Abstract

Different approaches of source apportionment of dust fractions have been reported world-over. Predicting source categories within receptor chemical profiles using regression and factor analysis using PCA has been reported to evaluate possible source/routes of air pollution mass. The present study is focused on the application of all three approaches to investigate higher degrees of significance in source apportionment of indoor dust fallout in the Raipur city district, Raipur, India, which is located at 21°14′22.7″ N latitude and 81°38′30.1″ E longitudes. Modeled source categories obtained from regression and factor analysis (using PCA) has shown potential support in the selection of source profiles in CMB. About 65-78% agreement has been obtained between results of source signatures of dust fallout obtained from the three approaches. The application of the combined approach has been extended to respirable fine particulates measured indoors. Both fractions have shown a different dominance of selected source of emissions. Major approaches of source signatures has been investigated in combination with the hypothesis that prediction and modeled source profiles will support the selection and inclusion of field based source profiles in source apportionment of indoor dust fractions using CMB. A stratified random sampling plan using the longitudinal study design has been adopted for dust fallout source apportionment.

Keywords: Source apportionment, CMB, Regression analysis, Indoor air

1. Introduction

The incidence of heavy metal contamination from both natural and anthropogenic sources has increased concern about the health effects of chronic low-level exposures, particularly on people living in urban environments who are more likely to be exposed to this threat. Natural and anthropogenic sources of soil contamination are widespread and variable. Heavy metals occur naturally in rocks, but most of the heavy metal occurrences in urban soils tend to originate from anthropogenic sources such as industrial, urban development and transport activities. Many researchers have shown that urban soils received a load of contaminants - usually greater than surrounding suburban or rural areas - due to the concentration of anthropogenic activities of urban settlements (Charlesworth et al. 2003; Farghaly and Ghandour 2005; Komarnicki 2005; Lee et al. 2006; Yang et al. 2006; Srivastava and Jain 2007; Gurugubelli et al. 2013). Researchers use several different approaches to assess indoor exposure to microbial bioaerosols and heavy metals. Several studies have reported concentrations of microorganisms in indoor air that range from 102 - 104 Colony Forming Units m-3 for both bacteria and fungi (Ross et al. 2000; Sessa et al. 2002; Bouillard et al. 2005; Balakrishna et al. 2015). There is an increasing concern about heavy metal contamination in the indoor environment since most people spend a great extent of their time indoors (e.g., offices, workplaces, houses, and so on). A number of studies (Farghaly and Ghandour 2005; Komarnicki 2005; Srivastava and Jain 2007) have suggested that contaminated soil or dust, ingested either directly or indirectly as a result of hand-to-mouth activity may represent a significant pathway of environment toxic metals to humans, with children representing the main sector of the population at highest risk. Children, who tend to play or crawl on the floor and place objects in their mouths that have been in intimate contact with dusty floors, are particularly at risk from such health complications. In certain environments, airborne particles and settled dust are especially undesirable, as they constitute contaminants that interfere with the activities conducted in these environments (Morawska and Salthammer 2006).

Increasing severity of dispersion and fallout of fugitive dusts in urban areas of India has shown spontaneous linkage with a higher degree of health disorders especially bronchial ailments (Quraishi and Pandey 1995; Goel and Trivedi 1998; Bohm and Saldiva 2000; Sharma and Pervez 2003; Sharma and Pervez 2005; Saxena et al. 2008). Due to the higher settling tendency of larger particles of dust fallout fraction near emission sources on a regional scale, researchers have classified its reception pattern as ambient-outdoor, street-outdoor and indoors dust fallout (Quraishi and Pandey 1993;
Sharma and Pervez 2004; Gadkari and Pervez 2007; Dubey and Pervez 2008). The present study has been focused on the various source roots of urban indoor particulate matters and its deviation pattern with the aid of the chemical mass balance and regression graph analysis.

2. Material and methods (study design, sampling and data analysis)

2.1. Study Design
The study was undertaken in urban areas (Fig 1). The goal of the study was to evaluate relative source contribution estimates of various routes of dust fallout in the urban residential indoor environment. The objectives are: (1) To measure and characterize dust fallout at identified sources (2) to analyze statistically, the relationship between dust fall measurements of source-routes and residential receptors and (3) to carryout apportionment of dust fall at residential receptors, taking identified atmospheric routes as possible sources using the chemical mass balance model (CMB8). A residential area (Birgaon) located in close proximity to a major industrial area (Siltara) was selected for the study.

Fig 1. Local map of source and receptor sites in Raipur city along with windrose of the region
2.2. Sampling Design

A comprehensive study about source contribution estimates of fallout of urban areas (residential, commercial, and sensitive regions) was started from December 2007. Source apportionment study of dust fallout of a specific urban-residential indoor region has been presented here. A non-probability based longitudinal stratified random sampling design in space-time framework has been chosen to achieve the objectives (Gilbert 1987; EPA 2003). Ambient-outdoor and local-outdoor has been decided as the atmospheric measurement levels at identified sources of dust emissions and residential-receptor, respectively.

2.3. Sampling method of indoor dust fallout

Dust emission sources were identified using the layout map, anthropogenic activity patterns, and urban-industrial development plan of the study area. The identified sources (Table 1) were classified in point, line, and regional sources of dust emission (Goel and Trivedi 1998). Dust collection jars (dimension: dia-23” ht- 45”) with standard specifications (Katz 1977; Thakur and Deb 2000) were placed for a month at a height of 1 ft. In case of sampling at a paved road, the sampler was installed at the height of 5 ft at major crossroad passing through the residential colony. As far as soil profile is concern, samples of soils (1 kg) were collected from the open land of the residential colony. Soil samples were collected after removing surface soils up to 6 cm depth (Gadkari and Pervez 2008). Frequency of sampling was 24 (one in each month) at each source receptor site throughout the sampling year. About a liter of double distilled water was placed in each jar and a net sheet (size: 20 mesh) was placed on the mouth of the jars. Five replicate measurements were done to minimize weighing error (Table 2). After the completion of the sampling period, filters were carried to the laboratory and dried in desiccators and weighed in an electrical 5 Digital Balance (DENVER model TB215D). Geometric mean and standard deviation of the 24 measurements (1 in each site) of residential indoor houses were recorded. Regression analysis of indoor dust-fall level has been done for each site (Fig 2). Geometric mean and standard deviation values of dust fall levels and their correlations are presented in Table 2. All statistical parameters are calculated using Microsoft Excel and Stats direct version 2.5.7 (EPA 2003).

![Fig 2. Regression analysis between selected dust fallout receptors and dust fallout at identified source sites.](image-url)
Table 1: Identification and grouping of defined sources and receptor in the study area

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Name of Source/receptor</th>
<th>Type</th>
<th>Classification of monitoring level</th>
<th>Site characteristics</th>
<th>Sampling Frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-1</td>
<td>Siltara industrial area</td>
<td>Stationary point</td>
<td>Ambient-outdoor</td>
<td>Most of the industries are: casting, sponge iron, steel foundries.</td>
<td>12 samples throughout the sampling year (one in each month)</td>
</tr>
<tr>
<td>S-2</td>
<td>Urla Industrial, area</td>
<td>Stationary point</td>
<td>Ambient-outdoor</td>
<td>Most of the industries are: casting, chemical, oil production, glass and plastics.</td>
<td></td>
</tr>
<tr>
<td>S-3</td>
<td>Paved road</td>
<td>Line</td>
<td>outdoor</td>
<td>Re-suspended dusts of road side runoff measured at 3ft height</td>
<td></td>
</tr>
<tr>
<td>S-4</td>
<td>Civil construction</td>
<td>Area</td>
<td>Ambient-outdoor</td>
<td>Dusts emitted from handling of raw materials used in civil construction site</td>
<td></td>
</tr>
<tr>
<td>S-5</td>
<td>Automobile</td>
<td>Point</td>
<td>Emission outlet</td>
<td>Mixed dust fraction emitted from silencer of truck, cars and two wheelers</td>
<td></td>
</tr>
<tr>
<td>S-6</td>
<td>Local soils</td>
<td>Area source</td>
<td>-</td>
<td>Re-suspension of soil dusts</td>
<td></td>
</tr>
</tbody>
</table>

Receptor site

| R-1   | Birgaon, Raipur         | Residential area | House-Indoor | Residential area located northeasterly and downwind to industrial complexes | 12 samples throughout the sampling year (one in each month) |

Table 2: Yearly average dust fallout monitored

<table>
<thead>
<tr>
<th>S. No</th>
<th>Site No</th>
<th>Minimum</th>
<th>Max</th>
<th>Geo. mean</th>
<th>STDV (Standard deviation)</th>
<th>R (Correlation)</th>
</tr>
</thead>
<tbody>
<tr>
<td>01</td>
<td>S-1</td>
<td>131.51</td>
<td>391</td>
<td>181.186</td>
<td>77.974</td>
<td>43.03%</td>
</tr>
<tr>
<td>02</td>
<td>S-2</td>
<td>178.54</td>
<td>245.29</td>
<td>217.429</td>
<td>24.414</td>
<td>11.23%</td>
</tr>
<tr>
<td>03</td>
<td>S-3</td>
<td>122.73</td>
<td>186.25</td>
<td>141.435</td>
<td>18.324</td>
<td>12.96%</td>
</tr>
<tr>
<td>04</td>
<td>S-4</td>
<td>67.71</td>
<td>116.54</td>
<td>87.845</td>
<td>16.366</td>
<td>18.63%</td>
</tr>
<tr>
<td>05</td>
<td>S-5</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>06</td>
<td>S-6</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>07</td>
<td>R-1</td>
<td>12.453</td>
<td>18.923</td>
<td>14.3144</td>
<td>2.3882</td>
<td>16.68</td>
</tr>
</tbody>
</table>

Yearly average of Chemical species in Dust fall (g/M²)

<table>
<thead>
<tr>
<th>S. No</th>
<th>Site No</th>
<th>Chemical</th>
<th>Minimum</th>
<th>Maximum</th>
<th>Geo. mean</th>
<th>STDV (Standard deviation)</th>
<th>R (Correlation)</th>
</tr>
</thead>
<tbody>
<tr>
<td>01</td>
<td>S-1</td>
<td>Fe</td>
<td>0.311</td>
<td>0.803</td>
<td>0.4188</td>
<td>0.1520</td>
<td>36.29</td>
</tr>
<tr>
<td>02</td>
<td>S-2</td>
<td>Cr</td>
<td>0.009</td>
<td>0.074</td>
<td>0.0284</td>
<td>0.0246</td>
<td>86.84</td>
</tr>
<tr>
<td>03</td>
<td>S-3</td>
<td>Mn</td>
<td>0.003</td>
<td>0.054</td>
<td>0.0184</td>
<td>0.0169</td>
<td>91.89</td>
</tr>
<tr>
<td>04</td>
<td>S-4</td>
<td>Ni</td>
<td>0.107</td>
<td>0.654</td>
<td>0.2578</td>
<td>0.1789</td>
<td>69.37</td>
</tr>
<tr>
<td>05</td>
<td>S-5</td>
<td>V</td>
<td>0.001</td>
<td>0.009</td>
<td>0.0028</td>
<td>0.0029</td>
<td>103.06</td>
</tr>
<tr>
<td>06</td>
<td>S-6</td>
<td>Zn</td>
<td>0.166</td>
<td>0.972</td>
<td>0.4389</td>
<td>0.2559</td>
<td>58.30</td>
</tr>
<tr>
<td>07</td>
<td>R-1</td>
<td>Cu</td>
<td>0.059</td>
<td>0.271</td>
<td>0.0948</td>
<td>0.0703</td>
<td>74.17</td>
</tr>
<tr>
<td>08</td>
<td>R-1</td>
<td>Pb</td>
<td>0.031</td>
<td>0.271</td>
<td>0.0553</td>
<td>0.0434</td>
<td>78.59</td>
</tr>
</tbody>
</table>
2.4. Source apportionment studies
Chemical mass balance model (CMB8, EPA) software has been used for source apportionment studies (Friedlander 1973; Cooper and Watson Jr 1980; Gordon 1980; Watson 1984; Watson et al. 1984; Gordon 1988; Hidy and Venkataraman 1996). Profiles used here are: (1) source compositional profile of all sources, (2) receptor residential indoor dust fall chemical compositional profile, (3) road-traffic borne dust and (4) soil-borne dust fraction. For road-traffic source, samples of dust were collected at a major traffic junction within the residential colony. Source profiles were documented using the Microsoft Excel worksheet. Receptor profiles of dust fall of selected subjects belonging to specific residential areas were also prepared using similar chemical constituents in a similar sequence. Source and receptor profiles along with their source and species selection files were applied using an extension file as input to the CMB 8 model. For each receptor subject’s profile, all source profiles prepared for related residential location were used. None of the species were excluded from the CMB execution. The important output parameters for good fit have been evaluated. The results of the CMB execution are presented in Table 3. Relative source contribution estimates are shown in Fig 3. A bar diagram of source profiles for each residential area are shown in Fig 3.

Fig 3. Relative source contribution estimation of dust fallout and chemical species at selected classified atmospheric levels at the receptor.
2.5 Chemical analysis of dust fallout

All dust samples collected in the sampling programs were subjected to chemical analysis. Samples were taken in the Teflon digestion bomb followed by the addition of 10 ml 1:1 acid mixture of HNO₃ and H₂O₂, and placed in an oven at 180°C for 6 h (Envirotech, 2000). The sample was then filtered through Whatman filter paper No. 42. The final volume was made up to 50 ml by double distilled water. The digested samples were then transferred into cleaned glass bottles. The digested samples were subjected to chemical analysis for major (Fe, Ca, Mg, Na and K) and minor (Cd, Hg, Ni, Cr, Zn, As, Pb and Mn) constituents (Xuan 2005). Fe, Al, Ca, Mg, Cr, Mn, Ni, As, Hg, V, Zn, Cu, Pb, Co and Sb were determined by using ICP-AES (Jobin Ywuan, version 3.0) by standard procedures (Montaser and Golightly 1987). Na and K have been evaluated flame photometrically (Systronics, Model 130) using standard procedures. Selected source indicator anions (SO₄²⁻, Cl⁻ and NO₃⁻) were also determined (Babko et al. 1976; Ramteke and Moghe 1988; Christian 2003). Five replicate determinations were made for all species. Repeatability of determination was increased where relative standard deviation was not within 5-8%.

3. Results and Discussion

Profuse and highly skewed dust fallout at the indoor receptor of the Birgaon residential area has been observed. It has been observed that the geometrical mean level of dust fallout at the residential outdoor receptor is a thousand times higher than the maximum permissible limits developed in Australia (Ferrari 2000) and has shown significant increase within a decade. Dust fallout levels in the Siltara industrial area has shown a higher deviation pattern in annual geometrical mean compared to that in the Urla Industrial area. However, the Urla Industrial area has shown higher dust fallout in all monitoring locations. Annual mean of dust fallout measured at a height of 3 ft on paved roads have also shown comparable levels with that measured in industrial sites due to a higher degree of re-suspension of dusts formed during eruption of low quality paved road material.

Linear regression analyses have shown that the receptor site (R-1) is best correlated with the Siltara Industrial area (S-1) and compared to other sources this has also been conformed by the Chemical Mass Balance model. Paved road also shows the significant contribution, this has been proved by both regression graph analysis and CMB8 model analysis. Dust fallout of paved roads have shown a dominating relationship with dust fallout of residential indoors similarly with coal fired industrial sources.

Annual mean of selected chemical species measured in dust fallout of S-1 to S-4 has been utilized as the source profile for the source apportionment of dust fallout at the Birgaon residential indoor (R-1). In addition, chemical profiles of vehicle exhaust and local soils have also been prepared and used for source apportionment modeling. The output of CMB8 with good fit parameters (chisquare- 2.37, R²- 0.61) has been presented (Fig 3). Multiple source contribution has been observed with the paved road dominance. Re-suspension of poor quality road dust has suppressed the soil dust contribution to a large extent. Lower contribution of the Urla Industrial source compared to the Siltara Industrial source has been observed and variation in contribution could be assessed using wind-rose of the study region. In contrast to the international scenario, vehicle exhaust has shown lower contribution due to the predominance of paved road dust source. Results showed clear agreement with those obtained by regression analysis and CMB of the dust matrix.

Manganese (Mn), nickel (Ni), vanadium (V) and lead (Pb) have shown major contributions from the Siltara Industrial area compared to other sources with the contribution percentage of 31%, 68%, 48% and 43% respectively. Iron has shown a different pattern of occurrence at the residential indoor site. Paved roads have shown 1.21 fold dominance in iron compared to industrial sites with a contribution of 35%. The zinc (Zn) industrial source (S-1) has shown a major contribution nearly similar to paved road (S-3) source. The paved road source (S-3) has shown good contribution for chromium (Cr) with 46%; this is two times greater than the industrial source (S-1). The copper industrial source (S-1) has shown similar contribution with the automobile source (S-5) with a contribution of 39% and 37% respectively. Finally, in this study we have found that the paved road source (S-3) has shown equivalent contribution with the industrial source (S-1). The construction source (S-4) has also shown significant contribution in all cases.

In conclusion, dust fallout at an indoor atmospheric level in the Birgaon residential area is affected by multiple sources. In the Siltara Industrial area, local construction activities and paved road dust have been identified as major precursors of dust fallout in the region. Both tests (regression analysis and receptor modeling) have shown a similar pattern of source dominance on receptor dust fallout. Except for iron and chromium, all other indicator species of industrial emissions (Mn, Ni, Cu, V, Zn and Pb) have shown a
similar pattern of relative contribution estimates in receptor dust fallout.

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