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Assessment of Road Dust Contamination in India

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Abstract

The road dusts (RD) are fugitive in nature causing potential health hazards to people living in highways. They are generated from different sources on the roads and being a valuable archive of environmental information. In the present work, contamination assessment of 18 heavy metals and ions in road dusts of the country are described. Techniques *i.e.* ion selective, ion chromatography and atomic absorption spectrophotometers were used for analysis of the ions and metals. The content of 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 was ranged from 75 - 895, 276 - 12718, 48 - 1423, 243 - 10,580, 11 - 539, 290 - 46,484, 110 - 7716, 84 - 1771, 595 - 15,955, 24 - 42, 164 - 526, 1711 - 5218, 63,850 - 144,835, 47 - 62, 81 - 720, 166 - 450, 92 - 295 and 0.05 - 0.12 mg/kg with mean value of 224 ± 43, 3734 ± 895, 592 ± 895, 2859 ± 662, 143 ± 29, 4826 ± 2049, 1565 ± 411, 837 ± 121, 8545 ± 1288, 31 ± 4, 246 ± 82, 3002 ± 851, 91,331 ± 18,587, 54 ± 4, 206 ± 145, 241 ± 64, 171 ± 42 and 0.08 ± 0.02 mg/kg, respectively (at 95% probability). The enrichment, variation, correlation and sources of the contaminants are discussed.

Keywords

Ions, Heavy Metals, Sources, Road Dust

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1. Introduction

Air pollution has become a growing problem in megacities and large urban areas of the World [1] [2]. The estimated number of light and heavy vehicles in India registered is >120 million. A large fraction (>40%) of the air pollution is contributed by road transport, emitting a wide range of gaseous air pollutants and suspended particulate matter of different sizes and compositions [3] [4]. Transport-related air pollution causes a number of health problems *i.e.* increased risk of death, particularly from cardiopulmonary causes, and it increases the risk of non-allergic respiratory symptoms and disease [5]-[7]. Urban street dusts are sinks of the various pollutants (*i.e.* ions, metals, organics, etc.) depositing by sources *i.e.* motor vehicles, industry, weathered materials, etc. [8]-[29]. Therefore, in the proposed work, contamination assessment of ions and metals *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 highway road dusts of India is described.

2. Materials and Methods

2.1. Study Area

The road dust samples were collected from 42 locations of the country, near high way (**Figure 1**). The most of sampling locations were chosen from the Chhattisgarh state of the country due to running of several industries and coal based thermal power plants. Other samples were taken from 5 cities and towns of India.

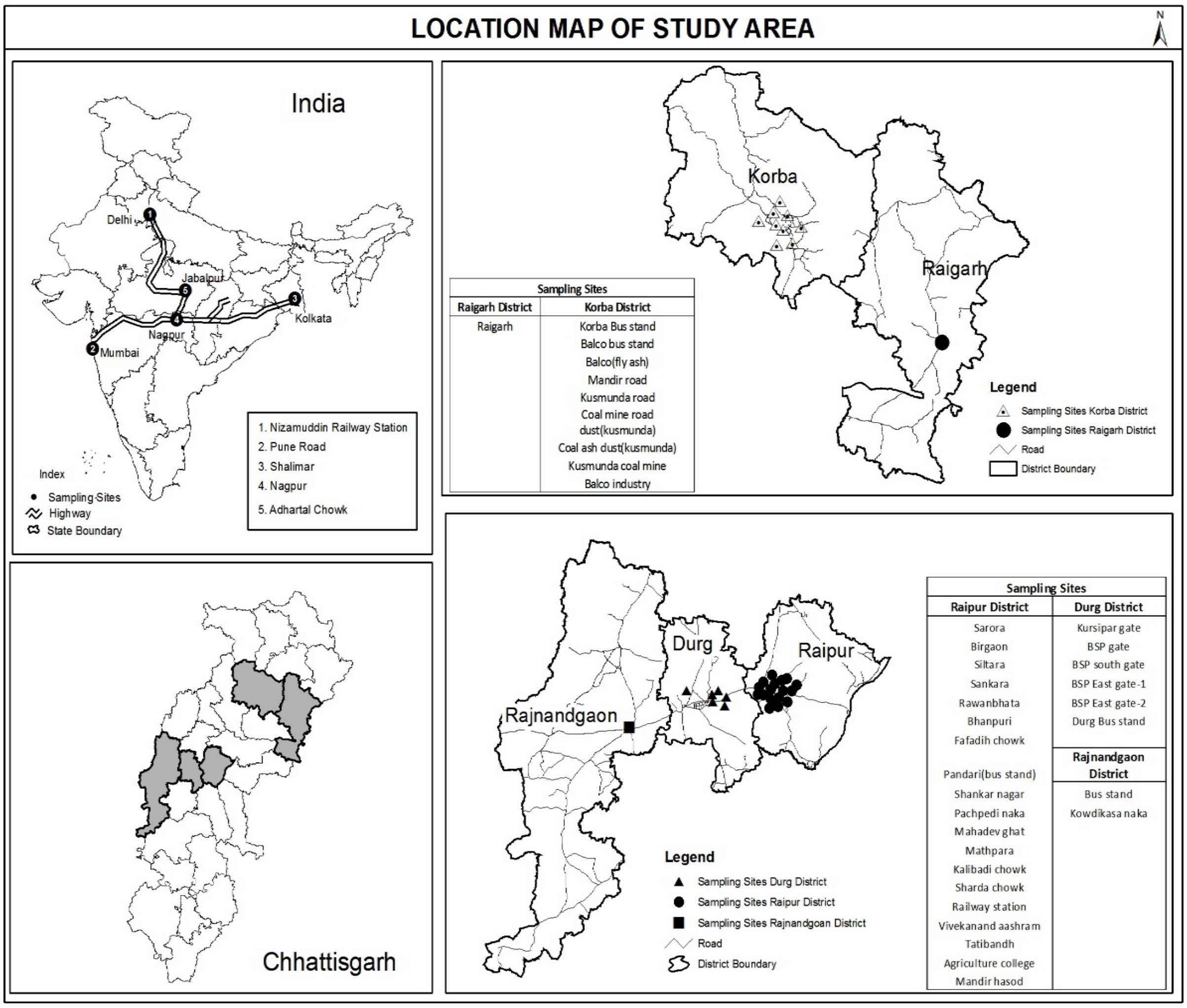

Figure 1. Representation of sampling locations in India.

2.2. Sample Collection

Total 42 surface road dust samples (0 - 10 cm) over area of 6 × 6 cm^2 were collected from various locations of the country in year, 2008. Four samples from different points of each location were collected, and a composite sample was prepared by mixing them in equal mass ratio. In years, 2009-2014, one composite sample from location: Siltara-I was collected in each year. The samples were collected by using plastic spoon in month of May during years from 2008 to 2014. They were kept in a glass bottle (250 mL) and dried at 60˚C in an oven for overnight (12 hr). The samples were crushed into fine particles by mortar and sieved out the particles of mesh size <0.1 mm.

2.3. Sample Preparation and Analysis

The color of the dust was differntiatted by using the standard color chart. A 10 g dust sample was extracted with 50 mL deionized hot water (≈50˚C) for 6 hrs in the shaker. The extract was filtered by using filter paper (pore size, 2 µm). The pH values were measured by using Hanna pH meter.The fluoride content was monitored with Metrohm ion meter-781 equipped with fluoride ion selective electrode and calomel electrode by using buffer in an equal ratio. The content of ions *i.e.* Cl^-, NO_3^-, SO_4^{2-}, NH_4^+, Na^+, K^+, Mg^{2+} and Ca^{2+} was analyzed by using Dionex DX1100 ion chromatography, equipped with anion separation column (AS9-HC, 250 × 4 mm), cation separation column (CS12A, 250 × 4 mm) and conductivity detector. The eluents, 9 mM Na_2CO_3 (1.4 mL/min) and 20 mM methyl sulfonic acid (0.8 mL/min) were used for leaching of the anions and cations, respectively. The content of ions was determined by using the standard calibration curves.

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) were used for analysis of the metals in the dust. The VARIAN "SpectrAA 55B equipped with hydride/cold vapor regenerator accessories was employed for analysis of elements *i.e.* 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 [30]. The statistical window software STATISTICA 7.1 was employed for the statistical analysis.

3. Results and Discussion

3.1. Dust Characteristics

The physical characteristics of the dusts are shown in **Table 1**. The color of dusts was varied from yellow to black. The urban dusts were blackish to black in color. The pH value of dust (n = 42) was ranged from 6.4 - 9.5 with mean value of 7.4 ± 0.2 at 95% probability. The dust of coal burning site of country like Korba was found to be slightly acidic due to the relatively higher content of ions *i.e.* Cl^- and SO_4^{2-}.

3.2. Ions in Road Dust

The contents of water soluble ions in the road dusts (n = 42) is summarized in **Table 2**. The concentration of ions *i.e.* Cl^-, NO_3^-, SO_4^{2-}, NH_4^+, Na^+, K^+, Mg^{2+} and Ca^{2+} was ranged from 276 - 12,718, 48 - 1423, 243 - 10,580, 11 - 539, 290 - 46,484, 110 - 7716, 84 - 1771 and 595 - 15,955 mg/kg with mean value of 3734 ± 895, 592 ± 895, 2859 ± 662, 143 ± 29, 4826 ± 2049, 1565 ± 411, 837 ± 121 and 8545 ± 1288 mg/kg, respectively. Ions *i.e.* Ca^{2+}, Na^+, Cl^- and SO_4^{2-} were found to be major contributing species in the road dusts. Their highest concentration was observed in the dust of Delhi followed by Jabalpur. The concentration of water soluble F^- in the road dust samples (n = 42) was ranged from 75 - 895 mg/kg with mean value of 224 ± 43 mg/kg (at 95% probability) (**Table 2**). The highest concentration of Ca^{2+} in all locations (except Delhi and Raigarh) was marked. In Delhi, >50% fraction of the road dust was contributed by Na^+. In all urban and industrial regions of the country, ≥25% fraction of the dust was contributed by anions *i.e.* Cl^- and SO_4^{2-} due to huge fuel burning. The highest concentration of F^- and NO_3^- was seen in the Raipur and Korba region due to running of Aluminium plant and thermal power plants (**Figure 2**). However, the highest concentration of NH_4^+ was marked in the remote area, Ambagarh Chouki. The [Σanion]/[Σcation] ratio (n = 42) was ranged from 0.05 - 0.77 with mean value of 0.27 ± 0.05, showing alkaline nature of the dusts. The temporal variation of ions from year 2008-2014 at site:

Table 1. Characteristics of road dust of India.

S. No.	Location	City	Color	pH
1	Urla	Raipur	DB	7.6
2	Siltara-I	Raipur	Bl	8.3
3	Siltara-II	Raipur	Bl	8.6
4	Sankara	Raipur	DB	7.7
5	Rawanbhata	Raipur	DB	7.6
6	Bhanpuri	Raipur	LB	7.3
7	Fafadih chowk	Raipur	LB	7.2
8	Pandari (Bus stand)	Raipur	B	6.9
9	Shankar Nagar	Raipur	B	7.3
10	Pachpedinaka	Raipur	B	7.4
11	Mahadevghat	Raipur	B	7.2
12	Mathpara	Raipur	LB	9.4
13	Kalibadi chowk	Raipur	B	9.5
14	Sharda chowk	Raipur	B	7.1
15	Railway station	Raipur	B	7.1
16	VivekanandAashram	Raipur	B	7.1
17	Tatibandh	Raipur	B	7.3
18	Agriculture college	Raipur	YB	7.3
19	Mandirhasod	Raipur	B	7.2
20	Kursipar Gate	Bhilai	B	7.7
21	BSP Gate	Bhilai	B	7.5
22	BSP South Gate	Bhilai	B	7.8
23	BSP East Gate-1	Bhilai	YB	8.1
24	BSP East Gate-2	Bhilai	OB	7.7
25	Durg Bus stand	Durg	B	7.1
26	Bus stand	Rajnandgaon	B	7.3
27	Kowdikasanaka	Ambagarh Chouki	B	7.0
28	Raigarh	Raigarh	Bl	7.4
29	Korba Bus stand	Korba	B	7.4
30	Balco Bus stand	Korba	B	7.2
31	Balco	Korba	G	6.8
32	Mandir road	Korba	B	7.6
33	Kusmunda road	Korba	Bl	7.2
34	Kusmunda-1	Korba	Bl	6.5
35	Kusmunda-2	Korba	LB	6.4
36	Kusmunda-3	Korba	Bl	6.5
37	Balco industry	Korba	B	7.2
38	Adhartal chowk	Jabalpur	B	6.7
39	Nagpur	Nagpur	B	7.7
40	Nizamuddin	Delhi	B	7.6
41	Shalimar	Kolkata	B	7.2
42	Pune road	Mumbai	B	6.8

B = Brown, Bl = Black, DB = Dark brown, LB = Light brown, YB = Yellow brown, G = Grey.

Table 2. Concentration of ions in road dust, mg/kg.

S. No.	F^-	Cl^-	NO_3^-	SO_4^{2-}	NH_4^+	Na^+	K^+	Mg^{2+}	Ca^{2+}
1	210	3428	1096	2810	163	2852	1391	707	7219
2	486	4634	835	3338	136	4059	958	950	8324
3	363	412	96	619	16	466	110	94	595
4	195	1615	416	1112	48	1902	785	699	8297
5	210	2498	428	1934	88	1896	991	526	7251
6	207	2697	491	1805	114	2859	1013	681	7202
7	168	6211	948	4120	188	5506	2247	1214	14,485
8	360	8559	1058	4656	178	6747	2596	1264	11,497
9	147	4873	823	3984	142	4308	1601	902	9203
10	204	3095	562	2186	130	2851	818	576	6958
11	174	276	48	243	11	290	127	84	1190
12	144	2926	531	1910	75	2846	1031	679	7767
13	158	10,605	1423	5682	141	8601	7716	1563	12,572
14	141	7733	1213	5033	197	6174	2792	1472	13,765
15	156	5707	897	4004	210	4478	2050	912	9239
16	141	6050	718	3250	204	4715	2910	1024	8566
17	210	7102	1230	4762	252	5803	1656	1250	13,708
18	153	884	271	1009	122	4083	904	1011	12,114
19	165	521	149	423	75	3692	2163	451	2925
20	171	7075	1225	6082	187	5825	1693	1577	15,955
21	192	4268	820	3130	160	3688	795	1771	15,941
22	216	4989	828	4010	176	4484	1101	1266	13,037
23	210	793	195	778	539	3177	592	864	7780
24	210	1009	216	860	149	4093	979	1009	8799
25	153	1082	280	876	139	3335	591	791	9181
26	156	492	101	540	109	1784	1271	600	7149
27	171	675	136	557	343	2644	2657	809	10,393
28	216	712	370	597	99	3990	1480	441	2508
29	138	5266	296	1279	195	3737	575	587	4839
30	726	3234	112	379	49	2952	599	473	4163
31	303	1910	404	1754	306	5488	2153	1100	14,064
32	240	3112	948	1936	98	2887	448	289	2608
33	192	3958	1072	2598	81	3061	1370	599	7533
34	198	4183	924	3258	97	4732	601	468	3150
35	207	3944	828	6504	132	3022	599	447	3821
36	192	5240	1080	3886	148	5775	859	536	3484
37	895	3179	493	2347	74	3426	2315	834	10,424
38	120	7116	351	7289	209	4774	4452	1309	13,904
39	75	505	468	2303	46	2605	995	434	4575
40	205	12,718	224	10,580	29	46,484	3740	1384	15,627
41	177	882	49	2833	16	3716	1576	713	6138
42	183	671	198	2830	114	2894	432	781	10,948

Siltara-I is presented in **Figure 3**. A temporal increase in the concentration of all ions was observed due to increase in the frequency of the vehicles at rate of ≥2% - 8% in the Raipur region of the country. In duration of six years (from 2008 to 2014), the sum of total concentration of 9 ions was increased >2-folds. The concentration of ions in the dust was observed in following increasing order: $NH_4^+ < F^- < Mg^{2+} < NO^{3-} < K^+ < SO_4^{2-} < Na^+ < Cl^- < Ca^{2+}$.

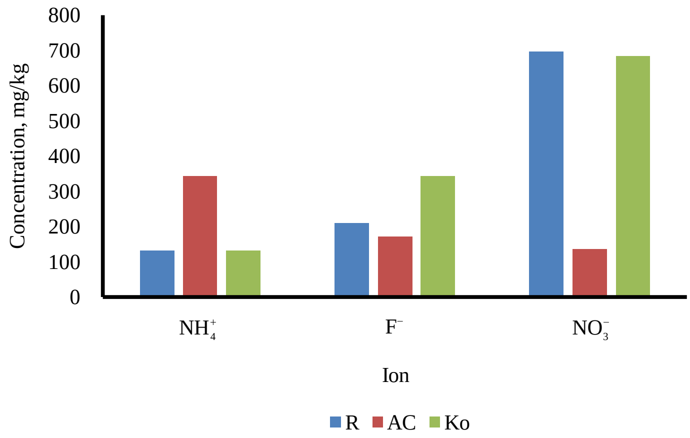

Figure 2. Spatial variation of ions, R = Raipur, Ko = Korba, AC = Ambagarh Chouki.

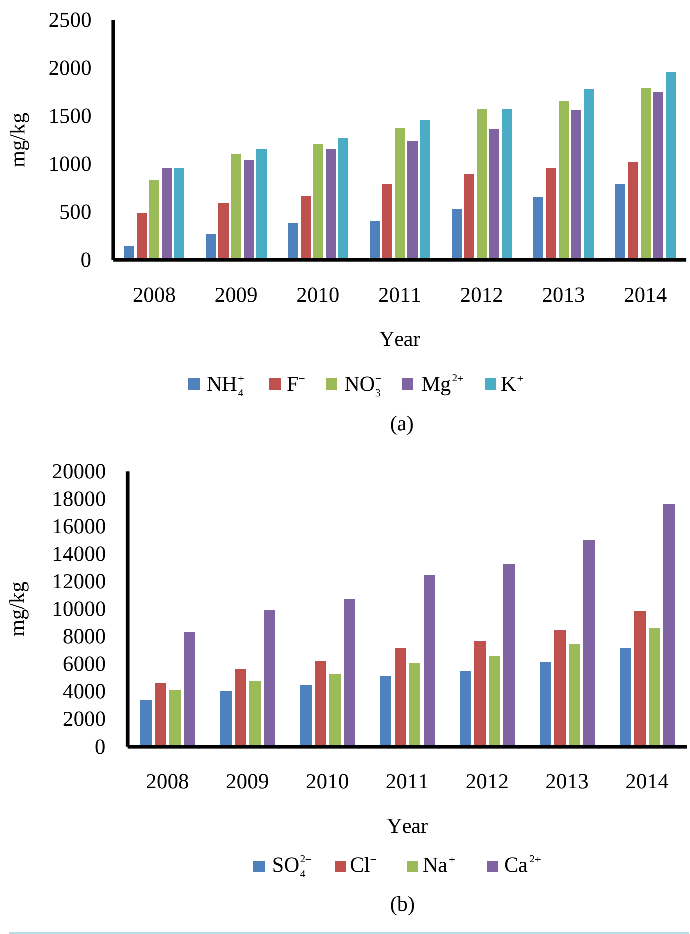

Figure 3. Temporal variation of ions at Siltara-I location.

3.3. Metals in Road Dust

The concentration of the metals *i.e.* As, Cr, Mn, Fe, Ni, Cu, Zn, Pb and Hg in the road dusts of Raipur city is shown in **Table 3**. The content (n = 9) of metals *i.e.* As, Cr, Mn, Fe, Ni, Cu, Zn, Pb and Hg in the road dusts was ranged from 24 - 42, 164 - 526, 1711 - 5218, 63,850 - 110,853, 47 - 62, 81 - 720, 166 - 450, 92 - 295 and 0.05 - 0.12 mg/kg with mean value of 31 ± 4, 246 ± 82, 3002 ± 851, 82,581 ± 11,214, 54 ± 4, 206 ± 145, 241 ± 64, 171 ± 42 and 0.08 ± 0.02 mg/kg, respectively (at 95% probability). Among them, Fe exhibited extremely high concentration in all locations of the Chhattisgarh state. The ferro-alloy metals *i.e.* Fe, Cr, Ni and Hg showed the higher concentration in the industrial locations. However, metals *i.e.* Cu, Zn and Pb exhibited the higher concentration in the highway sites *i.e.* Tatibandh due to vehicular and tire emissions. The concentration of the metals in the dust was seen in the following increasing order: Hg < As < Ni < Cu < Pb < Cr ≈ Zn < Fe. A temporal enhancement in the content of metals in the road dust of Siltara-I is shown in **Figure 4**. The metal content was found to increase at rate of >2% from year 2008-2014 due to an enormous increase in number of vehicles and iron industries. The content of metals in the road dust of studied area was found to be higher than other regions of the World due to increased mineral roasting and coal burning activities [10]-[29].

3.4. Salinity of Dust

The salinity is a sum of content of water soluble ions (*i.e.* Cl^-, NO_3^-, SO_4^{2-}, NH_4^+, Na^+, K^+, Mg^{2+} and Ca^{2+}), and ranged (n = 42) from 0.28% - 9.10% with mean value of 2.23% ± 0.44%, respectively. Among them, the highest value (9.10%) was observed at Delhi, may be due to highest vehicle frequency (>6,000,000). The mean salinity value was found to be at least 10-times higher than the recommended value of 0.25%.

3.5. ESP and SAR Values

The presence of excessive amounts of exchangeable sodium causes deflocculating of soil. A soil is considered "sodic" when the exchangeable sodium percentage (ESP) is 6% or greater. Sodium adsorption ratio (SAR) is a ratio of the sodium (detrimental element) to the combination of calcium and magnesium in relation to known effects on soil dispensability. The ESP and SAR value was ranged from 14.2% - 67.1% and 2.2 - 95.3 with mean value of 26.6% ± 3.4% and 13.1 ± 4.1, respectively. Among them, the highest value was recorded at Delhi, due to the largest anthropogenic activities in the capital city of the country. The higher ESP and SAR values were observed in the locations *i.e.* industrial area, bus stand, etc. due to increased human activities. The ESP and SAR value of the road dusts of the country were found to be much higher than recommended value of 15% and 6, respectively.

3.6. Contamination Factor

The contamination factor (C_f) is a concentration ratio of element from the road dust to the background level

Table 3. Concentration of metals in road dust, mg/kg.

S. No.	Metal	R1	R2	R3	R4	R5	R6	R7	R8
1	As	42	28	33	33	32	24	26	29
2	Cr	260	164	201	241	171	212	189	526
3	Mn	2241	5218	4336	3062	1711	2914	2778	1755
4	Fe	87,761	63,850	74,835	70,610	70,157	82,716	99,863	110,853
5	Ni	58	57	55	49	49	47	62	52
6	Cu	720	119	81	149	155	151	150	121
7	Zn	450	290	208	190	183	233	208	166
8	Pb	210	295	127	141	164	165	175	92
9	Hg	0.09	0.05	0.08	0.12	0.07	0.06	0.11	0.08

R1, R2, R3, R4, R5, R6, R7 & R8 = Tatibandh, Vivekan and Aashram, Fafadih chowk, Urla, Bhanpuri, Sankara, Siltara-I & Siltara-II.

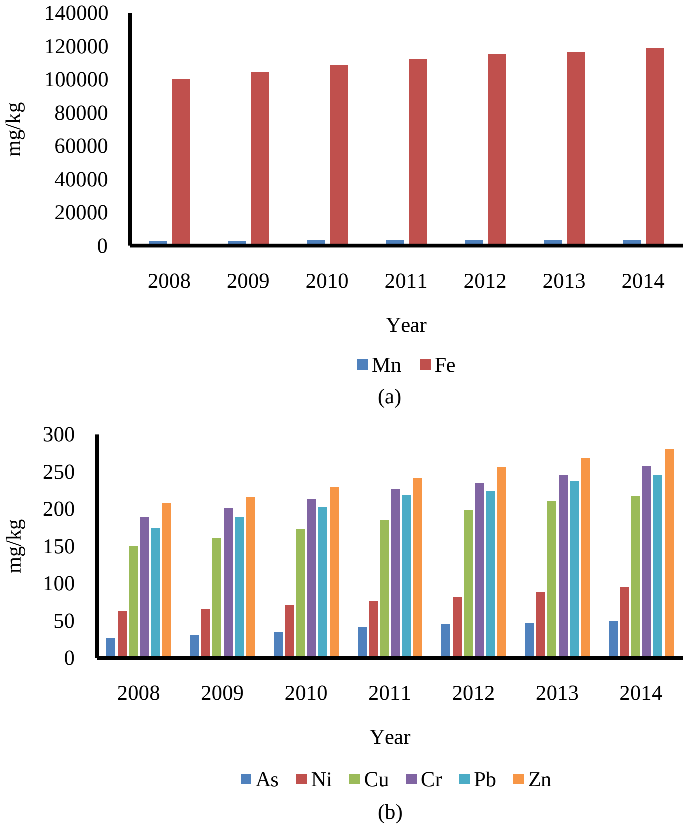

Figure 4. Temporal variation of metals in road dust at Siltara-I.

present in the earth crust [31]. The C_f value for F^-, Ni, Hg, Fe, Cr, Zn, Mn, Cu, Pb, Cl^- and SO_4^{2-} was found to be 1.1, 1.7, 2.1 2.2, 2.6, 3.9, 7.3, 10, 10 and 15, respectively. Among them, Cu, Pb, Cl^- and SO_4^{2-} were highly contaminated at all locations. However, other metals *i.e.* Hg, Fe, Cr, Zn and Mn were poorly contaminated in the road dust.

3.7. Cluster Analysis

The dendrogram of the sample sites is presented in **Figure 5**. Cluster analysis was performed on the dataset by Ward's method using Euclidean distance as similarity measure. The variables were interrelated to each other according their maximum similarities. First, the interrelation takes place between two variables which had the most similarity and the next repetition other similar pair clusters were related together [32]. Three groups of sample sites were observed: Group A (n = 1) with the sample site No. 40 which is Nizamuddin railway station located in Delhi. The sample site No.40 stands as an outlier. Group B (n = 10) which contained the sample sites nos. 7, 8, 13, 14, 17 located in Raipur, 20 - 22 in Bhilai, 31 in Korba and 38 in Jabalpur. Group C (n = 31) is formed by the rest of sample sites located in Raipur, Bhilai, Korba and the others locations, except Jabalpur. The discriminating parameters between the three groups were pH, F^- and inorganic nitrogen (NH_4^+ and NO_3^-) which are highlighted in **Figure 6**.

3.8. Correlation Matrices

The correlation matrices of the ions and metals in the dusts are presented in **Table 4**, **Table 5**. The F^- content of the road dust had either no correlation or poor negative correlation with other ions, may be due to its reactive nature. Other ions *i.e.* Cl^-, NO_3^-, SO_4^{2-}, NH_4^+, Na^+, K^+, Mg^{2+} and Ca^{2+} among themselves were well correlated, and expected their emission from multiple sources *i.e.* vehicular combustion, road material weathering, etc. Among heavy metals, four metals *i.e.* As, Cu, Zn and Pb were fairly correlated coming from similar sources. Iron was found to be well correlated only with Cr.

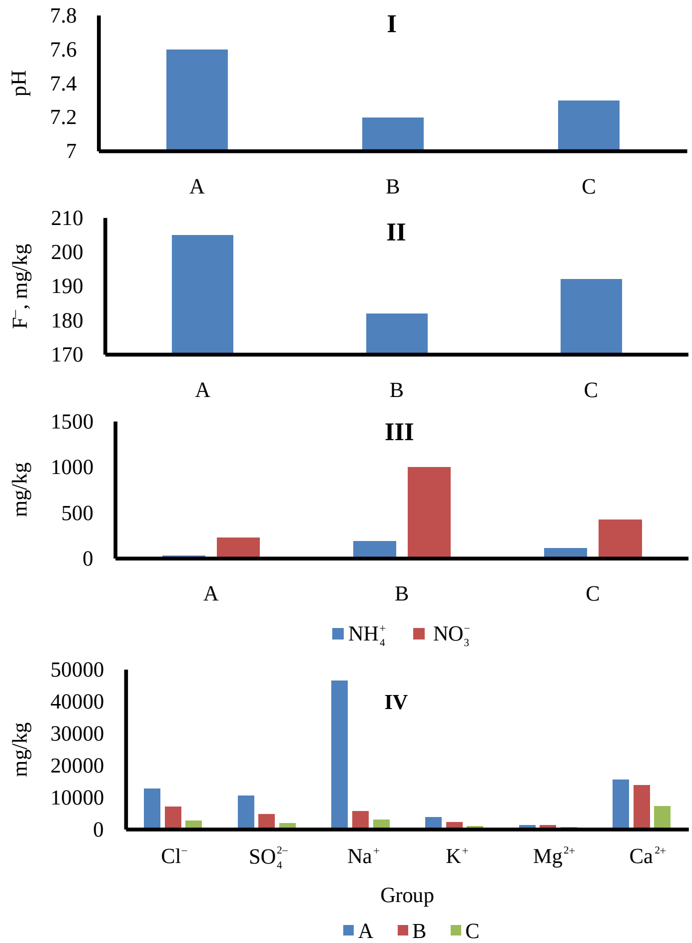

Figure 5. Discriminating parameters for groups.

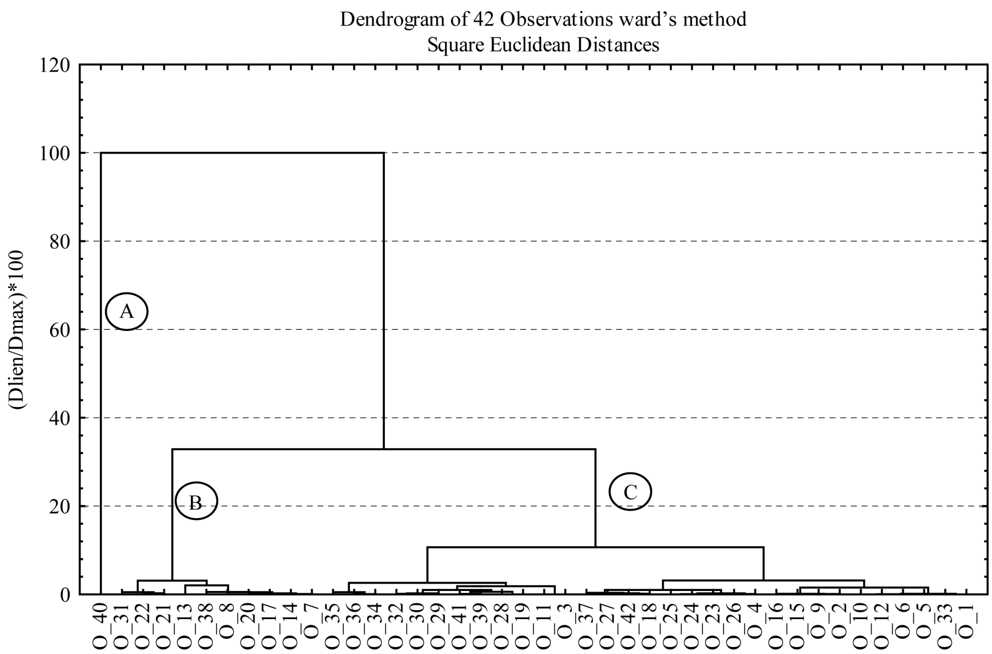

Figure 6. Dendrogram for differential of road dust samples.

Table 4. Correlation matrix of ions in road dust of Raipur city.

	F^-	Cl^-	NO_3^-	SO_4^{2-}	NH_4^+	Na^+	K^+	Mg^{2+}	Ca^{2+}
F^-	1.00								
Cl^-	0.00	1.00							
NO_3^-	0.00	0.93	1.00						
SO_4^{2-}	0.00	0.97	0.96	1.00					
NH_4^+	−0.14	0.75	0.81	0.82	1.00				
Na^+	−0.10	0.91	0.83	0.87	0.75	1.00			
K^+	−0.22	0.78	0.66	0.68	0.41	0.82	1.00		
Mg^{2+}	−0.14	0.89	0.86	0.88	0.80	0.94	0.71	1.00	
Ca^{2+}	−0.20	0.75	0.77	0.79	0.78	0.81	0.50	0.94	1.00

Table 5. Correlation matrix of metals in road dust of Raipur city.

	Cr	Mn	Fe	Ni	Cu	Zn	As	Pb	Hg
Cr	1								
Mn	**−0.48**	1							
Fe	**0.74**	**−0.57**	1						
Ni	−0.14	0.28	0.27	1					
Cu	0.03	−0.31	0.13	0.30	1				
Zn	−0.18	0.10	−0.09	**0.42**	**0.90**	1			
As	0.04	−0.19	−0.13	0.17	**0.78**	**0.64**	1		
Pb	**−0.58**	**0.56**	**−0.51**	0.40	0.26	**0.59**	0.03	1	
Hg	0.11	−0.31	0.29	0.22	0.16	−0.11	0.28	**−0.42**	1

3.9. Factor Analysis

Factor analysis was executed on 18 variables for the 8 sample sites. Four factors were extracted 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+} had each one a strong positive loading value. Na^+ and Cu showed some moderate loading values on Factor-1. It characterized 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 or Ni and Hg.

Factor-3 represented 14.23% of the total variance. Manganese and Pb showed absolute strong loading values on Factor-3. Manganese was in opposite relation with metals *i.e.* Pb, Zn, Cr, Cu, Ni and Fe. This can 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 also different sources between As and Pb or Zn. The results of factor analysis highlighted the complexity of the different sources of metals.

A higher concentration of Zn and Pb in the road dust was found, and their prominent sources expected were ZnO and Pb used in tire thread and in the motor vehicle wheel balance weights, respectively [10]. The possible source of the metals *i.e.* As, Cr, Mn, Fe, Ni and Hg are road materials, automobile rust, motorcar exhaust, steel plants and coal burning [18].

4. Conclusion

The main dominating species in the road dust is the Fe, contributing ≈75% fraction of the content of 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). However, the fraction of Na and Ca includes 4% and 8%, respectively. The road dust is a sodic in nature at hazardous levels. The motor vehicle exhaust emissions are expected to be main sources for contaminating the road dust with Cl^-, SO_4^{2-}, Cu, Zn and Pb nearby highways. The higher concentration of F^- was marked in two locations: Raipur and Korba of the country due to huge coal burning and running of an Aluminium Plant.

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