Vertical transport of PM 2.5 and PM 10 and its source identification in the street canyons of Chennai metropolitan city, India

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9 authors, including:

Ezhilkumar Marimuthu Rajendran
Sri Krishna College of Engineering and Technology

Karthikeyan Singaram
Anna University, Chennai

Elena Chianese
Parthenope University of Naples

Giuseppina Tirimberio
Università degli Studi della Campania "Luigi Vanvitelli

Some of the authors of this publication are also working on these related projects:

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Vertical transport of PM$_{2.5}$ and PM$_{10}$ and its source identification in the street canyons of Chennai metropolitan city, India

Marimuthu Rajendran EzhilKumar$^{a,b}$, Singaram Karthikeyan$^b$, Elena Chianese$^{c, *}$, Giuseppina Tirimberio$^c$, Alessia Di Gilio$^d$, Jolanda Palmisani$^d$, Valeria Daniela Miniero$^d$, Pietro Cotugno$^d$, Angelo Riccio$^c$

$^a$ Sri Krishna College of Engineering and Technology, 641 008, Coimbatore, Tamil Nadu, India
$^b$ Centre for Environmental Studies CEG, Anna University, 600 025, Chennai, Tamil Nadu, India
$^c$ Department of Science and Technology, University of Naples ‘Parthenope’, Centro Direzionale, Isola C4, 80143, Napoli, Italy
$^d$ Department of Biology, University of Bari, Via Orabona, 4, 70126, Bari, Italy

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ABSTRACT

Chemical characterization of particulate matter (PM) measured along trafficked roads in Chennai city was performed during the winter season. Several heights, from 3 m to about 38 m above the ground level, and road geometries were taken into account. The daily average coarse (PM$_{10}$) and fine (PM$_{2.5}$) particles concentrations were in the range 72–110 (for PM$_{10}$) and 34–57 μg/m$^3$ (for PM$_{2.5}$), depending on the site. Samples were analyzed in terms of inorganic ions using Ion Chromatography (IC) and elements by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Results indicated the dominance of SO$_4^{2-}$ followed by Na$^+$, Ca$^{2+}$, NO$_3^-$ and Cl$^-$ ions in the coarse fraction; similarly, in the fine fraction ion concentrations decreased in the following order: SO$_4^{2-}$, NH$_4^+$, K$^+$ and Ca$^{2+}$. Among the elements, crustal element (Al, Fe) and Zn concentrations were much higher (accounting about 90% of the total elemental concentration) than other toxic elements (Cr, Cu, Mn, Ni, Pb, Sn, Ti and V). No element showed a significant dependence on height, except for calcium at site ‘Velachery’ which contributed significantly to the abundance of the coarse fraction mass. In order to identify the major sources of air pollution, the collected data were analyzed using Positive Matrix Factorization (PMF), allowing to highlight five dominant pollution sources/factors: secondary PM, road traffic, biomass burning, sea spray and crustal erosion. Overall, the present study provided a new insight for the source apportionment of monitored pollutants in the Chennai city.

1. Introduction

Given the rapid rate of urbanization, in 2018 in India there were five megacities with a population of 10 million or more people: Delhi, Mumbai, Kolkata, Bangalore and Chennai (United Nations, Department of Economic and Social Affairs, 2019). Increasing urbanization, together with industrial development and vehicular emissions, contributed significantly to particulate matter (PM) concentration in the ambient atmosphere of plains (Safai et al., 2008), coastal areas (Sharma et al., 2012) and mountainous regions (Sharma et al., 2014b; Kuniyal et al., 2015). Interestingly, the contribution to aerosol from anthropogenic sources in the Asian region slightly decreased during the last decade, but not in India, where both PM$_{10}$ and PM$_{2.5}$ concentrations increased by more than 20% from 2006 to 2010 (Li et al., 2017), notably in urban and industrial locations (Mohan et al., 2012). Although there has been an increased focus on PM emissions control in recent years, concentrations are still found to exceed the Indian National Ambient Air Quality Standards (NAAQS), i.e. 100 μg/m$^3$ for the PM$_{10}$ daily average concentration and 60 μg/m$^3$ for the PM$_{2.5}$ daily average concentration (CPCB, 2020).

The analysis of data collected in Delhi by CPCB in the last months (in association with lock down due to Covid emergency) clearly indicate the influence of vehicular traffic and combustion due to industrial, residential and commercial activities. It was observed that in the pre-lockdown period (until 24 March 2020), PM$_{10}$ and PM$_{2.5}$ reached a maximum hourly concentration of 244 μg/m$^3$ and 114 μg/m$^3$.

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* Corresponding author.

E-mail address: elena.chianese@uniparthenope.it (E. Chianese).

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respectively, and decreased to 127 and 21 $\mu g/m^3$ during lockdown period (until mid-April), within NAAQS (CPCB, 2020). Therefore, identification of PM sources is necessary to develop air quality improvement strategies to control ambient PM concentrations through targeted actions; also, the different sources of PM may determine different PM chemical properties and, in this manner, they can exert various health effects (Deng et al., 2019).

The identification of air quality improvement strategies relies on the chemical composition and physical properties of PM. Indeed, it is widely known that the effects of PM depend on its size distribution and composition (Hwang et al., 2018; Mukherjee and Agrawal, 2017). The size distribution may vary over a wide range of values, from nano-to micro-particles, and composition mainly consists of inorganic ions, organic carbon (OC), elemental carbon (EC), crustal elements and toxic metals. In India, high enrichment factors have been reported for various metals including Pb, Zn, Cu, Ni and Cr in many studies (Meena et al., 2016; Masih et al., 2019). Using SEM-EDX analysis, Srivastava et al. (2009) reported that particles were primarily of anthropogenic origin irrespective of size in polluted areas, e.g., traffic intersections. High concentrations of inorganic ions have also been reported; they were generally reported to be alkaline with neutralization of acidity mainly due to cations like NH$_4^+$ and carbonates (Sharma et al., 2019). The natural sources of aerosols like minerals and sea salts have been found to affect the PM concentration and composition: marine aerosols dominate over coastal regions, while aerosols of a crustal and anthropogenic origin dominate over continental interiors (Kulshrestha et al., 2009; Amadio et al., 2011; Di Gilio et al., 2015). Further, using satellite fire radiative power (FRP) observations, Liu et al. (2018) found that biomass burning may explain a large part of the variance of PM$_{10}$ concentration in the pre- and post-monsoon season. Biomass burning has also been addressed as a major concern for the adverse effects on regional climate due to high loading of carbonaceous particles (Lawrence and Lelieveld, 2010).

In densely urbanized areas, the PM atmospheric pollution may be exacerbated at specific ‘hot spots’, e.g. traffic nodes. For example, the ground level PM$_{10}$ in Mumbai ranged from 50 to 200 $\mu g/m^3$ in residential areas (Kothai et al., 2009) but achieved about 1000 $\mu g/m^3$ at busy traffic nodes (Vinod Kumar et al., 2001). Traffic nodes also represent a privileged point of observations to study people’s exposure to PM atmospheric pollution, since footpaths are used by pedestrians in city centers and by vendors in suburbs. Moreover, they are generally surrounded by shops and commercial complexes with different height-to-width ratio, which may influence the dispersion of pollutants. At present, substantial efforts have been made to investigate the horizontal variability of air pollutants and epidemiological studies have taken advantage of resulting improvements in exposure assessment. However, little is known about the vertical distribution and only a few studies have investigated the vertical variability and their results are not consistent. Tripathi et al. (2004) selected different street configurations and street environments in Mumbai and found no significant difference in the concentration levels of particulate matter and trace metals at different heights, compared to the first-floor level. Kalaiarasan et al. (2009) studied traffic-generated airborne particles in naturally ventilated multi-storey residential buildings at different heights in Singapore, and found a mean particle mass concentration at high-level floors higher than at mid-level floors. Chan et al. (2005) studied the distribution of suspended particulate at different heights in Beijing, and found complex vertical profiles due to various factors considered to be influential, i.e., prevailing wind direction and street configuration, in particular height-to-width ratio, meteorological factors such as temperature inversions close to the surface, as well as the proximity of trunk road and construction activities. Shen et al. (2011) conducted an intensive sampling of aerosol particles from ground level and 100 m during a strong pollution episode during the winter in Xi’an, China, noting that major ionic species were slightly lower at the ground than at 100 m.

On the basis of these considerations, in this work, we sampled PM$_{10}$ and PM$_{2.5}$ at different heights in the urban area of Chennai. Here, we selected three different road geometries (a street asymmetrically surrounded by buildings of different heights, an open street, and a street canyon) and building types (commercial, residential, public offices and/or mixed) and attempted to identify PM sources at different heights using correlation matrix and factor analysis.

Results were interpreted in the light of possible sources, using positive matrix factorization (PMF).

Although many studies, based on chemical characterization of particulate matter and its source apportionment, have been reported from highly polluted Indian cities (Gummeneni et al., 2011; Gupta et al., 2007, 2012; Selvaraju et al., 2013; Sharma et al., 2014a), this is the first study concerning the influence of road geometries on PM concentration and composition in the Chennai region.

2. Materials and methods

2.1. Sites description

Chennai, formerly known as Madras, lies at the latitude between 12°50’ and 13°17’ N and longitude between 79°59’ and 80°20’ E and covers about 1189 km$^2$. It has a tropical wet and dry climate and is strongly influenced by the monsoon cycle. Chennai is the capital city of the Tamil Nadu state. Notably, the population in this state grew by 16% from 2001 to 2011, with an increase of the urban share of 27% (Commissioner for Census, 2014). The construction of skyscrapers has been discouraged and this has led to an expansion of the city in neighboring territories with an increase in commuting times and private vehicles. The total number of registered vehicles in Chennai city was 3,076,416 according to the 2011 census (Statistical Handbook of Tamil Nadu, 2014). Chennai also had the highest vehicle density, about 690 vehicles per km of road length, compared to the average of Tamil Nadu, 123 vehicles per km of road length (DEAR, 2019). It has a large industrial base anchored to automobile, software services, medical tourism, hardware manufacturing and financial services sectors. 30% of the Indian automotive industry is located in Chennai and for this reason it is often called the “Detroit of India” (Shira et al., 2012). Other important industrial sectors are petrochemicals, textiles and apparel. Based on the 2011 census, about 34,260 companies have been identified in this city. The Chennai and Ennore ports contribute greatly to its economy. Due to the high urban population share and number of economic activities, total suspended and respirable PM consistently exceeded the air quality standards during the last years, in particular at traffic junctions, according to the Environmental Information System Centre of Tamil Nadu (2019).

In this study, three different road geometries were selected to investigate PM distribution and composition. The first position (OS) is an asymmetrical canyon; one side of the road is occupied by tall commercial and residential buildings and the other side is an open ground with a vegetative cover. This site is closer to the coastline, which suffers from a high marine influence in terms of dispersion and contribution to air pollutants. The roadway serves as the main route for the IT (Information Technology) corridor along the Old Mahabalipuram Road (OMR) for commuters from the north and west. The second position (AS) is an asymmetrical canyon, with buildings on both sides of the road, but with different heights. This location is described as a residential area built with tall residential apartments and is close to an important public transport depot. The location is along a 100-foot road and another road to the IT corridor located along OMR for commuters from the western side of those who use Grand Southern Trunk (GST) road. The third (SC) position is a symmetrical canyon, with buildings of equal height on both sides and an elevated railway corridor along the median of the road. This area also has residential apartments and private hotels of high heights. There is a large public bus terminal located near the sampling location and the road connects the commuters entering Chennai from the
northwestern position. This study was focused to understand the vertical profile of air quality in the urban street canyons. The streets considered in this study where occupied by buildings ranging from 3 m to 38 m high. Therefore, based on the dwelling units’ height, we decided to study the air quality at three different heights, minimum, maximum and intermediate, along the buildings in each street corresponding to 3, 37 and 16 m from ground level, respectively.

In this work the results concerning both the coarse and fine fraction are presented and discussed.

2.2. Sampling

Samples were collected during the winter season (daily measurements, from 10 a.m. to 10 p.m.) from January to February, with a total of 90 valid samples, 45 for PM$_{10}$ and 45 for PM$_{2.5}$, including all locations, heights (3, 16 and 37 m from ground level) and size fractions. In this sampling campaign, three Ambient Fine Dustsamplers (AFDS) (model IPM FD5, made by Instrumex, India) were used for simultaneous sampling in all three selected heights. AFDS is capable of collecting PM$_{10}$ and PM$_{2.5}$ particles with a Well Impactor Ninety Six (WIN5) setup. The PM$_{10}$ and PM$_{2.5}$ particles were collected using polytetrafluoroethylene (PTFE) filters (46.2 mm diameter). The samples were collected at the flow rate of 16.67 L/min. Desiccation of filter papers were done in a controlled chamber for a period of 24-h before and after sampling to reduce the moisture in filter papers. Later the filter papers were weighed in a gravimetric balance with an accuracy of ±2.5µg in a stabilized laboratory condition under normal room temperature.

2.3. Analytical methods

PM filters were cut in different portions, each of them destined to a different analytical method (aimed to determine the inorganic and elemental costituents): a portion used for mineralization and elemental composition determination, a portion used for soluble fraction extraction and measurements with ionic chromatography, as described below.

2.3.1. Ionic analysis

The portion of each filter destined to the analysis of soluble components was extracted for 15 min with 15 ml of ultrapure water in a microwave system (SONICAL, Vetrochimica srl). Solutions were filtered (polar filters, porosity of 0.20 µm) and then analyzed for anions (Cl$^-$, SO$_4^{2-}$, NO$_3^-$, NO$_2^-$, PO$_4^{3-}$, HCOO$^-$, CH$_3$COO$^-$, C$_6$H$_5$O$_2^-$) and cations (Na$^+$, Ca$^{2+}$, K$^+$, NH$_4^+$, Mg$^{2+}$) contents, in a double column Dionex 1100 system. Eluents, standards and column characteristics, together with method compliance and accuracy, were described in Chianese et al. (2019).

2.3.2. Elemental analysis

The elemental composition (Al, Fe, Zn, Cr, Fe, Mn, Ni, Pb, Sn, Ti and V) of PM$_{10}$ and PM$_{2.5}$ samples was determined by ICP-MS (inductively coupled plasma-mass spectrometry). One-fourth of the filter had been acid digested in 8 ml nitric acid and 2 ml hydrogen peroxide solution, coupled plasma-mass spectrometry). One-fourth of the filter had been acid digested in 8 ml nitric acid and 2 ml hydrogen peroxide solution, according to the EN 14902:2005 procedure, in a microwave system (Milestone, Ethos D model). The digested solutions were diluted to 50 ml with deionized water and analyzed by ICP-MS (ThermoScientific™ iCAP Q system by ThermoFisher Scientific) (Amodio et al., 2014; Di Gilio et al., 2017). Multi-element standard solutions in a dynamic concentration range from 20 to 2500 ppt were daily analyzed for the quality control of the analytical procedure and samples quantification. Moreover, a multielement internal standard (20 ppb) was added both in standard solutions and digested samples. The determination of the recovery percentage of the analytical procedure was carried out according to EN 14902:2005 and recoveries varied in the range from 87% to 106%. The limit of quantification (LOQ) values for all the investigated elements were in the range from 0.23 ng/ml (0.84 ng/m$^3$) to 7.1 ng/ml (25 ng/m$^3$).

2.4. Source apportionment

In this work we used PMF, a well-known multivariate receptor model that analyze a series of observations simultaneously to determine the number of sources, their chemical composition and their contributions to each observation (Pant and Harrison, 2012; Banerjee et al., 2015; Kothai et al., 2011).

PMF decomposes the speciated data matrix X of dimensions n and m (where n is number of samples and m the number of chemical species) into two sub-data matrices, the factor profiles, g and factor contributions, f, by minimizing the residual error, e, according to the following formula:

\[ X = \sum_{i=1}^{p} g_{it}f_{it} + e 
\]

In equation (1), $p$ is the number of selected factors. For this, a weighted least square approach is used, which involves minimization of an objective function Q, given as:

\[ Q = \sum_{i=1}^{n} \sum_{j=1}^{m} e_{ij}^2/s_i 
\]

$s$ is a weight used to adjust the influence of each data point, depending on the confidence in the measurement. Further, each element of matrices $g$ and $f$ is constrained to be non-negative, e.g. $g_{ik}$ ≥ 0 and $f_{ij}$ ≥ 0.

The procedures of Hopke (2016) were applied to estimate the weights for the PMF analysis, based on the detection limit values. First, data below the minimum detection limit were identified; those data, as well as the missing values, were replaced by the geometric mean for that species; next, the uncertainty corresponding to these data was increased by three times the average geometric concentration of the species to impact its impact on the estimation procedure.

In the current study, different numbers of sources (from three to nine) were explored by applying a trial and error method in order to determine the optimal number of sources. In each instance, the model was run in the default robust mode to decrease the influence of extreme values in the PMF solution, with twenty replica and randomized initial values, to ensure the model least-squares solution represented a global rather than local minimum and the rotational FPEAK variable was held at the default value of 0.0. In this study the minimum number of samples (n) for factor analysis should be such that $n > 30 + (V + 3)/2$, where $V$ represents the number of variables; forty-five samples for each PM size fraction (aggregating all heights and sites) were considered for factor analysis. All the variables were analyzed using the signal-to-noise criterion and only strong variables (20 out of 29) were retained as inputs to PMF. Five factors were retained as an interpretable final solution in terms of the nature of the sources in the study area and their known physical meaning.

3. Results

Samples were collected at three sites: Taramani (OS), Velachery (AS) and Arumbakkam (SC). As indicated in Fig. 1, the highest concentrations for PM$_{10}$ occurred at sites AS and SC, with an overall median value over the three heights of 110 and 107 µg/m$^3$, respectively. Daily concentrations at site AS were within the range 77–180 µg/m$^3$ and within the range 22–133 µg/m$^3$ at site SC. The lowest concentrations were measured in OS (median value of 72 µg/m$^3$). Similarly, the highest PM$_{2.5}$ concentrations occurred in Velachery (47 µg/m$^3$) and Arumbakkam (57 µg/m$^3$).

Taramani was also a site monitored in previous studies. Gupta and Kumar (2006) monitored the PM concentration from 1991 to 2003 in
many Indian sites, including three locations in Chennai: Thiruvottiyur, an industrial site, General Hospital, a commercial site, and Taramani. The PM$_{10}$ concentration during the winter months in Taramani was in the range of 23–101 $\mu$g/m$^3$ with an average of 52 $\mu$g/ m$^3$, lower than that measured in both the industrial (in the range of 8–171 $\mu$g/m$^3$) and commercial sites (in the range of 18–212 $\mu$g/m$^3$). Gupta and Kumar (2006) also demonstrated that the PM$_{10}$ levels generally improved at many sites in that period but not in Taramani where it has increased by around 5% per year. Pulikesi et al. (2006) have monitored the respirable and total suspended particulate matter along with surface ozone concentration, NO$_x$, and meteorological parameters at five sites, including Taramani, in the summer of 2005, and found a concentration of respirable PM of 102 $\mu$g/m$^3$. The PM values in Chennai during the period of 2001–2004 were also monitored in upwind, traffic and commercial sites and reported by Oanh et al. (2006).

However, all these studies have been restricted at detecting the prevailing air quality levels, without speciation or differentiation with respect to vertical height (Chan and Kwok, 2000; Hang et al., 2018, 2017; He and Dhaniyala, 2012). The vertical distribution of pollutants in an urban context depends on the street configuration, e.g. the height/width ratio; the release height and distance from sources are other important factors influencing air pollutants dispersion in a street canyon. In this work, PM$_{10}$ and PM$_{2.5}$ levels have been monitored at three heights, approximately at 2, 16 and 37 m from the ground level. The concentration distributions of particulate fractions at each sampling point are presented in Fig. 1 as a function of height. The KruskalWallis H-test was used to test if the difference between medians within each site at different heights were statistically significant, i.e. if there was a significant trend along the vertical direction. No trend was detected for both the PM$_{10}$ and PM$_{2.5}$ fractions, apart for AS, for which the PM$_{10}$ concentration at the lower level was significantly higher than those at medium and higher levels (reduction of about 30% from the lowest to the middle level), and for SC, for which the PM$_{10}$ concentration at the lower levels was significantly higher than those at the higher level, probably due to resuspension effects. Actually, due to the geometry of the AS and SC, other factors may influence the PM vertical distribution. In fact, it was observed that the formation of air vortices related to the intrusion of air from the upper levels may generate a different pollutants distribution inside the canyon with, in specific wind condition, a decreasing concentration along with height above (Vardoulakis et al., 2003). In addition, in Wang et al. (2011) it was discussed the effect of the thermally induced buoyancy in determining air circulation and pollutants distribution within the street canyons; also in this case, thermal effects may determine an accumulation of pollutants within the street.

3.1. Ionic and elemental composition

Tables 1–3 and Fig. 2 show the ionic composition and elemental composition; these parameters allow us to evaluate PMs toxicity, to investigate some aspect as the formation of secondary PM, the contribution of biomass burning and of marine aerosol. A significant contribution in terms of total ion concentration was observed in all the three locations. Precisely, ions accounted for 40%, 48%, 32% of PM$_{2.5}$ and 30%, 38%, 27% of PM$_{10}$ mass at OS, AS and SC, respectively (data averaged over the three heights). Further, each single ion differently contributed to fine and coarse PM fractions, included in both fractions. Among secondary ions (i.e. sulphate, nitrate and ammonium), sulphate was the most abundant, followed by nitrate and ammonium; moreover, nitrate was predominantly present in the coarse fraction while ammonium in the fine fraction. The other two most abundant cations, i.e. calcium and sodium, together with chloride were mostly detected in the coarse fraction. The identified ionic composition in PM$_{2.5}$ was in the descending order of: $SO_4^{2-} > NH_4^+ > K^+ > Ca^{2+}$ with a negligible contribution from all others. Similarly, in the PM$_{10}$ fraction ions were in the order of: $SO_4^{2-} > Na^+ > Ca^{2+} > NH_4^+ > NO_3^- > Cl^-$ with a negligible contribution from all others. Similar reports were registered in previous studies at Chennai (Srimuruganandam and Nagendra, 2012a, 2012b; Chithra and Nagendra, 2013) and other urban areas (Aggrilo et al., 2013; Riccio et al., 2016, 2017; Jain et al., 2018). Since sampling was performed during winter, there were frequent biomass combustions by slum dwellers for heating and cooking (Marullo-Tovar et al., 2015; Kuniyal et al., 2015), and this may explain the abundance of potassium next to major secondary ions in PM fine fraction. It was also found that potassium and calcium may originate from lubricant oils used in vehicles (Popovicheva et al., 2014; Riccio et al., 2017), and potassium from tire and break wear (Srimuruganandam and Nagendra, 2012b). Ions such as Mg$^{2+}$, Na$^+$ and Cl$^-$ have possible origin from crustal and marine sources (Srimuruganandam and Nagendra, 2012b). The estimated chloride to sodium ratio was in the range 0.7–3.0 with an average of 1.0, slightly lower than the stochiometric value of 1.2 in sea water. Deviations from the sea water ratio may occur both because chlorine may desorb as hydrochloric acid during the aerosol aging process, due to sulphate (or nitrate) substitution, and because chloride emission may be also linked with soil dust, solid waste and biomass burning (Souza et al., 2014; Satasangi et al., 2017).

Since the study area is located close to the Bay of Bengal, sea spray may play a key role in PM source apportionment. Na$^+$ was used to determine the sea-salt (SS) contribution in the aerosol phase since the water-soluble Na$^+$ concentration is assumed to originate solely from seawater. Specifically, sea-salt aerosol concentration was calculated as:

$$\text{sea salt}(\mu g/m^3) = Cl^- + 1.47 \times Na^+(\mu g/m^3) \quad (3)$$

Fig. 1. Box-plots of PM$_{10}$ (left) and PM$_{2.5}$ (right) concentrations for the three sites, OS, AS and SC, and heights, L, M, U.
Table 1
Mean, standard deviation (SD), minimum and maximum of elemental concentrations in the coarse (PM10) and fine (PM2.5) fractions for the three sites. Concentrations are in ng/m3. ‘lod’ stands for ‘limit of detection’ and “SS” for sea salt.

<table>
<thead>
<tr>
<th>Element</th>
<th>PM10</th>
<th>PM2.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>2.9</td>
<td>6.2</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>2.2</td>
<td>5.0</td>
</tr>
<tr>
<td>K⁺</td>
<td>0.7</td>
<td>1.9</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>0.2</td>
<td>1.0</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>2.5</td>
<td>4.5</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>2.1</td>
<td>6.4</td>
</tr>
<tr>
<td>NO₂⁻</td>
<td>2.1</td>
<td>2.6</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>9.4</td>
<td>18.4</td>
</tr>
<tr>
<td>SS</td>
<td>6.3</td>
<td>15.6</td>
</tr>
<tr>
<td>Na⁺</td>
<td>3.4</td>
<td>5.4</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>1.0</td>
<td>0.8</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>&lt; lod</td>
<td>0.1</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>0.1</td>
<td>0.4</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>&lt; lod</td>
<td>0.6</td>
</tr>
<tr>
<td>NO₂⁻</td>
<td>&lt; lod</td>
<td>&lt; lod</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>6.5</td>
<td>10.8</td>
</tr>
</tbody>
</table>

Table 2
Mean, standard deviation (SD), minimum and maximum of elemental concentrations in the coarse (PM10) fraction for the three sites. Concentrations are in ng/m3. ‘lod’ stands for ‘limit of detection’.

<table>
<thead>
<tr>
<th>Element</th>
<th>OS</th>
<th>AS</th>
<th>SC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>2240</td>
<td>251</td>
<td>661</td>
</tr>
<tr>
<td>Ti</td>
<td>25.8</td>
<td>191</td>
<td>119</td>
</tr>
<tr>
<td>V</td>
<td>&lt; lod</td>
<td>&lt; lod</td>
<td>&lt; lod</td>
</tr>
<tr>
<td>Cr</td>
<td>28.9</td>
<td>71</td>
<td>17.2</td>
</tr>
<tr>
<td>Mn</td>
<td>60.6</td>
<td>50</td>
<td>85.3</td>
</tr>
<tr>
<td>Fe</td>
<td>685</td>
<td>182</td>
<td>304</td>
</tr>
<tr>
<td>Ni</td>
<td>0.7</td>
<td>0.7</td>
<td>11.2</td>
</tr>
<tr>
<td>Cu</td>
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<td>32.3</td>
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<tr>
<td>Zn</td>
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<td>Sn</td>
<td>347</td>
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<tr>
<td>Pb</td>
<td>83.8</td>
<td>150</td>
<td>117</td>
</tr>
</tbody>
</table>

Table 3
Mean, standard deviation (SD), minimum and maximum of elemental concentrations in the fine (PM2.5) fraction for the three sites. Concentrations are in ng/m3. ‘lod’ stands for ‘limit of detection’.

<table>
<thead>
<tr>
<th>Element</th>
<th>OS</th>
<th>AS</th>
<th>SC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>296</td>
<td>50</td>
<td>246</td>
</tr>
<tr>
<td>Ti</td>
<td>25.2</td>
<td>10.1</td>
<td>3.2</td>
</tr>
<tr>
<td>V</td>
<td>1.9</td>
<td>0.2</td>
<td>3.0</td>
</tr>
<tr>
<td>Cr</td>
<td>35.8</td>
<td>0.3</td>
<td>16.6</td>
</tr>
<tr>
<td>Mn</td>
<td>60.6</td>
<td>197</td>
<td>17.4</td>
</tr>
<tr>
<td>Fe</td>
<td>228</td>
<td>271</td>
<td>180</td>
</tr>
<tr>
<td>Ni</td>
<td>23.5</td>
<td>22.5</td>
<td>22</td>
</tr>
<tr>
<td>Cu</td>
<td>2.2</td>
<td>111</td>
<td>3.4</td>
</tr>
<tr>
<td>Zn</td>
<td>113.</td>
<td>186</td>
<td>180</td>
</tr>
<tr>
<td>Sn</td>
<td>25.0</td>
<td>182</td>
<td>83.0</td>
</tr>
<tr>
<td>Pb</td>
<td>45.4</td>
<td>18.2</td>
<td>83.0</td>
</tr>
</tbody>
</table>

where 1.47 is the seawater ratio of \((Na^+ + K^+ + Mg^{2+} + Ca^{2+} + SO_4^{2-} + HCO_3^-) / Na^+\) (Millero, 2006). This equation explicitly account for the contribution from other non-sea-salt components (K⁺, Mg²⁺, Ca²⁺, SO₄²⁻ and HCO₃⁻) in the sea-salt mass and by-pass the problem of the loss of Cl⁻ mass through Cl⁻ depletion processes (Di Giilo et al., 2015; Bigi et al., 2017). As can be seen from Table 1, chlorine and sodium are mainly concentrated in the coarse fraction (Kopanakis et al., 2012), and consequently marine salts.
contribute predominantly to the coarse mode. The contribution of sea salt to the PM$_{10}$ fraction varied between 4.8% and 15.6%, corresponding to an average contribution of 8.7% to overall PM$_{10}$ mass. Even though SO$_2^-$, K$^+$ and Ca$^{2+}$ can have a marine origin, more than 90% of their contributions derive from nSS (non sea salt) sources.

Zn, Al and Fe formed the dominant trace elements in the PM$_{10}$ fraction, with an average percentage of 2.8%, 1.5% and 0.6% for the three sites, respectively. The remaining elements altogether formed less than 0.7% of the total mass in this fraction. Zn, Al and Fe also constituted the dominant trace elements in the finer fraction, with a negligible contribution (< 0.8%) from all other elements. Tripathi et al. (2004) have reported a value of 1.7% (for the sum of Zn, Al and Fe) in suspended particulate matter for a site in a residential area in Mumbai.

The ionic and elemental contribution was also scrutinized in order to verify if there was a dependence on the height. In all cases, both for the coarse and fine fraction, no significant variation with height was found for any element or ionic species, apart for calcium in the PM$_{10}$ fraction at the AS site. In fact, the mean calcium concentration at the lower level in AS was $7.8 \pm 1.1 \mu g/m^3$, significantly higher than that measured at the medium and upper levels, $4.2 \pm 1.3$ and $3.1 \pm 0.9 \mu g/m^3$, respectively. This result confirmed the potential resuspension source responsible of the highest PM concentration reported above for the same site.

3.2. Source apportionment

The mass fraction distribution of species was used to identify the sources of PM. The most realistic solution comprised five factors, which were secondary PM, road traffic, biomass burning, sea spray and crustal erosion. Figs. 3 and 4 show the contribution of each element to PM$_{10}$ and PM$_{2.5}$. Fig. 5 also shows the contribution of each source to the PM composition for the two fractions.

The first source can be attributed to oil combustion and secondary PM, mainly composed by sulphate and nitrate, counterbalanced by ammonia. Moreover, other important elements, copper, vanadium, zinc and lead with abundances between 0.1% and 0.6%, are explained by this factor. Vanadium in crude oil is a key tracer of fossil fuel/heavy oil combustion from heavy fuel oil boilers and ship engines (Moreno et al., 2010). Sulphate may have different origins, because it is formed in the condensed phase of atmospheric aerosol, following oxidation of sulphur dioxide (Huang et al., 2014), but also from marine aerosol as documented in the EPA’s SPECIATE and European SPECIEUROPE databases (Simon et al., 2010); moreover sulphate has been identified as a distinct
secondary product of heterogeneous reactions in the atmosphere, such as in-cloud processing for sulphate neutralization with calcium and potassium ions (Liu et al., 2005). The oil refineries, oil-fired power plant, and ports near the sampling sites in addition to marine aerosol could have contributed to this factor in the study area.

The second source explains a large part of the variability of Fe, Cu, Sn, Cr, Ni, Sb, and Mo as markers of traffic (Liu et al., 2015; van der Gon et al., 2007). Although the profile of trace metal concentrations in non-exhaust particulate matter is unique for every region and varies based on parameters such as traffic volume and pattern, vehicle fleet characteristics, driving and traffic patterns, climate and geological characteristics of the region (Amato et al., 2011a; Duong and Lee, 2011), several elements, e.g. Cu, Zn, Ba, Sb, Mn, typically characterize non-exhaust emissions of tire wear, lubricating oil combustion, and vehicle brake abrasion (Pant and Harrison (2013) and references therein). Also, some elemental markers, Cu, Mn, Fe, Zn, Ba, Sn, Ni, Mo and Sb, have been used for exhaust vehicular emissions (Amato et al., 2011b; Waked et al., 2014; Pant et al., 2015).

The third factor can be a combination of biomass and garbage burning, and cooking, due to the contribution from potassium (Shivanagendra et al., 2018; Srimuruganandan and Nagendra, 2012a); this factor explains about 70% its abundance. It is widely known that biomass burning in India represents an important contribution to gaseous air pollutants (CO, NH₃, NOₓ, SO₂, volatile organic compounds),

Fig. 3. Element profiles for PM₁₀ (bars correspond to the left y-axis (in ng/m³) and red dots correspond to the right y-axis (in percentage) of the factors determined by positive matrix factorization.
and particulates matter, especially during the winter. The Tamil Nadu state, together with that of neighboring Andhra Pradesh, is one of the most important contributors to crop residue burning (Jain et al., 2014). The importance of the detrimental effects of biomass combustion was highlighted in a study concerning biomass combustion in the Tamil Nadu state (Balakrishnan et al., 2002). The authors reconstructed the 24-hr exposure profile; it was found that women involved in cooking activities, more than 60% of individuals in the sample, were exposed for more than 3 h in cooking activities; concentrations of respirable particulate matter ranged from 500 to 2000 μg/m³ during cooking in biomass-using households, and average 24-hr exposures ranged from 90 ± 21 μg/m³ for those not involved in cooking, to 231 ± 109 μg/m³ for those who cooked, while the 24-hr exposures were around 82 ± 39 μg/m³ for those in households using clean fuels (with similar exposures across household sub-groups). Nearly 10% of Chennai population lives in disadvantaged and slum-like settings where biomasses are systematically used for domestic cook stoves (De Gennaro et al., 2016; Dambruoso et al., 2014; Amodio et al., 2012).

Chennai is strongly influenced by the sealand breeze phenomena, since it is located near the Bay of Bengal; for this reason sea spray contributes significantly to PM, as evidenced by the fourth factor, enriched with sodium and chloride, which contributed > 80.0% of their total element concentrations. As mentioned above, the Cl/Na ratio in both size fractions was close to the ratio for seawater, and the Cl and Na

![Fig. 4. Element profiles for PM₂.₅ (bars correspond to the left y-axis (in ng/m³) and red dots correspond to the right y-axis (in percentage) of the factors determined by positive matrix factorization.](image-url)
concentrations correlated well ($R^2 > 0.8$), confirming the contribution of sea salt spray.

Finally, the last factor was associated to crustal material, due to the larger contribution from Al, Ca, Fe, and Ti then to the other factor profiles. These elements contributed over 90.0% to their total measured element concentrations in PM$_{10}$. The concentrations of these elements were highly correlated, indicating a probable common source. Roads and subways were being repaired and constructed around the sampling area during the sampling period, and these activities may have contributed to supplying these elements to PM.

4. Conclusions

PM sampling was carried out during the winter season along trafficked roads in Chennai city (India). The purpose was to identify potential PM sources and to related ionic and elemental components with heights and road geometries. Collected data highlighted that the mean daily concentration values of PM$_{10}$ and PM$_{2.5}$ varied in the range 72–110 and 34–57 $\mu$g/m$^3$ respectively, in the investigated sites, depending on the site characteristics and height from the ground. Anyway, no significant differences in PM concentrations were determined related to height except for urban residential site (AS), where the concentration at middle heights increased of about 30% respect to PM mean concentration, and in SC, although less evident, probably because of resuspension effects due to road abrasion and a contribution from air flow and thermal effects within the canyons.

Likewise, elemental and ion components generally showed no significant dependence on height, apart for calcium at the AS site. PMF data treatment allowed to highlight five dominant pollution sources/factors: secondary PM, road traffic, biomass burning, sea spray and crustal treatment. Overall, the present study provided a new insight for the source apportionment of elemental and ion components in PM of selected urban and residential sites in Chennai city.

Also, an elevated level of PM$_{10}$ in AS and of PM$_{2.5}$ in SC were observed in this work, which were higher than the National Ambient Air Quality Standards (NAAQS) prescribed for India. In general, the AS and SC sites showed a poor air quality in comparison to OS for both PMs. Further, in OS people residing in greater heights are exposed to higher PM concentration then AS, whereas, in case of SC, people residing at mid-level heights get maximum exposure due to the viaduct position. Hence, this study provides an evidence against the general thought that people living at greater heights avoid getting exposed to poor air quality, and the quality of air in urban street canyon is greatly influenced by the street geometry.

Credit author statement

Marimuthu Rajendran Ezhil Kumar, Conceptualization; Investigation; Methodology; Writing-original draft preparation; Writing - review & editing. Singaram Karthikeyan, Conceptualization; Project administration; Resources; Supervision; Writing-original draft preparation; Writing - review & editing. Elena Chiarese, Data curation; Investigation; Validation; Writing-original draft preparation; Writing - review & editing. Giuseppina Tirimiero, Investigation; Writing-original draft preparation. Alessia Di Gilio, Investigation; Writing-original draft preparation. Jolanda Palmisani, Investigation; Writing-original draft preparation. Valeria Daniela Miniero, Investigation. Pietro Cotugno, Investigation. Angelo Riccio, Data curation; Formal analysis; Methodology; Validation; Writing-original draft preparation; Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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