

Elemental Composition of PM_{2.5} and PM₁₀ in the Industrial Area of Yopougon, Abidjan, Côte d'Ivoire

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Abstract

This paper describes the evaluation of trace element composition of atmospheric aerosol particles (PM_{2.5} and PM₁₀) and their influence on air quality in the largest industrial area of Abidjan city, Côte d'Ivoire. Multi-week sampling was conducted in an urban site (industrial area) in Abidjan from April 2018 to July 2019. The mean mass concentration was $48.83 \pm 15.24 \mu\text{g}/\text{m}^3$ for PM_{2.5} and $77.34 \pm 10.91 \mu\text{g}/\text{m}^3$ for PM₁₀, with significant temporal variability. The average ratio of PM_{2.5}/PM₁₀ was 0.64 ± 0.21 . The concentration of BC in PM_{2.5} and PM₁₀ was respectively $52.32 \pm 7.48 \mu\text{g}/\text{m}^3$ and $52.26 \pm 12.07 \mu\text{g}/\text{m}^3$. Twenty-two elements: Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Rb, Sr, Zr and Pb were analysed by Energy Dispersive X-ray Fluorescence (EDXRF). Elemental composition data were modeled using principal component analysis (PCA) with varimax rotation to determine two (2) and four (4) dominant source categories contributing to PM_{2.5} and PM₁₀ respectively. In the case of fine particles PM_{2.5}, the possible sources were Industrial activities and non-exhaust emissions, exhaust emissions. The PM₁₀ sources were industrial activities and non-exhaust emissions, industrial processes, mineral dust, and waste combustion.

Keywords

Aerosol Particles, PM_{2.5}, PM₁₀, EDXRF, PCA

1. Introduction

Atmospheric particulate matter pollution is one of the main issues of public concern worldwide. The rapid industrialization and urban growth had been the major reasons for the frequent violation of the ambient particulate matter concentration standards, particularly in developing countries [1]. Particulate matter is introduced into the ambient air from a variety of natural and anthropogenic sources [2] leading to the deterioration of air quality and environmental degradation. It is known as a major component of this pollution and is one of the most concerning pollutants because of its strong impact on human health. Indeed, exposure to particulate matter can result in adverse human health problems such as acute respiratory illness, chronic cough and reduced lung function [3] [4].

It is important to study the chemical composition of atmospheric particulate matter because of its effects on human health [5] and climate change [6] [7]. In addition, such studies provide information on the origins of the particulate material and can reveal whether it was emitted as primary or secondary particles. Smaller particles can penetrate more deeply into the lungs than larger ones and thus cause more severe harm [8]. In addition, fine particulate matter affects the radiation balance of the earth [9] because it scatters and absorbs much of the incident visible light from the sun.

Coarse particles (PM_{10}) usually contain materials from the earth's crust and dust from vehicles and industrial plants, while fine particles contain the secondary formed aerosols, combustion particles, and re-condensed organic and metallic vapours [10]. Black carbon (BC) is one of the main-anthropogenic components of particulate air pollution, being produced by incomplete combustion. When it is formed, it is invariably mixed with other atmospheric constituents [11]. Generally, there are two important reasons for determining the elemental content in airborne particulate matter. First, it can contain heavy elements such as Cd, Pb, As and Sb, which are toxic to human health. It is of interest to follow the eco cycles of these metals as environmental hazards once they have been released into the atmosphere, biosphere and technosphere. The second aspect is that single elements or ratios of different elements can be used to fingerprint and monitor emissions from specific sources.

The results of previous studies in Côte d'Ivoire showed that the air quality situation in Abidjan was worrying, as the major cities of West Africa [12].

The aim of this study was to evaluate trace elemental concentrations in particles ($PM_{2.5}$ and PM_{10}) and to investigate their influence on local air quality. Thus, it will improve our knowledge of air quality associated with PM [13] in Abidjan.

2. Materials and Methods

2.1. Sampling

The sampling campaign was conducted at the industrial site of Yopougon with

an area of 153 km² [14]. This measurement site (red dot) corresponds to GPS the coordinates 5°23'18" North and 4°4'35" West (Figure 1). The collection of particles was carried out three times a week with LVS/LV-S6-RV Sven Leckel sampler, from April 2018 to July 2019 [13]. The meteorological parameters including temperature, relative humidity and wind speed were provided by the Société d'Exploitation et de Développement Aéroportuaire, Aéronautique et de Météorologique-Cote d'Ivoire (SODEXAM).

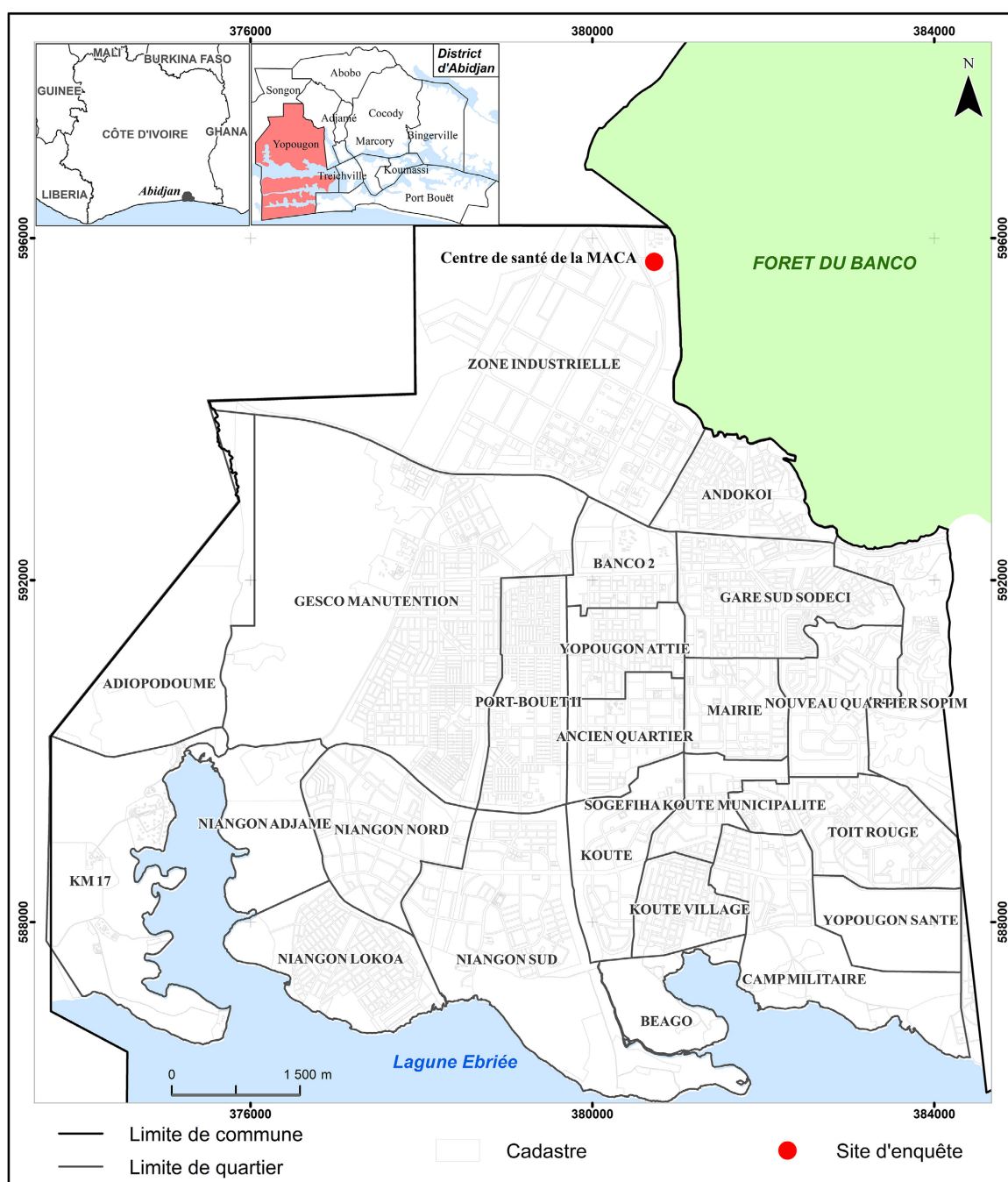


Figure 1. Localisation of the sampling site in the city of Yopougon.

2.2. Analysis

PM concentrations were determined by gravimetric mean. Black carbon measurements were performed using an EEL Smoke Stain reflectometer (Model 43 M, Diffusion Systems Ltd 43) **Figure 2**. A light source shines its light on the filter, and the reflected light is measured by photocells located in a black housing. The reflector reading is obtained directly from the universal digital readout and converted to output voltage. Both methods used are described elsewhere [13]. The particulate matter collected on the filters was quantitatively analyzed for trace elements by an Energy Dispersive X-ray Fluorescence (EDXRF) spectrometer of type X-123 (**Figure 3**). This spectrometer is composed of a fast SDD detector (25 mm diameter and 130 eV resolution), a mini X-ray tube with silver anode (30 kV and 25 μ A), an excitation and emergence angle of 67.5°, an X-ray tube-sample distance of 33.9 mm and a 15.9 mm detector-sample. The samples were irradiated during 300 seconds and the obtained X-ray spectra were processed using the XRS-FP software of CrossRoads Scientific Company. Then, the elemental contents given in μ g/g were converted into airborne concentrations in μ g/m³. This EDXRF method gives elemental concentrations with a typical error margin of 10%, which includes statistical counting errors of the detected elements in the sample. Twenty-two elements, namely Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Rb, Sr, Zr and Pb were detected and quantified.

2.3. Statistical Analysis

Principal Component Analysis (PCA) with varimax rotation was used to estimate and identify the possible sources of coarse and fine particles. Thus, the chemical elements with higher concentrations in each factor were interpreted as fingerprints of emission source that it represents. In the present study, SPSS software was used to perform multivariate factor analysis.



Figure 2. EEL 43M Smoke Stain Reflectometer developed in conjunction with DTI Warren Spring Laboratory.

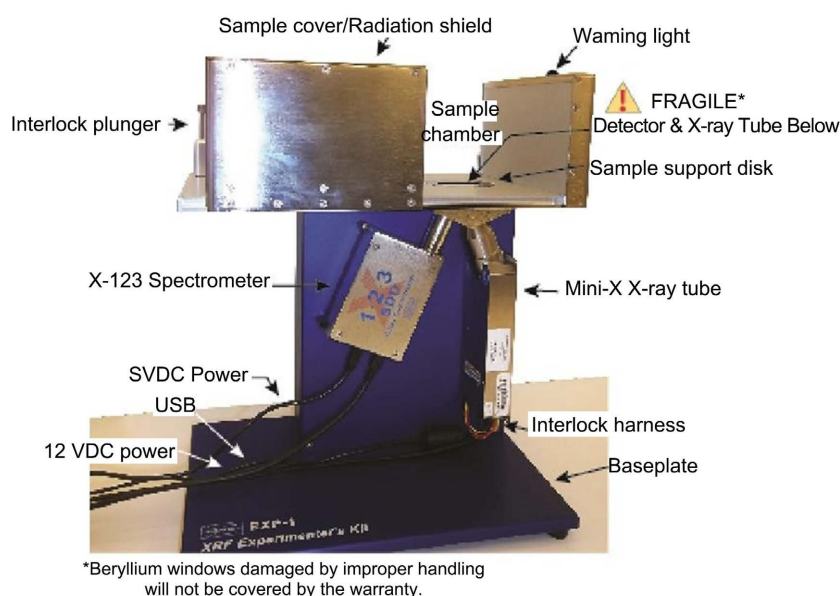


Figure 3. Simplified diagram of Energy Dispersion spectrometer type X-123.

3. Results and Discussions

This environmental study focused on the trace elements concentrations level of the PM and emission sources. But the influence of the meteorological parameters and BC content will also be discussed

3.1. Concentration Level of Particulate Matter (PM) and BC

The mean values concentration of fine ($PM_{2.5}$) and coarse (PM_{10}) particulates fractions were $48.83 \mu\text{g}/\text{m}^3$ and $77.34 \mu\text{g}/\text{m}^3$ respectively. The corresponding highest concentration was equal to $96.5 \mu\text{g}/\text{m}^3$ and $94.1 \mu\text{g}/\text{m}^3$. The time series plots of the particulate matter (PM) in both size particles and their respective content in BC are presented in **Figure 4** and **Figure 5**.

From the beginning of the great rainy season (May 2018) until October 2018, the fine particles showed an inverted behaviour to that observed for coarse particles (**Figure 5** and **Figure 6**). After this period, the fine particles increased and reached one significant peak at the beginning of the great dry season (December 2018) with a concentration of $93.5 \mu\text{g}/\text{m}^3$. Thereafter it decreased considerably until almost at the end of the great rainy season (June 2019 $37.64 \mu\text{g}/\text{m}^3$) before increasing slightly.

A variation of BC in both sizes ($PM_{2.5}$ and PM_{10}) was observed during the study period. A considerable peak of BC was recorded in PM_{10} in December 2018 (**Figure 4**). This could be justified by the industrial stacks releases into the air during this period of the year.

The times series plot indicated that the monthly concentrations of PM_{10} increased during the great rainy season (May 2018 to July 2018) samplings, decreased significantly from August 2018 to September 2018, followed by a slight increase at the beginning of the small rainy season. This seasonal trend could be attributed, in part, to the meteorological conditions. It was found that the higher

values of PM₁₀ corresponded to lower temperatures and higher wind speed values and vice versa except for April 2019 to May 2019 where PM₁₀, temperature and wind speed had the same evolution (Figure 6).

Table 1 presents the results of PM studies of some African cities. The PM values found in these studies exceeded largely the WHO standards (PM_{2.5}: 15 µg/m³/24h; PM₁₀: 45 µg/m³/24h) [15].

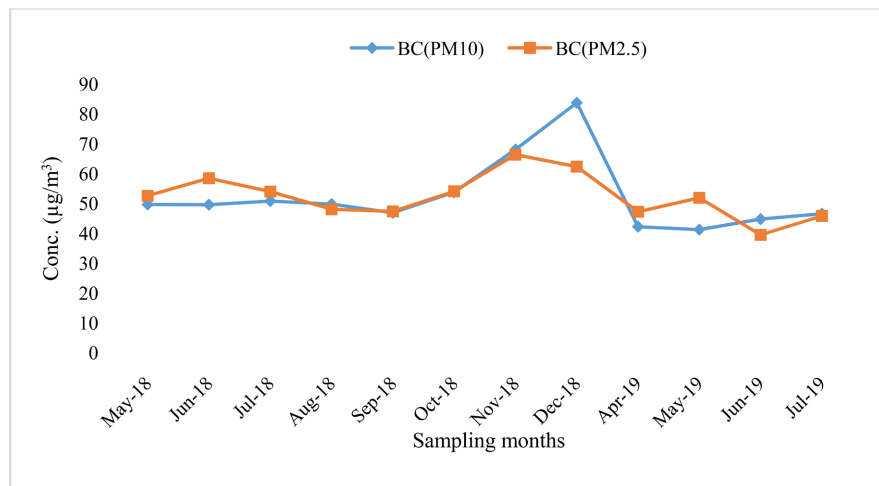


Figure 4. Mass concentration of black carbon in the particles.

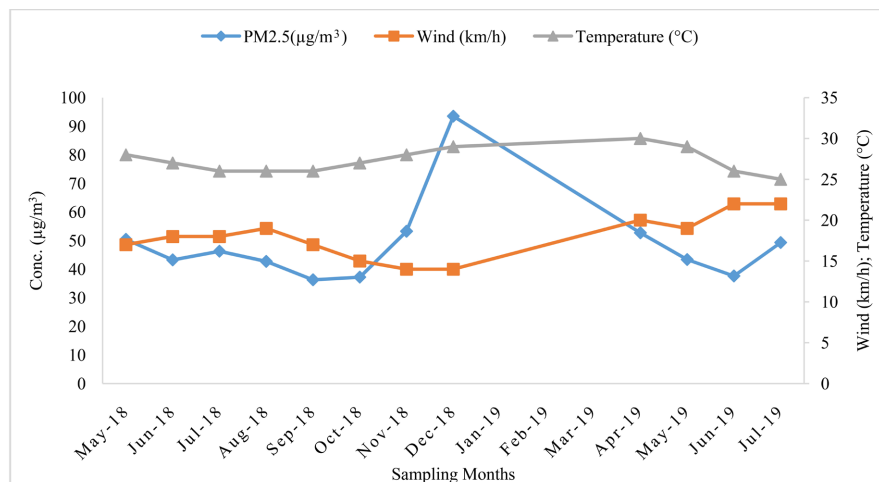


Figure 5. Variations of concentrations of fine particulates as the function of meteorological parameters.

Table 1. PM_{2.5} and PM₁₀ levels of Côte d’Ivoire (Abidjan) and some of other African countries.

Country	Type of site	Study periode	PM _{2.5} (µg/m ³)	PM ₁₀ (µg/m ³)	Reference
Côte d’Ivoire (Abidjan)	Industrial area	April 2018 to July 2019	48.83	77.34	The present study
Senegal (Dakar)	Urban/industrial area (Hlm)	2018-2019	280.56	246.16	Moustapha kebe <i>et al.</i> , 2021 [16]
Nigeria (Abuja)	Industrial area (M1)	May 2011 to April 2012	151.68	341.69	Lasun T. Ogundele <i>et al.</i> , 2016 [17]

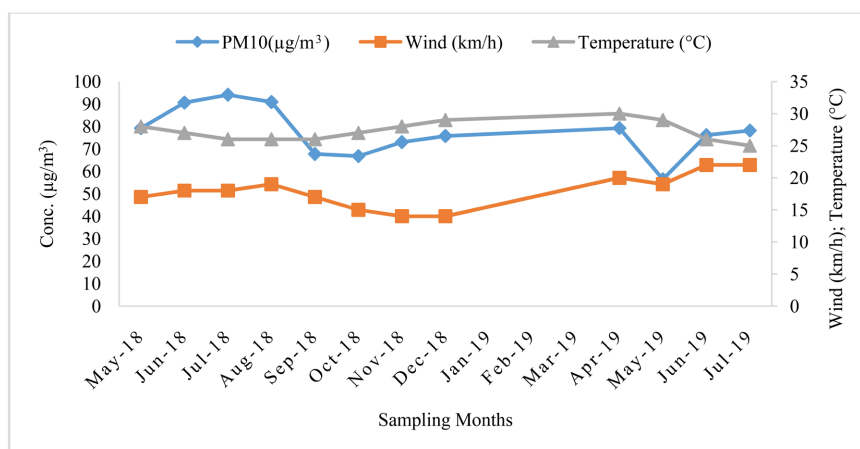


Figure 6. Variations of concentrations of coarse particulates as the function of meteorological parameters.

It can be noted that the values of our study are lower than those found in these different African countries, but they remain higher than the international standards [15].

3.2. Elemental Concentration in Particulate Matter

The elemental compositions, their average concentrations in $PM_{2.5}$ and PM_{10} and standard deviations are presented in **Table 2**. Thirteen elements were determined for all the samples in coarse and fine particles. The average concentrations of these elements ranged from $0.0010 \mu\text{g}/\text{m}^3$ for Zr in $PM_{2.5}$ to $0.487 \mu\text{g}/\text{m}^3$ for Ca in PM_{10} .

Figure 7 shows the concentrations level of the elements detected in fine and coarse particles at the industrial area of Yopougon, Abidjan. For both fine and coarse particles, Zr was the element with the lowest concentration ($0.0010 \pm 0.0005 \mu\text{g}/\text{m}^3$). However, the highest concentration was recorded for K ($0.202 \pm 0.080 \mu\text{g}/\text{m}^3$) in fine particles and Ca ($0.487 \pm 0.188 \mu\text{g}/\text{m}^3$) in coarse particles. A comparison of the metal concentrations in both particles indicated that the elements of crustal origin (Al, K, Ca, Mn and Zr) were more prevalent in PM_{10} than $PM_{2.5}$. Whole, the elements from anthropogenic sources (Cr, Ni, Cu, Zn and Pb) were less prevalent in fine particulates.

3.3. Multivariate Analysis

To further assess dominant source categories and quantify their contributions for coarse and fine aerosols, the principal component analysis (PCA) with varimax rotation was used. For coarse fraction (**Table 3**), four principal components (PCs) were extracted that, accounting for over 83% of the explained variance. The PCA results of PM_{10} showed that the first factor (PC1), with the maximum percentage of variance (27.18%), had high loadings of Mn, Cl, BC, Cu, Zr and Pb. PC1 could show a combined contribution of industrial activities and non-exhaust emissions. This factor includes the contribution from vehicle non-exhaust sources traced by Mn and Cu, but it also receives significant mass contributions

by combustion species like BC and Cl. BC can be found in combustion emissions [18] [19] and Cl can be considered as an elemental tracer for coal combustion [20] and industrial activities mainly composed of Zr and Pb which reflects the influence of ceramic industry processes [21]. PC2 mainly consisted of Zn, Ni, and Pb with 21.23% of the total variance, which was recommended as fingerprints for the metal processing industry. Oliveira *et al* pointed out industrial sources that had a strong contribution from Zn, Pb and Mn could be related to waste incineration or metallurgy [22]. PC3 showed a high loadings of Ca, Al, K, and Fe elements with a crustal origin, and explained 18.37% of the total variance. This factor is interpreted as a mixture of several sources including soil resuspension, urban works and regional mineral dust. PC4 explained 17.06% of the variance with high loadings of S, Cr and K. It would point out the role of waste combustion sources typically burning of woods [23].

Table 2. The mean and standard deviations of elemental concentrations of PM_{2.5} and PM₁₀ collected at Yopougon industrial area from May 2018 to July 2019.

Elements	PM _{2.5} (µg/m ³)		PM ₁₀ (µg/m ³)	
	Mean	S.D	Mean	S.D
Al	0.010	0.003	0.022	0.010
S	0.026	0.009	0.070	0.030
Cl	0.024	0.006	0.302	0.110
K	0.202	0.080	0.306	0.099
Ca	0.103	0.040	0.487	0.188
Cr	0.018	0.006	0.024	0.007
Mn	0.010	0.003	0.015	0.004
Fe	0.052	0.020	0.106	0.040
Ni	0.004	0.001	0.005	0.001
Cu	0.003	0.001	0.005	0.001
Zn	0.156	0.060	0.235	0.090
Zr	0.0010	0.0005	0.002	0.001
Pb	0.010	0.003	0.013	0.005
BC	52.32	7.48	52.26	12.07

*S.D. is Standard Deviation.

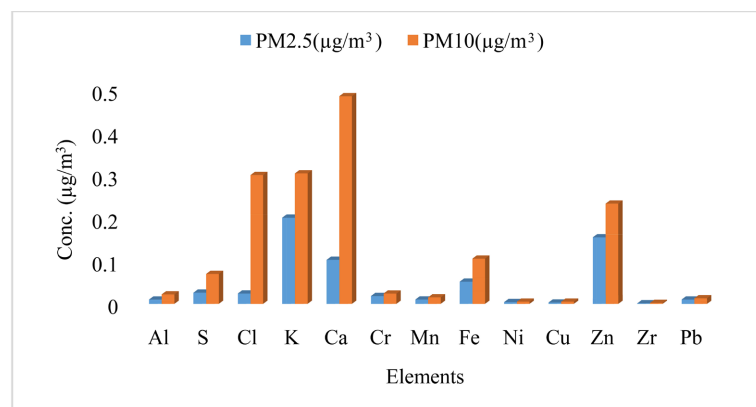


Figure 7. Comparison of metal contents in fine and coarse particles at yopougon site.

Table 3. Principal component analysis with varimax rotation for PM₁₀ dataset from Yopougon area.

Element	Factor			
	1	2	3	4
BC	0.795	-0.235	-0.272	0.322
Al	0.013	0.155	0.816	0.232
S	0.108	0.002	0.385	0.844
Cl	0.795	0.101	0.241	0.448
K	0.043	0.338	0.616	0.613
Ca	0.185	-0.229	0.838	0.253
Cr	0.303	0.211	0.163	0.834
Mn	0.804	0.395	0.167	-0.052
Fe	0.475	0.557	0.611	0.075
Ni	0.349	0.784	0.064	0.327
Cu	0.713	0.490	0.095	0.181
Zn	0.003	0.949	0.056	0.093
Zr	0.713	0.143	0.313	0.125
Pb	0.627	0.656	-0.058	-0.100
% of variance	27.18	21.23	18.37	17.06
Cumulative %	27.18	48.42	66.79	83.85
Source	Industrial activities and Non-exhaust emissions	Industrial processes	Mineral dust	Waste combustion

For PM_{2.5}, two principal components (PCs) were extracted by PCA analysis, accounting for over 81% of the explained variance. The PCA results of PM_{2.5} (**Table 4**) showed that the first factor (PC1), with the maximum percentage of variance (66.85%), had high loadings of Al, S, Cl, K, Ca, Cr, Mn, Fe, Ni, Cu, Zn, Zr, and Pb. This factor looked like a combination of different sources, according to their characteristic tracers, as Non-exhaust (Pb, Zn), Industry (Cu, Ni, and Cr), Combustion (S, Ni) and Crustal (Al, Fe) [24]. Therefore, this factor 1 could be assigned to sources such as scrap packaging, stainless steel, ceramics, electronic products, mechanical wear of electrical components, vehicles parts and metal parts of used equipment. The second factor, which explains 14.42% of the total variance, was strongly correlated with the BC. This factor originated from exhaust emissions [25] [26].

Table 4. Principal component analysis with varimax rotation for PM_{2.5} dataset from Yopougon area.

Element	Factor	
	1	2
BC	-0.009	0.880
Al	0.827	0.461
S	0.828	-0.061
Cl	0.874	0.405
K	0.897	0.288
Ca	0.820	0.018
Cr	0.846	0.439
Mn	0.792	0.303
Fe	0.844	0.417
Ni	0.838	-0.080
Cu	0.892	0.192
Zn	0.867	0.049
Zr	0.820	0.465
Pb	0.880	0.240
% of variance	66.85	14.42
Cumulative %	66.85	81.27
Source	Industrial activities and Non-exhaust emissions	Exhaust emissions

4. Conclusions

This study took place in the economic capital of Côte d'Ivoire, Abidjan. The measurement campaign was performed during the years 2018 and 2019. PM₁₀ and PM_{2.5} samples were collected three times per week. The elemental composition of the PM samples was determined using EDXRF. The elements that presented the highest concentrations were Ca, K, Cl, Zn and Fe. All these elements originated mainly from natural sources, except for K and Zn which could be soil components but could also be emitted from biomass burning.

Time series analysis of particulate matter revealed a seasonal trend with high concentrations during the end of the short dry season and the beginning of the great dry season period. The contents of chemical elements indicated that Zr was the element that showed the lowest concentrations for both fractions. However, Ca presented the highest concentrations in coarse particles and K the highest values in the fine particles. Using the Principal Component Analysis (PCA), four and two factors were obtained for coarse and fine particles respectively. The identified sources for fine and coarse particulates were respectively industrial activities and non-exhaust, exhaust emissions, and mineral dust and waste combustion. After the identification of the sources, further studies will be necessary

to quantify the contribution of each source.

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Conflicts of Interest

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

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