CHARACTERIZATION OF TRACE METALS IN TSP ALONG A DENSE TRAFFIC HIGHWAY IN OGBOMOSO, NIGERIA

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Abstract- Total Suspended Particles (TSP) in ambient air were collected at seven spots along a dense traffic highway in Ogbomoso, Nigeria. Particulate matters in TSP were extracted from filters by digestion method using a mixture of HNO₃ and H₂O₂ and the extract was analyzed for ten trace metals using Atomic Absorption Spectrophotometer (AAS). The concentration of TSP in air varied from 69.44 – 185.19 µg/m³ while the average concentration of the trace metals in TSP were 43.91, 36.99, 30.79, 48.28, 31.84, 302.5, 46.79, 105, 39.36 and 336 µg/m³ for Cd, Cr, Mn, Pb, Zn, Cu, As, Ca, Ni and Fe, respectively. The mean concentrations of trace metals in TSP were found in the order of Fe > Cu > Ca > Pb > As > Cd > Ni > Cr > Zn > Mn. Correlation studies showed that the trace metals originated from common source along the highway: Cd was highly correlated with Cu (r = 0.8516), Cr was highly correlated with Mn (r = 0.7844), Pb with Mn (r = 0.7455), Ca with Cr (r = 0.7581) and Zinc (r = 0.8471), and Ni with Cd (r = 0.7325). Trace metals concentration in TSP along Ogbomoso Section of Ibadan–Ilorin highway were higher than WHO and FEPA standard limits of trace metals in air but much lower than the values reported in other cities of the world. Enrichment factor analysis showed that Cd, Cr Zn, Cu, As, Pb and Ni originated from anthropogenic sources, majorly traffic and industrial activities while Fe, Mn and Ca were of crustal origin.

Keywords- TSP, Trace metals, Enrichment Factor, Highway.

I. INTRODUCTION

Atmospheric transport and deposition of aerosol is a significant source of trace metals to the earth surface. Total suspended particles (TSP) in ambient air are frequently considered as atmospheric pollutants due to their ability to bind to toxic substances and hazardous matter. Many studies have shown the close relationships between the high concentrations of TSP and an increased risk of respiratory symptoms, cancer and even mortality rates [1, 2]. Besides their adverse effects on visibility [3], TSP have been found to be the carriers of pathogenic bacteria that lead to fatal diseases [4] and toxic metals that result in human dysfunction and various diseases [5, 1]. Metals in particulate matter (PM) usually have both natural and anthropogenic origins. Natural sources such as crustal minerals, forest fires and oceans; and anthropogenic sources such as industrial activities, waste incineration, fossil fuel burning [6, 7, 1], traffic emissions [8], were the principal contributors to metals in the ambient air [9].

Traffic emissions have been reported as the most significant local particle source affecting urban air quality in metropolitan area [10, 11]. Non-crustal elements associated with particulate matter near the highways mostly come from vehicle emissions [12, 13]. Studies conducted on vehicular emissions along highway in several urban regions such as New Jersey, (US), Helsinki Metropolitan area (Finland) and Dhaka, (Bangladesh) [14, 15, 16], have shown that the concentration of trace elements varied as a function of distance from highway [17]. There is a major concern about trace metals, such as Ca, As, Cd, Cu, Fe, Pb, Zn, Cr, Ni, and Mn, because of their toxicity and potential carcinogenic property, increased mortality rates and their persistence in the environment [18, 19, 20, 21, 22].

Ogbomoso axis of Ibadan–Ilorin highway being a major route linking the Northern and Southern parts of Nigeria has witnessed an increased traffic level by cars and motor cycles due to the influx of both staff and students to the university and the university teaching hospital, which were not in existence some years ago, coupled with traffic
flow of heavy trucks along the highway. All these have given rise to high traffic emissions and dust generation. This paper presents the concentration level of total suspended particles (TSP) and the trace metal components (Ca, As, Cd, Cu, Fe, Pb, Zn, Cr, Ni, and Mn) in ambient air in Ogbomoso. The contributing source of the trace metals is investigated with the use of the enrichment factor analysis.

II. MATERIALS AND METHODS

2.1. Sampling site and sampling procedures

2.1.1. Sampling site

Ogbomoso city is a pre-colonial urban centre and the second largest city, both in terms of population and spatial extent, in Oyo State, Nigeria. The city is situated in South-Western Nigeria (4° 16' 0" East; 8° 8' 0" North) (Fig 1). It is located at a distance of about 100 km north of Ibadan, the Oyo State capital, and about 52 km from Ilorin, Kwara State capital. The map of the study area is shown in Fig. 2. It is one of the important gateways to the Northern part of Nigeria from the Yoruba land. It develops laterally towards the north and south along the Ibadan-Ilorin road [23]. The city is characterized by two distinct seasons: dry (November – March) and wet (April – October) with a mean annual rainfall of 1200 mm distributed seasonally. Temperature ranges are small and constant throughout the year. Its hottest month records 32.48 °C (90 °F) and its coolest month 26.88 °C (70 °F) with the temperature range of not more than 8 °C (20 °F). Being located along Ibadan – Oyo – Ilorin route, Ogbomoso has witnessed growth in road traffic. There has not been an increase in industrial activities along the highway. Major industries in the town include small agricultural processing industries, welders workshop, paint and pharmaceutical industries. On the other hand, there has been an increase in the number of vehicles for personal and commercial use in the town. Thus, traffic emission and road dust are expected to be the major sources of air pollution along the highway. The selection of the sampling site was based on several factors including nearness to the highway, minimizing potential for sample contamination, and ease of access. Based on the above criteria, seven sampling spots were chosen along Ogbomoso section of Ibadan-Ilorin highway. The characteristics of the sampling spots are given in Table 1. This research work was carried out along Ibadan-Ilorin highway that spans Ogbomoso town-ship. TSP samples were collected on filters and the filters were analyzed for ten trace metals using AAS.
Table 1: Characteristics of the Sampling Locations

| Sampling location | Height of sampling location (m) | Distance from the highway (m) | Description |
|-------------------|---------------------------------|------------------------------|-------------|
| High school       | 3.5                             | 12.5                         | Intersection with high traffic |
| Idi Oro           | 4.8                             | 6.7                          | Medium traffic, welder activities, filling station |
| California        | 10.6                            | 16                           | Medium traffic, welder activities |
| Olopemarun        | 5                               | 15.3                         | Medium traffic, welder activities, iron bender, animal feed |
| Takie             | 7.4                             | 4.2                          | High traffic, filling station, motor park, road construction, commercial activities |
| Starlight         | 4.67                            | 16.9                         | High traffic, filling stations, motor park |
| Sabo              | 6.5                             | 5.8                          | High traffic, commercial activities |

2.1.2. Sampling Procedure

Total suspended particles were collected on filters by gravimetric air sampling method using Negretti air sampler (Model NR 700). A sampling period of 6 hours was adopted. In this method, air samples were drawn from the atmosphere using a vacuum pump with a flow rate of 12 L/min through pre-weighed cellulose filters (Whatman) of size 2.5 cm diameter. Prior to use, the filters including the blank filters were desiccated and tarred, then placed in an aluminum foil and a zip-lock bag. After sampling, the filters were desiccated (to remove any moisture content) and re-weighed using a high-precision balance (Mettler Toledo XP6) to determine the change in the weight of the filters. The weight of TSP on the filters were determined by subtracting the initial weight from the final weight [24]. The loaded filters were then placed in an aluminum foil and sealed in a plastic zip-lock bag until analysis to minimize contamination and kept in freezer until chemical analysis to limit losses of volatile components [16]. Filter blanks were stored and processed in an identical manner as the loaded filters.

2.2. TSP Mass Concentrations

Mass concentrations of TSP was calculated using equation 1

\[
\text{Concentration of TSP} = \frac{10^6(W_2 - W_1)}{Q \times t}
\]

Where,

- \( W_1 \) = weight of the filter before sampling (g),
- \( W_2 \) = weight of the filter after sampling.

\( Q = \) volumetric flow rate of inlet air (m\(^3\) / hour), \( 10^6 = \) conversion from g to µg

\( t = \) time in hour

2.3. Concentration of Trace Metals in TSP

The concentrations of the selected trace metals: Ca, As, Cd, Cu, Fe, Pb, Zn, Cr, Ni and Mn in TSP, were determined as follows: the filters were separately digested in a 20ml mixture of nitric acid (HNO\(_3\)) and perchloric acid (HClO\(_3\)) in ratio 2:1 [25], and then diluted to 25 ml with distilled-deionized water. The digest (25 ml) was used to determine the concentrations of the selected trace metals (Ca, As, Cd, Cu, Fe, Pb, Zn, Cr, Ni and Mn) using Buck Scientific Atomic Absorption Spectrometer (AAS Buck Scientific VGP 210 Model) at the Centre for Energy Research and Development (CERD) at Obafemi Awolowo University, Ile Ife, Nigeria. The instrument was calibrated with appropriate standards to obtain calibration curves. The background contamination was monitored using blanks filters (unexposed filters) that were treated in a similar manner with field samples.

2.4. Enrichment Factor of Trace Metals in TSP

The concentrations of trace metals in TSP should be linked to natural sources in the absence of anthropogenic sources. However, emissions from the various anthropogenic sources have drastically increased the concentrations of trace metals in our environment. To identify the origin of trace metals in precipitation, enrichment factors (EF) analysis is always applied, to show the degree of enrichment of a given element compared to the relative abundance of that element in crustal material [26]. Na, K, Al, Mg, Ca, Mn and Fe are used as the reference metals in most cases. Concentration
of trace metals detected in TSP samples were correlated and Fe showed the best correlation with all other metals hence, selected as the reference element [27,28]. Efs < 10 indicate metals having crustal origin; 10 < Efs < 100 indicate moderate anthropogenic enrichment, showing greater concentrations of a particular metal in the TSP than would be expected from the crustal origin and metals with Efs >100 are considered to be of anthropogenic origin.

The enrichment factor was calculated using Equation (2)

$$EF(X) = \frac{(X/Fe)_{TSP}}{(X/Fe)_{Crust}}$$

Where: $EF(X) = \text{enrichment factor}$, $(X/Fe)_{TSP} = \text{mean concentrations of the target element and Fe in TSP}$, and $(X/Fe)_{Crust} = \text{mean concentrations of the target element and Fe in continental crust respectively}$. Efs < 10 indicate metals having crustal origin; 10 < Efs <100 indicate moderate anthropogenic enrichment, indicating greater concentrations of a particular metal in the TSP than would be expected from the crustal material and metals with Efs>100 are considered to be of anthropogenic origin.

III. RESULTS AND DISCUSSION

3.1 TSP Mass Concentration

The mass concentration of TSP determined at the seven sampling locations along the highway ranged from 69.444 µg/m³ to 185.185 µg/m³ as shown in Table 1. The lowest concentration of TSP was observed at Olopemarun, while the highest was observed at Takie, suggesting a strong influence from local sources like vehicle emissions at the location. The average concentration of TSP along the highway, 116.07 µg/m³, is much below the 250 µg/m³ maximum daily TSP concentration set by the national environmental pollution regulatory body, Federal Environmental Protection Agency of Nigeria [29]. The average concentration of TSP (116.07 µg/m³) obtained in this study is comparable with the result (138.88 µg/m³) obtained around a transportation area in Lagos [30], and with the average concentration of TSP 118.4 µg/m³, obtained Central Taiwan (Fang et al, 2014) but lower than the average concentration of TSP (269.93 µg/m³) obtained at Calabar [31].

| Sampling spots | Concentration of TSP (µg/m³) |
|----------------|-----------------------------|
| High school    | 115.70                      |
| Idi oro        | 138.89                      |
| California     | 92.59                       |
| Olopemarun     | 69.44                       |
| Takie          | 185.19                      |
| Starlight      | 115.74                      |
| Sabo           | 94.91                       |

Table 1. TSP Mass Concentration

3.2 Concentrations of Trace Metals in TSP

The concentrations of the trace metals components of TSP in ambient air ranged from 22.94 – 77.99 µg/m³; 31.84 – 59.43 µg/m³; 22.45– 40.41 µg/m³; 42.25 – 67.59 µg/m³; 29.18 – 47.76 µg/m³; 285.1 – 362.9 µg/m³; 39.80- 67.35 µg/m³; 97.96 – 125.7 µg/m³; 38.33 – 62.29 µg/m³ and 235.4 – 445.7 µg/m³ for Cd, Cr, Mn, Pb, Zn, Cu, AS, Ca, Ni and Fe, respectively (Table 2). Among the trace elements in TSP samples, major contribution was noted for Fe and Cu. Increasing trend of average trace metals concentrations in the TSP revealed the following order: Mn < Zn < Cr < Ni < Cd < As < Pb < Ca < Cu < Fe. These values are higher than the daily standard limit set by WHO and ATSDR [32,33].

The results of trace metals component of TSP clearly showed that vehicles as pollution emission sources contribute differently to different trace elements in the ambient air, and there are regional differences with respect to the strength of pollutant emissions. Almost all elements showed their maximum concentrations at Takie suggesting stronger influence from anthropogenic sources, such as the increased vehicular traffic at this site except for Zn, Cr and Ca, which have the highest concentration at Olopemarun.

| Sampling spots | Cd  | Cr   | Mn   | Pb   | Zn   | Cu   | As   | Ca   | Ni   | Fe  |
|----------------|-----|------|------|------|------|------|------|------|------|-----|
| High school    | 22.94 | 44.57 | 22.45 | 42.25 | 29.18 | 313.6 | 67.35 | 107.8 | 43.13 | 235.4 |
| Idi oro        | 36.70 | 31.84 | 24.69 | 42.25 | 37.14 | 323.9 | 64.29 | 114.3 | 45.52 | 306.3 |
The presence of Cd in the environment could be from natural sources but the other possible sources of Cd in this study may be through anthropogenic activities. It was concluded that the presence of industries and several combustion processes like the car emissions contributed to the atmospheric Cd in the study area [34]. Wear of the brake lining and of other metallic parts of vehicles have been reported to be the major source of Cd in the environment[35]. In a study [36], it was also discovered that the most concentration levels of Cd were recorded in traffic zone. Cd in the environment is traced to Di-methyl cadmium used in the production of tetraethyl lead and its emission could be linked to vehicle emissions[37]. The highest (77.99 µg/m³) and lowest (22.94 µg/m³) concentrations of Cd were detected at Takie and California, respectively. These concentrations are above the WHO, EPA and ATSDR standard value of 0.005 – 0.5 µg/m³ [32,33,38] (Table 3).

The average concentration of Pb (48.28 µg/m³) in TSP is higher than EPA standard value of 1.50 µg/m³ by EPA [38] and 0.50 µg/m³ by ATSDR [33] (Table 3). Lead is one of the major trace elements in urban environment due to its long residence time in the environment. The presence of Pb in the environment could be due to several emission sources such as carbon black plant, non-ferrous metal smelting, steel and pipe manufacturing plants, gas flare burning and heavy traffic of vehicles. However, the presence of Pb in TSP along Ogbomoso section of Ibadan-Ilorin highway could be attributed to heavy traffic of vehicles since most of these industrial activities are rare along the highway. A high concentration of Pb in zones with higher anthropogenic activities such as heavy traffic of vehicles [40].

### Table 3 Comparison of Concentration of Trace Metals in TSP with Regulatory Standards

| Body       | Cd     | Cr     | Mn     | Pb     | Zn     | Cu     | As     | Ca     | Ni     | Fe     |
|------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| WHO*       | 0.005 – 0.5 | NA     | 0.150  | NA     | NA     | 0.007  | NA     | 0.02   | NA     |        |
| EPA*       | 0.006  | 0.006  | NA     | 1.500  | 0.103  | 0.290  | NA     | NA     | NA     |        |
| ATSDR*     | 0.005  | NA     | NA     | 0.500  | NA     | NA     | NA     | NA     | NA     |        |
| This study | 43.91  | 36.99  | 30.79  | 48.28  | 31.84  | 302.5  | 46.79  | 105    | 39.4   | 336    |

*WHO, 2000; EPA, 2013; ATSDR, 2002

Reports of some studies carried out in urban areas have shown that, a high concentration of Pb in the atmosphere was due to the effect of industrial and traffic activities. It was also reported that a high concentration of Pb was always associated with high traffic density in Ogun state [34, 36]. Along Ogbomoso section of Ibadan-Ilorin highway, the primary source of Zn observed may be
probably from motor vehicle tyre wear caused by poor road surfaces, and the lubricating oils in which Zn is found as part of many additives such as zinc Dithiophosphates. This is because there are no major industrial activities, such as smelting operations, along the study area. [36] reported that the highest levels of Zn in wet deposition were shown in traffic and industrial stations. The highest and lowest concentrations of Zn were observed at Olopemarun (47.76 µg/m³) and High School and Starlight (29.18 µg/m³). [39] attributed the high concentrations of Zn in bulk depositions to the elevated concentrations of this metal in the atmosphere. [14] have reported tyre wear as one of the primary sources of Zn in the urban atmosphere. The fact that Zn primarily originates from the wear of vehicle tyre and other components can be further supported by the findings from the studies undertaken by [41,42]. The average concentration of Zn (31.84 µg/m³) in TSP is higher than EPA standard value of 0.103 µg/m³ [38] (Table 3).

The average concentration of Cu (302.5 µg/m³) in TSP is higher than EPA standard value of 0.290 µg/m³ [38] (Table 3). High Copper concentration in TSP along the highway could be due to vehicular emissions along the highway. In a study [43], the presence of Cu was attributed to vehicular emissions or oil combustion and re-suspended road dust. Wang et al [44] also attributed the presence of copper to chemical industries and intensive traffics. Most of man-made emissions of As originate from metal smelters which is emitted in form of arsenites or arsenates whereas natural sources are from volcanic activities. These activities are rare in the study areas and this explains the low concentration of As in the environment.

Ni pollution along the highway could be due to smoking of cigarette because WHO asserted that mainstream cigarette smoke contains 0.04-0.58 micrograms Ni/cigarette and consuming 20 cigarette/day will increase the ambient Ni value by 15 times [32]. The highest and lowest concentrations of Ni were observed at Olopemarun (62.29 µg/m³) and High School and Starlight (38.33 µg/m³). The average concentration of Ni (39.36 µg/m³) in TSP was above the WHO standard value of 0.020 µg/m³ [32] (Table 3).

For Fe, the highest (445.7 µg/m³) and lowest (235.4 µg/m³) concentrations were detected at Olopemarun and High School, respectively. The presence of Fe in TSP along the highway could be due to the natural origin of the studied area and tear of certain parts of vehicles moving on the road. It can also be from dropping of metal scraps by the roadsides. A very high concentration of Fe to the occurrence of Fe at high concentrations in Nigerian soils. The presence of Fe was also reported in emissions from heavy-duty vehicles [45,46].

### 3.3 Pearson’s Correlation Matrix among the Trace Metals Measured in Wet Deposition

Correlation coefficient is a measure of the linear correlation between two variables and giving a value between +1 and −1. Where 1 is total positive correlation, 0 is no correlation, and −1 is the total negative correlation. It is usually performed to distinguish the possible common sources of constituents [47,16].

The Pearson’s correlation matrix among the trace metals measured in TSP along Ogomoso section of Ibadan-Ilorin Highway are presented in Table 4. All positive and strong correlations indicate relationship among the trace metals in the same trend such that increase in the concentration of any suggests increase in concentration of the other. Concentration of Cd was moderately correlated with Cr (r = 0.5303) and Pb (r = 0.5303) and highly correlated with Mn (r = 0.8476), Cu (r = 0.8516), As (r = 0.9529) and Ni (r = 0.8653), Cr was highly correlated with Zn (r = 0.912), Cu (r = 0.824) and Ni (r = 0.81) and moderately correlated with Ca (r = 0.71). Mn was strongly correlated with As (0.8662) and moderately correlated with Fe (r = 0.741). This strong correlation among metals shows that they originate from common source along the highway; traffic source.

|       | Cd   | Cr    | Mn    | Pb    | Zn    | Cu    | As    | Ca    | Ni    | Fe    |
|-------|------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Cd    | 1    |       |       |       |       |       |       |       |       |       |
| Cr    | 0.5303 | 1    |       |       |       |       |       |       |       |       |
| Mn    | 0.8476 | 0.7844 | 1    |       |       |       |       |       |       |       |
| Pb    | 0.5228 | 0.4581 | 0.7455 | 1    |       |       |       |       |       |       |
| Zn    | 0.4485 | 0.6709 | 0.7055 | 0.2321 | 1    |       |       |       |       |       |

Table -4 Pearson’s correlation matrix among the trace metals measured in TSP

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3.4 Enrichment Factor Analysis

The result obtained for enrichment factors (EFs) is presented in Table 4. Cd, Pb, Cu and As were significantly enriched with EFs of 24438.6, 156.319, 745.017, and 3252.412 respectively (Table 5). High EFs (> 100) were obtained for Cd, Pb, Cu and As, indicating their anthropogenic origins. Among these elements, Cu is an additive in high-temperature lubricant and is present in brake linings, approximately 1–10% by weight [48], and it has been used successfully as a good tracer for wear emission of road traffic [49]. Zn is associated with wear tire debris because Zn is added to tires during vulcanization and is responsible for 1–2% of the tires by weight [50,51], and emissions from both vehicle exhaust and wear abrasion are important sources of Pb. Correlation analyses (Table 4) illustrated that Cd, Pb, Zn, Cu and As are well correlated with (r > 0.75), suggesting that, similar to Cu, these metals along Ogbomoso section of Ibadan-Ilorin highway originated mainly from wear-abrasive sources. This indicates that they are contributed primarily by traffic and industrial emissions, rather than a natural origin. This is in concert with previous results [52,53,54].

| Trace metals | Mean concentration in TSP (µg/m³) | Mean concentration in crust (µg/m³) | Enrichment factor |
|--------------|----------------------------------|-----------------------------------|------------------|
| Cd           | 43.911                           | 688.16                            | 24438.6          |
| Cr           | 36.991                           | 212244.89                         | 66.749           |
| Mn           | 30.787                           | 2132653.06                        | 5.529            |
| Pb           | 48.28                            | 118289.714                        | 156.319          |
| Zn           | 31.837                           | 185714.286                        | 65.657           |
| Cu           | 302.505                          | 155510.204                        | 745.017          |
| As           | 46.793                           | 5510.204                          | 3252.412         |
| Ca           | 104.96                           | 67755102.04                       | 0.593            |
| Ni           | 39.362                           | 201257.143                        | 74.906           |
| Fe           | 335.999                          | 128685714.3                       | 1                |

Cr, Zn and Ni were moderately enriched by anthropogenic activities with EFs of 42.745 and 5.408 respectively. EFs (> 10) was obtained for Cr, which was well correlated with Cu (r > 0.75), this suggests its anthropogenic origin. Mn and Ca were not enriched by anthropogenic sources due to very low EFs of 1.239 and 0.743 respectively. Enrichment factor of Ca was close to unity, which suggest that a dust source could account for at least half of the aerosol Ca budget. The EF values obtained for Ca was consistent with the results observed at Hsuehshan Tunnel in Taiwan [55]. The authors found out that Ca originated mainly from the resuspension of soil and road dust. The values showed that in the most cases, the heavy metals in TSP had anthropogenic origins. This result is similar to the results obtained by Farahmandkia et al [53], where the heavy metals in precipitation had anthropogenic
origins. Elements of anthropogenic origins (Cd, Pb, Zn, Cu and As) were highly enriched with respect to crustal composition indicating the influence of anthropogenic input for these metals. Iron (Fe), which is considered an important crustal element, correlated well with Mn (r = 0.8331, Table 3.), demonstrating that crustal source is the major source of Fe. This is different from the results obtained at Hsuehshan Tunnel in Taiwan where wear dust was the major anthropogenic source of Fe in Hsuehshan Tunnel [55].

IV. CONCLUSION

Concentrations of trace metals in TSP have been measured along a heavily trafficked highway in Ogbomoso, Nigeria. The peak values in the concentrations of the heavy metals were typically observed at Takie with the highest traffic density, regardless of the sample type. The Pearson’s correlation matrix among the trace metals measured in TSP along the highway ranged from 0.987- 0.8471. All positive and strong correlations indicate relationship among the trace metals in the same trend such that increase in the concentration of any suggests increase in concentration of the other. Enrichment factor ranged from 0.593 – 24438.6 Cd, Pb, Zn, Cu and As were highly enriched with respect to crustal composition indicating the influence of anthropogenic input for these metals. The concentration of TSP at the seven sampling spots along the highway ranged from 69.444 µg/m³ to 185.185 µg/m³. It was also found that the highest concentration of TSP at all the sampling locations were below the daily limit of 150 µg/m³ except at Takie where it was beyond the limit.

Several of our observations also support the need for extended observations and analysis of these heavy metals in the urban environment.

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