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Urban $PM_{2.5}$ Air Pollution in Sub-Saharan Africa: A Comparative Study Between Case of Benin, Côte d'Ivoire and Senegal

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ABSTRACT

The aim of this study is to investigate the Sub-Saharan Africa air pollution in Côte d'Ivoire, Senegal, and Benin by studying fine particles $PM_{2.5}$ and to bring out their physicochemical characteristics in order to have a better knowledge on the African air pollution. Though these countries don't share the same borders, their urban environments reveal similarities as regards higher concentrations of $PM_{2.5}$. Likewise, similar repartitions of trace elements were recorded in the three countries. The ratio of specific surface area to the proportion of 2.5 µm fraction was 0.1 in the three countries. This ratio could be used to investigate African urban air. Moreover, xylene/ethylbenzene ratio was very high (11.1 in Senegal and 4.2 in Benin). This suggests a high photochemical reactivity attributable to the greatest presence of ozone in atmosphere. All results indicated that its main cause is traffic emission. Others studies in African cities are necessary in order to exclude the possible industrial dust and soil influence.

Keywords: Air pollution, Particulate matter, Sub-Saharan Africa, Physicochemical characterization, Diagnostic ratio

INTRODUCTION

Urban air pollution is estimated to have been the cause of the 1.3 million annual deaths worldwide and 82,000 annual deaths in Sub-Saharan Africa in 2008 (1). Also, the World Health Organisation (WHO) reported an increase of 16 % of the total number of deaths attributable to outdoor air pollution as compared to the year 2004. In 2008, according to the WHO, African countries such as Côte d'Ivoire, Senegal and Benin, recorded 3,669, 1,441 and 916 annual deaths, respectively, caused by urban air pollution. Moreover, children under 5 years old are the most vulnerable group due to the immaturity of their respiratory systems. They represent 8, 20, and 13 % of the total number of deaths per year in Côte d'Ivoire, Senegal and Benin, respectively. This African outdoor air pollution is due to the migration of rural population to urban areas in search of better economic conditions, employment or sheer survival (2). It is also explained by the unplanned and unsustainable development of transports especially increasing second-hand cars (3,4) and motorbikes (5,6).

Accordingly, air pollution is becoming a major environmental and health concern in Sub-Saharan Africa. In recent decades, concerns have been raised and it indicated that VOCs, $PM_{2.5}$ and their toxic components (heavy metals, Paraffin, PAHs, water soluble ions, etc.) were responsible for adverse health and environmental effects (7–12). Urban air PM is mainly originated from incomplete fuel combustion of motors but they also depend on global characteristics of urban cities. For instance, Abidjan (Côte d'Ivoire) is characterized by 6.8 million inhabitants (in 2011), with high emission from buses and utility vehicles, oil refineries, gas flares, electrical power stations, biomass bush burning, biomass burning for cooking purposes, uncontrolled waste burning and blowing sand from the Sahara Desert (13,14). In Dakar (Senegal), the population is estimated to 3.2 million residents (in 2011). The majority of the population carry on their main activities in the center of Dakar and this brings about congestion and traffic jams. Dieme et al. (15) reported that the city develops many industrial activities but it is filled with diesel buses which are the main mode of transport. Some activities by their nature, as those related to lead, provoke a higher level of air pollution (16,17). Dakar is often swept across by laden wind of desert. In Cotonou (Benin), the population is estimated to 1.2 million of residents. Throughout the city, it is easy to note an exposition to gasoline cans and bottles along the roadside and to observe above the different crossroads, a thick layer of smoke which wraps the population. The town is identified by the lack of public transport and the galloping increase of the widespread use of motorbikes, particularly the phenomenon of motorbike-taxi drivers commonly known as "Zemidjan", which is the main means of transport both faster and cheaper with door-to-door trips. The city had more than 94,000 motorbikes and more than 350,000 old second-hand cars (5,18).

In addition, numerous epidemiological studies have shown the relationship between PM and harmful health effects (9,11,19) and assess these adverse impact using chemical and physical characterization of PM (source, size, mass, surface area, organic composition, metals, etc.) (20–23). Airborne PM with aerodynamic dynameters below 2.5 μm ($PM_{2.5}$) are the most toxic particles (13,24). In most of the developing countries, limited data are available about physicochemical characterization of urban particulate matter associated to adverse health effects assessment (13,25,26).

The aim of this study is to investigate Sub-Saharan Africa air pollution in three countries, Côte d'Ivoire, Senegal, and Benin by studying fines particles $PM_{2.5}$ through their physical and chemical characteristics in order to have a better knowledge on the African urban air pollution.

Analytical procedures

Sample collection

Comparative sampling sites were Abidjan (5°20'16.94"N, 3°59'59.86"W; Côte d'Ivoire), Dakar (14°40'14"N, 17°26'17"W; Senegal), and Cotonou (6°22'2.3"N, 2°25'46.4"E; Benin) (Figure 1). $PM_{2.5}$ samplings were carried out on continuous collection in each country and were performed from December 12, 2007 to

December 17, 2007 (Côte d'Ivoire), from July 2009 through September 2009 (Senegal), and from November 16, 2010 through December 08, 2010 (Benin). The trajectories of air mass were performed using the NOAA HYSPLIT model. This model is available on the Web (http://ready.arl.noaa.gov/hysplit.php).

Concerning the wind speed average during the period collection, it was 3.5 m/s in Côte d'Ivoire, 3.4 m/s in Senegal, and 3.0 m/s in Benin. As collection method, particles samplings were collected with by using high volume cascade impaction air samplers (Staplex, New-York, USA) as described by Billet et al. [27]. The impactor's plates were mounted without any filter and backup filter to maintain a constant aspiration flow rate (i.e., 80 m^3/h).

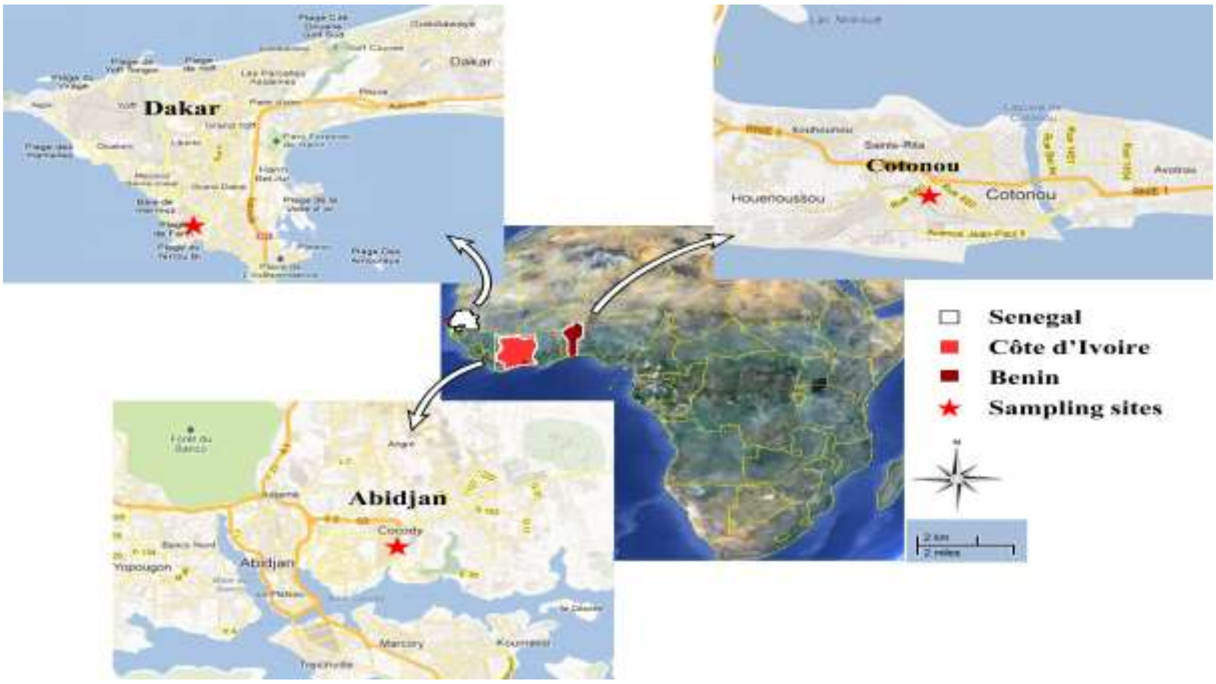

Figure 1: Map of urban sampling sites of the three countries

PM size distribution and specific surface area

Laser granulometry (Beckman Coulter LS13 320MW with Universal Liquid Module) has been used to study the PM size distribution. The laser granulometer measures particle size distribution over the range from 0.017 to 2,000 µm and based on polarization intensity differential scattering (PIDS). Duration of each measure was 1 min and limit of beam obscuration was 8 - 12 %. The power had been adjusted between -4 mV and +4 mV.

Specific surface area analysis was performed with Quantasorb® Surface Area Analyzer (Quantachrome Corporation, New York, U.S.A.) which is based on Brunauer Emmett Teller (BET) method. Particle samples placed in a small Pyrex U-shaped cell were outgassed at 200 °C and volumes of pure nitrogen gas adsorbed to their surface at -196 °C (liquid nitrogen temperature). Amount of nitrogen absorbed at various partial pressures was used to calculate sample's surface area.

Trace elements, soluble chemical species and organic compounds

PM samples were digested with HNO_3 and $HClO_4$ (ratio 1:2, v/v) using microwave digestion (MARS 5 XPRESS, CEM Corporation). Thereafter, the solutions obtained were filtered by Whatman cellulose filters and analysed by ICP-MS (Varian 820 MS) as described by Cazier et al. [28].

Soluble species were determined by ion chromatograph Dionex DX 100 coupled with Dionex ICS 900. Samples were previously extracted and filtered on cellulose acetate filter 0.45 µm and then 25 µL were injected in chromatograph. Soluble anions were determined by chemically suppressed ion chromatography (carbonate 1mM/bicarbonate 3.5 mM eluents and AG14A/AS14A columns, 1.2 mL/min, Dionex DX 100). Soluble cations were determined by chemically suppressed ion chromatography (methane sulfonic acid 20 mM eluents and CG12A/CS12A columns, 1 mL/min, Dionex ICS 900). Chromatographic data were analyzed by Chromeleon® software.

Volatile organic compounds (VOCs) analysis were carried out as published by Caplain et al. [29]. At the beginning, samples have been trapped in glass tubes prior and desorbed by thermal desorption between 220 and 300°C using GC/MS (Combi Injector/Desorber module - EM640 Brüker). Polycyclic aromatic hydrocarbons (PAHs) and paraffins adsorbed on PM samples were extracted with dichloromethane by soxhlet after the thermal desorption. Extracts were concentrated under nitrogen flux and injected in a gas chromatograph (VARIAN 3800) coupled to a mass spectrometer (VARIAN 1200 TQ). The capillary column is a Factor four VF-5 ms (30 m x 0.25 mm x 0.25 µm) and used helium as carrier gas. The total time for this analysis was 60 min; 40 °C for 5 min, 5 °C/min up to 310 °C and 310 °C for 3 min. The parameter of mass detector was impact electronic ion current = 70eV and temperature of source 280 °C. The samples were analyzed between 40 and 350 mass unit. Compounds were identified by comparing retention times of chromatographic peaks from samples with those from standard mixtures and by comparing mass spectra with those contained in NIST and/or WILEY libraries.

RESULTS AND DISCUSSION

Comparative table of demographic characteristics

PM studies were conducted in urban area of Côte d'Ivoire, Senegal, and Benin. These countries have enjoyed a strong demographic growth for several years. Table 1 summarized demographic changes in the three countries under study. Impact of air pollution PM on the health of the population, particularly on children living in city, would be associated to the main conducted activities. It is important to underline that despite the relatively low population density in Senegal, the rate of children death was higher than those reported in Côte d'Ivoire and Benin. This difference is most likely due to the activity relating to the smelting of lead performed by some companies [16,17] and high emission level of diesel old motors. In Benin, many women with small children sell gasoline in bulk along the roadside. Moreover, motorbike-taxi drivers generate a lot of exhaust gas in the air due to the poor maintenance of motors [6]. $PM_{2.5}$ physicochemical characteristics are necessary to explain potential sources of urban air pollution.

Table 1: Comparison of population characteristics of the three urban cities

Cities/Countries	City population (2011) x 10^6	Density x 10^3 resid/km^2	Main town characteristics	Annual deaths (AUP - 2008)	Children deaths under 5 years % (AUP - 2008)
Cotonou (Benin)	1.2	15	Zemidjan phenomenon, gasoline carboys along roadside, old second-hand cars	916	13
Abidjan (Côte d'Ivoire)	6.8	16	Old buses and vehicles, bush and waste burning	3669	8
Dakar (Senegal)	3.2	5.8	Many diesel buses, congestion and traffic jams, lead activities	1441	20
AUP = attributable to urban air pollution; resid = residents					

Sampling conditions and $PM_{2.5}$ concentrations

This comparative study focuses on $PM_{2.5}$ concentrations in ambient air and meteorological parameters that could influence their presence.

According to the NOAA Hysplit backward trajectories, the air masses originated from the sea and went through the three cities under study (Figure 2). Overall, Table 2 reported a relatively low wind speed during the collection period on the three sites. Prevailing wind direction showed that wind was blowing from Atlantic Ocean during that period and thus, the wind was not under the influence of the Sahara Desert (northeast wind called Harmattan) [30]. This is rather a maritime trade wind (southwest wind or monsoon). The highly relative humidity confirmed the origin of dominant wind. Temperature was relatively stable over the considered period as compared to West African average temperature (28 °C). Weinstein et al. [30] obtained in Guinea $PM_{2.5}$ concentrations (177 µg/m^3) near to those recorded in Benin; this value was found in harmattan period. It means that $PM_{2.5}$ concentrations in Benin would come at a very high level under harmattan influence. It is important to note that all values of $PM_{2.5}$ concentrations found in the three countries greatly exceed standards set by the World Health Organization [31] (25 µg/m^3 - 24h average concentration and 10 µg/m^3 annual average). Physicochemical characteristics provide more understanding on high level of PM concentrations.

Figure 2: Trajectories of air masses on sampling sites of the three countries

Table 2: Meteorological conditions during the different collections in the three countries

Cities/ Countries	**Period**	**Location site**	**Average temperature (°C)**	**Relative humidity (%)**	**Average wind speed (m/s)**	**Wind direction**	**PM concentrations (µg/m^3)**
Cotonou (Benin)	Nov-Dec	6°22'2.3"N 2°25'46.4"E	31.4	72	3.0	SSW	180.9
Abidjan (Côte d'Ivoire)	Dec	5°20'16.94"N 3°59'59.86"W	28.0	n.a.	3.5	SSE	105.6
Dakar (Senegal)	Jul-Sep	14°40'14"N 17°26'17"W	28.0	82	3.4	SSW	75.1
n.a. = not available							

$PM_{2.5}$ physical characteristics

Numerous studies established the correlation between particle characteristics and biological responses [22,32,33]. Table 3 showed up PM size distribution and ability to absorb chemical compounds on their surface.

According to Table 3, values of Cotonou, Abidjan, and Dakar indicated similar and significant proportions of $PM_{2.5}$ fraction in ambient air. PM fraction ranged from 1 µm to 0.5 µm were the same in the studied countries considering the ratio of this fraction against PM number below 2.5 µm. Contrariwise, Dakar's particles were abundant in ultrafine particles as compared to the ratio found in Benin. Moreover, $PM_{2.5}$ of the three cities presented the similar ratio of specific surface area/$PM_{2.5}$ proportion. This suggests that surface area of particles is strongly associated to the proportion of 2.5 µm fraction. This ratio could be used to estimate one of the parameters by knowing the other one and to appreciate ability of PM to absorb harmful compounds associated with adverse health effects. However, these findings need to be confirmed by future studies on West African particle samplings.

Table 3: PM size distribution and specific surface area in the three urban cities

Cities/Countries	PM number (%)								surface area (m^2/g)	ratio
	≤ 2.5 µm		1- 0.5 µm	ratio		0.5 - 0.33 µm	ratio			
Cotonou (Benin)	97.5		55.2	0.6		24	0.2		10.7	0.1
Abidjan (Côte d'Ivoire)	88.3		n.a.	n.a.		n.a.	n.a.		9	0.1
Dakar (Senegal)	94.7		61.4	0.6		35.5	0.4		12.7	0.1
The ratios have to be calculated in relation to PM number ≤ 2.5 µm; n.a. = not available										

Inorganic and organic compounds comparative study

Trace elements had been usually correlated to natural environment (e.g. Na, Mg, Ca, Ti) and anthropogenic origin (e.g. Fe, Al, Mn, Ba, Cr, Zn, Pb, Cu) [15,22]. In this comparative study, inorganic elements in urban air of Côte d'Ivoire, Senegal, and Benin are heterogeneous (Table 4).

Table 4: Inorganic elements on $PM_{2.5}$ air pollution in Abidjan, Dakar, and Cotonou

Metals	Percentage (%)				
	Cotonou		**Abidjan**		**Dakar**
Al	41.7		32.8		36.0
Ba	0.4		n.a.		0.3
Cr	0.1		0.8		0.0
Cu	0.3		0.1		0.1
Fe	34.4		29.4		39.1
Mg	7.0		3.9		8.4
Mn	0.6		0.4		0.3
Pb	0.2		0.3		0.1
Sr	0.2		n.a.		0.3
Ti	1.2		2.1		2.2
Zn	1.3		0.2		0.3
Others	0.2		0.1		0.1

Cities under study registered the greatest concentrations in Al, Fe, Mg, and Na and these values were similar. In African countries, there is red soil rich in iron which contains iron oxide (Fe_2O_3) and aluminium oxide (Al_2O_3) due to the strong presence of bauxite. Extraction activities with the processing of bauxite to final aluminium products can explain the high value of iron and aluminium in African ambient air. Moreover, urban $PM_{2.5}$ of the three countries hold in transition metals and alkaline soil metals which are usually found in African ground [34]. Among these trace elements there are Cr, Pb, Zn, Cu, V and Cd that are carcinogenic [35,36]. Many studies attributed the presence of atmospheric heavy metals to natural emissions, traffic emissions and industrial metallurgical processes [37–39]. However, it is crucial to investigate West African soil in order to discount the possibility of soil pollution influence.

With regards to ionic species concentrations (Figure 3), PM were abundant in calcium, nitrate, sulphate, sodium, and chloride ions. Sodium and chloride ions profiles are similar and likely due to the marine dust influence [28,40]. Significant amounts of calcium could come from natural erosion and/or dust of cement industry. In Cotonou (Benin), cement industry is located at about 1 km of the sampling site. Furthermore, sulphate and nitrate are anthropogenic activities [15,22,28,41,42]. High nitrate value observed in Abidjan (Côte d'Ivoire) indicated an anthropogenic contribution particularly animal and human waste [43].

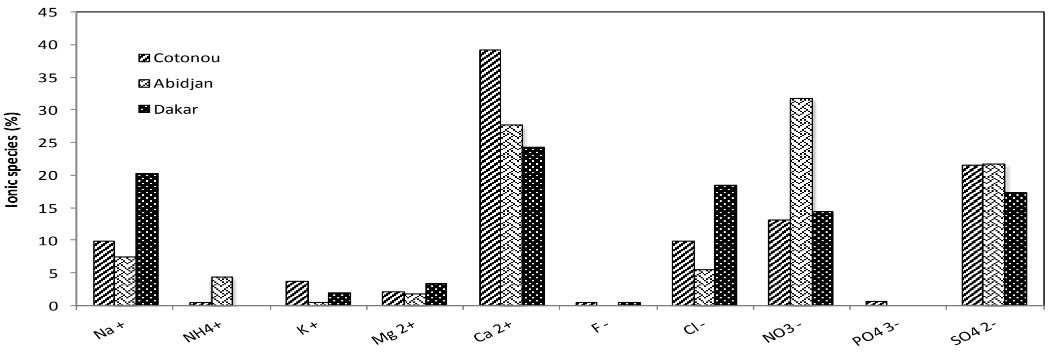

Figure 3: Ionic species profile in $PM_{2.5}$ of the three countries under study

In this study, West African countries under study recorded heterogeneity of paraffins (Figure 4). High level in C_{16} and C_{25} were found in urban $PM_{2.5}$ of Abidjan and high C_{33} in Cotonou. Overall, urban ambient air of studied countries was abundant in C_{20}-C_{30}. In the literature, paraffins ranged from C_{13} to C_{19} indicated microbiota and diesel influence and C_{20}-C_{37} are attributed to fossil fuel rubbish and plant waxes [28,44,45]. Kotianová et al. [46] reported that *n*-alkanes up to C_{20} are attributed to gasoline powered vehicles and until C_{25} are due to heavy duty diesel trucks. In short, in West Africa, paraffins could come from emissions of gasoline and/or diesel vehicles. Study of PAHs ratios provides also more information about possible urban sources.

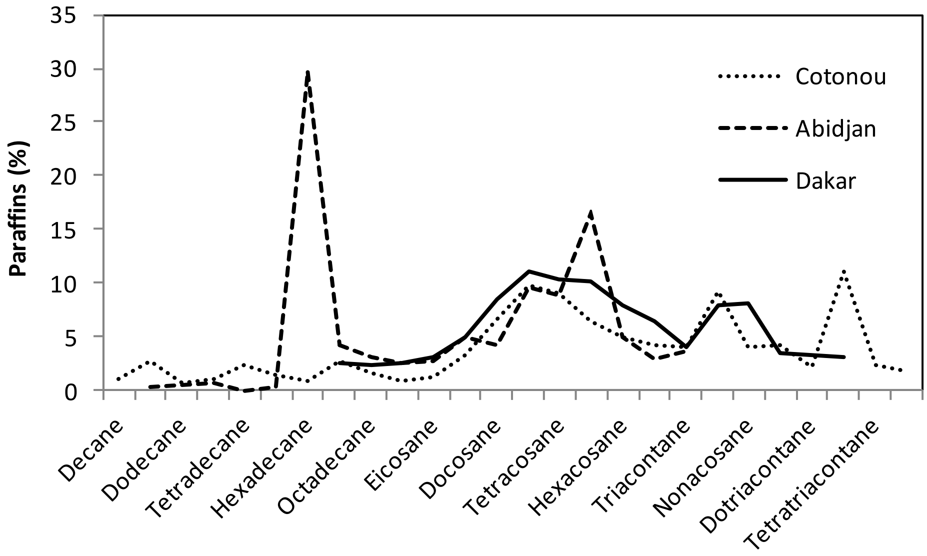

Figure 4: Paraffins profile in air particulate matter of Abidjan, Dakar, and Cotonou

In this work, we focus on BTEX of VOCs (Table 5). We had limited data in Abidjan. However, benzene value was similar in Abidjan and Cotonou, and twice higher than those found in Dakar. Contrariwise, Dakar recorded a high xylene level (53.5 %) compared to Cotonou (39.0). It is difficult to forecast the true influence of different emission sources. Some researchers have generally used diagnostic ratios of BTEX to identify the possible sources [47–49]. Toluene/benzene (T/B) ratio found in $PM_{2.5}$ samplings was 3.9 and 3.2 in Benin and Senegal, respectively. According to the literature, T/B ratio ranged from 1.5 to 4.0 in urban areas indicated traffic emissions [50–53]. Ethylbenzene/benzene (E/B) values in this study were 1.8 and 2.3 in Benin and

Senegal, respectively. They were relatively higher than E/B ratio (1.2) found in Tokyo [(54)]. Furthermore, xylene to ethylbenzene ratio (X/E) has been widely used an indicator for photochemical reactivity from OH-oxidation in the atmosphere. Recent studies showed that this ratio (o-X/E) was ranged from 0.2 to 0.9 worldwide [(55)]. In the present study, o-X/E ratio was remarkably higher in Benin (4.2) and Senegal (11.1). This ratio of xylene to ethylbenzene could be a good tool to assess air quality in African countries. Moreover, benzene/toluene ratio (B/T) recorded was similar in $PM_{2.5}$ in urban African cities under study. These values were near to those found by Wang et al. [(56)] and they indicated vehicular exhaust origin [(49)].

Table 5: Comparative study of VOCs and PAHs in $PM_{2.5}$ urban air of the three countries and diagnostic ratios of source identification

VOCs		Percentage (%)				
		Cotonou		Abidjan		Dakar
Benzene		5.2		5.7		2.1
Toluene		20.3		n.a.		6.7
Ethylbenzene		9.3		4.1		4.8
o-Xylene		39.0		n.a.		53.5
Other		26.2		90.2		32.9
VOCs Ratios						
T/B		3.9		n.a		3.2
B/T		0.3		n.a		0.3
X/E		4.2		n.a		11.1
E/B		1.8		0.7		2.3
PAHs						
Naphtalene	Nap	0.5		n.a.		2.0
Phenanthrene	Phe	1.0		n.a.		4.1
Fluoranthene	Flu	5.5		n.a.		4.7
Pyrene	Pyr	14.1		n.a.		5.8
Benzo[a]Anthracene	BaA	9.5		n.a.		9.3
Chrysene	Chr	13.1		n.a.		7.8
Benzo[b]Fluoranthene	BbF	n.a.		n.a.		18.0
Benzo[k]Fluoranthene	BkF	15.1		n.a.		7.0
Benzo[a]Pyrene	BaP	12.1		n.a.		9.4
Dibenzo[a.h]Anthracene	DahA	10.6		n.a.		n.a.
Indeno[1.2.3-c.d]Pyrene	Ind	n.a.		n.a.		15.5
Benzo[g.h.i]Perylene	BghiP	18.6		n.a.		16.4
PAHs Ratios						
∑COMB/∑PAHs		0.9		n.a.		0.9
BaP/BghiP		0.6		n.a.		0.6
BaP/(BaP + Chr)		0.5		n.a.		0.5
BaA/(BaA + Chr)		0.4		n.a.		0.5
BbF/BkF		n.a.		n.a.		2.6
Flu/(Flu + Pyr)		0.3		n.a.		0.4
Ind/(Ind + BghiP)		n.a.		n.a.		0.5

VOCs = Volatile Organic Compounds; PAHs = Polycyclic Aromatic Hydrocarbons; ∑PAHs = sum of total non-alkylated PAHs; ∑COMB = ∑ BaP, Chr, Flu, Pyr, BaA, Ind, BkF, BbF and BghiP; T/B = toluene/benzene; B/T = benzene/toluene; X/E = xylene/ethylbenzene; E/B = ethylbenzene/benzene; n.a. = not available

PAHs data in $PM_{2.5}$ were unavailable in Côte d'Ivoire. So, at this level, comparative study considers the values just in Senegal and Benin. Several studies used PAHs ratios to identify their possible source [(57–60)]. Percentages of PAHs were similar in Dakar and Cotonou, and present the same ratios. Flu/(Flu + Pyr) was 0.4 and 0.3 in Dakar and Cotonou, respectively. This indicated gasoline emissions [(61)]. The ratio of BaP/(BaP + Chr) suggests that PAHs in urban African $PM_{2.5}$ were from diesel emissions [(28)]. Further, BaA/(BaA + Chr), BaP/BghiP, and ∑COMB/∑PAHs reveal that PAHs of West African $PM_{2.5}$ are attributed to combustion and traffic emissions [(62–64)]. In Dakar, ratios of BbF/BkF and Ind/(Ind + BghiP) indicate aluminium smelter emissions [(65)] and diesel emissions [(61)], respectively.

CONCLUSION

The purpose of this study is to compare the physicochemical characteristics of PM in urban air of Sub-Saharan countries. This work focuses particularly on three West

African countries: Senegal, Côte d'Ivoire, and Benin. Though these countries don't share the same borders, their urban environments reveal similarities as regards higher concentrations of particles. Higher concentrations of $PM_{2.5}$ were recorded especially in Cotonou (Benin). The same distribution of PM and similar specific surface areas were found in these countries. Further, the ratio of specific surface area to the proportion of 2.5 µm fraction could be used to investigate African urban air. Likewise, similar repartitions of trace elements were recorded in the three countries. These metals can come from African soil and it is crucial to investigate West African ground to clarify pollution source. Identification tools of pollution source as VOCs ratios and PAHs ratios were used to detect pollutants origin. Concentrations of ozone could be high in West African ambient air. All results suggest mostly traffic emissions. However, other studies are necessary to exclude the possible industrial dust influence in African urban areas.

Declaration by Authors

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