

Exposure to coarse and fine particulate matter at and around major intra-urban traffic intersections of Ilorin metropolis, Nigeria



J.A. Adeniran^a, R.O. Yusuf^a, A.A. Olajire^{b,*}

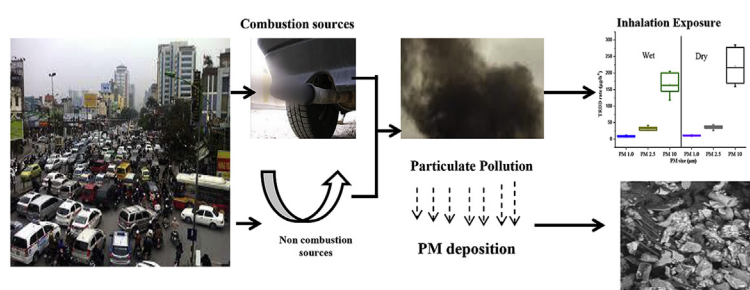
^a Environmental Engineering Research Laboratory, Department of Chemical Engineering, University of Ilorin, Ilorin, Nigeria

^b Industrial and Environmental Chemistry Unit, Department of Pure and Applied Chemistry, Ladoke Akintola University of Technology, Ogbomoso, Nigeria

HIGHLIGHTS

- Concentrations of ambient PMs at six major TIs were above statutory limits.
- TP and RDD values indicate that road users are exposed to high concentrations of PMs.
- Pb and Zn are anthropogenically-derived while the rest elements are of crustal origin.
- Deposition fluxes of NEEs are higher than AEEs.
- PCA indicates particulate emission data to be related to exhaust and non-exhaust sources.

GRAPHICAL ABSTRACT



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ABSTRACT

This study aims to determine the seasonal variations and composition of suspended particulate matter in different sizes PM_{1.0}, PM_{2.5}, PM₁₀ and the total suspended particles (TSP) emitted at major intra-urban traffic intersections (TIs) of Ilorin metropolis. The concentration levels of PM (PM_{1.0}, PM_{2.5}, PM₁₀) obtained at the TIs during the rush hours (45.1, 77.9, and 513 µg/m³) are higher than the levels obtained for the non-rush hour periods (42.3, 62.7, and 390 µg/m³). The average on-road respiratory deposition dose (RDD) rates of PM_{1.0}, PM_{2.5} and PM₁₀ during the dry period at TIs types was found to be about 24%, 9% and 25% higher than those obtained during the wet period. Based on EF values calculated, Pb and Zn were anthropogenically-derived while Fe, Mn, Cr, Cu and Mg were of crustal source. Principal component analysis (PCA) has been applied to a set of PM data in order to determine the contribution of different sources. It was found that the main principal factors extracted from particulate emission data were related to exhaust and non-exhaust emissions such as tyre wears, oil and fuel combustion sources.

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1. Introduction

In recent years, a global tendency toward air quality degradation has been observed in several urban areas of the world due to rapid industrialization, urbanization, population growth and increased

vehicular emissions, which have critically affected the atmospheric environment especially with regards to contamination of atmospheric particulate matter (PM) (Delkash and Mir, 2016; Singh et al., 2014; Das et al., 2015). The increase in number of vehicles is directly associated with changes in societal lifestyles, economic development and fuel consumption which subsequently lead to incessant traffic congestions at and around intra-urban road intersections and are therefore very common sources of particulate emissions in

* Corresponding author.

E-mail addresses: aaolajire@lutech.edu.ng, olajireaa@yahoo.com (A.A. Olajire).

the urban cities (Gokhale and Raokhande, 2008; Police et al., 2016). Traffic related emissions have been recognised as one of the major sources of air pollutants (Thorpe and Harrison, 2008; Adiang et al., 2016), where portion of pollutants emitted is directly deposited on surfaces, whilst the remainder remained airborne particles for a period of time (Gunawardena et al., 2012). Road deposited particulate (RDP) can therefore be used as an indicator of metal emission and pollution around road traffic environment since it is a complex mixture of particulates and contaminants (Pal et al., 2012). The free movement of vehicles on the road also results in resuspension of road dust while the slow movement of vehicles at traffic intersections (TIs) causes incomplete combustion of fuel, leading to the release of harmful pollutants into the atmosphere (Gokhale and Raokhande, 2008). Major intra-urban traffic intersections (TIs) are well known as pollution hotspots but studies focusing on determination of concentration of $PM_{1.0}$, $PM_{2.5}$ and PM_{10} particulates at and around such TIs are sparse, and therefore taken as the focus of the present study.

Previous studies have indicated the adverse effects of PM on visibility, global climate change and human health (Correia et al., 2013). In particular, PM_{10} fraction was studied as a carrier of many harmful chemicals into human respiratory tracts and are therefore associated with respiratory and cardiovascular diseases, aggravation of asthma, especially in kids (Vallero, 2014). Sources of particulates at and around traffic intersections have also been reported to include dust re-suspension (Thorpe and Harrison, 2008), tyre wears (Dahl et al., 2006) and brake wears (Hulskotte et al., 2007), due to vehicle movements at and around TIs. The impetus of the present study lies on the fact that information about air quality status in most cities of Nigeria is scanty in the literature as compared to other parts of the world. Commuters, roadside hawkers and pedestrians are exposed to high concentration of these particulate matters and little quantitative information is currently available especially in the developing countries. It is therefore imperative to carry out in-depth study of the relationship between traffic characteristics and key particulate matter loads at (i.e on-road) and around (i.e pedestrian, hawkers) TIs. This will assist in formulating appropriate policy strategies to mitigate the adverse impacts of these particulate matters on atmospheric air quality. In the present study however, coarse and fine PM monitoring and their source apportionment were carried out at two different periods (wet and dry periods) *visa-vis* traffic volumes change during the rush and non-rush hours in order to achieve the following objectives (i) to determine the distribution of different PM types (PM_{10} , $PM_{2.5}$, $PM_{1.0}$ and TSP), (ii) to assess human exposure level using RDD, (iii) to identify sources of particulate-bound metal species (iv) to measure dry deposition fluxes of mass particulates and seven metal species (Fe, Zn, Cu, Pb, Mg, Cr, and Mn) and finally (v) to carry out source apportionment of these particulate emission data using PCA.

2. Material and methods

2.1. Study area

The sampling was carried out in Ilorin, the capital of Kwara State and one of the largest cities in Nigeria. The city of Ilorin lies on longitude $8^{\circ}30'N$ $4^{\circ}33'E$ and latitude $8.500^{\circ}N$ $4.550^{\circ}E$ with daily average temperature ranges of $25^{\circ}C$ and $35^{\circ}C$. The climate is equatorial with distinct wet and dry periods—dry period (October–March) and wet period (April–September). Particulate matter measurements were carried out at six different major traffic intersections (TIs) (Fig. 1) spatially located in the city: Tanke tipper garage (SP1), Post office (SP2), Unity (SP3), Oja-Oba (SP4), Gari-Alimi (SP5) and Offa-garage (SP6). Vehicular traffic snarls are

rampart in the selected locations as they lead to other locations within and outside Ilorin. The study was carried out 1-hourly and 8-hourly at the two seasons. We also covered both the rush and non-rush hours at the selected locations. Rush hours (7.00–10.30 h) when offices and schools open in the morning and (15.30–17.30 h) when offices and schools close in the evening during weekdays. Non-rush hour (19.30–22.00 h) and weekend measurements were taken in the selected location when traffic volume is usually light. The average traffic fleets on the routes are approximately 7.2×10^3 vehicles/hr at non-rush hours (low traffic density) and about 1.3×10^4 vehicles/hour at rush hours (high traffic density), considering the four lanes leading to the roundabouts and the roads being double-lane with the roundabouts being cross-junctions. Various types of vehicles such as motorcycles, tricycles, cars, lorries and trucks ply the road for commercial, industrial activities and personal services. The diurnal variations of fleet compositions were almost the same each day, with relatively low traffic density during non-rush hours (17.30–22.00 h) and high traffic density during rush hour (7.00–10.30 & 15.30–17.30 h).

2.2. Sampling protocol

Two-channel particle counter (model GT-531 S), (Met One Instruments, Inc., Rowlett, Texas, USA) which employs light scattering technology and a laser diode optical sensor to detect and count particles in three size ranges was used. The instrument continuously samples air at $2.83 L min^{-1}$. The average number of particles counted ($L min^{-1}$) in each channel was recorded by the data acquisition system. Air leaks or debris in the particle sensor which may result in false counts when sampling was taken into consideration. Zero count test was performed hourly to ensure proper operation of the particulate counter using zero count filter (PN G3111). The continuous measurement of mass concentration of $PM_{1.0}$, $PM_{2.5}$, PM_{10} , TSP with range of $0-1 mg/m^3$ and the following micron diameters 0.3, 0.5, 1.0, 5.0 with range of $0-3,000,000$ were measured at a distance of 50 m from the roundabout of each locations during the rush and non-rush hours at about 1.5 m from the ground at all sampling locations. The atmospheric temperature and humidity were measured for the whole sampling period using the Kestrel 4500 Weather Tracker.

2.3. Calibration of equipment

A stationary HazDust™ instrument with a low-flow pump and filter (47 mm FRM style) was used for calibrating the optical light scattering technique (GT-531 S) used for the measurement of TSP, PM_{10} , $PM_{2.5}$ and $PM_{1.0}$ concentration levels. A gravimetric analysis technique was employed for measuring filter weights before and after sampling, with strict adherence to quality control procedure in order to minimize error. The monitoring was carried out at SP3 location in Ilorin metropolis and comprised the same sampling protocols during the rush hour.

The measurements acquired with the gravimetric analysis and the GT-531 S using the above sampling protocols were used to derive the correction equations for the different particulate sizes used in this study as illustrated in Fig. S1. Exposure data were adjusted according to derived calibration equations for the four particulate sizes as follows:

$$CorrectedPM_{1.0} = (0.646 * MeasuredPM_{1.0}) + 8.6 \quad (1a)$$

$$CorrectedPM_{2.5} = (0.924 * MeasuredPM_{2.5}) + 8.21 \quad (1b)$$

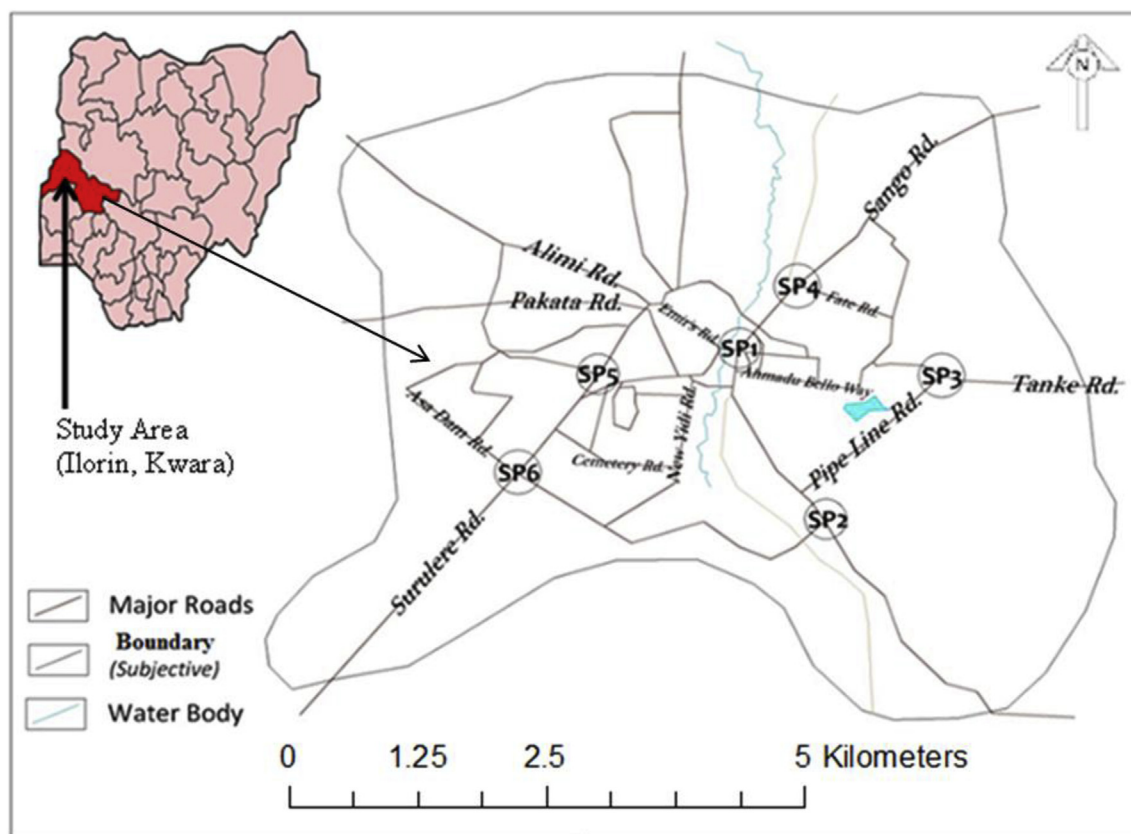


Fig. 1. Map showing the traffic intersections of the study area.

$$\text{CorrectedPM}_{10} = (0.869 \times \text{MeasuredPM}_{10}) + 48.19 \quad (1c)$$

$$\text{CorrectedTSP} = (0.990 \times \text{MeasuredTSP}) + 47.7 \quad (1d)$$

The agreement between the GT-531 S and gravimetric measurements was further investigated using Bland and Altman plots of the PM calibration data (Fig. S2).

2.4. Adjustment of PM values for relative humidity

Studies have shown that high relative humidity will have a strong effect on light scattering (Chakrabarti et al., 2004; Karagulian et al., 2012; Cropper et al., 2013), thereby leading to overestimation of PM concentration (McMurry et al., 1996). To account for the influence of relative humidity (RH) in GT-531 S measurements, a correction factor is typically applied, especially when RH exceeds 65%. This correction factor can be calculated as the ratio of the humidity influenced PM GT-531 S concentration to

empirical adjustment equations derived from experimental data of Laulainen (1993) which also fits well with data from several studies (Day and Malm, 2001; Chakrabarti et al., 2004) were adopted in this study:

$$CF = \frac{GT - 531 \text{ SPM}}{\text{Gravimetric PM}} = 1 + 0.25 \frac{(RH)^2}{(1 - RH)} \quad (2)$$

$$PM - \text{humidity bias} = \frac{GT - 531 \text{ SPM}}{CF} \quad (3)$$

2.5. Human exposure assessment

Human exposure to airborne pollutants at the TIs was assessed using respiratory deposition dose (RDD) estimates. The RDD rates for PM₁₀, PM_{2.5} and PM_{1.0} were estimated by using the approach suggested by Kumar and Goel (2016) as in Equation (4);

$$\text{Deposited doses (in thoracic, tracheobronchial, alveolar regions) of PM fractions} = (V_T \times f) \times DF_i \times PM_i \quad (4)$$

the humidity independent PM GT-531 S concentration. Dividing the GT-531 S measurements by this correction factor will adjust for the PM-humidity bias. Previous studies demonstrated humidity adjustment equations to estimate the correction factor (CF). The

where V_T is the tidal volume, f is the frequency of breathing, DF_i and PM_i are the deposition fraction and mass concentration of particle size i in μm . Values of V_T and f were taken as 800 cm³ per breath and 0.35, respectively for men during light exercise conditions

(Hinds, 1999; Kumar and Goel, 2016). Estimates of DF_i for PM_{10} , $PM_{2.5}$ and PM_1 were calculated according to equation proposed by Hinds (1999) given in Equation (5) and inhalable fraction (IF) as given in Equation (6).

$$DF = IFx \left(0.058 + \frac{0.911}{1 + \exp(4.77 + \ln d_p)} + \frac{0.943}{1 + \exp(0.508 - 2.58 \ln d_p)} \right) \quad (5)$$

$$IF = 1 - 0.5 \left(1 - \frac{1}{1 - 0.00076 d_p^{2.8}} \right) \quad (6)$$

2.6. Deposition flux and elemental composition

Deposition gauges were placed at a height of 5 m above the ground and were left for 28 days at each sampling location after which they were collected for laboratory analysis. Deposited particulate collected with deposition gauges were washed with deionised water and filtered using pre-weighed Whatman 41 Grade I ashless filters. The filter papers were dried after which they were re-weighed and the final mass deposition of the particulates was determined gravimetrically by subtracting the pre-weighed filter papers from post-weighed filter papers. The atmospheric dust deposition flux was obtained using the following equation:

$$\varphi_f = \frac{W_p}{A_d t} \quad (7)$$

where, φ_f = dry deposition flux, W_p = weight of deposited PM, A_d = area of deposition and t = time (s).

One half portion of post-weighed filter papers was analyzed by scanning electron microscopy (SEM) (The FEI Quanta™ 50 series from Aspex/FEI Corporation, USA) for the morphological characterization of the deposited PM. Another half portion of post-weighed filter papers were soaked in 15 mL of mixed acid (HNO_3 and $HClO_4$) and boiled at high temperature on a hot plate until a clear solution of the mixture was obtained. After complete digestion, sample solution was reduced to near dryness by boiling slowly at low temperature to remove excess acid. Then, 0.20% HNO_3 was added to the above mixture and resulting solution was filtered into 25 ml volumetric flask. The analysis of metals associated with particulate matter (Fe, Zn, Cu, Pb, Mg, Cr, and Mn) was carried out using flame atomic absorption spectrometry (IS BUCK 210 VGP by Buck Scientific Inc., USA). Standard reference material, (NIST SRM1648; urban particulate matter) and filter blanks were subjected to analytical protocols for quality control and assurance purposes. The percentage recovery of individual metal of interest was in the range 97.6–105.4%.

The dry deposition fluxes of metallic elements were calculated using the following equation:

$$F_d = 86400 C_i x V_d \quad (8)$$

where F_d is the atmospheric metal dry deposition flux of particulate matter in g/m^2 . day, C_i is the measured ambient mean metal concentration of particulate matter in mg/m^3 , and V_d is the metal settling velocity of particulate matter in cm/s . The values used here follow the mean values used by Duce et al. (1991), where for anomalously enriched elements (AEEs) such as Cu, Zn, Pb, and Cr

which are mainly associated with submicrometer particles, a mean value of 0.1 cm/s was applied, and for crustal or non-enriched elements (NEEs) such as Fe, Mn and Mg which are present mainly in the coarse fraction, a mean value of 2 cm/s was used, as already been used in other studies (Rojas et al., 1993; Migon et al., 1997; Herut et al., 2001; Pereira et al., 2007).

2.7. Multivariate analysis

In factor analysis, we have used the technique of Principal Component Analysis (PCA). The method of principal components (PCs) can be applied by using the original values of variables (X_j 's) (where $j = 1, 2, 3, \dots, n$) or their deviation from their means ($x_j = X_j - \bar{X}_j$), or the standardized variables given as;

$$Z_j = \frac{X_j - \bar{X}_j}{S_j} \quad (9)$$

where S_j is the standard deviation, X_j is the variables and $\bar{X}_j$ is the mean of variable X_j (Chen and Zhu, 2004; Zhang et al., 2014).

In present study, we have used original variables X_j 's ($j = 1, 2, 3, \dots, n$) in the principal component model, X_j is expressed as a linear combination of the principal component as (Olajire et al., 2011):

$$X_j = \sum_{i=1}^n a_{ji} P_i \quad (10)$$

where $j = 1, 2, \dots, n$; P_i is the i th principal component; a_{ji} is the factor loading of the j th variable on the i th principal component. Basically the factor loading is the j th component of the i th eigen vector of the correlation matrix multiplied by the square root of the corresponding eigen value. The principal components (Lohani, 1984) are given by:

$$P_i = \sum_{j=1}^n \frac{a_{ji} X_j}{\lambda_i} \quad (11)$$

where λ_i is the eigen-value associated with P_i .

In this study, our X_j is the primary data or variables, such as suspended particulates - $PM_{1.0}$, $PM_{2.5}$, PM_{10} , TSP; RDD of $PM_{1.0}$, $PM_{2.5}$, PM_{10} ; Fe, Zn, Cu, Pb, Mg, Mn and Cr in the deposited particulates; traffic count (TC) and the deposition flux rate (φ_f); $\bar{X}_j$ is the average value of X_j ; and S_j is the standard deviation.

3. Results and discussion

3.1. Microclimatic parameters

The mean wind speed (WS) were between 0.6 and 1.2 m/s for the six TIs. Also, the minimum temperature was 31.50 °C, while the maximum recorded temperature was 38.0 °C with mean temperature of 33.8 °C for the TIs types. The highest recorded result for relative humidity (RH) was 69.2% while the lowest was 53.6%, with an average RH of 62.9. The obtained results are consistent with the historical microclimatic parameter of the study area (NIMET, 2011).

3.2. Methods inter-comparison and humidity effects

The measured concentrations of TSP, PM_{10} , $PM_{2.5}$ and PM_1 with GT-531 S were compared to the gravimetric analysis as shown in Fig. S1. There was a very good correlation (eqn. (1)) between the two methods of determining mass concentrations of the different

particulate sizes. The regression analysis of the scatter plot of four particle sizes gave the slopes of less than unity with the R^2 values following the order: TSP ($R^2 = 0.90$) > PM_{10} ($R^2 = 0.88$) > $PM_{2.5}$ ($R^2 = 0.85$) > $PM_{1.0}$ ($R^2 = 0.71$). Overall, the results give reassurance that both monitors correlate well with each other in the determination of the ambient concentration of particulate matters. To establish the agreement between the GT-531 S and gravimetric measurements, the Bland-Altman plots (Bland and Altman, 1999; 2010) of TSP, PM_{10} , $PM_{2.5}$ and $PM_{1.0}$ calibration data were drawn as shown in Fig. S2. From the Figure, it could be seen that the limits of agreement (LoA) are not exceeded, hence further supporting that the two methods are in agreement with each other and may be used interchangeably for the determination of ambient concentration of particulate matters.

Particle-bound water significantly increases above 80% and 62% humidity, which are deliquescent points of $(NH_4)_2SO_4$ and NH_4NO_3 respectively. Thus, the increase in mass of particles above 68% RH and 80% RH causes more light scattering, leading to overestimation of PM values being recorded in PM monitors that utilize light scattering (McMurry et al., 1996; Chakrabarti et al., 2004; Karagulian et al., 2012; Cropper et al., 2013 such as the instrument used in this study. Therefore, for RH levels measured above 65%, PM values were adjusted according to a correction factor in equation (2) to obtain PM-RH bias values (eqn (3)). There was no significant difference in the calculated mean PM concentration values after humidity adjustment that incorporated >65% RH threshold ($p < 0.05$) during the wet period measurements.

3.3. Mass concentration of particulate matters

Fig. 2 shows the 8-hourly total particulate mass concentrations (TPMC) at different TIs types during the dry and wet periods. The dry period witnessed the highest total particulate mass concentration (TPMC) at SP2 with a total concentration of $2.2 \times 10^3 \mu g/m^3$, followed by SP3 and SP1 with total particulate mass concentration of $2.1 \times 10^3 \mu g/m^3$ and $1.9 \times 10^3 \mu g/m^3$ respectively. These high concentrations are related to the heavy traffic density at these TIs types. The TIs at SP6, SP5 and SP4 had the least total particulate mass concentration of $1.4 \times 10^3 \mu g/m^3$, $1.2 \times 10^3 \mu g/m^3$ and $1.3 \times 10^3 \mu g/m^3$ respectively, as a result of the low traffic density. On the other hand, in wet period, the highest mass concentration was recorded at SP4 and SP5 with a total particulate mass concentration

of $1.5 \times 10^3 \mu g/m^3$, followed by SP6, SP1 and SP2 with total particulate mass concentrations of $1.4 \times 10^3 \mu g/m^3$, $1.2 \times 10^3 \mu g/m^3$ and $1.2 \times 10^3 \mu g/m^3$ respectively while SP3 has the least total particulate mass concentration of $9.2 \times 10^2 \mu g/m^3$.

Particle size is an important parameter for fingerprinting of sources and behavior in the respiratory tracts. Particulate matters (PMs) have been categorized into three different sizes (i.e PM_{10} , $PM_{2.5}$ and $PM_{1.0}$) in this study. Different sources have been reported to characterize the contribution to coarse ($PM_{2.5-10}$) and fine ($PM_{2.5-1.0}$) particles, for instance coarse particles have been reported to be dominated usually by non-exhaust sources such as brake and tyre wear while fine particles are mainly due to fuel combustion in engines (Ketzel et al., 2007). The hourly averaged particulate mass concentration (PMC) range from 5.9×10^2 – $1.0 \times 10^3 \mu g/m^3$, 4.2×10^2 – $7.2 \times 10^2 \mu g/m^3$, 91.1 – $143 \mu g/m^3$, 46.6 – $84.5 \mu g/m^3$ for TSP, PM_{10} , $PM_{2.5}$ and $PM_{1.0}$ respectively during the wet period and 8.9×10^2 – $1.9 \times 10^3 \mu g/m^3$, 5.6×10^2 – $1.0 \times 10^3 \mu g/m^3$, 89 – $148 \mu g/m^3$, and 51.5 – $90.4 \mu g/m^3$ respectively for TSP, PM_{10} , $PM_{2.5}$ and $PM_{1.0}$ during the dry period. Fig. 3 shows hourly average mass concentration of PMs at different TIs types during different periods. The highest hourly mass concentration of TSP ($1.9 \times 10^3 \mu g/m^3$) at SP2; PM_{10} ($1.0 \times 10^3 \mu g/m^3$) at SP2; $PM_{2.5}$ ($147 \mu g/m^3$) at SP3 and $PM_{1.0}$ ($90 \mu g/m^3$) at SP2 are observed in dry period, while lower values of mass concentrations were observed for TSP, PM_{10} , $PM_{2.5}$ and $PM_{1.0}$ at all TIs types except at SP4 and SP5 for coarse particles in the wet period. The higher mass concentration of these PMs during the dry period than wet period at most of these TIs types might be due to different impact of resuspension of particles in dry and wet periods, resulting from various factors such as traffic flows of different types of vehicle that were present in the fleet, the influence of rain and winds as observed in other research works (Cao et al., 2006; Amato et al., 2009b; Norman and Johansson, 2006; de la Paz et al., 2015; Fernandez et al., 2017). In wet period however, factors such as wind speed, rainfall, the high relative humidity and lush vegetation can accelerate force deposition of particles (Jones and Harrison, 2004; Chate, 2005) and thus reached its lowest level in the atmosphere (Qiu et al., 2015). This observation is in agreement with the results of Teri et al. (2015) who noted that seasonal variation has effect on ambient PM load.

The ratios of $PM_{2.5}$ to PM_{10} , $PM_{1.0}$ to PM_{10} , and $PM_{1.0}$ to $PM_{2.5}$ are illustrated in Fig. 4. The average $PM_{2.5}/PM_{10}$, $PM_{1.0}/PM_{10}$ at all the TIs types are very low (generally below 20%), indicating that coarse particles were the greatest contributor to PM air pollution in these TIs types and thus confirming the dominance of non-exhaust sources such as brake and tyre wear. In addition, mass concentration levels of PM increased with increasing aerodynamic diameter. This is because, the larger the particulates, the longer the time for evaporation and agglomeration, whereas smaller particles ($PM_{1.0}$ and $PM_{2.5}$) evaporate faster and form agglomerates of larger particles within seconds due to condensation (Dasch and D'Arcy, 2008). This further corroborates the fact that concentration increases with increasing particle size due to agglomeration, accretion, coagulation and secondary formation processes (Sugimoto, 2000). The average $PM_{2.5}/PM_{10}$ and $PM_{1.0}/PM_{10}$ ratios were 16.2% and 10.1% respectively in dry period, lower than in wet period with 19.5% and 10.3% respectively. The average $PM_{1.0}/PM_{2.5}$ values were 62.6% and 51.9% in dry and wet period respectively, and ranged between 54.6% at SP3 – 72.1% at SP1 and 43.5% at SP4 – 59% at SP3 in dry and wet periods respectively. The proportions of $PM_{1.0}$ contained within $PM_{2.5}$ were quite high, further proving that ultra-fine particles were the greatest contributor to fine particulate air pollution that could be due to the anthropogenic emissions, primarily from fossil fuel combustion by vehicles and heavy duty generators used for industrial activities at these TIs types.

Fig. 5 shows the box plot of the mass concentration of PM during

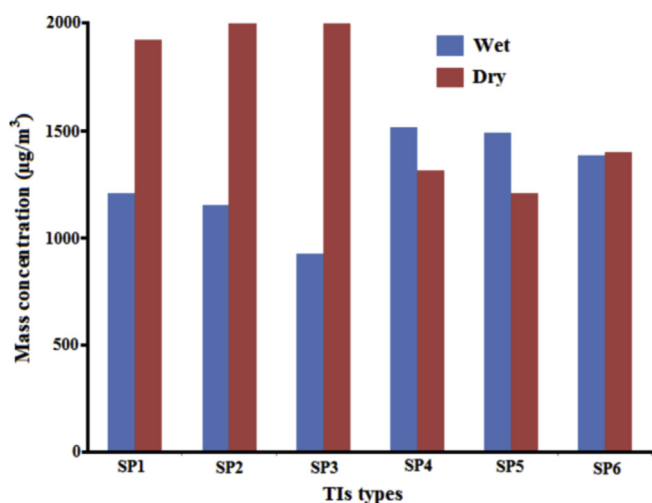


Fig. 2. 8-Hourly average total particulate mass concentration at different TI types during different periods.

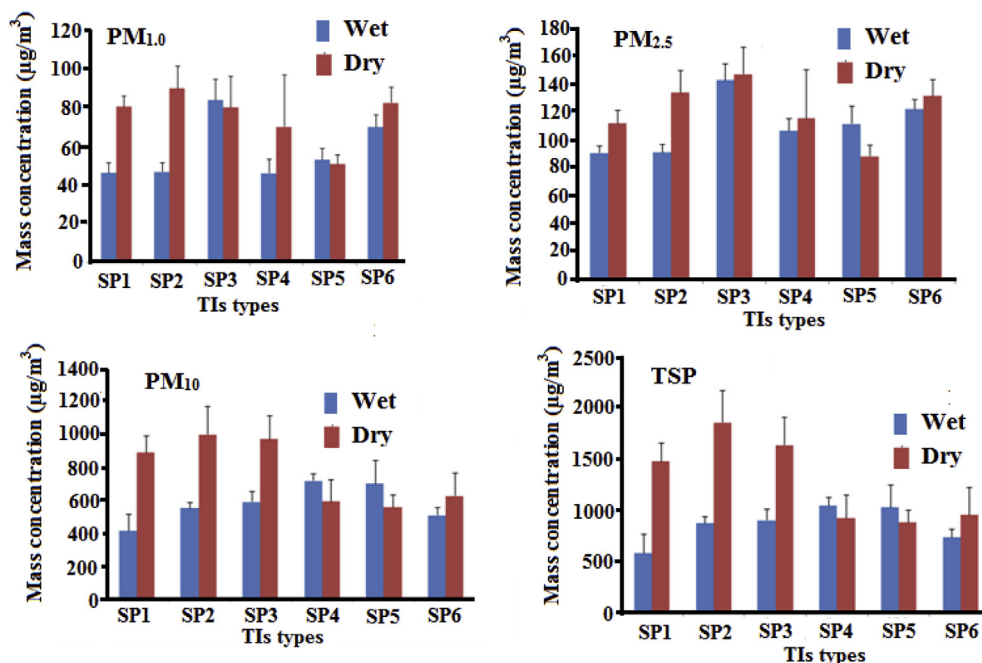


Fig. 3. Hourly average mass concentration of PMs at different TIs types during different periods.

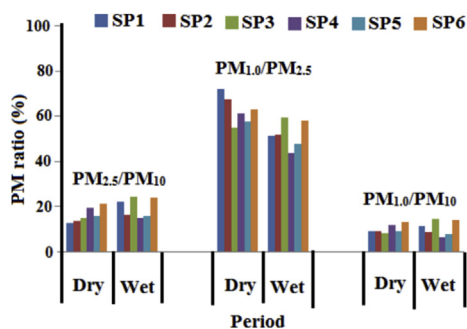


Fig. 4. PM ratio of TIs types at different periods.

rush (high traffic density) and non-rush hours (low traffic density), where we observed that the mass concentrations for rush hour periods are higher than those obtained for the non rush hour periods for all the particulate sizes. The average PM concentration levels during the rush hour periods were 1.1–3.7 times (PM_{1.0}), 1.3–3.4 times (PM_{2.5}), 1.2–3.7 times (PM₁₀), and 1.1–4.3 times of the concentration levels measured during the non-rush hour periods (low traffic density). Previous studies have shown that pollutants emission during traffic congestion are 2–4 times manifolds of those obtainable during the free flow traffic periods (Zhang et al., 2011, 2012; Shirmohammadi et al., 2017). The higher particulate emissions during rush hour are due to increase in vehicle population and increase in idle time they spend in traffic snarl while undergoing numerous acceleration and decelerations. Literature has also established that vehicular fuel consumption and associated pollutants emission during rush hour congestion are higher than the amount during free-flow traffic condition (Zhang et al., 2011).

3.4. Respiratory deposition dose

The average respiratory deposition dose (RDD) for PM₁₀, PM_{2.5} and PM_{1.0} for both periodical variation and traffic flow density

presented in Fig. 6. The average on-road RDD rate obtained during the dry period at TIs were $10.8 \pm 1.9 \mu\text{g h}^{-1}$, $35.7 \pm 6.1 \mu\text{g h}^{-1}$ and $221 \pm 58 \mu\text{g h}^{-1}$ for PM_{1.0}, PM_{2.5} and PM₁₀ respectively; while the estimated average on-road RDD rates during the wet period at TIs were $8.2 \pm 2.2 \mu\text{g h}^{-1}$, $32.6 \pm 5.8 \mu\text{g h}^{-1}$ and $166 \pm 33 \mu\text{g h}^{-1}$ for PM_{1.0}, PM_{2.5} and PM₁₀ respectively. The average on-road RDD rates of PM_{1.0}, PM_{2.5} and PM₁₀ during the dry period at all the TIs were found to be about 24%, 9% and 25% higher than those during the wet period (Fig. 5).

Similarly the average on-road RDD rate obtained during the rush hour (high traffic density) at TIs were $6.9 \pm 2.8 \mu\text{g h}^{-1}$, $24 \pm 11 \mu\text{g h}^{-1}$ and $159 \pm 74 \mu\text{g h}^{-1}$ for PM_{1.0}, PM_{2.5} and PM₁₀ respectively; while the estimated average on-road RDD rates during non-rush hours (free flow periods) at TIs were $4.0 \pm 1.4 \mu\text{g h}^{-1}$, $16.1 \pm 4.2 \mu\text{g h}^{-1}$ and $102 \pm 41 \mu\text{g h}^{-1}$ for PM_{1.0}, PM_{2.5} and PM₁₀ respectively. RDD rates obtained during the rush hour periods (high traffic density) were found to be about 42%, 33% and 36% higher than those obtained during the non-rush hours (free flow periods) (Fig. 6). Previous studies have pointed out that short term peak exposure levels may trigger acute health condition such as sneezing, coughing and asthma (Manigrasso and Avino, 2012), and have been linked with short-term cardiovascular and respiratory health effects (Zuurbier et al., 2010). PM_{1.0} and PM_{2.5} which are often referred to as ultrafine and fine particulate fractions, respectively are inhaled deeply into the alveoli of the lungs causing extensive damage to the body. PM₁₀ are generally associated with inflammatory responses (Zwozdziak et al., 2017). RDD estimated values were calculated on hourly basis and can be used to quantify pedestrian exposure. However, the values could be in several multiples for traffic delay conditions (rush hour periods) and roadside hawkers who often spend majority of their time at the TIs.

3.5. Particulate-bound metals

Table 1 shows the mean concentration and standard deviation of metals determined in the deposited particulate matters at the TIs types. Fe, Mn, Pb and Zn were the most abundant elements at all the

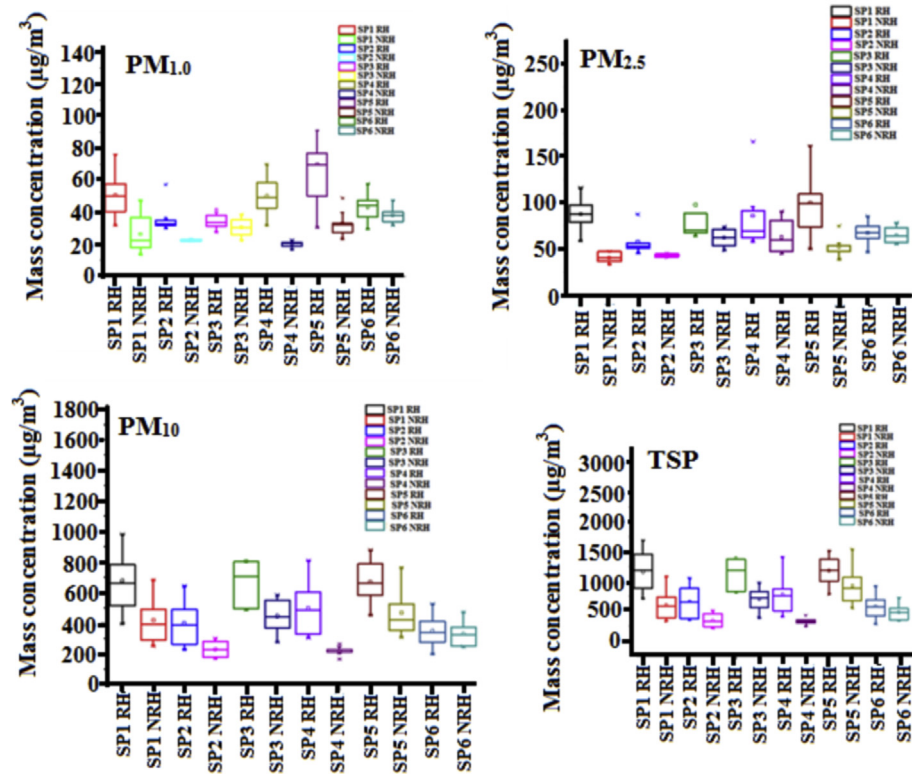


Fig. 5. Box plot showing the mass concentration of PM for rush (high traffic density) and non-rush hour (low traffic density) periods.

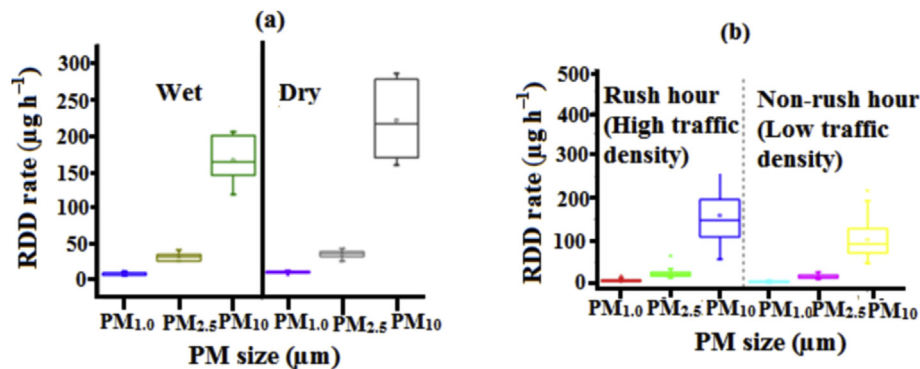


Fig. 6. Average RDD rate of PM_{1.0}, PM_{2.5} and PM₁₀ for periodic variation (a), and traffic flow density(b).

Table 1

Summary of particulate –bound metal concentrations in air (mg/m³) at TIs types of Ilorin metropolis.

TIs type	Fe × 10 ³	Zn	Cu	Pb	Mg	Mn	Cr	T _m × 10 ³
SP1	24.8 (1.4) ^a	351 (47.8)	53.7 (9.6)	294 (21.7)	91.1 (7.9)	584 (56.5)	13.2 (2.6)	26.2
SP2	10.5 (0.7)	210 (29.6)	35.4 (2.8)	236 (22.1)	105 (12.3)	185 (15.9)	36.2 (4.9)	11.3
SP3	14.5 (1.0)	405 (41.6)	36.9 (3.8)	403 (39.4)	101 (14.8)	303 (28.9)	61.7 (11.2)	15.8
SP4	26.8 (1.5)	413 (38.7)	68.8 (11.2)	672 (55.9)	99 (6.5)	594 (61.2)	34.8 (3.9)	28.6
SP5	9.8 (0.5)	127 (14.5)	63.6 (8.4)	118 (10.2)	88.6 (5.6)	169 (14.7)	16.8 (2.1)	10.4
SP6	31.1 (1.8)	911 (77.2)	76.8 (10.5)	513 (41.4)	100 (9.6)	803 (78.9)	46.3 (2.6)	33.5

^a Values in parenthesis are the standard deviation(±SD), σ_{n-1} ; T_m, total metal concentration.

TIs, and accounted for about 91.2–94.6%, 1.6–2.4%, 1.1–2.5% and 1.2–2.7% of the total metal contents at each TIs respectively. Fe is a major component of crustal materials and soil and is mainly attributed to resuspension of dust resulting from vehicular movement around the TIs and those blown by wind in the surrounding (Lough et al., 2005). The high Zn level may be related to metal-based oil additives containing zinc, anti-wear agents (Zn-based), while Pb and Mn can be associated with the use of lubricating oil containing trace amounts of Pb and Mn as additive (Lim et al., 2007). Cu, Mn, Cr, Pb levels could also be related to dusts originating from brake and tyre wears (Minguillón et al., 2014). The total metal concentrations at the TIs types follow the order: SP6>SP4>SP1>SP3>SP2>SP5. The high total metal load at these TIs types can be attributed to vehicular emission as well as tyre and brake wear in automobiles (Grigoratos and Martini, 2015) and local fuel combustion sources (Olatunji et al., 2015).

In order to elucidate the sources of particulate-bound metal

Table 2
Enrichment factors (EF_{crust}) based on mean and relative to Fe for all TIs types.

Metal	SP1	SP2	SP3	SP4	SP5	SP6
Cu	2.8	4.3	3.2	3.3	8.3	3.2
Fe	1.0	1.0	1.0	1.0	1.0	1.0
Mn	1.2	0.9	1.1	1.2	0.9	1.4
Zn	6.4	9.0	12.6	7.0	5.8	13
Cr	0.2	1.3	1.6	0.5	0.6	0.6
Pb	19	36	44	40	19	26
Mg	0.0	0.0	0.0	0.0	0.0	0.0

Upper crust Concentration($\mu\text{g/g}$): Pb = 20, Zn = 71, Cu = 25, Cr = 85, Mn = 600, Fe = 32000, Mg = 20900 (Taylor and McLennan, 1985).

species, enrichment factor (EF) of all the metal species in the atmosphere relative to natural (crustal) material was calculated using the following equation;

$$EF_{crust} = (C_x/Fe)_{air} / (C_x/Fe)_{crust} \quad (12)$$

where $(C_x/Fe)_{air}$ is the concentration ratio of mean trace metal to Fe in the air suspended particulates and $(C_x/Fe)_{crust}$ is the ratio in the average crustal materials. The equation above (Eq. (9)) was applied in this study by using the average chemical composition of the upper continental crust given by Taylor and McLennan (1985). Going by the general norm, where EFs <10 is taken as an indication of crustal-derived trace metals source in the atmosphere and these are termed the non-enriched elements (NEEs). In contrast, an EF value of >10 is considered to indicate non-crustal source or anthropogenically-derived trace metal source, and these are referred to the anomalously enriched elements (AEEs) (Caroli, 1996; Cheng et al., 2005). In this study however, EFs were calculated based on Fe natural abundance in crustal materials (Table 2). High EF values (>10) were calculated for Pb at all the TIs types, and for Zn at SP3 and SP6 TIs only (Table 2), due to dominance of anthropogenically– derived source and thus representing the group of the so-called anomalously enriched elements (AEEs). The sources of these metals at these TIs may include metal smelting, coal combustion, vehicle exhaust and incineration. Relatively low EF values ($EF < 10$) were calculated for Cu, Fe, Mn, Cr and Mg and thus belonging to the non-enriched elements (NEEs). Although Fe and Mn have been reported to originate from metal smelting while Cr, Cu, and Fe have been linked to vehicle exhaust (Thorpe and Harrison, 2008; Zhou et al., 2014; Świetlik et al., 2015; Kelepertzis et al., 2016; Yıldırım and Tokaloğlu, 2016; Crilley et al., 2017; Gope et al., 2017), but they exhibit a dominance of crustal-derived source in this study.

The SEM imagery of the deposited PM (Fig. S3) at the TIs show morphologies dominated by particles of different compositions, sizes and shapes in the particle populations. These particles are mostly rich in Fe, Mn, Pb and Zn suggesting that the deposited particulate matter is a mix of combustion derived and traffic induced dust resuspension. This finding is in agreement with the findings of Mitchell and Maher (2009). The clustered particulate formed as observed from the SEM images indicates that the particles are formed under gravitational sedimentation in consistent with the prevailing microclimatic condition in the study area.

3.6. Estimates of dry deposition flux

The estimated dry fluxes of the trace elements at the TIs types are presented in Table 3. The average flux of deposited particulates ranged from 7.2 g/m²/day for SP3 to 16.0 g/m²/day for SP1. The fluxes of the crustal-derived elements such as Fe, Mg and Mn, that is, the NEEs were higher than the fluxes of other anthropogenically-derived elements such as Pb, Zn, Cu and Cr, that is, the AEEs, at all

Table 3
Average estimates of dry deposition flux ($\text{g m}^{-2} \text{ day}^{-1}$) of mass deposited particles and metallic elements at the TIs types of Ilorin metropolis.

TIs type	PM ^a	Fe x 10 ^{4b}	Zn ^b	Cu ^b	Pb ^b	Mg x 10 ^{2b}	Mn x 10 ^{2b}	Cr ^b
SP1	16.0	4.3	30.3	4.6	25.4	1.6	10.1	1.1
SP2	7.3	1.8	18.1	3.0	20.4	1.8	3.2	3.1
SP3	7.2	2.5	35.0	3.2	34.8	1.7	5.2	5.3
SP4	11.4	4.6	35.7	5.9	58.1	1.7	10.3	3.0
SP5	15.2	1.7	11.0	5.5	10.2	1.5	2.9	1.4
SP6	10.9	5.4	78.7	6.6	44.3	1.7	13.9	4.0

^a Deposition flux of atmospheric dust deposited particles.

^b Dry deposition flux for seven metal species (Fe, Zn, Cu, Pb, Mg, Mn and Cr) in total suspended particulates.

the TIs types due to their higher concentrations and settling velocities. Fluxes for NEEs follow the sequence Fe > Mn > Mg at all the TIs types, while there is no regular trend among the TIs types for AEEs but flux for Cr appears to be the least at most of the TIs types.

3.7. Factor analysis

Factor analysis (FA) was applied to interpret relationships between variables and we have used the technique of Principal Component Analysis (PCA). The basic purpose of PCA is to account for the total variation among the variables in p -dimensional space by forming a new set of orthogonal and uncorrelated composite variates. Each member of the new set of variates is a linear combination of the original set of measurements (Henry and Hidy, 1979; Liroy et al., 1989). The linear combinations are generated in such a manner that each of the successive composite variates will account for a smaller portion of the total variation. The first composite (principal component) will have the largest variance; the second will have a variance smaller than the first but larger than the third, and so on (Table S1). Strong correlations were observed among the particulates of different sizes. Strong correlations also exist among the measured particulates of different sizes and the traffic counts as the obtained value were generally above 0.70. Weak correlations exist between ambient particulates measured and Fe. The same trend was observed for deposited PM. Measured ambient PM have low correlation (>0.4) with Zn and Cd. PM_{1.0} and PM_{2.5} exhibited strong positive for Mg and Cr. Weaker correlations exist between PM and Pb as values obtained were generally <0.3. Coarse particles are richer in Mn. Very strong negative correlation existed between the deposited PM and ambient fine PM fractions (PM_{1.0} and PM_{2.5}). This is expected because higher PM fractions will settle faster due to the influence of force of gravity. PM with smaller aerodynamic diameters tend to stay airborne for a longer period than the larger fractions. Deposited PM are richer in Cu, Mn and Fe. The elements have good correlations among themselves and they are typically associated with exhaust and non exhaust sources. Pb and Zn have very good correlations with other metals. Pb is usually associated with antropogenic sources while Zn is of crustal origin. High correlation values were obtained for RDDs and their respective concentration levels. This suggests that the higher the concentration, the higher the amount deposited in the respiratory tracts of exposed individuals. Traffic counts (TC) has positive impact on the amount of pollutants emitted as observed. TC has high correlation values with concentration levels and deposited doses.

Table S2 displays the factor loadings with a varimax rotation as well as the eigenvalues, percentile of variance and cumulative percentage. The communalities are inserted in the diagonal of the correlation matrix (Table S3). In reference to the eigenvalues, three factors were extracted as they have eigenvalues greater than 1 (Table S3). Factor one accounted for 52.2% of total variance with

high loading of PM_{1.0}; factor two accounted for 30.9% of the total variance with high loading of PM_{2.5} while factors 3 accounted for 11.2% for PM_{1.0}. Our data therefore resulted in three PCs with eigenvalues greater than 1, accounting for 94.3% of the variance. We applied a varimax rotation in order to simplify the interpretation of these three components and with a view to finding variables that have an interpretation in terms of different sources of pollution. When we considered the correlation loadings of rotated components, we observed that the first component (vcPC1) is highly correlated with the pollutants PM_{1.0}, PM_{2.5}, PM₁₀, TSP, RDDPM_{1.0}, RDDPM_{2.5}, RDDPM₁₀, Mg, and moderately correlated with Cr and Traffic count/min (Table S4). This might indicate a relation with fuel and oil combustion (Barrientos et al., 2016; Shi et al., 2016) by vehicles as well as industrial sources or continuously working energy production related sources. Thesecond component, (vcPC2), has its strongest correlation loading (>0.9) with Fe, Zn, Mn and Pb and moderate correlation with Cu (Table S4). This seems to point to a source that mainly includes road dust resuspension and brake wears (Lawrence et al., 2016). The third component (vcPC3) is weakly correlated with traffic count/min and deposition flux (DF) (Table S4), further supporting traffic related emission sources. Fig. S4 shows the component plot in rotated space for these three components.

4. Conclusion

This study has identified the sources of high concentration levels of ambient particulate matter in the locations of major TIs in Ilorin metropolis. It has given a good insight of exposure to particulate matter at and around six major traffic intersections (TIs) in the study area. The ambient PM concentration levels obtained were generally above the prescribed WHO air quality standards. Higher concentration levels were observed for rush hours and dry period. Mass concentration levels of PM were observed to have increased with increasing PM aerodynamic diameters. SEM images indicate that the particle populations are dominated by spherical, iron-rich particles. RDD values indicate that road users are exposed to high concentrations of these particulates. The results of our analysis revealed existence of strong relationships among the measured data which had physical meanings. More specifically, PCA applied on measured particulate data resulted in components generally related exhaust and non exhaust emissions such as tyre wears, oil and fuel combustion sources. The results can be useful in the design of lasting pollution mitigation strategies such as the use of cleaner fuels and pollution abatement methods such as decongestion of these TIs by providing alternate routes for heavy duty vehicles.

Conflicts of interest

The authors declare no conflict of interest regarding the publication of this paper.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.atmosenv.2017.07.041>.

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