Effect of modes of transportation on commuters' exposure to fine particulate matter (PM$_{2.5}$) and nitrogen dioxide (NO$_2$) in Chennai, India

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ABSTRACT
Daily commuting increases level of contaminants inhaled by urban community and it is influenced by mode and time of commuting. In this study, the commuters' exposure to ambient particulate matter (PM$_{2.5}$) and nitrogen dioxide (NO$_2$) was assessed during three modes of travel in six different road stretches of Chennai. The mean distance of road stretches was 25 km and the exposure to pollutants was assessed during peak hours and off-peak hours. The average travel duration was in the range of 39 to 91 min in motorbike, 83 to 140 min in car and 110 to 161 min in bus. Though there was variation on exposure to concentration in modes of transportation, the maximum exposure concentration of PM$_{2.5}$ was observed as 709 μg/m$^3$ in bus and the minimum exposure concentration was 29 μg/m$^3$ in closed car. Similarly, the maximum exposure concentration of NO$_2$ was observed to be 312 μg/m$^3$ in bus and the minimum exposure concentration was 21 μg/m$^3$ in car. The concentration of elements in PM$_{2.5}$ was in the order of Si > Na > Ca > Al ≥ K > S ≥ Cd, with Si and Cd concentration as 60% and < 1% of the PM$_{2.5}$ concentration.

Keywords: Commuter exposure, Fine particulate matter, NO$_2$, Particulate bound heavy metals, Traffic pollution

1. Introduction
The transportation micro-environment increases the exposure of humans to respirable particulate matter by about 50% [1], which depends on mode of transportation [2]. The transportation environment is considered to have serious impact on the people's health, as in most of the developed countries a person spends about 1.5 to 2 h in a day on road for traveling. The CPI (Commuter Pain Index) has reported that on an average, people in India spend around 1.5 h daily for commuting. Daily commuting increases level of pollutant exposure significantly [3, 4] and any physical activity such as speed walking and cycling during commuting, increases the inhalation intake rate of air, resulting in an increased level of pollutants inhaled [5]. Commuting by public modes of transport increases the pollution exposure which results in physiological changes [6], and also continuous exposure to PM$_{2.5}$ in closed cabin mode of transportation, results in exposure to other oxidative compounds in addition to PM$_{2.5}$ [7]. Traffic-bound pollutants include NO, CO, CO$_2$, diesel-exhaust particles, fuel combustion, pollutants that arise from brake wear, tire wear and re-suspended particles (e.g., trace metals) and pollutants like ozone, NO$_x$, secondary aerosol formed through physical and chemical processes [8]. The roadway exposure is high for motorists than the cyclists and least for pedestrians [9-11]. It may be due to that motorists ride at middle of road, whereas cyclists ride on the pavements and pedestrians use sidewalks [12]. The choice of routes on which the commuter travels also influences the exposure to pollutants and also plays a significant role in energy consumption [13]. Chennai, being one of the fastest developing metropolitan cities, the vehicle count has increased from 1,20,000 in 1981 to 44,70,328 as on 01.05.2015 (source: Regional Transport Office, Chennai south). Out of the total number of registered vehicles in the State of Tamil Nadu, Chennai alone accounted for 24.5% during the year 2012.

2. Material and Methods
This work focuses on assessing the commuters' exposure to partici-
ulate matter PM$_{2.5}$, NO$_2$, and heavy metals bound to particulate matter on most prevalent, three different modes of transportation viz., motorbike, car, and bus in Chennai. During commuting, samplers for both PM$_{2.5}$ and NO$_2$ were attached to the commuter, and cyclone along with the filter assembly was clipped to the collar of the commuter, such that it is held near the point of inhalation. The commuter on motorbike was wearing a helmet, the commuter in car kept the windows closed with A/C ON, and the commuter on bus was seated right behind the driver's cabin, during sampling (Fig. S1). The study was carried out along six busy road stretches having distance in the range of 21 km to 33 km, with a mean distance of 25 km (Fig. S2). The six stretches were chosen from a common diverging point Thiruvanmiyur, so that all possible directions of road stretches are covered in entire Chennai. The sampling time has been divided into three categories, i.e., morning-peak from 8 A.M to 11 A.M, off-peak 11.30 A.M to 3.30 P.M and evening-peak 5.30 P.M to 8.30 P.M. The details of prevalent mode of transportation, distance and travel time during sampling in the stretches are given in Table S1.

It may be noted that, travel time by bus was twice than motorbike and slightly higher than car. It might be due to busses having predetermined stops along the route, whereas motorbikes occupy less space on the road unlike bus and car. The maximum time of travel taken by bus was on road stretch S6 (Thiruvanmiyur to Avadi), since this road stretch is lined with thirty three traffic signals and has more number of bus stops than the other routes. The average travel time in stretch S4 (Thiruvanmiyur to Thiruvottiyur), was very close to S6, though the distance, the number of signals and stops are comparatively lesser than stretch S6. This was due to the fact that the road is always lined with container vehicles. The average time of travel for the six stretches, is in the order of S6 > S4 > S1 > S2 > S5 > S3, irrespective of the mode of transportation. The stretches along which sampling was carried out is given (Fig. S2).

2.1. Instrumentation

2.1.1 Particulate matter PM$_{2.5}$

A personal sampler (Model: PCXR-8, make SKC. USA) that has a flow rate ranging from 1 L/min to 5 L/min, fitted with an aluminum cyclone that has a cut-off point of 50% of 4 μm (NIOSH 0600), was used to collect the fine particulate matter. The aluminum cyclone was attached to a three stage filter cassette, assembled with a Whatman glass fiber filter paper, of Ø37 mm and pore size 0.6 μm. The sampler was attached to the collar of commuter while travelling in motorbike, car and bus so as to get a reliable amount of exposure by the commuter during travelling. The filter papers were dried in a hot air oven, at 120°C for about 10 min to remove any moisture content and were cooled in a desiccator for about 30 min before and after collection of samples. The weights of the filter papers were obtained using a Shimadzu’s, semi-micro weighing balance and the particulate matter (PM$_{2.5}$) concentration was determined by, IS 5182 - 23 (2006). From the total particulate matter concentration collected, the concentration of PM$_{2.5}$ was found out by, Particle Size Analyzer (make: Malvern, UK). It is designed to measure particle size distribution and particle mass based on a light scattering measurement of individual particles in the sampled air. Each single particle is illuminated by a defined laser light and each scattering signal is detected at an angle of 90° by a photo diode. In accordance with Mie theory, each measured pulse height is directly proportional to the particle size [14].

The filter paper used for sampling is weighed, before and after and the sampling and the weight difference obtained is expressed in grams. From the total weight of the particles obtained the concentration of PM$_{2.5}$ in μg/m$^3$ is obtained using (Eq. (1)).

\[
\text{PM}2.5\text{ Concentration (μg/μm$^3$)} = \frac{\text{Difference in weight (g)} + 1.00E+6}{3.00E-3 \times \text{Duration of sampling (min)}}\]

In the above Equation, 10$^6$ is multiplication factor to convert the weight in (g) to (μg), and the flow at which the sampler was operated was converted from (L) to (m$^3$) by a multiplication factor of 10$^3$.

2.1.2. Nitrogen dioxide NO$_2$

Another personal sampler (Model: SKC 107, make: India), that has a flow rate ranging from 1 L/min to 5 L/min, was used to collect NO$_2$. The sampler was fitted with a glass impinger of capacity 50 ml, using the scrubber solution of NaOH (sodium hydroxide) and Na$_2$AsO$_4$ (sodium arsenate) in the ratio of 3:1 in 1 L of distilled water. The sampler was run at a flow rate of 3 L/min. The impinger solution after sampling was analyzed using, UV-Vis Spectrophotometer at a wavelength of 540 nm, and the NO$_2$ concentration was obtained as per IS 5182 – 6 (2006). NO$_2$ concentration was calculated from the collected samples from the below (Eq. (2)).

\[
\text{Nitrogen dioxide concentration (μg/m$^3$)} = \frac{\text{Absorbance graph value in μg/D+Vs}}{Vt \times 0.82} \times Vt
\]

Where, the graph value is obtained by plotting absorbance against the standard graph, D is the dilution factor, Vs is the volume of sample taken for analysis, Vt is the volume of air during sampling, Vt is the volume of aliquot taken for analysis and 0.82 is the sampling efficiency. A photographic representation of the samplers used are given in the (Fig. 1).

2.1.3. Elemental composition

The elemental composition of collected PM$_{2.5}$ samples was subjected to quantitative analysis in an EDAX (Energy Dispersive X-Ray Analysis). EDAX is an analytical technique used for elemental analysis or chemical characterization of a sample. It is based on the investigation of a sample through interactions between electromagnetic radiation and matter, analyzing X-rays emitted by the matter in response to being hit with the electromagnetic radiation. The position of the peak with appropriate energies gives information about the qualitative composition of sample. The number of X-ray quanta is the measure for concentration of elements (peak height) [15].

2.1.4. Modes of transportation

A survey was conducted among various groups of commuters, in order to determine the prevalent modes of transportation in Chennai. It was found that a commuter from a middle class working group uses motorbike for 20 to 25 d in a month which is about 56.25%
of total respondents. In contrast, high income group uses car which is 20.39% of the total respondents, and on very few days motorbike was used as a mode of transportation. The remaining 16.78% preferred public mode of transportation and 6.58% of the respondents preferred other modes of transportation such as cycling, walking when the distance is < 5 km and metro trains when the distance in > 25 km (Fig. S3). The data obtained from, Directorate of Economics and Statistics of respective State Governments and for all India and survey conducted by the traffic police of Chennai showed that, of the total vehicle fleet in Chennai, 78% comprised of motorbike, 14% comprised of car, and remaining 8% comprised other modes of transportation. Therefore, three modes of transportation taken up for air sampling are bus, car and motorbike.

2.1.5. Type of road
Type of roads play an important role in commuters’ exposure to air pollutants [16]. A study carried out for underground subway passengers in four locations, which were near ticket counter, in subway while waiting, in subway while travelling and outside the subway on the road, showed maximum PM2.5 concentration of 361 µg/m³ in Yangjae and minimum concentration of 227 µg/m³ in Chungmuro both of which were observed while travelling in the subway, and it shows, location act as an important factor in the exposure to pollutants [17] and also commuters exposure to traffic pollutants depends upon the mode, fuel and road conditions [2]. Chennai has been subdivided in to three zones namely, North Chennai, South Chennai, Central Chennai and into three suburbs namely Northern Suburbs, Western Suburbs and South Eastern Suburbs. Each region in the study area has been lined with different institutions and commercial activities. The northern part of Chennai mainly comprises of industrial establishments that use heavy duty vehicles, though the vehicle volume and density are less in these zones they contribute majorly to the commuters’ exposure since these routes are lined with diesel vehicles that emit a huge amount of PM and NO2. The southern zone is lined with numerous educational institutions which use busses as mode of transportation during, morning and evening peak hours of the day, and commercial vehicles resulting in an increased traffic density comprising of mixed modes of transportations. Whereas the central zone of Chennai, always has a considerable amount of traffic throughout the day as these zones are lined with numerous government establishments and commercial establishments. The zones and directions of the stretches are given in Table S2 and depicted in (Fig. S4).

2.1.6. Time, duration and distance of travel
The time of travel and commuting route influences the commuters’ exposure to pollutants [9, 18]. For a stretch to be travelled, when there is more than one route to reach the destination, the person commuting by the normal route in which majority of the vehicles are operated gets exposed to a higher pollutant concentration than the alternative route which passes through the streets, but in general, the motorists were exposed to a much higher concentration, irrespective of the routes they travel [19]. The time duration for travelling the same distance on the same mode of transportation during peak hours and off-peak hours will be different depending upon various factors such as traffic intensity and metrological conditions. Therefore the study was conducted during morning-peak, evening-peak and off-peak hours on all six stretches in three modes of transportation.

2.1.7. Ventilation Conditions
The ventilation conditions could be open or closed ventilation in car and bus and it influences the exposure of commuters in many ways. Travelling by open ventilated cars and busses has the highest exposure to air pollutants [12], since the open ventilated cars have their cabin at the level of exhausts of other vehicles, whereas in busses the people get exposed to a significantly lesser level of pollutant concentration compared to cars [20]. A study showed that the commuters in closed busses get exposed to lower concentration of pollution, irrespective of the time of travel and the season when compared to the people travelling in open modes of transportation in ventilation nil zones, or half ventilated zones, where windows are closed and ventilation off [21]. Commuting in car with open ventilated conditions showed an increase when compared to the motorbike [3]. Air conditioning in cars was found to reduce the PM levels but it had no such significant influence on CO [22]. Therefore the study was carried out in cars under closed ventilation conditions and under open ventilated conditions in bus.
2.2. Exposure Assessment

Epidemiological and toxicological studies showed a close link between cardiovascular diseases and roadway traffic emissions [23, 24] and the fuel type also influences the cardiovascular effects, as it showed higher detrimental effect on asthma patients from diesel engine exhausts [25]. The value of minute ventilation (total volume of air entering the lungs per minute, m³/min) or respiratory minute volume was determined as given by, [26, 27] as given in (Eq. (3)).

\[
\text{Minute ventilation } Ve \left( \frac{\text{cu. m}}{\text{min}} \right) = \text{Tidal volume (cu. m)} \times \text{Respiratory rate (bpm)}
\]  

(T3)

Tidal volume represents the normal volume of air displaced between normal inhalation when extra effect is not applied and the tidal volume under such conditions is 500 ml [28]. The exposure to the pollutant concentration for a commuter is obtained from (Eq. (4)).

\[
\text{Exposure concentration } \left( \frac{\text{ug}}{\text{min}} \right) = Ve \left( \frac{\text{cu. m}}{\text{min}} \right) \times \text{Concentration } \left( \frac{\text{ug}}{\text{cu. m}} \right)
\]  

(4)

The respiratory rates for different age group of people is given in the Table 1 [29].

<table>
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<th>Respiratory rate (bpm)</th>
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<td>6-12 years</td>
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<td>4</td>
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<td>5</td>
<td>&gt; 65 years</td>
<td>12-28</td>
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3. Results and Discussion

Sampling of PM_{2.5} and NO_{2} was carried out to arrive at their exposure concentration while commuting on three modes of transportation along six roads stretches in the Chennai city. The total number trips were one hundred and eight (108) with thirty six trips in each mode of transportation. Eighteen trips were made in three modes of transportation on each road stretch so as to cover the three different commuting times, morning-peak, off-peak and evening-peak of a day. The average distance travelled on all trips was 25 km. The average travel time of each mode of transportation (Fig. 2(a)) and the average pollutant concentration (Fig. 2(b)) are depicted.

The mean exposure concentration of PM_{2.5} was 251 ± 56 μg/m³ while commuting on motorbike, whereas it was 224 ± 82 μg/m³ and 225 ± 104 μg/m³ in car and bus respectively. However, the mean exposure concentration of NO_{2} was 132 ± 29 μg/m³, 88 ± 24 μg/m³ and 97 ± 19 μg/m³ while commuting on motorbike, car and bus, respectively. The average time of travel was 62 ± 18 min, 110 ± 25 min and 115 ± 24 min while commuting in motorbike, car and bus, respectively.

It may be noted, though the overall mean travel time on motorbike was 50% lesser than in car and bus, whereas the overall mean exposure concentrations of PM_{2.5} and NO_{2} were higher while commuting in motorbike than in car and bus. This may be attributed to the fact that, motorbike commuters would travel closer to the exhaust levels of the preceding vehicles and they don’t travel in a closed environment unlike commuting by car and bus. Lesser concentration of the pollutants that was observed in car and bus in spite of a higher travel time, is attributed to the closed mode of transportation and ventilation conditions inside a closed cabin transportation system. A similar study, showed that air-conditioning system reduces particulate level in two ways, (i) closed window can act as a physical barrier to separate the vehicle interior air from the roadway air, thus to prevent direct influence of vehicle exhaust, (ii) part of the coarse size particulate is filtered out from the air stream by filter during fresh air intake or when the air inside is recirculated [30].

3.1. Effect of Travel Time on Exposure Concentration of PM_{2.5} and NO_{2}

The concentration of PM_{2.5} and NO_{2} on three modes of transportation for three different time periods viz., morning-peak (MP), off-peak (OP) and evening-peak (EP) are presented (Fig. S5).

On road stretch S1, the maximum exposure concentration of
PM$_{2.5}$ was observed as 417 $\mu g/m^3$ during the off-peak hours and minimum concentration was observed as 148 $\mu g/m^3$ during the evening-peak hours. In contrary to that, the maximum exposure concentration of NO$_2$ was observed as 196 $\mu g/m^3$ during the evening-peak hours, whereas minimum exposure concentration of 50 $\mu g/m^3$ was observed during the off-peak hours of the day. The maximum and minimum concentrations were exposed while commuting on motorbike and car, respectively.

The maximum and minimum exposure concentration of PM$_{2.5}$ was 500 $\mu g/m^3$ and 126 $\mu g/m^3$ were observed, during off-peak hours and evening-peak hours respectively on stretch S2. Nevertheless, the maximum and minimum exposure concentration of NO$_2$ was 134 $\mu g/m^3$ and 58 $\mu g/m^3$ respectively during the evening-peak hours and off-peak hours of a day. Unlike S1, the maximum exposure concentrations were observed while commuting on motorbike and car, whereas the minimum concentrations were exposed while commuting on bus in S2.

However, the maximum and minimum exposure concentrations of PM$_{2.5}$ and NO$_2$ were recorded during commuting on motorbike and bus respectively, in Stretch S3. The maximum PM$_{2.5}$ exposure concentration of 616 $\mu g/m^3$ and minimum concentration of 173 $\mu g/m^3$ were observed during off-peak hours and evening-peak hours respectively. But, in the case of NO$_2$, maximum exposure concentration of 203 $\mu g/m^3$ was observed during evening-peak hours and minimum exposure concentration of 89 $\mu g/m^3$ was observed during off-peak hours of the day.

On stretch S4, the exposure concentration of PM$_{2.5}$ was 228 $\mu g/m^3$ during morning-peak hour, and increased to its peak of 400 $\mu g/m^3$ in off-peak hour and then decreased to the minimum value of 87 $\mu g/m^3$ during evening-peak hours. However, the exposure concentration of NO$_2$ was 123 $\mu g/m^3$ during morning peak and decreased to the minimum value of 43 $\mu g/m^3$ during off-peak hours and increased to a maximum of 137 $\mu g/m^3$ during evening-peak hours. The maximum concentration was observed, while commuting on bus and motorbike, whereas the minimum concentration on car.

Similar to stretch S4, the exposure concentration of PM$_{2.5}$ has increased from morning-peak hour, attained its maximum at off-peak hour and then decreased to minimum in the evening-peak hours on stretch S5. The exposure concentration of PM$_{2.5}$ was 325 $\mu g/m^3$, 268 $\mu g/m^3$ and 68 $\mu g/m^3$ during morning-peak hour, off-peak hour and evening-peak hour respectively. Whereas, the exposure concentration of NO$_2$ was maximum with 133 $\mu g/m^3$ during morning-peak hour, decreased to 116 $\mu g/m^3$ during off-peak hours and further decreased to the minimum of 61 $\mu g/m^3$ during evening-peak hour.

The effect of time of travel on exposure concentration of PM$_{2.5}$ and NO$_2$ in stretch S6 was similar to that of S4 and S5. The exposure concentration of PM$_{2.5}$ has increased from 179 $\mu g/m^3$ during morning-peak, attained its maximum at off-peak with 333 $\mu g/m^3$ and then decreased to 79 $\mu g/m^3$ during evening-peak hour. The exposure concentration of NO$_2$ was maximum with 225 $\mu g/m^3$ during the morning-peak hour, decreased to 59 $\mu g/m^3$ during the off-peak hour and even further decreased and attained a minimum concentration of 55 $\mu g/m^3$ during the evening-peak hour of the day respectively. It may be noted that, the exposure concentration NO$_2$ decreased from morning peak, towards off-peak hour and further decreased towards the evening-peak hour, in contrary to PM$_{2.5}$. As far as mode of transportation is concerned, the maximum and minimum exposure concentrations were observed while commuting on motorbike and car, respectively on stretch S5 and S6.

Among the six stretches studied, the mean exposure concentration of PM$_{2.5}$ was maximum during off-peak hour in five stretches, which were S1, S2, S3, S4 and S6. In different stretches, different modes of transportation recorded maximum exposure concentration in the off-peak hour. The maximum exposure concentration was observed while commuting on bus in stretch S3 as 616 ± 132 $\mu g/m^3$, while commuting on cars in stretches S2 and S4 as 500 ± 0 $\mu g/m^3$ and 401 ± 23 $\mu g/m^3$ respectively, and while commuting on motorbike in stretches S1 and S6 as 417 ± 302 $\mu g/m^3$ and 333 ± 279 $\mu g/m^3$. On stretch S5, maximum mean exposure concentration of PM$_{2.5}$ of 325 ± 118 $\mu g/m^3$ was observed during morning-peak hour while commuting in motorbike. In none of the stretches, maximum concentration was observed during evening-peak hour. However the minimum average concentration of PM$_{2.5}$ was observed only while commuting by bus as 177 ± 42 $\mu g/m^3$ and 122 ± 14 $\mu g/m^3$ on stretches S1 and S6 during the evening-peak hour of the day, whereas it was observed as 126 ± 73 $\mu g/m^3$, 321 ± 25 $\mu g/m^3$, 143 ± 60 $\mu g/m^3$, 126 ± 18 $\mu g/m^3$ on stretches S2, S3, S4 and S5 respectively during the morning-peak hour of the day.

The maximum mean exposure concentration of NO$_2$ was observed on motorbike, irrespective of stretch and time of travel. The maximum mean concentration of NO$_2$ was observed during morning-peak hour on stretches S2, S3 and S4 as 134 ± 20 $\mu g/m^3$, 133 ± 30 $\mu g/m^3$ and 86 ± 37 $\mu g/m^3$, during off-peak hour on S3 and S4 as 204 ± 28 $\mu g/m^3$ and 130 ± 16 $\mu g/m^3$, and during evening-peak hour on stretch S1 with 196 ± 24 $\mu g/m^3$. However the minimum mean exposure concentration of NO$_2$ was observed during morning-peak hour, in S3, S4 and S5 as 43 ± 14 $\mu g/m^3$, 62 ± 12 $\mu g/m^3$, 56 ± 5 $\mu g/m^3$ while commuting on car and in S6 as 97 ± 22 $\mu g/m^3$ while commuting on bus, whereas during off-peak hour on S1 as 50 ± 37 $\mu g/m^3$ and S2 as 58 ± 16 $\mu g/m^3$ while commuting on car and bus, respectively. The mean exposure to PM$_{2.5}$ and NO$_2$ per minute and km travelled has been represented in (Fig. 3 (a) and (b)).

The mean exposure to PM$_{2.5}$/min of the time travelled, in six stretches are 2.00 ± 0.4 $\mu g/m^3/min$, 1.80 ± 0.2 $\mu g/m^3/min$, 1.86 ± 0.1 $\mu g/m^3/min$ while commuting in motorbike, and car and bus respectively, whereas the mean exposure to NO$_2$/minute of the time travelled, in six stretches are 1.04 ± 0.4 $\mu g/m^3/min$, 0.69 ± 0.3 $\mu g/m^3/min$, 0.77 ± 0.5 $\mu g/m^3/min$ while commuting in motorbike, and car and bus respectively. In contrary to that, the mean exposure to NO$_2$/km of the distance travelled, in six stretches are 4.9 $\mu g/m^3/km$, 7.9 $\mu g/m^3/km$, 8.3 $\mu g/m^3/km$, while commuting in motorbike, car and bus respectively, whereas the mean exposure to NO$_2$/km of the distance travelled, in six stretches are 0.26 $\mu g/m^3/km$, 3 $\mu g/m^3/km$ and 3.5 $\mu g/m^3/km$ while commuting in motorbike, car and bus, respectively.

It may be noted that, though the mean average exposure concentration while commuting in motorbike is twice than that of commuting in car and bus, the mean average exposure concentration/km of the distance travelled for car and bus is twice than that of the concentration while commuting in motorbike, and this is due to the fact that, motorbike commuters spend a comparatively less time on roads than commuters’ on car and bus. A similar study, showed that the geographical patterns and road characteristics
influence, commuters’ exposure to air pollutants [31]. The difference in overall mean average exposure concentration to the mean average exposure concentration/km is attributed to the fact, the time travelled to cover 1 km of the stretch is 2.48 min while commuting by motorbike, whereas the travel time by car and bus was more or less similar with 4.4 min and 4.6 min, respectively.

Similar studies conducted in Mexico and Netherlands for different modes of transportation during different time periods, reported that commuters’ exposure concentration varied with respect to mode of transportation and also during morning and evening-peak hours of a day [2, 32].

The peak exposure concentration of PM$_{2.5}$ during off-peak hour and NO$_2$ concentration during evening-peak hour may be attributed to the fact that, since Chennai being a metropolitan city, the vehicle count increases from mid-morning and keeps on increasing towards afternoon and further increases towards evening hours of the day. Since dampness prevails in the atmosphere, concentration of PM$_{2.5}$ and NO$_2$ exposed during the morning will be primarily from the vehicular emissions [33].

There was a consistent trend observed in stretches, the exposure concentration of NO$_2$ was higher during morning-peak and evening-peak and that of lowest was during off-peak of the day. This could be due to increased traffic volumes that tend to occur during these time periods and influence of local meteorological factors which affects the dilution rates, which in turn influences the exposure to NO$_2$. The effect of increased daytime temperatures on NO$_2$ concentrations may be explained by the process of thermally-induced convection. As the ground heats up during the day, gusts and winds increase, leading to increased diffusion of NO$_2$. Therefore, NO$_2$ gets dispersed resulting in exposure to lower concentrations [34].

Unlike NO$_2$, which is primarily from vehicle exhaust, particulate matter observed on road traffic comes from other sources as well, such as tyre wear, brake-wear and vehicle induced re-suspension of road dust. Hence, in case of PM$_{2.5}$, the re-entrained dust particles account more in addition to vehicular emission during midday than during morning and evening-peak hours, and also the speed of the vehicle and driving conditions influences the pollutants that are emitted in the atmosphere [35]. The heated road surface entrains more amounts of dust particles during off-peak hour than when the road surface gets damped during morning-peak and evening-peak hours. Studies carried out to study the dispersion of particulate matter (PM$_{2.5}$, PM$_{1.5}$ and PM$_{10}$) in Chennai showed a similar pattern of diurnal variation [14].

### 3.2. Elemental Analysis of PM$_{2.5}$

Fourteen (14) representative PM$_{2.5}$ samples, from one hundred and eight (108) samples, were subjected to nondestructive testing for the quantification of predominant elements. The fourteen representative samples were chosen, as two samples for each stretch (one maximum and one minimum), and two additional samples for stretches S3 and S4 were taken for consistency. The major elements observed from Scanning Electron Imaging under 5,000 times the magnification of filter papers were Silica, Sodium and Aluminum (Fig. 4(a), (b), (c), (d)). The elemental concentration in PM$_{2.5}$ while commuting in three modes of transportation during three time periods of travel is presented in (Fig. 5(a), (b), (c)).

It was observed that, major constituent of PM$_{2.5}$ is Silica (Si) which further confirms our above statement that, in addition to vehicular exhaust, the road dust is one of the major sources of commuters’ exposure to PM. The concentration of elements were in the range of, 45 $\mu$g/m$^3$ to 190 $\mu$g/m$^3$ of Si, 13 $\mu$g/m$^3$ to 74 $\mu$g/m$^3$ of Sodium (Na), 4 $\mu$g/m$^3$ to 13 $\mu$g/m$^3$ of Aluminium (Al), 4 $\mu$g/m$^3$ to 19 $\mu$g/m$^3$ of Potassium (K) and Calcium (Ca), 0.5 $\mu$g/m$^3$ to 2 $\mu$g/m$^3$ of Cadmium (Cd), and 0.5 $\mu$g/m$^3$ to 5 $\mu$g/m$^3$ of Sulphur (S). The concentration of elements analyzed were in the order of Si $\geq$ Na $>$$ Ca >$$ Al \geq$$ S \geq$$ Cd$. Studies carried out in Canada and Barcelona showed that, elemental concentration differs with respect to mode of transport and time of exposure i.e. travel time on which the commuters use the roads [3, 36].

It was found that, the concentration of Si was maximum, among all elements analyzed. Concentrations observed during morning-peak were 105.75 $\mu$g/m$^3$, 190.68 $\mu$g/m$^3$, 75.69 $\mu$g/m$^3$, during off-peak were 72.41 $\mu$g/m$^3$, 44.68 $\mu$g/m$^3$, 46.67 $\mu$g/m$^3$, and during evening-peak were 82.31 $\mu$g/m$^3$, 54.42 $\mu$g/m$^3$, 56.39 $\mu$g/m$^3$ while commuting on motorbike, car and bus modes of transportation. Whereas concentration of Na was next to concentration of Si,
which was observed as 39.24 μg/m³, 30.16 μg/m³ and 27.31 μg/m³ while commuting on motorbike, 72.11 μg/m³, 14.04 μg/m³ and 15.88 μg/m³ while commuting on car and 23.88 μg/m³, 13.3 μg/m³ and 18.75 μg/m³ while commuting on bus during morning-peak, off-peak and evening-peak hour of a day.

The concentration of Ca dropped down by 60% when compared to Na, irrespective of time and mode of transportation. The concentration while commuting on motorbike was observed as 10.62 μg/m³, 8.33 μg/m³ and 8.07 μg/m³, while commuting on car as 18.34 μg/m³, 4.23 μg/m³ and 5.62 μg/m³ and while commuting on bus it was 10.74 μg/m³, 4.75 μg/m³ and 5.31 μg/m³, during morning-peak, off-peak and evening-peak hours of the day, respectively.

Concentration of Al was similar to concentration of K on all modes of transportation. The concentration of Al and K observed while commuting on motorbike were 7.48 μg/m³, 5.16 μg/m³, 6.65 μg/m³ and 7.16 μg/m³, 5.34 μg/m³, 5.24 μg/m³, whereas while commuting in car the concentration of Al and K observed were 12.51 μg/m³, 4.24 μg/m³, 4.33 μg/m³ and 12.85 μg/m³, 3.15 μg/m³, 4.16 μg/m³. The concentration of Al observed while commuting on bus 8.01 μg/m³, 4.56 μg/m³, 5.12 μg/m³ and K were 5.07 μg/m³, 3.36 μg/m³, 3.93 μg/m³ during morning-peak, off-peak and evening-peak hours of the day, respectively.
The concentration of S, observed while commuting on motorbike were 4.68 μg/m³, 1.56 μg/m³ and 3.34 μg/m³, while commuting on car were 4.22 μg/m³, 2.18 μg/m³ and 0.77 μg/m³ and while commuting on bus were 4.68 μg/m³, 1.56 μg/m³ and 3.34 μg/m³ during morning-peak, off-peak and evening-peak hours of a day.

Off all the elements studied, Cd concentration observed was the lowest with a morning-peak concentration of 1.85 μg/m³, 1.31 μg/m³ and 1.67 μg/m³, an off-peak concentration of 0.95 μg/m³, 0.41 μg/m³ and 0.61 μg/m³ and an evening-peak concentration of 0.92 μg/m³, 0.84 μg/m³ and 1.02 μg/m³ while commuting on motorbike, car and bus, respectively.

It can be observed from graphs that, elemental concentration of all elements are high in car mode of transportation only during morning-peak hours of the day, whereas during off-peak and evening-peak hours of the day, the elements concentration was dominant in two wheeler mode of transportation followed by bus and car mode of transportation. This hike in concentration of elements, while commuting in car during the morning-peak might be due to the initial ignition of the car [37], idling time of cars during the mornings where there is a very low possibility of the pollutants getting dispersed, initial start of the ventilation systems, air recirculation efficiency etc. [38]. The percentage contribution of various elements is depicted in the (Fig. 6 (a), (b), (c)).

Even though the concentration of PM bound elements varies from mode to mode, percentage contribution of those elements are almost the same for each mode of transportation irrespective of time of travel. The percentage contribution of elements analyzed are as follows, Si- 60.87% and Na- 18.37% which is attributed to the re-entrained dust particles, road dust, construction activities, condition of roads [39], 5.90% of Al is attributed to processing of aluminum ores or production of aluminum metal, alloys, and compounds [40], Cd- 2% and S- 2.5% which is attributed to wear and tear of brake fluids and tires wear and tear [41] and K- 4.3% and Ca - 6.02% that is attributed to mineral processing and foundry industries. Particulate matter can be bound by black carbon, soot, and various compositions of heavy metals, mostly particulate matter will be bound by silica particles since most of the dust that is suspended around in the atmosphere is a result of vehicular movement on road [42].

### 4. Conclusions

From the study carried out during summer season of 2018 in Chennai on six stretches, it was found out that, the maximum average PM₂.₅ and NO₂ concentration observed were 435 ± 157 μg/m³ and 167 ± 51 μg/m³ while commuting on bus and motorbike respectively on stretch S3, whereas the minimum average PM₂.₅ and NO₂ concentration observed were 204 ± 132 μg/m³ and 57 ± 15 μg/m³ while commuting on motorbike and car on stretch S4 and S6 respectively. Taking into consideration the total average concentrations, mean exposure concentration of PM₂.₅ of 251 ± 56 μg/m³ was obtained while commuting on motorbike, whereas mean exposure concentration of PM₂.₅ was more or less same i.e. 224 ± 82 μg/m³ and 225 ± 104 μg/m³ in car and bus respectively. However, mean exposure concentration of NO₂ were 132 ± 29 μg/m³, 88 ± 24 μg/m³ and 97 ± 19 μg/m³ was obtained while commuting on motorbike, car and bus respectively. The average time of travel was 62 ± 18 min, 110 ± 25 min and 115 ± 24 min while commuting in motorbike, car and bus respectively. The overall PM₂.₅, NO₂ and elemental concentration during the summer season has been summarized in Table 2.

From the above study, it is concluded that, in Chennai, a road commuter’s mean exposure concentration of PM₂.₅ is 2.0 ± 1 μg/m³/min, 1.8 ± 1 μg/m³/min and 0.9 ± 0.4 μg/m³/min, if he/she

### Table 2. Average Concentration of NO₂, PM₂.₅ and Elemental Composition of PM₂.₅

<table>
<thead>
<tr>
<th>Mode</th>
<th>Na</th>
<th>Si</th>
<th>Al</th>
<th>K</th>
<th>Ca</th>
<th>Cd</th>
<th>S</th>
<th>PM₂.₅</th>
<th>NO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Motorbike</td>
<td>32.24</td>
<td>86.82</td>
<td>6.43</td>
<td>5.91</td>
<td>9</td>
<td>1.24</td>
<td>0.98</td>
<td>251</td>
<td>132</td>
</tr>
<tr>
<td>Car</td>
<td>34.01</td>
<td>96.59</td>
<td>7.03</td>
<td>6.72</td>
<td>9.40</td>
<td>0.85</td>
<td>2.39</td>
<td>224</td>
<td>88</td>
</tr>
<tr>
<td>Bus</td>
<td>18.64</td>
<td>59.58</td>
<td>5.86</td>
<td>4.12</td>
<td>6.93</td>
<td>1.10</td>
<td>3.19</td>
<td>225</td>
<td>97</td>
</tr>
</tbody>
</table>
travels by motorbike, car and bus respectively. Similarly, the unit time exposure to NO2 is 1.04 ± 0.4 μg/m³/min, 0.69 ± 0.3 μg/m³/min and 0.89 ± 0.3 μg/m³/min while travelling by motorbike, car and bus, respectively.

The effect of modes of transportation on exposure concentration of PM2.5 and NO2 per unit distance travelled is concluded as follows. PM2.5/μg/m³/km of the distance travelled was 4.9 μg/m³/km, 8.3 μg/m³/km while commuting in motorbike, car and bus respectively, whereas for NO2 it was 2.6 μg/m³/km, 3.2 μg/m³/km and 3.5 μg/m³/km, while travelling by motorbike, car and bus, respectively.

Of the three travel times during a single day, the most polluted time of the day wherein the commuters get exposed to a maximum exposure concentration of pollutants is during off-peak hour commuting, irrespective of the modes of transportation and time of travel throughout the day, whereas the minimum exposure concentration of pollutants is during morning and evening-peak hours of the day. Thus, the commuters’ exposure is influenced by several factors including mode of transportation, time of day, time of travel, and ventilation conditions.

Author Contributions

M.G.R. (Ph.D. Student) conducted all the field works and experiments. Dr. S.K. (Associate Professor) is the research supervisor and structured the manuscript.

References