Chapter 7

Atmospheric Concentration of Trace Elements, Dry Deposition Fluxes and Source Apportionment Study in Mumbai

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Additional information is available at the end of the chapter

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1. Introduction

Presence of toxic elements in the atmosphere is of a great concern due to their adverse affect on human health and ecosystem. Despite the requirement of some of the elements for all living organisms, certain elements cause various toxic effects on accumulation in animal tissues (Yasutake and Hirayama 1997). There are various types of sources emitting these elements into the atmosphere, e.g. fossil fuel combustion contributes Al, Fe, Ca, Mg, K, Na, As, Pb, Cd, Sc, Hg elements (Furimsky 2000), elements like Pb and Zn are contributed by wood combustion (Mohn *et al.,* 2002), vehicular traffic contributes Cd, Cr, Cu, Ni, Pb, Zn (Westerlund 2001), electroplating contributes Cr (Flower *et al.*1994) metal alloy industries emit different elements like Cd, Cr, Al, Fe, Ni, Zn, Pb, Cu, etc. in the air (Harrison *et al.,* 1986). Dry deposition of trace elements has gained the importance due to its environmental significance and concerns. There have been many studies undertaken over the past decade to estimate the dry deposition (Injuk *et al.,* 1998; Jiries *et al.,* 2002; Fang *et al.,* 2004; Sakata *et al.,* 2006; Herut 2001). Recently, measurement on dry deposition fluxes of elements and their velocities studies were also reported at Brazil, Taiwan and Tokyo (Fang *et al.,* 2007; Pedro *et al.,* 2007; Sakata *et al.,* 2008). In India, status of airborne toxic elements at different land used pattern locations in major urban cities has been reported (Tripathi *et al.,* 1993; Gajghate and Hasan, 1999; Gajghate and Bhanarkar 2005a, b; Gajghate *et al.,* 2005). Bhanarkar *et al.,* (2005) have been carried out inventory of toxic elements for industrial sources in Greater Mumbai. Atmospheric deposition of trace elements like Pb, Cd, Cu and Zn was studied at Deonar, Bombay, India (Tripathi et al., 1993). They indicated that dry deposition flux of these trace elements was in the range of 0.2 to – 104.6 kg km^{-2} yr^{-1}. Mudri *et al.,* (1986) reported the dry deposition of dust fall on monthly basis for whole year at the Visakhapatnam, which amounted to 12.35 MT km^{-2} $month^{-1}$. However, in comparison, there is still relatively little

known about atmospheric fluxes in India. This paper presents concentration and estimated dry deposition flux of selected trace elements (Zn, Pb, Al, Cd, Ni, Sr, Mn, Fe, Cr, Cu, Mg, V and Ca) in the atmosphere of Mumbai. Estimates the elements loading from the atmospheric deposition over the Mumbai are also presented. Enrichment factors (EFs) of elements with respect to crustal composition and source apportionment are also discussed.

1.1. Study area

Greater Mumbai is located on the western coast of India and above 11 m mean sea level. The city is spread over an area of 603 km^2 extending from Island city in the south to Borivali and Mulund in the north. It is one of the largest metropolises of the world with a population of 12 million in 2001 which is expected to touch 15 million in 2011. There are a large number of small and big industries include thermal power plant, refineries, petrochemicals, fertilizer, textiles mills, and engineering and foundry units in the city. Mumbai has a tropical savanna climate with relative humidity ranging between 57% and 87%, and annual average temperature of 25.3^{o}C, with a maximum of 34.5^o C in June and minimum of 14.3^o C in January. The average annual precipitation is 2078 mm, with 34% of total rainfall occurring in July. The prevailing wind directions are from West and northwest, with West and southwest shifts during monsoon. Some easterly component is observed during winter.

2. Materials and methods

2.1. Sample collection and analysis

Four sites were selected to represent different segments of the region and activities, which include one control/reference (C), one industrial (I), and two kerb sites (K-1 and K-2) for sampling of PM_{10} in ambient air of Mumbai. Details of sampling location are presented in Table 1 and also shown in Figure 1.

Site	Classification of area	Description
1	Control (C)	Protected area under Indian Navy, minimum traffic
2	Kerbside (K-1)	Commercial area, only four wheelers and buses are plying, 6 roads junction, cinema theatre, educational institutions
3	Kerbside (K-2)	Busy Swami Vivekanand Marg, Pawan Hans Civil air port, Santacruz BEST Bus Depot
4	Industrial (I)	Heavy traffic of trucks, tankers, multi wheeler dockyard activity

Table 1. Description of sampling sites

24-hrly sampling was carried out round the clock during the winter season using respirable high volume sampler with a flow rate of 1 m^3 min^{-1}. PM_{10} collected on glass fibre filter paper were determined by gravimetric method (Katz, 1997). PM_{10} samples collected from various sites were analyzed for selected trace elements (Zn, Pb, Al, Cd, Ni, Sr, Mn, Fe, Cr, Cu, Mg, V

and Ca). A known portion of the filter paper is taken and digested with high purity HNO_3 in clean Teflon bombs using microwave digester. Then the digested solution was filtered through glass fibre filter and make up to a final volume of 100 mL with double distilled water. Blank samples were extracted and concentrated with the same method described. Trace elements analysis was performed with Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES, Model: JY-24, Jobin Yvan, France).

2.2 QA/QC protocol

QA/QC protocol is undertaken for precise measurement of particulate matter by calibrating the air flow measurement device using top load calibrator prior to sampling and air flow is corrected at STP. Blank test background contamination was monitored by using operational blanks (unexposed filter) which were processed simultaneously with field samples. The field blanks were exposed in the field when the field sampling box was opened to remove and replace field samples. Blanks were cleaned and prepared with the same procedures applied to the actual samples. Concentration of particulate matter was determined by gravimetrically using calibrated balance (Mettler AE 163). Element analysis was carried out using Inductively Coupled Plasma - Atomic Emission Spectroscopy. High quality glass wares were preferred, throughout the sampling, digression and analysis steps, to prevent any metal contamination. The filter paper were digested with concentrated nitric acid (Merck) in Teflon vessel in a microwave digestion chamber (ETHOS make-milestone, Italy).The sample was digested for twenty minutes and then filtered through Whatman 42 (Ashless filter papers 125mm, cat No 1442 125) filter paper into properly cleaned volumetric flask. Calibration standards of 0.5ppm, 1ppm and 2ppm were prepared through serial dilution of standard stock solution of multi element having concentration of 1000 mg/lit (Merck, Cat No.1.11355.0100) and used for the calibration of the instrument. Samples are analyzed by spiking with a known amount of elements to calculate recovery efficiencies. The analysis procedure for the recovery test is the same as that described for the field samples. The recovery tests of elements were 102%, 95.5%, 106.5%, 94%, 98.0 114%, 103.5%, 96.5 %, 94.5%, 98.0%, 90.0%, 93.0% and 95.5 % for Al, Zn, Fe, V, Pb, Ca, Mg, Cd, Ni, Mn, Cr, Cu and Sr respectively. The reproducibility test indicates the stability of the instruments. Analysis of elements of the same concentration standard solution is repeated for many times. The standard solution of 0.5 mg/lit was repeated and reproducibility of results indicates that 103.9%, 96.65%, 96.61%, 97.5%, 99.40%, 96.02%, 99.2%, 99 %, 97.24%, 98.62%, 94.4%, 96.6% and 98.02 % for Al, Zn, Fe, V, Pb, Ca, Mg, Cd, Ni, Mn, Cr, Cu and Sr respectively was observed.

3. Results and discussions

3.1. Concentration of PM_{10}

The air quality was determined in the activity zones namely control, industrial zone and high traffic area (Kerbside). The average PM_{10} concentration for control site was observed to be 78 $\mu g/m^3$ with minimum and maximum of 29 $\mu g/m^3$, 146 $\mu g/m^3$ respectively. Ambient air

quality in industrial site showed the average PM_{10} was 135 μg/m³.The average concentration of PM_{10} were maximum at all kerbsides. Average level of PM_{10} was 186 μg/m³ and 315 μg/m³ at K-1 and K-2 respectively. Concentration of PM_{10} has been exceeded CPCB standards for mixed area at all the sampling location except at control site. Kerbside K-2 showed the 315μg/m³ as higher average concentration of PM_{10} with 450 μg/m³ and 166 μg/m³ as maximum and minimum concentration respectively.

3.2. Concentration of toxic elements

The measured average elemental concentrations at various sites were presented in Fig 1 (a & b). Average individual trace element concentrations fluctuated between 0.003 μg/m³ (Cr) and 3.432 μg/m³ (Zn). Average concentration of Zn was found to be ranged from 2.59 μg/m³ to 5.45 μg/m³. A minimum average Zn concentration of 2.59 μg/m³ at control site and maximum concentration of 5.45 μg/m³ at industrial location. Average concentration of Fe varied from 0.23 μg/m³ to 3.5 μg/m³ with average mean concentration of 1.69 μg/m³. Similarly average minimum Ca concentration of 0.61 μg/m³ observed at control site and maximum concentration of 3.07 μg/m³ at kerbside (K-1) with average mean concentration of 2.28 μg/m³. Average mean V concentration of 0.52 μg/m³ was found with maximum of 1.2 μg/m³ at kerbside (K-2). As regards to Al, average concentration was found to be 0.60 μg/m³ with minimum of 0.01 μg/m³ and maximum of 1.22 μg/m³ at industrial site. The highest mean concentration are found for Zn (3.43 μg/m³),following Ca (2.28 μg/m³), Fe (1.69 μg/m³), Al (0.60μg/m³), V (0.52μg/m³), Mg (0.19 μg/m³) and Pb (0.13 μg/m³). The remaining elements (Ni, Mn, Cd, Cu, and Cr) were found to follow a sequence of decreasing concentration starting from Mg (0.10 μg/m³) and terminating at Cr (0.003 μg/m³). Overall average basis decreasing element concentration trend was Zn>Ca>Fe>Al>V>Mg> Pb>Ni>Mg>Cd>Cu>Cr. However, overall average basis decreasing anthropogenic element concentration trend was Zn>V>Pb>Ni>Cd>Cr and crustal elements trends as Ca>Fe> Al >Mg>Mg>Cu respectively.

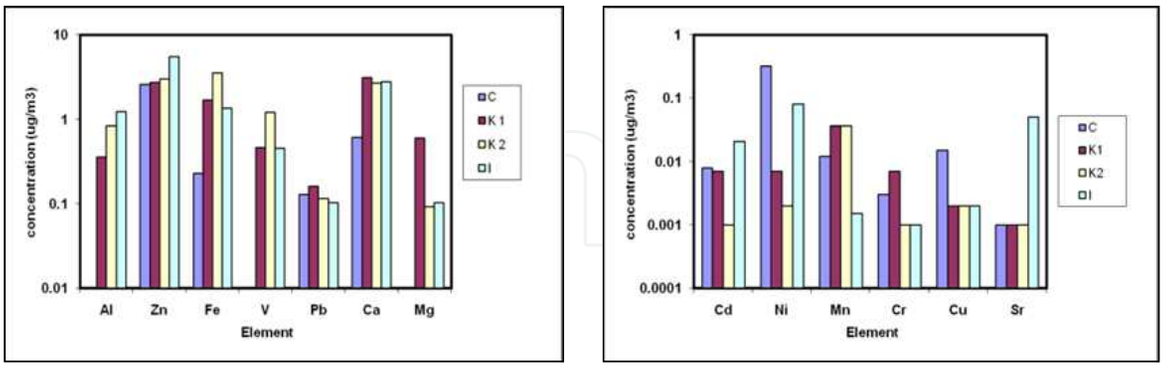

Figure 1. (a & b) Average trace element concentrations at various sites

3.3. Dry deposition estimation

Dry depositions flux for the various elements are estimated as the product of the atmospheric concentration and a suitable deposition velocity. Dry deposition fluxes were calculated using the equation:

$$F = C_i \times V_d \quad (1)$$

Where, F is the dry deposition flux, C_i trace element mean concentration and V_d is the elemental settling velocity.

GESAMP,(1989) suggested that the best values for the dry deposition velocities of Zn, Pb and Cd should be 0.1 cm s^{-1} and those for Al, Fe and Mn should be 1.0 cm s^{-1}. Dry deposition velocities reported by Wu *et al.,* (1994) for Cr and Cd are 0.26 cm s^{-1} and 0.47 cm s^{-1} respectively. In our study, dry deposition estimate for Al, Mn, Fe, Zn, Pb have been undertaken using dry deposition velocity values adopted from GESAMP (1989) and for Cr and Cd dry deposition velocity values adopted from Wu *et al.,* (1994). Deposition velocity values for V, Ca, Sr, Cu and Ni have been adopted from Injuk *et al.,* (1998) and for Mg from Wu *et al.,* (2006).

Site wise variation in dry deposition fluxes of selected trace elements is shown in Fig 2 (a & b). Dry deposition fluxes of elements at industrial site showed the dominance of Ca (1401.63 μg/m²/d) followed by Fe (1162.94 μg/m²/d), Al (1054 μg/m²/d), Zn (470.88 μg/m²/d) and Mg (124.58 μg/m²/d) was observed. At control site, prominent elemental fluxes were Ca (305.68 μg/ m² /d), Zn (223.77 μg/m²/d), V (207.36 μg / m² /d), Fe (198. 72 μg / m² /d) and Ni 168.65μg / m² /d). Whereas at kerb site, the highest dry deposition fluxes were observed for Fe (3024 μg/m²/d), Ca (1538.43 μg/m²/d), Mg (725.76 μg/m²/d), Al (717.12 μg/ m²/d), Zn (258.33 μg/m²/d) and V (248.83 μg/m²/d).

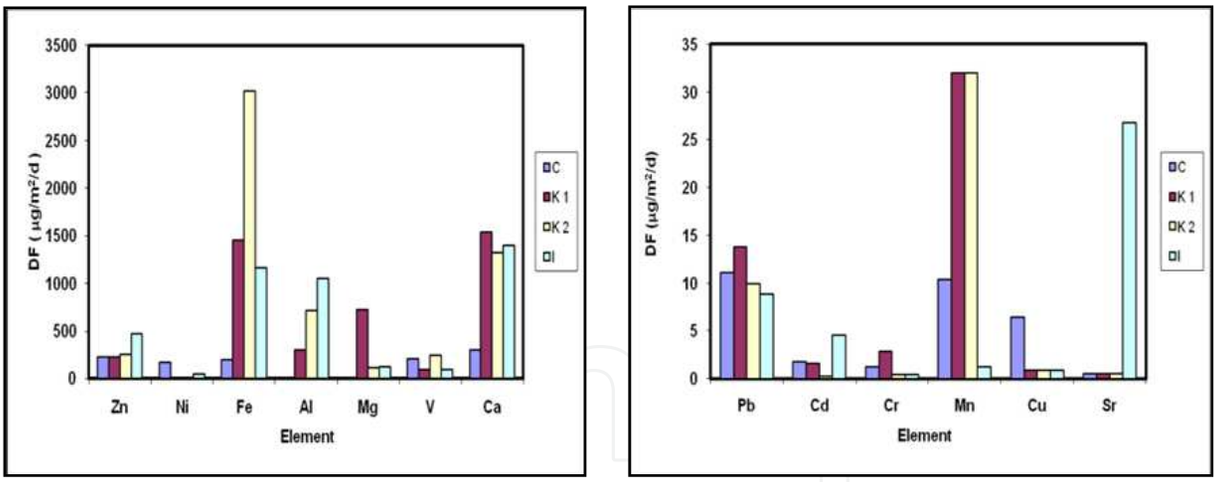

Figure 2. (a & b) Average dry deposition fluxes of trace elements

The average estimated trace element fluxes ranged between 1.218 (Cr) and 1461 (Fe) μg m^{-2} d^{-1}. The dry deposition fluxes for dominant elements were Fe (1461.45μg/m²/d), Ca (1143.43 μg/m²/d), Al (521.64 μg/m²/d), Zn (296.56 μg/m²/d) and Mg 241.014 μg/m²/d) were observed. The deposition fluxes for remaining metal (V, Pb, Cd, Ni, Mn, Cr, Cu, Mg and Sr) ranged from highest of V (161.27 μg/m² /d) to minimum of Cr (1.21 μg / m² /d).

Average deposition fluxes of preliminary crustal elements were significantly higher than the anthropogenic elements. Fe, Mg and Ca were the most significant crustal elements followed

by abundant anthropogenic elements (Zn, V and Ni). However, anthropogenic element Cd and Pb were comparatively small. Al was most abundant crustal elements.

Dry deposition loading (Mg yr^{-1}) of trace elements to the Greater Mumbai was calculated using the elemental dry deposition fluxes from Table 2. Loading of Al, Mn, Fe, Zn, Pb, Cd, V, Ca, Ni, Mg, Sr, Cu and Cr to the entire area of Greater Mumbai ranged from 0.27 Mg yr^{-1} for Cr to 321.7 Mg yr^{-1} for Fe. Fe, Ca, Al, Zn Mg and V were found the highest loading to the Greater Mumbai, which may support the atmospheric pathway as an important source of this metal.

Elements	Estimated deposition rates (Mg yr^{-1})
Al	114.8
Mn	4.2
Fe	321.7
Zn	65.3
Pb	2.4
Cd	0.45
Cr	0.27
Cu	0.50
Ni	11.9
Mg	53.0
Ca	251.7
Sr	1.56
V	35.5

Table 2. Estimate of yearly element deposition rates to Mumbai

3.4. Enrichment of elements

Enrichment factor (EF) is a measure to which trace elements are enriched or reduced relative to a specific source. The enrichment factor (EF) is the ratio of the concentration of any trace metal or ion (X) to Fe in the sample divided by the corresponding ratio in crustal material (Weisel *et al.,* 1984). If the EF is less than 10, trace metal in aerosol has a significant crustal source but elements with enrichment factors greater than 10 are assumed to be due to the other sources rather than background contribution in that sampling region.

Results of the EF computation are plotted in Fig 3. Iron is the common reference element for crustal particles in EF calculations. The order of EF values were Cd>Zn>Pb>V>Ni > Cu> Ca >Sr>Mn>Cr >Mg>Al. Crustal elements such as Al, Ca, Mg, Mn, Cr, Cu and Sr were not enriched to higher than 10 (log EF < 1) indicating that they have originated from local soil dust. Elements such as Cd, V, Ni, Zn and Pb have enrichment factors higher than 10, indicating these elements had significant anthropogenic sources.

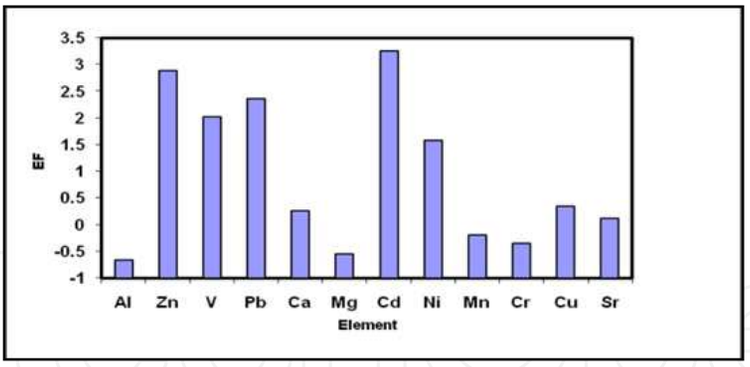

Figure 3. Enrichment of elements in the study area

3.5. Source apportionment

The varimax rotated factor analysis technique based on the principal components (Zhou *et al.,* 2004) has been used in the determination of the source contribution of PM_{10} pollution in Mumbai city. The components or factors rotated had eigen values greater than one after rotation. Based on the results, contribution of ambient PM_{10} by each source at different sites is presented in Fig 4.Overall, the study indicates the diesel and gasoline vehicle exhaust emissions contribute to the extent of 6% to 14% ambient PM_{10} levels. The contribution of vehicular exhaust emissions at kerb side however, varies between 33% and 54%. Resuspended dust due to movement of traffic also contributes significantly (10% to 20% in ambient air and 9% to 17% to kerbside). Marine sources contribute 13 %to 14% to ambient PM_{10} and upto 12% to kerb side PM_{10} levels.

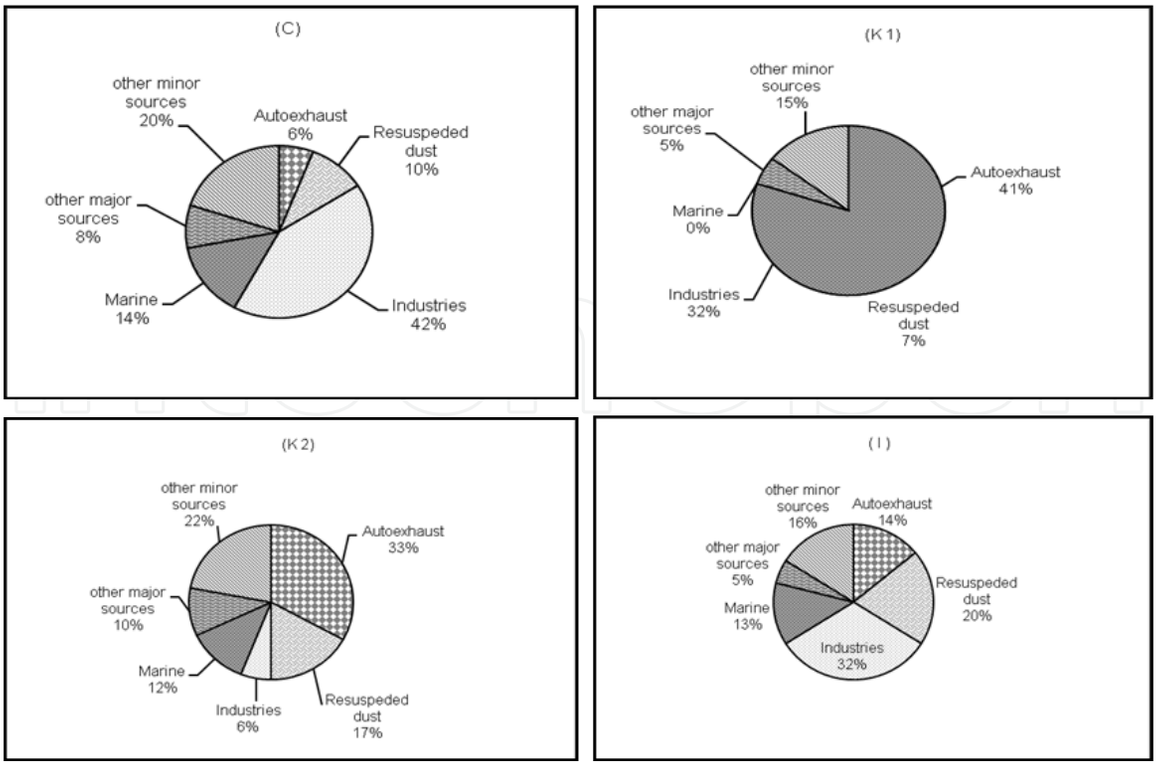

Figure 4. Source apportionment study for PM_{10} using factor analysis

4. Conclusions

Airborne PM samples collected from Greater Mumbai area was used for examine the concentrations of selected trace elements (Zn, Pb, Al, Cd, Ni, Sr, Mn, Fe, Cr, Cu, Mg, V and Ca) and to perform dry deposition flux estimates. Average individual trace element concentrations fluctuated between 0.003 μg/m^3 (Cr) and 3.43 μg/m^3 (Zn). The primarily crustal elemental concentrations were higher than the primarily anthropogenic elemental concentrations. Zn, Fe, Ca, Al, V, Mg and Pb had the highest measured concentration followed by Ni, Mn, Cd, Cu, Cr and Sr. The estimated trace element flux values ranged between 1.2 (Cr) and 1461 (Fe) μg m-2 d-1. The study indicates that crustal elemental fluxes were significantly higher than anthropogenic elemental fluxes. Estimated loading of trace elements to Mumbai region ranged from 0.27 Mg yr-1 for Cr to 321.7 Mg yr-1 for Fe. Higher crustal trace element concentrations and fluxes in this study may be due to re-suspension of dust released during traffic activities and soil erosion. However, the concentration and fluxes of Zn and V (anthropogenic elements) may be attributed to industrial emission. Source apportionment study reveals that PM_{10} is contributed by vehicles exhaust, followed by resuspension of dust and marine sources in Mumbai city.

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