Monitoring Particulate Matter Air Pollution in Urban Centers: New Insights from Douala, Cameroon

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Air quality progressively deteriorates as urbanization, motorization and economic activities increase. Aerosol particles smaller than 2.5µm (PM_{2.5}), a widespread form of pollution is an emergent threat to human health, the environment, quality of life, and the world's climate. The composition of these particles is an important aspect of interest not only related to possible health and environmental effects of the elemental content but the elemental determination which also adds valuable information for source apportionment. This study investigates and evaluates the level of PM_{2.5} in Douala, Cameroon. Particles were collected using a cyclone that separates the PM_{2.5} from the air stream and impacts them on polycarbonate filters which were changed every 24-hour sampling period. Samples were analyzed for particulate mass concentration, black carbon (BC) and trace elements. Trace element analysis was done by EDXRF (energy dispersive x-ray fluorescence spectroscopy). Cl, K, Ca, Ti, Mn, Fe, Ni, Cu, Zn, Br, Sr, and Pb were identified and quantified for samples. Local meteorology was used to study variations in PM_{2.5} mass concentrations. Possible sources for the pollutants were also investigated. The mean particle mass concentration was $252 \pm 130 \mu\text{g}/\text{m}^3$ while BC attained a maximum of $6.993 \mu\text{g}/\text{m}^3$. The influence of leaded gasoline was inferred while combustion and road traffic were identified as the major anthropogenic sources. Trends in meteorological parameters were influenced by thunderstorms. Sea spray was identified as another major contributor to aerosol PM. This study highlights high pollution levels in Douala.

Keywords: PM_{2.5}, air quality, aerosol, mass concentration, source identification

Introduction

With the recent upsurge in globalization and industrialization coupled with increasing pressures of global climate change, deforestation and shifts in land use pattern, air pollution is emerging as one of the major factors influencing human health, agriculture and natural ecosystems (Agrawal et al. 2003, Kuan et al. 2017, Sánchez de la Campa et al. 2018). Air quality is of particular concern due to the degradation of human health attributed to it. Air borne particles that play pivotal roles in human health and atmospheric processes such as fog and cloud formation, visibility, solar radiation and precipitation, acidification of clouds, rain and fog, and climate change as a whole are of particular interest (Goldoni et al. 2006,

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Dawson et al. 2007, Kawata et al. 2007, Donaldson et al. 2009, Kelly and Fussell 2011, Tiwari et al. 2012, Amodio et al. 2013).

The health burden due to particulate matter (PM) air pollution (PM₁₀ and PM_{2.5}) is one of the biggest environmental health concerns globally (Kuan et al. 2017, Loxham and Nieuwenhuijsen 2019). According to Loxham and Nieuwenhuijsen (2019) and Ariundelger et al. (2020), exposure to ambient airborne PM is a major risk factor for mortality and morbidity, associated with asthma, lung cancer, heart disease, myocardial infarction, and stroke, and more recently type 2 diabetes, dementia and loss of cognitive function especially in urban centers where urbanization, motorization, and rapid economic growth rapidly deteriorate the quality of the air (Boman et al. 2009a, Bell et al. 2009, Kuan et al. 2017, Cao et al. 2018). The size of particles affects their ability to penetrate the human respiratory system causing adverse health effects (Schwarze et al. 2006, Seinfeld and Pandis 2006, Kaonga and Ebenso 2011). Exposure to fine particles especially PM_{2.5} which are aerosol particles with aerodynamic diameter $\leq 2.5\mu\text{m}$ can cause short and long term effects such as decreased lung function, alterations in tissue and lung structure, increased respiratory symptoms, alterations in the respiratory tract and even premature death (Tsai et al. 2003, Katsouyanni et al. 2009, Kuan et al. 2017). Increased toxicity and PM carcinogenicity have been strongly associated with the elemental composition of PM and the presence of polycyclic aromatic hydrocarbons (PAHs) in the finer particles. New evidence shows that long-term exposure to air pollution not only affects outcomes such as premature deaths but also contributes to the development and progression of subclinical and clinical disease such as serious cardiopulmonary defects, as well as some unexpected responses in the liver and brain (WHO 2007).

More attention is required for "Heavy metals", usually referred to as metallic chemical elements having a relatively high density and toxic or poisonous at low concentrations (Hg, Cd, As, Cr, Ni and Pb). In addition, trace metals are proven to be useful tracers and are extensively used to identify sources of emissions to be targeted by the emission reduction policies (Gotschi et al. 2005, Querol et al. 2006, 2007, Viana et al. 2007, Jeong et al. 2008).

According to WHO (2005), Forster (2007) and Tai et al. (2012), climatic conditions have direct effects on the concentration, dispersion and life time of aerosol particles in the atmosphere. The dynamics of the atmosphere and the meteorological conditions play a vital role in governing the fate of air pollutants. Lecoeur et al. (2012) states that concentrations of PM are strongly dependent on meteorological conditions of which temperature, wind speed, humidity, rain rate and mixing height are the variables that impact PM concentrations the most. In this study, the relationship between ambient PM concentration and meteorological variables, such as temperature, rainfall, wind speed and direction and relative humidity is statistically analyzed.

In Cameroon, Douala is of particular interest for air pollution studies because of its dense population coupled with intense industrial and commercial activities (Kemajou et al. 2007). However, there has been limited air pollution research in this city.

With focus on PM_{2.5}, spatial analysis and temporal variations of air pollution in areas of different development typology in Douala, the economic capital of Cameroon was studied. Detailed measurements of air pollution (PM_{2.5}) were carried out at street sites in 2 industrial zones (1 semi industrial interspersed with residential and commercial neighborhoods, and 1 absolute industrial zone) and a residential neighborhood all of which were centrally located and paved neighborhoods.

Literature Review

Ambient PM is a complex mixture of solid and liquid particles suspended in air (Seinfeld and Pandis 2006, Adams et al. 2015). The size, chemical composition, and other physical and biological properties of particles vary with location and time. This variability in pollutant levels derives from differences in pollutant sources, and the characteristic weather parameters of the area (Pinto Miranda Garcia et al. 2018). The sources may be natural, such as forest fires volcanoes, dust storms, forest and grassland fires, living vegetation and sea spray (Omidvarborna et al. 2015, Adams et al. 2015, Loxham and Nieuwenhuijsen 2019), or the result of human activities, such as the burning of fossil fuels in vehicles (Omidvarborna et al. 2015), stubble burning, manufacturing and power plants (Adams et al. 2015), wet cooling towers in cooling systems and various industrial processes, also generate significant amounts of particulates. Coal combustion in developing countries is the primary method for heating homes and supplying energy thus a significant source of PM (Omidvarborna et al. 2015). Salt spray over the oceans is the overwhelmingly most common form of particulate in the atmosphere. As stated by Webb and Pierre (2018) and Wang et al. (2018), anthropogenic aerosols currently account for between 10% and 60% of the total mass of global aerosols in the atmosphere.

According to Seinfeld and Pandis (2006), Brook et al. (2010), Heal et al. (2012), Adams et al. (2015) and Manisalidis et al. (2020), air pollutants may either be emitted directly into the atmosphere (primary pollutants) or formed within the atmosphere itself through chemical reactions and physical processes (secondary pollutants). Heal et al. (2012), further classifies them as inhalable, thoracic and respirable dust fractions depending on the depth of penetration of the particle into the respiratory system. The inhalable dust fraction with a size threshold of about 50µm can be captured by inhalation in the nasal cavity (easily filtered by cilia or mucus). The dust fraction reaching all the way to the lungs (lower respiratory tract) is the thoracic dust fraction. These are particles ≤ 10 but $> 2.5\mu\text{m}$ (Boman et al. 2010, Fortoul et al. 2012, Manisalidis et al. 2020), and the fine dust that can penetrate even further into the bronchioles and alveoli (gas exchange region) is known as the respirable dust fraction. These particles are not ejected by breathing out, coughing, or expulsion by mucus, and approximate a particle size threshold of about 3.5–4µm. In effect, they are $< 2.5\mu\text{m}$ (WHO 2003, Boman et al. 2010, Fortoul et al. 2012, Heal et al. 2012), and are capable of reaching the gas exchange surfaces of the alveoli (Heal et al. 2012).

It should be noted that ambient PM levels in any particular location are also affected by local ambient mixtures of gaseous pollutants, meteorology, geography, and seasonal patterns (Adams et al. 2015, Pinto Miranda Garcia et al. 2018).

Meteorological Implications of Particulate Matter

According to Tai et al. (2012), Lecoeur et al. (2012) and Li et al. (2017), the fate of air pollutants is influenced by the movements and characteristics of the air mass into which they are emitted. The measurements of wind speed and direction, temperature, humidity, rainfall and solar radiation are important parameters used in the study of air quality and can assist in furthering understanding of the chemical reactions that occur in the atmosphere (Lecoeur et al. 2012, Wei et al. 2012, Pinto Miranda Garcia et al. 2018).

As stated by Tai et al. (2010) and Li et al. (2017), $PM_{2.5}$ concentrations depend on meteorological conditions, suggesting that climate change could have significant effects on $PM_{2.5}$ air quality and vice versa. PM is comprised of many different species, and meteorology can have complex effects on total PM concentrations due to its impacts on individual species (Dawson et al. 2007, Zhou et al. 2020). Aerosol SO_4^{2-} concentrations depend on the temperature-dependent oxidation of SO_2 in both the gas and aqueous phases, and sunlight intensity (Seinfeld and Pandis 2006, Dawson et al. 2007, Zhou et al. 2020). On the other hand, concentrations of semi-volatile NO_3^- and organic aerosols are temperature and relative humidity dependent; they can also vary with the amount of oxidants present, which is linked to photolysis rates and, therefore, cloud cover (Dawson et al. 2007). Tai et al. (2010), Dawson et al. (2007) and Tsigaridis and Kanakidou (2007) report that SO_4^{2-} concentrations are expected to increase with increasing temperature due to faster SO_2 oxidation, but semi-volatile components such as NO_3^- and organics are expected to decrease as they shift from the particle phase to the gas phase at higher temperature.

Higher relative humidity (RH) promotes the formation of ammonium nitrate, but an increase in precipitation causes a decrease in all $PM_{2.5}$ components through scavenging and since all species have wet deposition as a sink, precipitation is expected to have a significant effect on aerosol concentrations (Dawson et al. 2007). During a study by Dawson et al. (2007), it was observed that the changes in $PM_{2.5}$ resulted even in areas with little or no base-case precipitation indicating that changes in precipitation in upwind areas affected $PM_{2.5}$ concentrations in downwind areas. Seinfeld and Pandis (2006) conclude that changes in absolute humidity have the largest effects on concentrations of ammonium nitrate aerosol with concentrations increasing with increased absolute humidity and that increases in humidity shift the equilibrium of the ammonia-nitric acid system toward the aerosol phase, resulting in higher concentrations of ammonium nitrate aerosol.

Finally, mixing and dilution influence PM concentrations, so wind speed and mixing height are expected to have an impact as well. According to Tai et al. (2010), if the air is calm and pollutants cannot disperse then the concentration of these pollutants will build up. Conversely, if a strong, turbulent wind is blowing any pollution generated will be rapidly dispersed into the atmosphere resulting in

lower pollutant concentrations in the air. Wind speed changes affect all species that comprise $PM_{2.5}$, with increases in wind speed generally leading to decreases in $PM_{2.5}$ concentrations, and decreases in wind speed generally leading to increases in $PM_{2.5}$ (Dawson et al. 2007, Ya-Gao et al. 2019). According to Brook et al. (2010), increases in wind speed leads to changes in advection and transport resulting in decreases in $PM_{2.5}$ concentrations.

Objectives

This study seeks to investigate and evaluate the level of PM in the industrial town of Douala in Cameroon. The objectives of the study were to analyse and quantify $PM_{2.5}$ in terms of mass and mass concentration and the elemental composition of the PM found in Douala. The study also focused on determining the influence of meteorological parameters on $PM_{2.5}$ concentration in Douala, embarked on apportioning sources to the different PM components that would be identified, and analyzing the variation of fine particles with meteorological parameters, and determine the sources of the $PM_{2.5}$ in the area.

Methodology

Sample Collection

Sampling was done using an electrically powered cyclonic sampler (Casella Group Ltd) capable of collecting PM in $PM_{2.5-10}$ size fractions. The cyclone separates the $PM_{2.5}$ particles from the air stream and impacts them on polycarbonate filters. Operating at a constant volumetric flow rate of 3L/min, $PM_{2.5}$ particles were collected for a period of 1 month. The flow through the cyclone was kept constant by a critical orifice (accuracy of $\pm 15\%$) to maintain a particle cut off diameter of 2.5 μ m. Sample collection was done at a daily temporal resolution and temporal coverage from 30/10/2012–29/11/2012. The set up was mounted at each location for 9 sampling days after which it was mounted at the next location. Filters were changed after every 24h sampling period. Since the same setup was used during the whole campaign the different samples can be compared with each other without being influenced by possible differences in sampling flow (Boman et al. 2010)

Purposefully, samples were collected at 3 sites in the industrial town of Douala (Figure 1); Site 1, the Bonaberi industrial zone (longitude 09°74" East and latitude 04°09" North), Site 2, the Bassa industrial zone (longitude 09°68" East and latitude 04°07" North) and Site 3, the Bonamoussadi residential zone (longitude 09°75" East and latitude 04°04" North). At site 1, the sampler was placed at a height of 8.5m above ground with the intake nozzle placed 1.5m above the platform on which the sampler was placed. The nozzle was placed such that airflow was unobstructed (at all sites) about 200m away from the industrial area and 50m away from the road. The Bassa site saw similar sampling conditions. The sampler was placed facing the industrial zone but away from the road 100m away.

It was placed 8.0m above ground and 80m away from the railway. At site 3 the sampler was placed on the flat roof 5m above ground with the nozzle position 2m above the roof and 100m away from the roadside. The sampler was placed such that air flow was unobstructed. Effective sampling time was ± 24 hours.

Particle collection was done on 25mm diameter Teflon filters with a pore size of $0.4\mu\text{m}$. The polycarbonate filters were initially preconditioned at 45% relative humidity and 20°C (equilibrium conditions intended to minimize the liquid water associated with soluble compounds and to minimize the loss of volatile species as stated by Chow and Watson (1998). These conditions ensure that particle growth due to accumulation is minimized) before they were weighed and placed in Petri dishes. After sampling, the filters were again placed and stored in the same dishes. An OHAUS Adventurer Pro electronic analytical microbalance with a sensitivity of 0.0001 mg was used for gravimetric determination of the sampled particle mass. The set up was mounted at each location for 9 sampling days. Since the same setup was used during the whole campaign the different samples can be compared with each other without being influenced by possible differences in sampling flow.

Figure 1. Map of Study Area showing Sampling Sites in Douala

Source: Fieldwork 2012.

The climate of this region is uniform and is described as a particular equatorial type marked by a lengthy rainy season (at least nine months), abundant rainfall (about 4000 mm per annum), high and stable average annual temperatures (26.7°C) (Siegfried et al. 2009). The mean of the minimum temperature calculated in Douala for 30 years is 22.6°C in July and the mean of the maximum temperature

is 32.3°C in February. The relative air humidity remains high throughout the year with a mean value of 82.6%; the lowest value being around 60% in February and the highest is 100% in the rainy season (Din et al. 2008). Rainfall is bimodal, peaking at July and August with minimal rainfall in January and February and varies from 78.0–1215.0 mm/month and an average rainfall of 2900 mm/year (Djuikom et al. 2011, Fonge et al. 2011).

Sample Analysis

The samples were analyzed for PM mass concentration, elemental composition and black carbon. A principal component analysis (PCA) was conducted to apportion PM sources.

Gravimetric analysis was performed to determine the mass concentration of the sample aerosol.

The total volume of air sampled was determined from the volumetric flow rate of 3L/min. The concentration of PM_{2.5} in the ambient air is computed as total mass of collected particles divided by the volume of air sampled in actual conditions. The concentrations are expressed in micrograms per actual cubic meter (µg/m³). The equation governing the gravimetric analysis is given below:

$$C_{PM} = \frac{M}{V}$$

Where,

C_{PM} = PM Mass Concentration

M = Net mass of the particulate matter collected on the sample filter

V = The volume of air sampled

Samples obtained were analyzed for elemental composition by Energy Dispersive X-Ray Fluorescence (EDXRF) spectrometry (Van Grieken and Markowicz 1993). The spectrometer based on a three-axial geometry consisted of a Siemens Mo-anode X-ray tube with a Mo secondary target that facilitated a good signal to background ratio giving low detection limits (Table 2), and a Kevex Si (Li) detector. According to Boman et al. (2009a) and Gatari et al. (2006), the spectrometer was operated at 50kV and 25mA and the samples were analyzed for 1000s. To ensure and verify the validity of the results obtained, a certified reference material (#2783, Air Particulate on filter media, NIST, USA) was used. For spectrometer calibration, thin film standards with specified uncertainty of 5% in the elemental concentration were used (Micromatter Inc., Seattle, WA, USA). By repeatedly analysing two aerosol filter samples the mean analytical precision of the spectrometer was determined to be 5% (Molnár et al. 2006). Sample elemental spectra were obtained and evaluated by a quantitative x-ray analysis system (QXAS) software provided by the International Atomic Energy Agency (IAEA) laboratories, Seibersdorf, Austria. Atmospheric concentrations and detection limits (DLs) were determined and several of the elements below detection limits were excluded from analysis.

BC concentrations were determined by a Black Smoke Detector Model FH 621-N (ESM Emberline, Erlangen, Germany). This instrument is a reflectometer that has light emitting diodes (LEDs) and photosensors enclosed in a completely black casing. The LEDs (red light emitting diodes for this case) illuminate the sample with optimized light that is tuned at a wavelength of 0.6 μ m. The reflected light intensity is sensed by the photosensors that translate the light intensity to electrical current. The voltage reading is related to the level of sample blackness and subsequently recalculated into BC concentrations. For QC/QA (quality control and Quality assurance) measures, appropriate filter substrate was selected and tested for sampling effectiveness prior to field sampling. The filters were pre-conditioned to removed contaminants and ensure quality of air sampled. Laboratory accredited program was used to assure the quality. The sensors in the instrument used were also calibrated for purposes of QC/QA.

Principal Component Analysis

Factor analysis with Principal Components as extraction method known as Principal Component Analysis (PCA) in air quality studies is widely used to provide information on PM or gaseous pollutant sources (Querol et al. 2001, Amodio et al. 2010). The PCA technique identifies components that explain the common variation pattern of the included variables (elements, and BC) based on the principle that elements with similar concentration patterns most likely originate from a common source. The components are identified by the PCA, and possible sources of the components ascribed. Values < 0.3 have low loading, those between 0.3 and 0.6 are considered to have moderate loadings, those with 0.8 are said to be moderately high loadings and values > 0.8 are considered as high loadings (Boman et al. 2009a).

Meteorological Conditions

Since PM_{2.5} concentrations are strongly dependent on meteorological conditions, it is important to investigate the relationships between PM_{2.5} and meteorological parameters (Lecoeur et al. 2012). The meteorological information during the measurement campaign was obtained from the Douala Meteorological centre which records such data for the entire city. The website "<http://wunderground.com>" was also valuable in getting certain daily variations for some climate parameters.

Results and Discussion

Mass and Mass Concentration

The mean mass and mass concentration of PM collected from the 3 sites is as shown in Table 1.

Table 1. Mass and Mass Concentration for All Sampling Sites

Sample Code	Mass(g)	Mass Conc ($\mu\text{g}/\text{m}^3$)	Sample Code	Mass(g)	Mass Conc ($\mu\text{g}/\text{m}^3$)	Sample Code	Mass (g)	Mass Conc ($\mu\text{g}/\text{m}^3$)
Bonamoussadi 1	0.0010	224	Bonaberi 1	0.0005	116	Bassa 1	0.0010	236
Bonamoussadi 2	0.0003	77.2	Bonaberi 2	0.0003	78.4	Bassa 2	0.0020	463
Bonamoussadi 3	0.0010	224	Bonaberi 3	0.0015	347	Bassa 3	0.0010	232
Bonamoussadi 4	0.0006	147	Bonaberi 4	0.0025	579	Bassa 4	0.0013	307
Bonamoussadi 5	0.0010	232	Bonaberi 5	0.0012	270	Bassa 6	0.0003	77
Bonamoussadi 6	0.0014	316	Bonaberi 7	0.0000	0	Bassa 7	0.0013	309
Bonamoussadi 7	0.0010	224	Bonaberi 8	0.0017	386	Bassa 8	0.0010	232
Bonamoussadi 8	0.0010	232	Bonaberi 9	0.0018	424	Bassa 9	0.0013	307
Mean	0.0009	209	Mean	0.0012	275	Mean	0.00115	271
Standard Dev.	0.000327	70.2	Standard Dev.	0.000856	197	Standard Dev.	0.000475	109
Range	0.0003–0.0014	77.2–316	Range	0–0.0025	0–579	Range	0.0003–0.002	77–463
Median	0.001	224	Median	0.00135	309	Median	0.00115	273

Source: Fieldwork 2012.

The cumulative mean concentration for all sites is $252 \pm 130 \mu\text{g}/\text{m}^3$ which is relatively higher than the WHO Guideline of $25 \mu\text{g}/\text{m}^3$ for $\text{PM}_{2.5}$ (24-hour mean), as stated by Heal et al. (2012). The daily variation in particle mass concentration of $\text{PM}_{2.5}$ in Douala is clearly shown in Figure 2.

Figure 2. Daily Variations in Particle Mass Concentration of $\text{PM}_{2.5}$ in Douala

Source: Fieldwork 2012.

The huge population of the city, the wide range of commercial and industrial activities, variety of old and new, maintained and poorly maintained vehicles, large scale two wheel activities, and the dependence of the population on biomass significantly contribute to the high value of $PM_{2.5}$ mass concentration. According to UN (2018), most vehicles imported into the country range are used or old vehicles (emit a disproportionate amount of pollutants) which between 6–9 years. Nonetheless, JV (2013) puts forward that some of these second hand vehicles are as old as 20 years, although the 2011 financial law of the country permits only the entry of cars of maximum 7 years of age. Mercedes Benz MB 100 D that was first manufactured in 1981 is still being imported into the county. Named "cargo", this wagon carries up to 25 persons within the Douala city. Similarly, vehicles on Cameroonian roads such as taxis date between 1980 and 1990, states the paper.

Open burning and the high dependence on fuel wood and charcoal for domestic and commercial purposes significantly contributes the high BC concentrations for all sampling sites.

Elemental Analysis

EDXRF was run for 22 elements, and a total of 12 elements were identified (above detection limits as shown in Table 2), and quantified in most of the samples; Cl, K, Ca, Ti, Mn, Fe, Ni, Cu, Zn, Br, Sr, and Pb (Table 2).

Sample collection was done at a daily temporal resolution and temporal coverage from 30/10/2012–29/11/2012. The set up was mounted at each location for 9 sampling days after which it was mounted at the next location. Filters were changed after every 24h sampling period implying that after every 24 hours the filters were changed. Since the same setup was used during the whole campaign the different samples can be compared with each other without being influenced by possible differences in sampling flow.

Table 2. Detection Limits (DL) in $\mu\text{g}/\text{m}^3$ for the Analysed Elements

Elt	Cl	K	Ca	Ti	Mn	Fe	Ni	Cu	Zn	Br	Sr	Pb
DL	0.12	0.024459	0.017763	0.007277	0.002214	0.002029	0.002	0.00159	0.001724	0.0011	0.0011	0.001299
NB: Three axial geometry with Mo secondary target. X-ray tube operated with 50kV and 25mA. Lifetime of 1000s. A collection time of 24h.												

Source: Fieldwork 2012.

Full campaign concentration means with standard deviations in $\mu\text{g}/\text{m}^3$ for the analysed elements and the $PM_{2.5}$ mass concentrations at the three sites including BC concentrations in $\mu\text{g}/\text{m}^3$ are given in Table 3. Reported elemental concentrations are those above DL and blank filter concentrations while N is the number of samples with concentrations above DL. DL for analysed elements ranged from $0.0011\mu\text{g}/\text{m}^3$ for Br and Sr to $0.12\mu\text{g}/\text{m}^3$ for Cl as shown in Table 2 while Figure 3 shows how the elemental concentration varied at different sites.

Table 3. Average Elemental Concentrations for the Entire City

Parameter	Range	Average ($\mu\text{g}/\text{m}^3$)	N (Max = 24)
Particle mass concentration ($\mu\text{g}/\text{m}^3$)	0–578.7	251.4 ± 133.7	24
Black Carbon	0–7.0	1.9 ± 1.815	21
Cl	0.131–0.760	0.347 ± 0.189	9
K	0.048–0.507	0.164 ± 0.103	19
Ca	0.027–0.810	0.190 ± 0.195	23
Ti	0.008–0.085	0.029 ± 0.020	18
Mn	0.003–0.126	0.017 ± 0.033	13
Fe	0.035–0.917	0.248 ± 0.216	24
Ni	0.003–0.009	0.005 ± 0.002	4
Cu	0.002–0.013	0.005 ± 0.003	17
Zn	0.004–1.777	0.296 ± 0.469	24
Br	0.017–0.040	0.022 ± 0.005	24
Sr	0.001–0.022	0.004 ± 0.005	15
Pb	0.007–2.075	0.292 ± 0.48	24

Source: Fieldwork 2012.

Figure 3. Variation of Elemental Concentration at Different Sites

For Bonaberi, Ca, Fe, Zn, Br and Pb were present in all samples while for Bassa only Fe, Zn, Br and Pb were identified in all samples. Cl and Ni have the lowest frequencies of occurrence with Cl appearing only once in Bonamoussadi, Ni appearing twice in Bonamoussadi, once in Bonaberi and Bassa with the highest concentration recorded in Bassa.

All concentrations but for Fe, Zn and Pb have concentrations $< 0.3\mu\text{g}/\text{m}^3$ for Bonaberi. But for Cl, all other elements have concentrations $< 0.3\mu\text{g}/\text{m}^3$ for Bonamoussadi and Bassa. Ca presents relatively high concentrations in Bonaberi than for the other zones most probably due to the presence of the cement industry which is present in Bonaberi and absent in the other zones.

While the concentration of Br is relatively low for the other zones, Bonamoussadi presents a higher Br concentration. The high Br concentration could be explained by a high input of particles from biomass burning, since Br can be tracer element for pyrogenic biomass burning.

The possible contribution of Br from sea spray or some combustion source especially vehicle exhaust cannot be excluded (Boman et al. 2009b). Apart from Cl, K and Ca which are higher in Bonamoussadi than in Bassa, Bonamoussadi generally has lowest concentrations. It can then be concluded that Bonaberi has highest elemental concentrations followed by Bassa then by Bonamoussadi. The industrial zones therefore contain more $PM_{2.5}$ than the residential zone.

The lone appearance of Cl in Bonamoussadi indicates there is no local source in that locality. The high Cl concentration could either be from a sporadic source or blown in by the wind. PM concentrations here seem to be higher than for Bonamoussadi. Ca, Fe, Zn and Pb have highest concentrations as can be seen in Figure 3. Unlike in Bonamoussadi, Ca has peaks higher than the 0.3 line which can be explained by the presence of the cement industry in Bonaberi. Cl also presents concentrations higher than the other sites.

The relatively high concentration of Pb especially in Bonaberi can be accounted for by the presence of fuel from unofficial markets (locally known as "fungeh"). Lead paint is also being scrapped from walls and spread in both old and new construction sites and also at the shipyard (eye witness account). Chronic exposure to low concentrations of Pb is very dangerous and can lead to reduction of intelligence, increased blood pressure and a range of behavioral and developmental effects (WHO 2005).

The results show a large variation in sample mass, BC concentration as well as in the concentrations of the analyzed elements. A look at the individual samples from the different sites (Figure 4) signifies that the variation of the different constituents does not show the same pattern. This adds to the picture of different sources for different pollutants and to the influence of meteorology on PM concentration. The different patterns are as shown in Figure 4(a–c).

Figure 4a. Individual Element Pattern for Elements Found in $PM_{2.5}$ in Bonamoussadi

Figure 4b. Individual Element Pattern for Elements Found in PM_{2.5} in Bonaberi **Figure 4c.** Individual Element Pattern for Elements Found in PM_{2.5} in Bassa

Black Carbon (BC)

Very high concentrations of BC are recorded for Bonaberi, high concentrations for Bonamoussadi and averagely high concentrations for Bassa. The mean concentration of Bonaberi, $3.17 \pm 2.376 \mu\text{g}/\text{m}^3$ as opposed to $1.42 \pm 0.459 \mu\text{g}/\text{m}^3$ for Bonamoussadi and $1.10 \pm 1.566 \mu\text{g}/\text{m}^3$ for Bassa is relatively very high (there is high use of fuel wood for household and commercial purposes in the area hence the high BC concentration for Bonamoussadi). The sampling site for Bonaberi is the gateway to and away from the Wouri Bridge hence very dense traffic for most parts of the day hence emissions from vehicle exhaust can explain the high BC concentration. The industrial zone also has very high dependence on fossil fuel for energy production. Bonamoussadi concentrations can be due to the burning of biomass for domestic purposes while vehicle emissions cannot be ignored. Traffic also accounts for that of the Bassa area which is a gateway from Douala to

Yaoundé with high traffic at Ndokotti Market. Open burning and the high dependence on fuel wood and charcoal burning for domestic and commercial purposes significantly contribute the high BC concentrations for all the areas.

Factor Analysis

Three components were extracted by the analysis explaining a total of 76.8% variance for the whole data set as shown in Table 4. The first component is characterized by high loadings of Fe, K, Zn, and moderately high loadings for Cu, Cl, Sr, Br, Ti, and Ca. This component accounts for 50.5% of the total variance obtained. The component could be interpreted as a combination of geological (soil/crust) origin and combustion aerosols. There is a combination of high and moderately high loadings for elements which are derived from these sources. K and Fe for example have high loading and indicate soil originated aerosols, Ti and Ca have moderately high loadings and indicate soil originated aerosols while Zn with High loading indicate industrial activity (Boman et al. 2009a) especially metallurgical activities (Heal et al. 2012). The moderately high Cl and Br loadings also indicate industrial combustion. Zn and Fe could also be emitted from lubricating oil additives (used in two-stroke engine where engine oil is mixed with fuel), combustion of impure fuel, vehicle engine and brake tire wear.

Table 4. *Component Matrix for Source Apportionment for Elements in Air Samples from Douala*

Elements	Components		
	1	2	3
Cl	0.754	-0.021	-0.518
K	0.882	0.367	-0.130
Ca	0.668	0.538	0.141
Ti	0.721	0.050	0.517
Mn	0.345	0.748	0.289
Fe	0.946	-0.207	-0.063
Cu	0.779	0.147	-0.191
Zn	0.818	-0.158	-0.150
Br	0.727	-0.357	0.168
Sr	0.753	-0.242	-0.358
Pb	0.394	-0.730	0.394
BC	0.450	-0.049	0.581

The first component has high loading for all detected elements but for Mn, Pb and BC. Zn compounds are extensively employed as lubricants, antioxidants and as detergent/dispersant improvers for lubricating oils (Begum et al. 2007). The high and moderately high loadings are of more mixed character, possibly representing both soil and combustion origin. To confirm this mixed character, Fe, K, and Ca are characteristic to road dust attributed to diesel vehicle emissions. The industrial and petrochemical waste managing companies that incinerate most

of these wastes could also be a significant source for these elements in the atmosphere.

The second component is characterized by moderate loading from Mn, and this component accounts for 15.0% of the total variance obtained. Moderate loadings of Mn bear sign of aerosol from the metallurgical industry (Heal et al. 2012). This could be confirmed by the moderate loading of Ca in this component. Other activities generating Mn include vehicle engine, brake and tyre wear, and during combustion of impure fuel (particularly coal), and fuel and lubricating oil additives (Heal et al. 2012). Nonetheless, Mn and Ca are typical mineral elements and consequently, this factor could be associated with the crustal fraction of PM_{2.5} (Heal et al. 2005). The presence of these elements in PM_{2.5} could mainly be a result of local and regional dust re-suspension by wind, convection and other natural processes. However, if the emissions from incomplete and complete combustion of biomass have different sources, this could explain the appearance in two different components in the analysis.

The third component had moderate loading for BC accounting for 11.4% of the obtained variance. BC is a good marker for combustion – derived component of airborne particles. It is also a good marker for traffic-related PM pollution (Heal et al. 2012).

PCA for individual sampling sites showed same results as above implying that the individual sites have similar sources of particulate pollution.

Ni which was not included in the PCA due to its being below detection limits for most samples mainly comes from dust and re-suspended soil particles. It is also a tracer for the combustion of heavy fuel oil (Boman et al. 2010).

Influence of Meteorology on PM Concentration

Diurnal temperatures varied between 23°C and 31°C and relative humidity between 81 and 95%. Winds in Douala were westerly, showing a diurnal pattern with gusts of up to 10m/s during daytime, while evenings and nights were generally calmer with very stable atmospheric conditions.

Scattered plots showing variation of meteorological variables with the elemental concentration for the sampling period are given in Figure 5.

Trends for the plot for temperature against mass concentration (A) show that as temperature increases in Bonaberi, the mass concentration reduces while mass concentration increases with increase in temperature for both Bonamoussadi and Bassa. These variations can be explained by the chemical species present in the PM_{2.5}. The mass concentration reduction with increasing temperature for Bonaberi could be explained using the species present in the PM_{2.5}. This trend may indicate the dominance of nitrates in this area since nitrates are semi-volatile. It could also indicate the dominance of primary particulates in this region (Seinfeld and Pandis 2007).

For Bonamoussadi and Bassa, mass concentration increases with increasing temperature indicating the probable presence of sulphates and dust. According to Seinfeld and Pandis (2007), the oxidation of SO₂ to SO₄²⁻ is temperature dependent and increases as temperature increases thus increasing the aerosol concentration. This also indicates that these two areas are dominated by secondary

particulates. From literature, one of the precursor gases for the formation of secondary particulates is SO_2 thus confirming the above assertion. On another hand, these variations can be explained by wind speeds and direction. The wind blows away from Bonaberi hence transporting away a bulk of the mass of particles with it, whereas for Bonamoussadi and Bassa, the wind blows to their direction bringing in more particles from the upwind. This confirms the theories of Brook et al. (2004), Dawson et al. (2007) and Tai et al. (2010).

Figure 5. Variation of PM Mass Concentration with Meteorological Parameters: (A) with Temperature, (B) with Rainfall, (C) with Wind Speed and (D) with Relative Humidity

Mass concentration of $PM_{2.5}$ shows a slight decrease with increasing rainfall for Bassa. A slight increase is noticed for Bonaberi and a sharp increase for Bonamoussadi. This can be explained by the nature of rainfall which is predominantly thunderstorms. Depending on the strength of the wind during the storm, the process of wet deposition can be counteracted and the particles blown away in the wind faster than they are deposited or washed out by the rain. In this case, the particles are blown downwind and mass concentration can then increase in the downwind area with increasing rainfall. This confirms Dawson et al. (2007)'s conclusion that changes in precipitation in upwind areas affect $PM_{2.5}$ concentrations in downwind areas and also explains the slight increase in PM mass concentration in Bonaberi as rainfall increases. The degree of change could be affected by the aerosol concentration of the upwind area.

PM mass concentration increases with increasing wind speed increases in all the locations contradicting the theories of Dawson et al. (2007) and Tai et al. (2010) which states that if the air is calm and pollutants cannot disperse then the concentration of these pollutants will build up. Conversely, if a strong, turbulent wind is blowing any pollution generated will be rapidly dispersed into the atmosphere resulting in lower pollutant concentrations in the air. This contradicting behaviour could be explained by the thunderstorm effect. However, it should be noted that the month of November which should be dry recorded quite some rainfall which could affect the behaviour of aerosols. In the dry season, there is the general tendency of particles to build up. And if suddenly strong winds and heavy rainfall come to play, patterns could be altered.

$PM_{2.5}$ mass concentration generally decreases as relative humidity increases. According to Dawson et al. (2007) this trend can be explained by the different species in the $PM_{2.5}$. Nitrates are semi-volatile thus, when relative humidity and temperature increase, they are taken out of the atmosphere by volatilisation hence reducing the mass concentration of $PM_{2.5}$. This trend could be an indication that the $PM_{2.5}$ in these areas is dominated by primary particulates. Tsigaridis and Kanakidou (2007) states that nitrates shift from particle phase to gas phase as temperature and relative humidity increase.

Comparing the average elemental concentrations in this study with selected studies from some African and European cities (Table 5), it can be seen that the concentrations of Ca, Ti, Mn, and Fe are much higher in Ouagadougou than in Douala, and lower for the other regions than for these two cities.

In the comparison, the concentrations of Br and Pb are relatively low for all the other areas indicating a low influence of leaded fuel. For this study Pb is present in all the samples and in relatively high concentrations (Mean value of 292 ng/m^3) indicating the influence of leaded fuel and leaded paints. Zn also presents higher concentrations in this study than for the others. Apart from Ouagadougou, elemental concentrations are higher for this study than for the other studies.

Table 5. Summary of Selected Elemental Concentrations in Fine Aerosol Particles from Different Measurements in Cities in Africa and Europe

Dataset	This study	Boman et al. 2009b	Gatari et al. 2006	Heal et al. 2005	Rodriguez et al. 2004
Location	Douala, Cameroon	Ouagadougou, Burkina Faso	Nairobi, Kenya	Edinburg, UK	Barcelona, Spain
Year	2012	2007	2001	1999–2000	1999–2000
Particle size range	$d_a < 2.5\mu\text{m}$	$d_a < 2.5\mu\text{m}$	$d_a < 2.5\mu\text{m}$	$d_a < 2.5\mu\text{m}$	$d_a < 2.5\mu\text{m}$
Cl	347	900	<DL		
K	167	290	730		229
Ca	190	690	70		516
Ti	29	240	8.7	0.4	16
Mn	17	61	12	0.7	14
Fe	248	3000	130	27.6	258
Zn	296	41	100	7.5	162
Br	22	8.7	36		
Pb	292	11	76	11.36	120

All Concentrations are in ng/m^3 , year is the year of sample collection, <DL is below detection limit.

Conclusions

$\text{PM}_{2.5}$ for the city of Douala was collected over a 24-hour sampling period and analysed for mass, mass concentration and elemental composition. The cumulative mass concentration of $252 \pm 130.8\mu\text{g}/\text{m}^3$ which is critically higher than the WHO standard of $25\mu\text{g}/\text{m}^3$ was recorded. Cl, K, Ca, Ti, Mn, Fe, Ni, Cu, Zn, Br, Sr, and Pb were identified in the PM collected. The high concentration of Pb indicated the possible use of leaded fuels and/or paints in the vicinity. The industrial zones exhibited higher PM concentrations than the residential areas. Meteorological parameters greatly influenced the PM concentration. However, the "thunderstorm effect" counteracted the normal variation of $\text{PM}_{2.5}$ with wind speed and precipitation.

Diurnal patterns in concentrations suggested a common PM source. From PCA it was concluded that anthropogenic activities like traffic, biomass burning and industrial activities were the major PM sources. Old fleet and poorly maintained vehicles exacerbate the situation. Despite the high emission from these sources, natural sources such as sea spray and windblown dust significantly contribute to the PM load of this city.

Conclusively, the results presented in this study indicate that the majority of the Douala inhabitants are exposed to high air pollution levels in their everyday life.

Recommendations

Given the high values of both elemental and PM concentrations in Douala, the following actions to reduce particulate matter and black carbon emissions are recommended:

- There should be very regular vehicle emissions tests, retirement, or retrofitting (e.g. adding particulate traps, including penalties for failing to meet air quality emissions standards, and heightened penalties for on-the-road "super-emitting" vehicles);
- The sale of certain fuels should be banned or strictly regulated. The use of cleaner fuels encouraged.
- The installation of a shore-based power/electrification of ships at port, regulating idling at terminals, and mandating fuel standards for ships seeking to dock at the Douala port.
- Banning or regulating slash-and-burn clearing of forests and burning of agricultural waste
- Biomass burning in urban and non-urban areas should be regulated and/or limited.
- Permits should be issued to operate industrial, and power generating, facilities, and periodic permit renewal and/or modification of equipment.
- Filtering technologies should be introduced together with high-temperature combustion for existing power generation plants. Annual emissions from such plants should also be regulated.

For BC it is necessary to focus on primary PM emission abatement measures such as:

- End-of-pipe technologies, i.e., diesel particle filters for road and off-road vehicles or machinery.
- Technologies allowing the reduction of emissions from medium- and small-scale combustion facilities, including domestic stoves (e.g., pellet stoves and boilers; product standards).
- Better implementation of the ban of open field burning of agricultural waste; such a ban has already been introduced in many EU Member States.

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