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ARTICLE

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Chemical characterization of urban aerosols in Abidjan and Korhogo (Cote d'Ivoire) from 2018 to 2020 and identification of their potential emission sources

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As part of the Air Pollution and Health in Urban Environments (PASMU) project, equipment was installed in urban sites of Abidjan and Korhogo (Ivory Coast) in West Africa, with the aim of monitoring the chemical composition of PM2.5 aerosols. These installations were used to collect PM2.5 aerosols on a weekly basis, with the determination of PM2.5 mass, EC, OC and water-soluble ions (WSI). This database will enable us to analyse 2-year trends (2018-2020) of the chemical composition of PM_{2.5} aerosols in the two cities. In addition, this database was used to assess the sources contributing to these aerosols, using both PCA (Principal Component Analysis) and the US Environmental Protection Agency's EPA PMF 5.0 software. The results show that the PM_{2.5} concentrations observed during the 2 dry seasons are more than 2 times higher than those during the 2 wet seasons. Also, over the 2 years studied, the PM_{2.5} concentrations observed, were above the WHO, 2021 standards. Analysis of the chemical composition of PM2.5 shows that organic matter (OM) is the majority fraction in the 2 cities, followed by EC in Abidjan and Dust in Korhogo. Similarly, the observation of trends shows greater variations in OC concentrations between the dry and wet seasons, compared with the EC. 5 contributing sources are identified, with very disproportionate contributions. In Abidjan, these sources are road traffic (44.7%), domestic fires (40%), natural and road dust (11.2%), sea salt (3%) and construction dust (1.2%). In Korhogo, the sources are biomass burning and domestic fires (70.7%), road traffic (16%), road dust and sea salt (8.1%), natural dust (2.6%) agriculture (2.5%). This study offers vital insights into identifying the primary sources of urban air pollution in the west Africa cities. Tailored strategies based on these sources can effectively mitigate urban particulate pollution, leading to reduced emissions, enhanced air quality, and improved public health in densely populated urban regions.

1. Introduction

Particulate pollution is a real public health problem worldwide, with an even more dramatic situation in developing countries, where its impacts are still poorly understood.¹ They are the cause of many deaths worldwide, 4.2 million in 2016 according to the WHO. Cohen *et al.*² are shown the impact of anthropogenic fine particles in West Africa on premature deaths from cardiovascular and respiratory causes (e.g. lung cancer). Concentration levels of particulate matter (PM) depend on several processes that transform emissions into concentrations, be they meteorological, climatic, physicochemical, urban morphology, etc.

To understand the impact of particulate pollution on the health of populations, it is necessary to be able to characterise the chemical composition of aerosols. Indeed, the health impact of aerosols is highly related to the chemical species that compose it, less to the levels of aerosol mass concentrations.³

In West Africa, Adon et al.4 showed a strong dependence between the inflammatory impact of aerosol and its soluble organic carbon (WSOC). In addition, links between oxidative activity (measured using DTT) and carbon species concentrations (OC, EC, WSOC and WIOC) have been established between in areas subject to source road traffic.5 In Abidjan, Kouassi et al.6, established the toxicity induced by the chemical composition of PM_{2.5} from rural, urban and industrial sites. Furthermore, the chemical composition of $PM_{2.5}$ is dependent on the contributing sources.4,7-11 Therefore, to limit the health impacts of aerosols, it is necessary to study their chemical composition and identify their contributing sources, in order to be able to take better action. This work is particularly important in West African cities which are experiencing a real population explosion, associated with increasing emissions of air pollutants since the 1990s (Keita et al. 12). This study aims to investigate the chemical characteristics of PM_{2.5} aerosols in Abidjan and Korhogo in Cote d'Ivoire, using a database of several years. It is based on sampling techniques using aerosol collectors placed at 1 site in each city, in Abidjan (site A1, UFHB) and 1 site in Korhogo (site

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[†] Footnotes relating to the title and/or authors should appear here. Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

K1, UPGC). The samples collected allow several analyses to be carried out in order to obtain numerous physical-chemical parameters of the aerosols collected. The analysis of this database will be presented as follows: interannual and seasonal evolutions of PM_{2.5} concentrations on the 2 sites, including the evolutions of the carbonaceous species; the evolutions of the mineral composition of PM_{2.5} aerosols, the analysis of the chemical composition (carbonaceous and mineral species) with the aim of explaining the masses of PM_{2.5} aerosols collected on the 2 sites, and finally the analysis of the contribution of sources to the concentrations of PM_{2.5} aerosols in Abidjan and Korhogo. This work is carried out within the framework of the project Air Pollution and Health in Urban Areas, Cote d'Ivoire (PASMU).

2. Methodology

2.1. Study areas

Data collection took place jointly in Abidjan and Korhogo, the two cities of the PASMU project study. Fig. 1 shows a map of Cote d'Ivoire with the location of these two cities with Abidjan in the south and Korhogo in the north. The morphological, geographical and anthropogenic differences of these cities allow the study of air pollution in two distinct urban configurations of Cote d'Ivoire.

The city of Abidjan has been for a long time the political capital of Cote d'Ivoire and is still the centre of most of the economic activities. Indeed, with its large coastline Abidjan shelters the main industrial activities of the country. This city is divided into 10 communes and 3 sub-prefectures (peripheral communes) with a population of 6,321,017 inhabitants according to the 2021 General Census of Population and Housing, or 21.5% of the national population, for an area of 2,119 km². Abidjan is an autonomous District with different levels of urbanization and populations of different social classes. The main sources of anthropogenic pollutant emissions are traffic, domestic fires (use of wood and charcoal), waste combustion and industrial activities.

The city of Korhogo is the third most populous city in the country (440,926 inhabitants, 1.5% of the national population). Much of the city's land area is unbuilt and used for agriculture, with an urbanization rate of 42.9% in 2021.13 Korhogo is then a city marked by agricultural activities with a few rare factories processing and packaging agricultural products. Consequently, the activities of these factories are strongly linked to local agricultural production. The main sources of emissions in the city of Korhogo are domestic fires and traffic, with an intense activity of heavy trucks, intercity buses but also 2- and 3-wheel motorized vehicles. Moreover, in this city, only the main roads are paved and represent less than 10% of urban roads.14 This implies an important resuspension of aerosols present on the roads, which is also a major source of particulate emissions. The domestic fire source is very important with the use of firewood for economic reasons or convenience because these resources are available in the surrounding villages. In addition to the local anthropogenic sources present in Korhogo, an important impacting source is provided by the harmattan winds. This

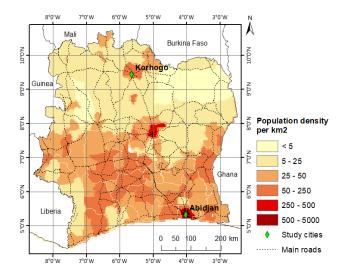


Fig. 1. Population density map of Cote d'Ivoire, with the 2 study towns in green, adapted from *Gnamien et al.2020*.

predominant air mass during the dry season is an important source of dust from the Sahara and aerosols from surrounding or regional savanna fires.

In conclusion, these two cities differ in terms of economic and social activities, and infrastructure: the usual means of transportation and types of roads, the fuels used for cooking, the practices of the population, and finally the local weather as described in the paragraph 2.6.

On the map of the population density distribution in Cote d'Ivoire (Fig. 1), it can be seen that the population densities of these two cities are also very different, with Abidjan's population density 10 times higher than that of Korhogo. However, even though population densities in the south-central Cote d'Ivoire are generally higher than in the more northern regions, Korhogo's population density is still high for a northern region. This is due to the existence of industries in the city.

2.2. Measurement sites

As mentioned above, medium-term measurements were carried out at 2 sites, in Abidjan (UFHB) and in Korhogo (UPGC). Measurements at the medium-term sites are weekly and/or daily in the 2018 and 2019 dry seasons and in the 2019 wet season.

2.2.1. Abidjan (site A1, University Felix Houphouet-Boigny UFHB)

Site A1 is the main measurement site (reference site) of the PASMU project. It is located within the University Felix Houphouet-Boigny (UFHB) in Abidjan at 5°20′47,58″N latitude and 3°59′23,96″W longitude. According to LCSQA¹⁵, Site A1 is an urban site. Indeed, it allows the monitoring of the average exposure of the population to air pollution known as "background" of urban centers. It is located on the roof of the building of Representation of Institut de Recherche pour le Developpement (IRD) in Cote d'Ivoire at 12 meters from the ground.

2.2.2. Korhogo (site K1, University Peleforo Gon Coulibaly UPGC)

The K1 site is located within the University Peleforo Gon Coulibaly in Korhogo (UPGC). It is located at 9°25′37,09′′N latitude and 5°37′47,17′′W longitude at the entrance of the city,

near one of the main roads. The privileged position of this site allows to monitor the urban background pollution. The site allows to follow the average exposure levels of the population to the atmospheric pollution phenomena called "background" at the periphery of the urban centre, thus allowing to better observe the external influences such as road traffic. It also allows to follow the primary pollutants from domestic fires.

2.3. Sampling methods

Samples are collected on quartz and Teflon filters, depending on the analytical techniques further considered. Quartz filters are used to obtain mass concentrations, carbonaceous aerosol, especially elemental carbon (EC) and organic carbon (OC), while Teflon filters are used to quantify the content of water-soluble ions (WSI). The measurements are carried out using aerosol collectors developed in INDAAF project (https://www.aerisdata.fr/projects/indaaf/) and have been used in the DACCIWA project in Cote d'Ivoire and Benin (https://www.imktro.kit.edu/10052.php), notably in the work of Djossou et al. 16. These collectors are composed of 2 independent measurement lines and each line is composed of a counter (GALLUS type G4), a ball flowmeter (with a Cole Palmer micrometric valve including flow rate adjustable from 0 to 10 l/min, accuracy 5%), a pump (KNF, 9 I/min N89 KNE-K), a watertight filter holder (47 mm size) and a cut-off head (Rupprecht and Patashnik), to select aerosol by size class, either PM_{2.5} or PM₁₀ particles. The pump flow rate of 5 liter/min is necessary for the proper operation of the cut-off head. In addition to this collector, another measurement line with URG cyclone to select PM_{2.5} particles, is used on each site. This line has the same operating principle as the collectors: atmospheric aerosols are sucked in by a fixed flow pump and collected on filters. For weekly measurements, a measuring line operates for 15 minutes per hour (i.e. 6 hours per day) thanks to an electric programmer in order to avoid the overheating of the pumps. This sampling method was used in the DACCIWA project. The filter holders used to expose the filters are cleaned regularly with alcohol. All handling of the filters is done with dedicated tongs. The type of filter used depends on the chemical parameters of interest.

2.3.1. Quartz filters

Quartz fibre filters are used both in the collector and in the measurement line to collect PM_{2.5} aerosols respectively at the

A1 (UFHB) and K1 (UPGC) sites. They are from the Whatman brand and require preparation before use. Each quartz filter is burned for 48 hours at 400° C in an oven to remove impurities, then referenced, weighed on a submicron balance (SARTORIUS) and stored in a Petri dish (single use). These references make it possible to identify the filter throughout its journey from preparation to the various analyses, including exposure at the measurement sites. The analysis carried out on these filters are to measure aerosol mass and carbonaceous aerosol (EC and OC) concentrations in PM_{2.5} and PM₁₀ aerosols.

2.3.2. Teflon filters

Teflon filters or polytetrafluoroethylene (PTFE) are used in the collector to sample $PM_{2.5}$ aerosols at the A1 (UFHB) and K1 (UPGC) sites. These filters are produced by PALL Corporation and also used in several other programs and projects. As with the quartz filters, the Teflon filters are stored individually in referenced petri dishes. The collected Teflon filters are used to analyse the mineral composition of $PM_{2.5}$ aerosol.

2.4. Gravimetric and chemical analysis

The analyses of the collected samples were performed at the Laboratoire d'Aerologie (Laero) in Toulouse (France). The analyzers of the Laero are regularly tested for certification. In addition, the Laero is the reference laboratory for several international programs and projects (such as INDAAF) and its results are published in international journals.^{4,17–19}

2.4.1. Gravimetric analysis

The mass concentrations are calculated by the equation 1.

$$C = \frac{\Delta M}{\Delta V}$$
 (1) with,

$$\Delta M = M_f - M_i$$
 et $\Delta V = V_f - V_i$

where,

 $\mathit{M_fet}\ \mathit{M_i}$ are the masses (in µg), respectively weighed after and before exposure;

 V_f et V_i are the volumes (in m³), respectively given by the counters, after and before exposure.

For each quartz filter, a weighing is performed before and after sampling. The mass difference (ΔM) is used to obtain the mass of aerosols collected. This technique is a reference method and the equipment used has already been used in several studies^{4,17,19}. Prior to each weighing, the filters are exposed for 24 hours in a dedicated chamber installed in the clean room.

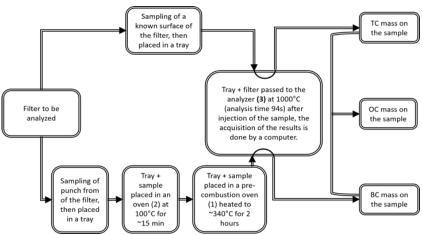


Fig. 2. Scheme of carbon analysis of quartz filters.

This allows the filters to adapt to the ambient air of this room, which houses the submicron balance. This balance is indeed very sensitive to temperature and humidity. Some filters are weighed twice in order to evaluate the uncertainty of the weighing.20

The volume of air sampled (ΔV) is given by the difference between the final volume and the initial volume given by the counters at the site before and after each filter is exposed. Pump flow checks are regularly performed on each measurement line.

2.4.2. Carbonaceous aerosol analysis

The carbonaceous aerosol analysis is performed by two-step thermal method developped by Cachier et al.21 and used in several works including Doumbia al.9, Keita et al.19 and Adon et al.4 Fig. 2 shows the analysis scheme for carbonaceous species. The sample boat where the filter will be installed are first run through an oven at 1000°C to be cleaned. The machine blank is obtained when the analyse is performed without anything in the oven whereas the operational blank combines the machine blank with an empty sample boat in the oven. These blank measurements are performed before, in between and after the sample's analysis.

During the analysis performed by a BRUKER G4 ICARUS analyser, TC (total carbon) and EC (Elemental Carbon) are directly obtained. A portion of the filter with a known surface area is first passed directly into the G4 ICARUS analyser to obtain TC concentrations present on the analysed portion of the filter. In parallel, another portion of the same filter is precombusted in an oven heated to ~340 °C under an oxygen flow for 2 hours, to remove the organic carbon (OC) fraction. After this step, this portion is analysed by the G4 ICARUS to obtain the amount of EC. Moreover, at the exit of the pre-combustion step, the samples awaiting EC analysis are placed in an oven heated to 100°C to protect them from impurities.

Finally, the difference in mass between TC and EC $(M_{TC} - M_{EC})$ gives the mass of OC.

Note that a multi-point calibration of the analyser is performed using tests with a sucrose solution (concentration of 1 μ gC/ μ L). Indeed, regression lines are drawn for low total carbon and high total carbon conditions, comparing the values of the integrals obtained by the G4 ICARUS and the known sucrose concentrations.

2.4.3. Water-soluble ions (WSI) chemical analysis

Mineral species concentrations (Na⁺, NH₄⁺, K⁺, Mg²⁺, Ca²⁺, SO₄²⁻, NO₃-, Cl-, etc.) are assessed from Teflon filter analyses, collected on sites A1 and K1. These analyses are performed at the Laboratoire d'Aerologie with Thermo Dionex chromatographs (ICS 1000, ICS 1100, and ICS 5000).

Table S1 shows the different species analysed by each of the chromatographs used. Before each series of analysis, 3 standard solutions (standard 1, 2 and 3) with known concentrations are analysed. The results of the analyses of the standard solutions must have a correlation coefficient, R² greater than 0.99. The concentrations of the standard solutions 1 and 3 form an interval [min, max] able to contain the concentrations of the solutions to be analysed. The filters to be analysed are first put in solution in vials with 20 ml of ultrapure water and then passed through an ultrasound tank for 30 minutes. More description of this methodology may be found in Adon et al.²²

2.4.4. Calculation of uncertainties

Uncertainty is systematic or statistical. The systematic error usually occurs, and is attributed to the quality of the measuring instrument or measurement protocol and to poor knowledge of the measurement process. The statistical or random error occurs when the analysis of a quantity is performed several times. Thus, the error or uncertainty, whether systematic or statistical, must consider these two aspects. For the types of analysis (mass of aerosols, mass of carbonaceous species and mass of mineral species) the uncertainties (Unc) are calculated by the formula given by the equation 2:

$$Unc = \sqrt{(ErR * V_0)^2 + (0.5 * LoD)^2}$$
 (2) where,

ErR is the relative error;

Vo is the observed value of the parameter;

LoD is the Limit of Detection

The relative error (ErR) and the detection limit (LoD) depend on the method of analysis.

Table 1 shows the methods for determining the uncertainties and the values obtained for the 3 types of analyses, i.e. mass of PM, masses of carbonaceous species and masses of mineral species. The uncertainties will be used for the analysis of the contribution of the sources.

| Unc | ertainties | ErR | LoD |
|-----|------------|----------------------------|--|
| | | Determination: This | Determination: this is a specific |
| | | is the average of the | characteristic of the device, |
| | | differences between | given by the manufacturer, i.e. |
| | | the results of double | 2 μg, based on an average |

Table 1 Method for determining uncertainties in sample analysis

PM mass after

Carbon

species mass

EC and OC

weighing the filters exposure. Indeed, one filter out of 10 was weighed twice. ErR = 2 %

Determination: This this Determination: calculated from the values of is the average of the deviations between the blank filter analyses, which the double analysis include the uncertainties results of 10 blank related to the materials filters. These values (machine, tray and blank filter). varied between 19.6 The detection limit is equal to and 21.4 µgC. Thus the average of the blanks +3xthe standard deviation, i.e. differences represent 1 to 6% of 22.01 μgC, which will be related the mass of carbon to the average volume of air obtained. sampled of 12.65 m³. It was determined on a series of 20 samples

| | ErR = 3% | | | | |
|--------------|------------------------|--|--|--|--|
| | Determination: | | | | |
| | Samples are only | | | | |
| | analysed if the | | | | |
| | coefficient of | | | | |
| 14/-1 | determination, R2 > | | | | |
| Water- | 0.99. It would be fair | | | | |
| Soluble Ions | to take ErR ~ 0%, but | | | | |
| (WSI) mass | in order to take this | | | | |
| | component into | | | | |
| | account. we took ErR | | | | |

=1%, i.e. 0.01.

ErR ~ 0%

the

Value: 1,74 μgC/m³ Determination: calculated from white filter values. It was determined on a series of 20 samples.

sampling volume of 12.65 m^3 .

Value: 0,16 μg/m³

Thus, for each species, a LoD was determined. However, the zero LoDs obtained will be replaced by the lowest LoD.

Value: Ossohou, 2020²³

2.5. Analysis of the contribution of the sources

As described in Doumbia *et al.*⁹, two multivariate statistical analysis methods are used to establish source apportionment of $PM_{2.5}$ in our study: The Principal Component Analysis (PCA) and the Positive Matrix Factorization (PMF). These methods allow to study the dependence between several variables (p). These methods make it possible to reduce a number p of variables to a number k of factors (p > k) while keeping the most information from the variables. These 2 methods are complementary and their combination allows to obtain quantifiable information on the contribution of the sources to the atmospheric concentrations of $PM_{2.5}$.

2.5.1. Principal Component Analysis

Principal Component Analysis (PCA) is a statistical method for studying dependencies between multiple variables or parameters. It allows the grouping of variables that present statistical similarities around a factor.

It has its origins in Pearson in 1901 and since then, its fields of application have continued to grow.²⁴ Today, PCA is applied in several fields for the analysis of large databases.

PCA transforms a large number (p) of variables into factors (k), based on the similarities detected in the analysis of the variables. A reduced number of factors will eventually represent almost all the information from the variables.²⁵

Assuming a linear relationship between the variables (which are here the species concentrations) and a number of p factors (which are here the number of sources), the PCA is expressed as follows:

$$Z_{ij} = \sum_{k=1}^{p} g_{ik} * h_{kj} \qquad (3)$$
where

 Z_{ij} is the reduced mass concentration of the species (i) in the sample (j), with k the number of factor (from 1 to p, which represent the number of species)

 $m{g}_{ik}$ is the contribution of the species (i) to the component at the source (k)

 $m{h}_{kj}$ is the contribution of the component from the source (k) to the sample (j)

In the context of air pollution, the variability of observed concentration levels requires the use of normalized PCA. The normalization of values is done through the centring and reduction of the series of each variable. Centring allows the impact of extreme values to be reduced by making the mean of the series equal to zero, without changing the nature of the point distribution (point cloud). The reduction process allows to obtain a variance equal to 1. These transformations applied to each of the variables put them in a normalized form that allows us to get rid of the dimensions of the variables. Following the normalization, the calculation of the factors allows to compose factorial plans, from the axes defined by the most significant factors, with the aim of restoring almost all the variance of the data set. In the context of particulate pollution, these factors represent a grouping of variables (chemical elements). According to the source profiles (given in the literature) these factors are associated to the different emission sources. The contribution of each variable to each factor gives additional

elements of interpretation. Eventually, the application of the PCA upstream of the PMF allows to identify the number of factors to retain.

2.5.2. Positive Matrix Factorization (PMF)

Positive Matrix Factorization (PMF) is a quantitative multivariate analysis method. It was created by Paatero. ^{26,27} The PMF method consists in decomposing a database into nonnegative matrices, allowing to explain the original data. Like PCA, it is not necessary to know the source profiles of the emission beforehand. As a complement to the PCA results, the PMF allows the quantification of the contribution factors of the different sources and requires a large data set and a large time series of variables in order to work.

PMF was originally developed and is used for the study of sources of particulate matter in ambient air, based on model input chemical species such as metals, major inorganic species (anions or cations) or specific organic tracers.^{27–30}

Receptor models are mathematical approaches to quantify the contribution of sources to samples based on source composition or speciation. Composition or speciation is determined using analytical methods appropriate to the environment, and associated with key species, where combinations of species are required to separate impacts.

As shown in equation 4, the X matrix is decomposed into: the matrix F (source), the species profile matrix in each source, and the matrix G, the contribution matrix by each factor (source) to the chemical equilibrium of each sample.³¹

$$X_{ij} = \sum_{i=1}^{p} G_{ik} \times F_{kj} + e_{ij}$$
 where. (4)

p is the number of factors.

 ${\bf X}$ is the concentration matrix collected at the site, composed of the samples (by dates) in rows (i) and the measured species in columns (j), with for each ${\bf X}_{ij}$.

G is the contribution matrix of sources (k), for each sample (i).

F is the matrix of species profiles (j) versus source (k).

e is the matrix of residual errors, function of the samples and the species.

Moreover, the elements of the matrices G and F are constrained to be non-negative.

To this end, a weighted least squares approach is used, in order to minimize the Q function, called the objective function.

To achieve this objective, the Q function (equation 5), also called objective function or cost function, must be evaluated and minimized through several randomized simulations.

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \left[\frac{x_{ij} - \sum_{k=1}^{p} G_{ik} \times F_{ki}}{u_{ii}} \right]^{2}$$
 (5

For a species, the sum of the concentrations from the factors (sources) cannot be greater than the concentration.

The PMF analysis uses sample time series, containing the concentrations of each of the chemical species, and the associated uncertainties. This feature allows us to account for confidence in the measurement. For example, data below the detection limit can be retained for use in the model, with the associated uncertainty adjusted so that these data points have less influence on the solution than measurements above the detection limit.

2.6. Meteorology

Local meteorology (wind direction and intensity, specific humidity, and rainfall) has a proven influence on air pollution.³² It conditions the emissions, transformations, and transport, but also the removal (deposition) of air pollutants. In addition, regional winds carry desert dust and combustion aerosols from, for example, nearby and/or regional biomass burning that greatly influence the observed concentrations and chemical composition of collected aerosols. The intensity of these parameters varies greatly during the year depending on the season. Moreover, the analysis of some meteorological parameters allows a seasonal breakdown of the year, in order to better understand the variations of the measured concentrations.

The analysis of specific humidity and rainfall data measured on the synoptic stations managed by the *Agence pour la Sécurité de la Navigation Aérienne en Afrique et à Madagascar (ASECNA*) at the Félix Houphouet-Boigny airport in Abidjan (station no. 65578) and at the Korhogo airport (station no. 65536) was carried out. Daily rainfall was collected at each station and the parameters collected were used to calculate specific humidity. In Abidjan, the specific humidity is almost constant over the three years (Fig. 3). This is due to the position of the city on the coast of the Atlantic Ocean. On the other hand, rainfall shows differences over the year, but similarities from one year to another. We note that the months of January and February have very low rainfall. This observation is also valid for the months of August.

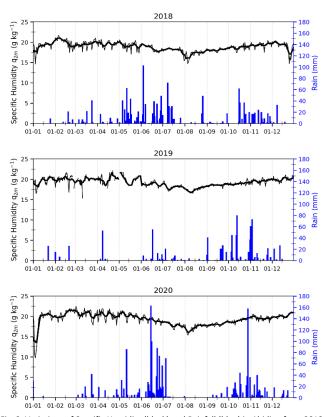


Fig. 3. Variations of Specific Humidity (black) and Rainfall (bleu) in Abidjan from 2018, 2019 and 2020.

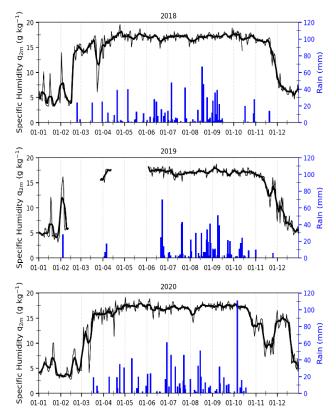


Fig. 4. Variations of Specific Humidity (black) and Rainfall (blue)in Korhogo from 2018, 2019 and 2020.

In Korhogo, Fig. 4 reveals another picture: specific humidity is low from December to February of the following year, and rainfall is concentrated between March and November over the three years. In Korhogo, the observation of these two parameters allows us to clearly define the seasons. Indeed, the low values of specific humidity reveal an atmosphere poor in water and therefore a dry season from December to February. Conversely, from March to November the atmosphere is more humid with high rainfall, hence a wet season.

Given the marine influences on Abidjan, we will not be able to establish specific seasons for Abidjan. Thus, we will use this division of seasons, namely: a dry season from December to February and a major wet season from March to November. In accordance with our study period, we define the dry season 1 (DS1) from December 2018 to February 2019 and the dry season 2 (DS2) from December 2019 to February 2020. As for the periods of March to November of 2018 and 2019, they are wetter, so are respectively the wet seasons 1 (HS1) and 2 (HS2). The dry seasons are recognized as periods of high pollution, because during this period, the phenomenon of atmospheric particles wet deposition is low, or even zero, which increases their concentrations in the atmosphere and promotes the aging of aerosols. Moreover, biomass burning is recurrent, as well as strong resuspension of aerosols due to the dryness of the soils and desert dust transported.

3. RESULTS

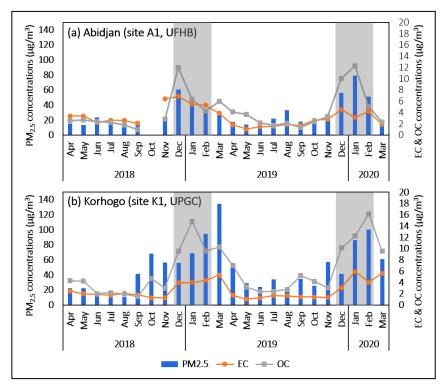


Fig. 5. Monthly average concentrations of PM_{2.5} aerosols and their EC and OC contents at (a) Abidjan (site A1, UFHB) and (b) Korhogo (site K1, UPGC). The gray-shaded areas represent the dry seasons (DS), from left to right, DS1 and DS2.

3.1. Temporal variations of $PM_{2.5}$ aerosol concentrations and their EC and OC content in Abidjan (site A1, UFHB) and Korhogo (site K1, UPGC)

Fig. 5 (a and b) shows the interannual evolution of monthly average $PM_{2.5}$ concentrations in Abidjan (a) and Korhogo (b), as well as their content in EC and OC, over the period from December 2018 to March 2020.

In Abidjan, PM_{2.5} concentrations range from 7.5 to 127.6 $\mu g/m^3$, with an average of 29.4±22.9 μg/m³ over the entire period. This average concentration is above the respective WHO standards (2021). The medians of the $PM_{2.5}$ concentrations are 20.5 μg/m³. As a reminder, the median gives statistical information on the data set, i.e. the value for which we have as many samples of higher and lower concentrations. Here, these medians allow to say that almost half of the year, the concentrations are higher than the daily standards of the WHO³³ (15 μ g/m³). The concentrations of EC and OC in PM_{2.5} vary respectively from 0.3 to 9.3 $\mu g/m^3$ and 0.2 to 23.9 $\mu g/m^3$. On average, the concentrations of EC and OC are 3.2 µg/m³ and 4.3 µg/m³, respectively. The TC content of PM_{2.5} is 27±13% on average. The OC/EC ratio is 1.6 over the study period. Concentrations during the two dry seasons DS1 (Dec2018, Jan2019, Feb2019) and DS2 (Dec2019, Jan2020, Feb2020) and those for the rest of the year (wet season and shoulder season) are shown in Fig. 3 and Table 2. The mean PM_{2.5} concentrations are $44.9\pm26.5 \,\mu\text{g/m}^3$ for DS1 and $61.8\pm31.3 \,\mu\text{g/m}^3$ for DS2. The concentrations during DS2 are thus almost twice as high as those during DS1. It is interesting to note that OC concentrations are also increasing from DS1 to DS2 whereas EC is decreasing.

Consequently, the OC/EC ratio in PM_{2.5} is approximately 1.3 in DS1 and 3.5 in DS2. This increase in the OC/EC ratio in DS2 can be attributed to a higher contribution of secondary organic aerosols, as suggested by Satsangi *et al.*³⁴. This could be associated with weather conditions that are more conducive to the formation of secondary aerosols, such as reduced rainfall and lower cloud cover during DS2 in comparison to DS1. Therefore, there is a greater contribution from incomplete combustion sources during DS2. An analysis of the backtrajectories to Abidjan, in conjunction with regional active fires in DS1 and DS2 (Fig. 3 and 4), does not provide evidence linking the increase in OC/EC to the impact of biomass burning.

For PM_{2.5}, the concentrations during HS1 and HS2 are 17.5 \pm 6.8 μ g/m³ and 21.3 \pm 7.3 μ g/m³, respectively, which are 2-3 times lower than the concentrations during the following dry season. The difference in higher concentrations during the dry seasons than during the wet seasons is mainly due to the low rainfall observed during the dry seasons, limiting the removal processes of particles by wet deposition.

In Korhogo (Fig. 5(b) and Table 2), the mean concentrations of $PM_{2.5} \mu g/m^3$ are 46.8±36.5 $\mu g/m^3$, and range from 6.9 to 165.3 $\mu g/m^3$, with a median concentration of 36 $\mu g/m^3$. We note that the average concentrations observed are 2 to 3 times higher than the standards and recommendations of the WHO³³ and Cote d'Ivoire. The concentrations of EC and OC are on average 2.6±1.8 $\mu g/m^3$ and 6.1±5.3 $\mu g/m^3$. On average, the TC represents 23±14% of $PM_{2.5}$ with an average OC/EC ratio of 2.3. This OC/EC ratio value is higher than that observed in Abidjan. This could be due both to a greater contribution of incomplete sources such as the domestic fire source and two-wheeled vehicles more important in Korhogo than in Abidjan, but also to

a more important secondary aerosol formation. The mean concentrations of PM_{2.5} during DS1 are 71.9 \pm 33.4 µg/m³ against 82 \pm 42 µg/m³ during DS2, representing a 20% increase whereas OC/PM_{2.5} and OC/EC ratios remain of the same order of magnitude. The back-trajectories to Korhogo (Fig. S7) during DS1 originate from the African continent while those of DS2 originate from the Atlantic Ocean. The influence of regional continental (Fig. S7 and S9) sources on Korhogo could explain the differences observed between DS1 and DS2. This hypothesis will be confirmed with the analysis of mineral species. PM_{2.5} concentrations during HS1 (27.0 \pm 22.9 µg/m³) and HS2 (40.7 \pm 35.2 µg/m³) are 2 to 3 times lower than during the dry seasons. It is interesting to note that the concentrations are generally higher in Korhogo than in Abidjan either in dry seasons or in wet seasons, in agreement with Gnamien *et al.*²⁰.

In Abidjan, the OC/EC ratio values (Table 2) are generally between 0.7 and 3.5 in all the seasons, with an average of 1.6, that could be suggest a link with the road traffic source^{35–37}, as on the road traffic site of Djossou *et al.*¹⁷, which had found a value of 2. However, the standard deviations of this ratio are very large, reflecting the wide variability of the ratio values and therefore the significant influences of various sources. In Korhogo, the OC/EC ratios are generally greater than 2 (with the exception of HS1), with smaller standard deviations from the ratio values. This may reflect the predominance of biomass combustion sources at this site. In fact, an OC/EC ratio greater than 2 indicates both a strong contribution from biofuel and biomass burning^{38–40} and the presence of secondary organic aerosols (AOS).³⁴

Table 2. Average concentrations in $\mu g/m^3$ of PM_{2.5}, EC, OC and OC/EC ratio over the whole study period (04/2018 - 03/2020), the wet seasons HS1 (04/2018 - 11/2019) and HS2 (03/2019 - 11/2019), and the dry seasons DS1 (12/2018 - 02/2019) and DS2 (12/2019 - 02/2020).

| City (site id, site name) | Period | PM _{2.5} | EC | ОС | OC/EC |
|---------------------------------|-----------------|-------------------|---------|----------|---------|
| | Study period | 29.6±22.9 | 3.2±1.9 | 4.3±4.1 | 1.6±2.1 |
| A la : al : a . a | HS1 | 17.5±6.8 | 3.2±1.7 | 2.3±1.2 | 0.7±0.4 |
| Abidjan (site A1, UFHB) | DS1 | 44.9±26.5 | 6.0±1.2 | 7.9±5.7 | 1.3±0.7 |
| • | HS2 | 21.3±7.3 | 2.0±0.8 | 2.8±1.4 | 1.7±1.8 |
| | DS2 | 61.8±31.3 | 4.0±1.8 | 9.2±5.5 | 3.5±4 |
| | Study period | 46.8±36.5 | 2.6±1.8 | 6.1±5.3 | 2.3±1.4 |
| Varbaga | HS1 | 27.0±22.9 | 1.8±0.5 | 2.7±1.7 | 1.5±1.0 |
| Korhogo (site K1, UPGC) | DS1 | 71.9±33.4 | 4.1±1.3 | 11.2±4.3 | 2.8±1.2 |
| • | HS2 | 40.7±35.2 | 1.7±1.0 | 4.1±3.1 | 2.5±1.4 |
| | DS2 | 82.0±42.0 | 4.2±2.4 | 12.6±7.1 | 3.2±1.9 |

The average PM_{2.5} concentrations of this study in Abidjan are of the same order than those obtained with the same procedure by Djossou *et al.*¹⁷ on traffic sites in Abidjan (32±32 μ g/m³) and Cotonou (Benin) (32±24 μ g/m³) and on a landfill fire site in Abidjan (28±19 μ g/m³) whereas they are higher in Korhogo. However, both of them remain lower than those of a domestic

fire site in Abidjan (149±69 μ g/m³), which was a site very close to the source. In addition, other studies have been conducted in West African cities. Thus, in Accra Dionisio $et~al.^{41}$ obtained 21 μ g/m³ and 39 μ g/m³, for PM_{2.5} at sites located in areas with a high and low socioeconomic status respectively. These concentration levels, as well as those observed by Arku $et~al.^{42}$, Boman $et~al.^{43}$, Dieme $et~al.^{7}$, Doumbia $et~al.^{9,44}$ and Garrison $et~al.^{45}$, respectively in Accra (Ghana), Ouagadougou (Burkina Faso), Dakar (Senegal) and Bamako (Mali) are of the same order of magnitude as those obtained on our sites.

3.2. Variations in the concentrations of water-soluble ion (WSI) species in $PM_{2.5}$ aerosols

At Abidjan site A1, the sum of water-soluble ions (WSI) represent 10.6±8.8% of the PM_{2.5} mass (Fig. 6(a)), with sulfate (1.16±1.25 μ g/m³) and potassium (0.41±0.52 μ g/m³) being the most abundant anion and cation respectively. Fig. 6(a) shows that sulfate, nitrate, and ammonium, also called SNA are major species of WSI.⁴⁶ The average level of SNA is 1.87 μ g/m³, contributing to 7% of the PM_{2.5} mass. SNA (SO₄²⁻, NO³-, and NH₄+) account for 4.1%, 1.5%, and 1.4% of the PM_{2.5} mass, respectively. The proportions of K+ (1.3%), Na+ (0.7%), Ca²+ (0.5%), oxalate ions (0.4%), Cl- (0.3%), and Mg²+ (0.2%) are relatively small compared to SNA. The rest of the ions, acetate ions (0.09 μ g/m³), formate ions (0.05 μ g/m³) have contributions less than 0.1%.

The highest peak is observed for the month of December 2018, with a WSI concentration (excluding acetate and formate ions) of $10.6~\mu g/m^3$, or 12.8% of the $PM_{2.5}$ mass. These high values appear on 3 of the 4 weeks of December 2018. Also, we observe lower WSI concentrations (mainly sulfate, nitrate and potassium) during DS2 compared to DS1. This high value in December 2018 is reflected in the average observed during DS1, $13.5\pm12.6\%$ (caused mainly by SNA which represent 4.1 and 1.5 and 1.4% of $PM_{2.5}$, respectively), compared to $6.3\pm4.1\%$ of WSI in $PM_{2.5}$ during DS2. SNA alone accounts for 6.51% and 4.13% of WSI during DS1 and DS2, respectively.

As shown earlier, the analysis of the December 2018 back trajectories in A1 shows a difference compared to December 2019. Indeed, in December 2018, the back trajectories (Fig. S6) and wind roses (Fig. S8) all originate from the west coast of South Africa, in the Atlantic Ocean whereas in December 2019, 2 origins are observed: part of them is coming from the Atlantic Ocean as in 2018 when the other part takes their origins on the African continent, more precisely in West and Central Africa. These observations allow us to link variations in WS1 concentrations to a greater contribution of marine source in DS1 than in DS2.

During the wet seasons (HS1 and HS2), the WSI are of the same order of magnitude, $11.2\pm9.6\%$ and $11.4\pm7.9\%$ of $PM_{2.5}$, respectively. In contrast to EC and OC, WSI concentrations are significant in the summer period, for the months of June, July and August (Fig. 6(a)) compared to the other months of the wet season, with a predominance of SNA followed by K^+ , Ca^{2+} and Na^+ . These variations suggest the influence of meteorology on the chemical composition of aerosols.

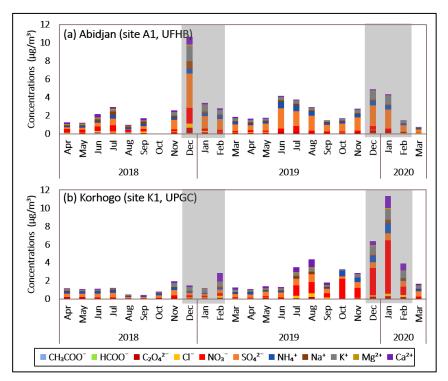


Fig. 6. Monthly mean concentrations of soluble ions (CH₃COO⁻, HCOO⁻, C₂O₄²-, Cl⁻, NO₃⁻, SO₄²-, NH₄⁺, Na⁺, K⁺, Mg²⁺ et Ca²⁺) contained in PM_{2.5} aerosols collected on (a) Abidjan (site A1, UFHB) and (b) Korhogo (site K1, UPGC). The gray-shaded areas represent the dry seasons (DS), from left to right, DS1 and DS2.

Fig. 6(b) shows the interannual evolution of WSI concentrations at Korhogo (site K1). The sum of water-soluble ions (WSI) represents 6±8.7% of the PM_{2.5} mass collected at site K1, with nitrate (0.77±1.81 μ g/m³) and K⁺ (0.34±0.33 μ g/m³) being the most abundant anion and cation, respectively.

The annual average level of SNA (SO $_4^{2-}$, NO $_3^-$ and NH $_4^+$) is 1.51 $\mu g/m^3$, contributing 3.16% of the PM_{2.5} mass in Korhogo. SNA account for 1.4%, 1.5% and 0.69% of PM_{2.5} aerosols, respectively, and 60% of WSI. K+, Ca2+, oxalate, Na+, Cl- and Mg2+ ions account for 0.78%, 0.70%, 0.32%, 0.27%, 0.25% and 0.1%, respectively. Acetate (0.02 μ g/m³) and formate (0.02 μ g/m³) ions have contributions less than 0.1% as for the Abidjan A1 site. The largest peak is observed in January 2020 and more generally during DS2. In January 2020, the WSI concentration is 11.3 μg/m³, or 10.8% of PM_{2.5}. During DS1, WSI accounts for $2.6{\pm}1.7\%$ of $PM_{2.5}$ versus $8{\pm}7.8\%$ during DS2, with SNA contributing 0.83% and 4.91% of WSI during DS1 and DS2, respectively. This agrees with our earlier. The back-trajectories (Fig S7) and wind roses (Fig. S9) to Korhogo during DS1 originate from the African continent while those of DS2 originate from the Atlantic Ocean. In DS2, a greater contribution of marine sources is then expected with larger WSI concentrations. Also, to our knowledge, it is difficult to perform any comparison with previous studies here, since previous studies of WSI when existing in West Africa deal with intensive campaigns results. These chemical compounds, combined with carbonaceous species, can be used to quantify the various chemical fractions included in PM_{2.5} aerosols at the Abidjan and Korhogo sites.

3.3. Analysis of chemical composition of PM_{2.5} aerosol

Carbonaceous aerosol and soluble ions concentrations from the different analyses allow us to reconstruct the different aerosol type fractions included in the PM $_{2.5}$ aerosol. Thus, the concentrations of WSI, EC and OC, allow us to determine 5 main type fractions, and to evaluate the fraction not determined from our chemical and mass analyses of PM $_{2.5}$. These are:

Elemental carbon: EC obtained directly from the thermal analysis used in this work developed by Cachier *et al.*²¹ and applied by Keita *et al.*¹⁹ and Adon *et al.*⁴;

Organic matter: OM = 1.8*[OC] from Temesi *et al.*⁴⁷ and Maenhaut *et al.*⁴⁸; [OC] being analysed in this study following the methodology of Cachier *et al.*²¹;

Dust = $10.96*[nss-Ca^{2+}]$, avec $[nss-Ca^{2+}]=[Ca^{2+}]-0.038*[Na^{+}]$ from Sciare *et al.*⁴⁹, all ions being analysed in this study;

Sea salt = $[Cl^-]$ + $[Na^+]$ + $[Mg^{2+}]$ + $[ss-K^+]$ + $[ss-Ca^{2+}]$ + $[ss-SO_4^{2-}]$, avec $[ss-K^+]=0.036^*[Na^+]$; $[ss-Ca^{2+}]=0.038^*[Na^+]$; $[ss-SO_4^{2-}]=0.252^*[Na^+]$ from Sciare *et al.*⁴⁹, all ions being analysed in this study;

nss-lons = $[NH_4^+]$ + $[NO_3^-]$ + $[Mg^{2+}]$ + $[nss-SO_4^{2-}]$ + $[nss-K^+]$ + $[CH_3COO^-]$ + $[HCOO^-]$ + $[C_2O_4^{2-}]$, all ions being analysed in this study:

n.d. = $[PM_{2.5}]$ - ([EC] + [OM]+ [Dust] + [Sea salt] + [nss-lons]), where $[PM_{2.5}]$ is the $PM_{2.5}$ concentration obtained in this study.

Fig. 7 (a and b) show the evolution of the chemical composition of PM $_{2.5}$ aerosols at sites A1 and K1 respectively. The 5 identified type fractions explain on average 56.7% and 50.5% of the PM $_{2.5}$ aerosol mass, respectively at Abidjan (site A1, UFHB) and Korhogo (site K1, UPGC). In decreasing order of contribution, at Abidjan, we have 26.7±13.2%; 13.2±8.4; 8.2±7.1%; 5.6±5.9%

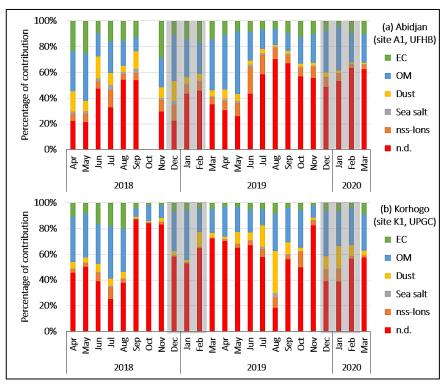


Fig. 7. Main chemical fractions included in PM_{2.5} aerosol from (a) Abidjan (site A1, UFHB) and (b) Korhogo (site K1, UPGC). The gray-shaded areas represent the dry seasons (DS), from left to right, DS1 and DS2.

and 1.4±1.6%; respectively for organic matter (OM), EC, nsslons, Dust and Sea salt (Fig. 7 (a)).

In Korhogo, $28.2\pm18.1\%$, $9.4\pm18.4\%$, $7.1\pm6.1\%$, $4.4\pm6\%$ and $0.8\pm1.6\%$ are the contributions of OM, Dust, EC, nss-lons and Sea-salt respectively (Fig. 7 (b)).

The major fraction is organic matter in both Abidjan and Korhogo sites, with close contributions. EC is the 2nd most important fraction in Abidjan (13.2%), but 3rd in Korhogo (7.7%), as it is supplanted by Dust, with 6.1% and 9.4% in Abidjan and Korhogo respectively. The nss-lons, with 9.1% and 4.4% respectively in Abidjan and Korhogo are in 4th position. The contribution of Sea salt is the lowest with 1.5% in Abidjan and 0.8% in Korhogo. The carbonaceous fractions (EC and OM) participate to 40% and 36% of the chemical composition of PM_{2.5} respectively in Abidjan and Korhogo, underlining the importance of the contribution of combustion sources to PM_{2.5} aerosols. Also, as expected, dust contribution is more important in Korhogo than in Abidjan.²⁰ However, the unexplained fractions are very large, sometimes exceeding 50%. The absence of trace elements and metals from the analyses underestimates the dust fraction, according to Guinot et al.50

Then multivariate analyses will allow to identify and quantify the contributions of the different sources.

3.4. Analysis of source apportionment of PM_{2.5} aerosol

3.4.1. Number of contributing sources

Principal component analysis (PCA) is one of the most common methods of multivariate analysis. It is applied to types of data in order to find dependencies between variables in order to reduce their number by grouping them. In this study, the variables are the chemical species (EC, OC and WSI). In addition,

since EC and OC are considered independently, TC will not be included in the analysis to avoid double counting. From April 2018 to March 2020 (i.e. 105 weeks), the 84- and 83-week samples were retained in Abidjan and Korhogo respectively. Indeed, when the concentrations of a species or a group of species is missing, the week is indeed excluded from the study. The species are then grouped around the principal components also called factors. In the following, we will use the term, factor, as a linear combination of species with specific coefficients for each variable, and within each factor. These coefficients represent the degrees of correlation between the variables and the factor. 9 Thus, the stronger a species correlates with a factor, the more it influences that factor, and that could be used to identify the source associated with the factor. In this type of study, a small number of factors that can explain most of the variance is desirable. In order to determine the number of factors to retain, several methods (criteria) are available. Doumbia et al.9 proposes the following criteria: criterion 1 retains as many axes as necessary to reach the desired threshold of explained variance, a threshold to be defined; criterion 2 retains eigenvalues greater than the value of 1 (following the Kaiser-Guttman criterion, commonly called Kaiser criterion) and criterion 3 is based on scree plot criterion using the curve of eigenvalue decay, with the number of factors to be retained corresponding to the first inflection point detected on the curve.

Fig. 8, illustrating the criterion 2, shows the eigenvalue curve as a function of the number of factors (in blue), with the Kaiser criterion in red. This figure reveals the difficulty of applying

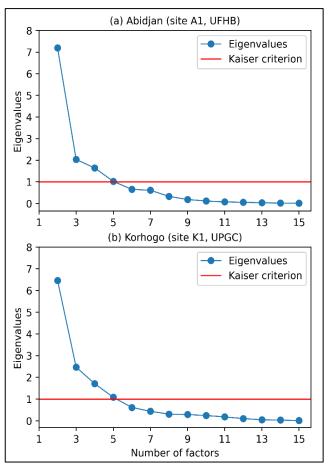


Fig. 8 Eigenvalue decay curves as a function of the number of factors, for sites A1 (Abidjan) and K1 (Korhogo), with criterion 2 (Kaiser criterion) in red.

Criterion 2 in both Abidjan and Korhogo, because the inflection point is not always clearly identifiable.

Moreover, the application of criterion 1 poses a problem in the threshold to choose. Indeed, the choice of the threshold could appear subjective, i.e., made according to the number of factors sought. Pires et al.51 chose a threshold of 90% of variance explained. In our case, this threshold would lead us to 6 sources (factors) respectively in Abidjan and Korhogo. On the other hand, a threshold of 80% leads us to 4 sources in Abidjan and Korhogo. As a reminder, the choice of the number of factors must allow for the restitution of almost all the information in the database. In order to avoid grouping of sources, we will take criterion 1, with a maximum threshold of 90%. However, we note that 88% and 89% of the variance explained in Abidjan and Korhogo respectively leads to 5 factors. This choice seems appropriate to us because it seems inappropriate to add a 6th factor that represents less than 4% of the variance, to reach 90%. Indeed, in the absence of trace elements, the identification of certain sources is difficult. Thus, we retain 5 factors (contributing sources) in Abidjan and Korhogo.

3.4.2. Sources contributing to $PM_{2.5}$ aerosols

The application of PMF (Positive Matrix Factorization) is based on the number of 5 factors identified by the PCA, both in Abidjan and Korhogo. In this study, version 5 of the EPA PMF software, developed by the US Environmental Protection Agency (US EPA), is used. This software uses as input the time series of weekly concentrations of chemical species and the associated uncertainties. Thus, the weekly concentrations each represent an independent sample. It is possible to replace the missing data by the median of the series, but this option was not retained, because we have a significant number of validated samples. Indeed, in the dataset, 84 weeks were retained out of 91 weeks actually sampled in Abidjan. On the other hand, in Korhogo, all 83 weeks sampled were retained. As we have shown above, the concentrations of the chemical species do not allow the reconstruction of the whole mass of the collected PM_{2.5} aerosols. In order to account for the undetermined mass, and as it is recommended, PM_{2.5} was added to the species for PMF, with an uncertainty equal to 4 times the observed PM_{2.5} concentration.52-54

The uncertainties were calculated based on recommendations provided by the U.S. EPA (2014) software user manual. If the species concentration is below the limit of detection (LoD), the concentration is replaced by half the LoD, and its uncertainty is 5*LoD/6. According to the species, at site A1, the number of samples involved is 0 for C₂O₄²⁻, Cl⁻, NO₃⁻, Na⁺, NH4+, K+, Mg $^{2+}$, Ca $^{2+}$ and PM $_{2.5}$, 3 for SO $_4^{2-}$, 17 for OC, 21 for EC, 34 for HCOO⁻, and 39 for CH3COO⁻, out of 84 samples included in the analysis. While for site K1, the number of samples involved is 0 for PM_{2.5}, 1 for Cl⁻, NH₄⁺, K⁺, Mg²⁺and Ca²⁺, 2 for $C_2O_4{}^{2-}$, $NO_3{}^{-}$, 4 for $SO_4{}^{2-}$, 6 for Na^+ , 12 for OC, 35 for $HCOO^-$, 36 for EC and 46 for CH₃COO⁻, out of 83 samples.

The application of PMF, successively to the Abidjan (site A1) and Korhogo (site K1) datasets, allows us to quantify the contribution of the different sources to PM_{2.5}. Thus, according to the tracers and species that contribute to each factor, a source is identified and attributed to each factor, here 5 factors. It often happens that the profile of the contributing species to a factor does not allow to identify a source, but rather an association of source.

Abidjan (site A1, UFHB): The simulations of the PMF analysis at Abidjan considering 5 factors give coefficients of determination (R²) between the concentrations predicted by the PMF and the observed concentrations of each species. We observe 3 classes: R² < 0.4 for EC, CH₃COO⁻, HCOO⁻, 0.4 < R² < 0.7 for PM_{2.5}, Na⁺, Mg²⁺, OC and R² > 0.7 for C₂O₄²⁻, Cl⁻, NH₄⁺, NO₃⁻, K⁺, Ca²⁺ and SO_4 ?. Species with R² <0.4 correspond to samples for which the concentrations are often below the respective LoD. In this case, as mentioned above, it is recommended to replace the concentration by LoD/2 and the uncertainty by 5*LoD/6 from *U.S. EPA*. ⁵⁵ Fig. 9 (a) presents the relative contribution to PM_{2.5} of the 5 sources, obtained by our receptor model at A1 site of Abidjan.

Abidjan source 1 (Factor 2): it contributes to 44.7% of PM_{2.5} and 60.6% and 38.1% of EC and OC respectively. According to Gupta $et\ al.^{54}$ and Watson $et\ al.^{56}$, this source is <u>Road traffic.</u> The OC/EC ratio in this source is 0.9 less than 2, which according to Guinot $et\ al.^{50}$, Pio $et\ al.^{57}$ and Sandradewi $et\ al.^{58}$ is consistent with that of the traffic source. This value is close to that of sites heavily influenced by the traffic source. The high contribution of NH₄+ (69.6%), associated with that of NO₃-

(21.3%) and SO_4^{2-} (24.2%) to this factor, highlights the presence of secondary aerosols. Indeed, NH_4^+ , after its formation, remains present in the atmosphere as NH_4NO_3 and $(NH_4)2SO_4$. 62 This process is confirmed by the correlation coefficient of 0.75 (p-value<0.05) between NH_4^+ , and the sum of SO_4^{2-} and NO_3^- . The presence of carboxylic acids (CH_3COO^- with 22.7%, $HCOO^-$ with 29.2%) confirms the enrichment of this source by secondary aerosols according to Wang *et al*. 63

Abidjan source 2 (Factor 4): it corresponds to 40.5% of the PM_{2.5} mass, contributing respectively to 57.4% and 26.5% of the OC and EC concentrations, both tracers of <u>Domestic fires</u> sources from biofuels according to Cachier and Ducret⁶⁴, Chow and Watson⁶⁵, Rogge *et al.*⁶⁶ and Fine *et al.*⁶⁷. Domestic Fires source can be confided by the good correlations between K⁺, and OC (0.72) and K⁺ and NH₄⁺ (0.71), with p-values < 0.05, which are all 3 tracers of combustion sources. Also, this source contributes to 61.5% of the mass of K⁺, who is tracer for this source according to Adon et al.⁴, Sharma et al.⁶², and Wu et al.⁶⁸.

Abidjan source 3 (Factor 1): it participates in 11% of the PM_{2.5} mass, contributing to 42.53% and 18% of the concentrations of Ca²⁺ and Mg²⁺, respectively, which are <u>Natural dust</u> tracers according to <u>Pant and Harrison</u>⁶⁹. In addition, Source 3 contributes of concentrations respectively to 84.7% for C₂O₄²⁻, 41.38% for CH₃COO⁻, 40.9% for Na⁺, 12.9% for EC, 12.1% for Cl⁻ and 4.5% for OC. These contributions can be explained by the resuspension of <u>Road dust.</u> According to Gupta *et al.*⁵⁴, Ca²⁺, Cl⁻ and OC can be considered as tracers of the latter source.

Abidjan source 4 (Factor 3): It contributes to 3% of the PM_{2.5} mass, with only soluble ion (WSI) contributions. Thus it participates in 50.2%, 23.8%, 19.2%, 17.7% and 13.4% respectively to NO₃-, SO₄²⁻, Na⁺, Cl⁻ and K⁺, which highlight the <u>Sea salt</u> source. To Also, the lack of contribution to EC and OC (0% contribution) helps to confirm that they are marine Salts. The absence of the contribution to Mg²⁺ highlights the inaccuracy of the receptor models in dealing with species that are lower in mass, but have multiple sources.

Abidjan source 5 (Factor 5): with 1% of the PM_{2.5} mass, this source contributes mostly to Mg²⁺ (78.5%) and Ca²⁺ (15.4%), both dust tracers. In addition, this source contributes to 59.8% and 15.4% of the Cl⁻ and Na⁺ concentrations respectively, tracers of the marine source. Considering the marine origin of the construction sand ⁷¹, this factor represents the <u>Dust from Construction</u> ⁷² showing its importance on some of the species studied.

In Abidjan, the profile of the Road traffic source (Fig. S3) does not show any seasonal variation, as expected, because this source is not seasonally dependent. However, the profile of the Biomass and Domestic Fire Sources shows peaks during the dry seasons, with larger peaks during DS1 than DS2. The Natural Dust and Road Dust source profile shows larger contributions during year 1, with large peaks during DS1, but smaller contributions during the 2nd year of sampling. The marine salt source profile also shows a larger contribution in year 1 than in year 2. Finally, the profile of the construction dust source is similar to that of the natural and road dust sources. The analysis of the contribution profiles reveals seasonal specificities of some sources, particularly for OC. However, the large peaks

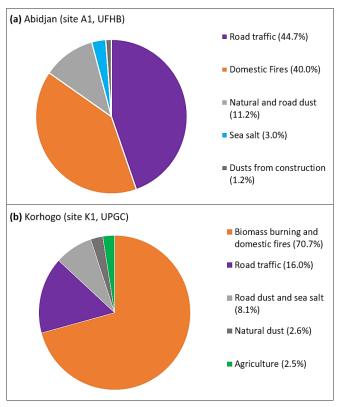


Fig. 9. Apportionment of sources contributing to the PM_{2.5} aerosol mass identified at (a) Abidjan (site A1, UFHB) and (b) Korhogo (site K1, UPGC)

observed during DS1 compared to DS2 should be put into perspective, as this analysis is based on species that can only explain 56.7% of the collected aerosol mass. Thus, it would be important to reduce the undetermined fraction of the aerosol, a fraction that includes a large part of the trace elements, to better explain these seasonal variations.

Korhogo (site K1, UPGC): The application of the PMF model to the K1 site of Korhogo results in R² coefficients of determination that can be grouped into 2 classes. These are species with R² < 0.4 for PM2.5, EC, OC, CH3COO-, SO4²- and NO3-, and those with R² > 0.6 for HCOO-, C2O4², Cl-, Na+, NH4+, K+, Mg²+ and Ca²+. Species with R² < 0.4 show high values relative to seasonal trends, peaks likely due to localized events in time. However, because the uncertainties are a function of the concentration of the species in each sample, they increase with concentration. Fig. 9 (b) and Fig. S1 show the contributions of the 5 different sources determined in our PMF study, to carbonaceous and inorganic species contained in the PM2.5 sampled at site K1 of Korhogo.

Korhogo source 1 (Factor 4): Source 1 contributes to 70.7% of the PM_{2.5} mass in Korhogo, making it the main source in Korhogo. This source is responsible for 79.9% and 62.3% of OC and EC respectively according to Cachier and Ducret⁶⁴ and Chow and Watson⁶⁵, tracers of Biomass burning source. In addition, it provides 77.3% of K⁺ also recognized as a tracer of this source (Wu et al.⁶⁸ and Sharma et al.⁶²). However, these tracers are also associated with the Domestic Fire Source.^{67,73–75} Thus, this source combines both <u>Biomass burning and domestic fires</u>

source. It can thus be local or regional (driven by regional winds). Observation of the evolution of this source (Fig. S4) shows higher contributions during the dry seasons (DS1 and DS2) compared to the wet seasons (HS1 and HS2).

Korhogo source 2(Factor 2): This source participates in 16% of the PM_{2.5} mass, and contributes 22.7% and 13.2% respectively of EC and OC, tracers of the *Road traffic* source. The OC/EC ratio of 1.46 in the source profile is close to the values of urban areas (influenced by the same source) in Europe^{76,77} and Morocco⁷⁸. In addition, it is responsible for the emissions of 82.5% NH₄+; 43.4% NO³⁻ and 32.9% SO₄²⁻, secondary aerosol tracers according to Sharma *et al.*⁶² The presence of sulphate, a tracer of the secondary aerosol component of this factor, could result from photochemical interactions with atmospheric SO₂, and improved photochemistry during the warm season would promote these reactions.^{78,79} Figure S3 shows very little seasonality in the contribution of this source to PM_{2.5} concentrations, which is typical of the traffic source, as is the case for Abidjan.

Korhogo source 3 (Factor 1): it contributes to 8.1% of the PM_{2.5} mass, with contributions of 30% and 11.5% respectively to the dust tracers Mg²⁺ and Ca⁺.69 The low contribution to carbonaceous species (EC, OC) excludes the combustion source, but reveals an indirect link: it is a dust source from the resuspension of Road dust.⁵⁴ In addition, the 41.4% participation in Na⁺, 21.8% in Cl⁻ and 15.7% in K⁺ reveals the presence of sea salt.⁷⁰ The association of these 2 sources is confirmed by Fig. S4, where we observe a contribution of this factor that increases both in the dry season (dust) and in the wet season (in Sea salt).

Korhogo source 4 (Factor 5): it participates in 2.6% of the PM_{2.5} mass, with contributions of 67.5% and 57.2% respectively to Ca²⁺ and Mg²⁺, tracers of desert dusts, *Natural dust*.⁶⁹ The 9.6% contribution to EC but 0% to OC, but also 27.1% and 21.1% to C₂O₄²⁻ and CH₃COO⁻, respectively, could underline the remote origin of a carbonaceous particle source. Indeed, only the inert fraction (EC) is observed and the reactive fraction (OC) seems to have given way to carboxylic acids.

Korhogo source 5 (Factor 3): This source, which contributes to 2.5% of the PM_{2.5} mass, participates in 78.2% and 42.7% respectively in Cl⁻ and NO₃⁻; according to Nyilitya *et al.*⁸⁰, these species are tracers of the Agriculture source, through the use of pesticides, Animal manure and fertilizers. Furthermore, Chlorine (Cl⁻), nitrogen (NO₃⁻, NH₄⁺) and potassium (K⁺) are the main constituents of pesticides, representing 98.9% of this source: this confirms the link with *Agriculture*, which is a very preponderant activity in the area. Indeed, Korhogo is the main cotton and mangoes production area of Cote d'Ivoire. These crops are grown with the use of fertilizers and pesticides. It should be noted that Koh *et al.*⁸¹ recommend an isotopic study to confirm the choice of the source Agriculture from these results.

In Korhogo, profile for the Biomass burning and Domestic Fires source (Fig. S4) shows a contribution of equal magnitude for DS1 and DS2 for the existing samples (indeed, note the absence of data during DS2), much larger than in the wet season. Therefore, this source does not clearly explain the variations in

PM_{2.5} concentrations observed between DS1 and DS2. The Traffic source profile shows no seasonal or interannual variation, despite some significant peaks. The Road dust and Sea salt source is a grouping of sources that could not be separated. However, from the figure, it can be assumed that (1) the highest contributions to PM_{2.5} during DS1 and DS2 are due to Road dust, a source increasing in the dry season, and (2) the high contributions to PM_{2.5} during the wet season (HS2) are associated with marine salts. The Natural dust source has a larger contribution during DS1 than during DS2 which explains the higher particle concentrations during DS1. However, the larger contributions during HS2 suggest the influence of a third, unidentified source that may be related to a dust event. The Agriculture source has a larger contribution during the 2nd studied year than during the 1st. Thus, the appearance of this source in the second year may be attributed to the start of a new agricultural activity or a change in agricultural practice nearby the study site.

4. Conclusions

This study presents temporal trends in the chemical composition of PM_{2.5} aerosols in two cities, Abidjan in the south and Korhogo in the north in Côte d'Ivoire (West-Africa). PM2.5 concentrations consistently exceed both WHO recommendations and Cote d'Ivoire's air quality standards, with dry seasons (DS1 and DS2) showing concentrations more than twice as high as wet seasons (HS1 and HS2). Carbonaceous species (EC and OC) account for 27% in Abidjan and 23% in Korhogo, with Abidjan indicating a significant influence of traffic emissions and domestic fires (OC/EC ratios < 2), while Korhogo reflects biomass and domestic fires (OC/EC ratios > 2). Chemical composition analysis explains 56.7% and 50.5% of PM_{2.5} at the A1 and K1 sites, respectively. Five contributing sources were identified at each site. In Abidjan, these are Road traffic (44.7%), Domestic fires (40%), Natural and Road dusts (11.2%), Sea salt (3%), and Dusts from construction (1.2%). In Korhogo, it is biomass burning and domestic fires (70.7%), road traffic (16%), road dusts and sea salt (8.1%), natural dusts (2.6%), and agricultural activities (2.5%). PM_{2.5} concentrations in Abidjan and Korhogo exhibit strong links to rainfall and regional sources (dusts and biomass fires) in the dry seasons in Korhogo. The observed seasonal variations emphasize the importance of long-term aerosol composition monitoring to track the effectiveness of pollution source reduction efforts.

To conclude, this study provides crucial information for identifying the main sources contributing to air pollution in each of the cities studied. By understanding the main sources of these emissions, it becomes possible to put in place targeted strategies aimed at mitigating the impact of urban particulate pollution, which are specific to each city. This approach will not only reduce atmospheric emissions, but also improve air quality and, consequently, public health in these highly urbanised areas.

Author Contributions

S.G. directed the work on this study, C.L. was the scientific leader, S.K., S.S. and J.B. took part in the design and analysis of the results, E.G. carried out the chemical analyses, K-D. M. and A.O. were involved in data collection in Abidjan and V.Y. was the P.I. of the PASMU project.

Conflicts of interest

There are no conflicts of interest to declare.

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