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Physico-chemical caracterization of PM_{2.5} and PM₁₀ collected in dry savanna of Banizoumbou in Niger and wet savanna of Djougou in Benin

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Abstract

This study, carried out in the context of climate change (greenhouse effect, rainfall acidity, atmospheric pollution), is part of the INDAAF (International Network to study Deposition and Atmospheric chemistry in Africa) program. It allowed the chemical characterization of the soluble part of fine particles whose diameter is less than 2.5µm (PM_{2.5}) and 10µm (PM₁₀). These particles were collected in the dry savanna of Banizoumbou in Niger from 2005 to 2007 and in the wet savanna of Djougou in Benin from 2005 to 2009. Inorganic ions (CI, NO₃⁻, SO₄²⁻, Na⁺, NH₄⁺, K⁺, Mg²⁺, Ca²⁺) and organic (HCOO⁻, CH₃COO⁻, C₂H₅COO⁻, C₂O₄²⁻) were analyzed by ion chromatography. In Banizoumbou, high concentrations of Ca²⁺ (0.91µg.m⁻³), NO₃⁻ (0.49µg.m⁻³) and SO₄²⁻ (0.36µg.m⁻³) were obtained in the dry season against 0.25, 0.65 and 0.18µg.m⁻³, respectively in the wet season. In Djougou, the most dominant ions are: Ca²⁺(0.59µg.m⁻³), NO₃⁻(0.28µg.m⁻³) and SO₄²⁻ (0.25 µg.m⁻³) in the dry season against 0.05, 0.15 and 0.16µg.m⁻³, respectively in the wet season. The NH₄⁺ concentration is not negligible in the wet season: 0.25µg.m⁻³ in Banizoumbou and 0.10µg.m⁻³ in Djougou. At the same time, the organic ions are in the trace state. The results show that the atmosphere is more charged with particles in dry savanna than in wet savanna. Ca²⁺ and NH₄⁺ have a strong capacity to neutralize rainwater in Banizoumbou during the wet season. In Djougou, only the NH₄⁺ has significant effect as the concentration of SO₄²⁻ increases due to phytoplankton activity. These findings partly explain the alkaline character of the rains at Banizoumbou and acid at Djougou. The neutralization process involves oxidation, heterogeneous nucleation, condensation and coagulation of fine particles.

Keywords: Fine particles, physicochemical processes, neutralization, nucleation, condensation, coagulation.

Introduction

African ecosystems represent the site of significant biogenic gaseous and particulate emissions. Moreover, the growing population pressure will lead to a significant increase in these emissions in the next years. These emissions have an impact on the additional greenhouse effect, the change in the oxidizing capacity of the atmosphere, the acidification of precipitation, etc. However, studies on biogeochemical cycles in the tropical atmosphere and the influence of tropical ecosystems on the global atmosphere remain very limited.

Thus, the INDAAF program has as scientific objectives the study of atmospheric deposition in Africa. It is within this program that this study focuses on fine Particle Mater (PM) collected at two stations, Banizoumbou in Niger representing the dry savannah and Djougou in Benin representing the wet savanna. Recent studies on precipitation chemistry have been carried out in tropical regions. These works include those made in African ecosystems¹⁻⁹. They have allowed to quantify wet deposition of important biogeochemical species and to estimate the contributions of the different sources. These studies are supplemented by those made on dry deposition in the dry savanna of Banizoumbou in Niger, wet savanna of Lamto in

Ivory Coast and equatorial forest of Zoetele in Cameroon which did not take in account the aerosol sizes^{10,11}.

The effects of aerosols on health and climate change, depend on their chemical composition, their toxicity, their sizes and their concentrations. The recent study by Wang et al. showed that exposure to $PM_{2.5}$ can lead to various diseases in humans and animals¹². In Western Africa, particulate and gaseous pollutants are emitted from biomass burning, domestic fires, fossil fuel and dust particles from the Sahel and Sahara^{13,14}. Biomass burning pollutants are only emitted during the dry season while domestic fires, traffic and industrial aerosols as well as dust particles are also produced all year around. Secondary aerosols have been studied by Rastogi et al.¹⁵. These polluants result into deterioration of air quality causing problems of human health and environmental degradation¹⁶⁻¹⁸.

In this work, we study the monthly, seasonal and annual variations of concentration of the ionic species in $PM_{2,5}$ (particles with diameter $< 2.5 \mu m$) and PM_{10} (particles with diameter $< 10 \mu m$) collected at Banizoumbou and Djougou. PM_{10} are mainly primary particles made up of terrigenous materials (metal oxides, etc.), carbon, sulfates, nitrates and ammonium, elements resulting from erosion. $PM_{2,5}$ consist

essentially of carbon from the condensation of very hot vapors during the combustion of fossil organic materials (coal, fuel, ...) or biomass (wood), but also nitrates, sulfates and Polycyclic Aromatic Hydrocarbons (PAHs). PM_{2.5} is divided between primary and secondary particles. They are said to be nonsedimentary because they travel very great distances under the effect of winds, very numerous and difficult to quantify because of their negligible masses¹⁹.

Materials and methods

Presentation of the sites and meteorology: Banizoumbou is a village located 65km from Niamey. It is populated by a few dozen people who live mainly from agricultural activities. The INDAAF station at Banizoumbou (13°31'N, 02°38'E) is located on this site, which is part of the Niamey square, study area of the Hapex-Sahel experiment. This region has a seasonal semiarid climate with alternatively a dry season from October to May, and a wet season from June to September. The mean annual rainfall and temperature, calculated from the measurements taken during the study period are of the order of 500mm and 30°C, respectively. The resort is subject to two main wind regimes; i. from October to March-April, the Harmattan. It is a hot and dry wind, which is characterized by a very low relative humidity (5%), little local erosion, the contribution of dust of distant origin during several days (the dry mists); ii. from March-April to October, the monsoon. It is a less hot and humid wind, which is characterized by a high relative humidity (50%), a very intense local erosion mainly at the beginning of the period preceding the rain, and therefore of short duration.

The transitions between the two periods corresponding to the passage of the Intertropical Front (FIT) last several days. The seasonal shift in the latitude of the FIT determines the wet and the dry seasons¹¹.

Djougou is a village situated in Northwest Benin. The INDAAF site is located at Nangatchori (9°65'N, 1°74'E) near Djougou, approximately 460km from Cotonou. The average altitude is 430 m. Nangatchori belongs to the wet savanna region of Benin. The climate of Djougou is sub - sudanese with a mean annual rainfall of 1190mm, measured over 50 years 20 . It is characterized by a wet season from April to October, and a dry season from November to March. These seasons are schematically determined by the position of ITCZ. The daily mean temperatures vary from 25°C in August to 31°C in March. Approximately 70% of the population of this region dedicates itself to agricultural activities²¹. It is also necessary to notify that this region is just in the South of the Atakoramountain, thus explaining that the rainfall amount is higher compared to more Eastern zones in Benin. Vegetation is composed of a mosaic of dry forests and savanna, with dense and tall herbaceous strata, mainly composed of perennial grasses, and more or less dense woody strata. We assume that the INDAAF site of Djougou is rural and representative of a remote site of African wet savanna⁹.

Collection and analysis method: Sample collection: The aerosols are collected by means of an autonomous system including a pump and a gas meter. A volume of air is filtered through a Teflon filter for the ions or a quartz filter for carbon. The pumping system operates continuously for 48 hours with an average hourly flow of 5 l/min. Samples are taken once a week. At the beginning and at the end of the sampling the flows read on the 4 flowmeters are noted and then the pumps with the circuit breakers are switched off before recording the values of 4 gas meters. Afterwards, the 2 filter gates per box PM_{2.5} and PM₁₀ are removed and replaced by those that have been prepared for the following week. The circuit-breaker is started and the flow rates are maintained at 51/min for the duration of the pump operation. The treated filters are cleanly removed and placed in petri dishes and then refrigerated before being sent to the Toulouse Aerology Laboratory.

Method of chemical analysis of aerosol samples: The chemical composition of the collected aerosol samples was measured by liquid chromatography. Before proceeding with the chemical analysis, each aerosol sample is subjected to preliminary treatment; half of the filter is added 2 cm³ of deionized water and the soluble portion of the aerosol is extracted by ultrasonic stirring.

Weighted Average Concentrations at the two stations studied: The weighted average concentrations by volume of pumped air in the collected $PM_{2.5}$ and PM_{10} are determined from the following formula:

$$C_{a} = \frac{\sum (C_{i} \cdot V_{i})}{\sum V_{i}}$$
(1)

Where: C_a , C_i , and V_i represent the weighted average concentration ($\mu g/m^3$), the ionic concentration ($\mu g/m^3$), and the sampling air volume (m^3), respectively.

Monthly, seasonal and annual trends in weighted average concentrations in the soluble part of PM2.5 and PM10 are determined at the two stations studied. These results will enable us to estimate the different emission sources of these particles and to investigate the possible meteorological conditions and physicochemical process leading to their formation in the atmosphere.

Results and discussion

Monthly mean Concentrations of $PM_{2.5}$ and PM_{10} at the two stations: In the dry savanna of Banizoumbou: The variation of PM_{10} concentration at Banizoumbou is irregular during the dry season (Figure-1a). This would be due to abrupt changes in weather parameters at the local scale that could lead to atmospheric instabilities capable of suspending large quantities of dust. Irregularly produced biomass fires are also another reason for this phenomenon. The peak of concentration of PM_{10} observed in February corresponds to the high intensity of the Harmattan which carries enormous quantities of dust serving as nuclei for gas condensation, thus leading to the formation of the coarse fraction of aerosols¹¹. High solar intensity in May and gaseous emissions from biomass fires and domestic fires could explain the peak concentration of PM_{10} while the peak in June (early rains) is due to high emissions of NO_x and NH_3^{22} and the dust raised by the winds accompanying the first rainy - stormy manifestations. During the rainy season, the concentration of PM_{10} is relatively low since this period is neither favorable to biomass fires nor to the durable suspension of terrigenous dust. Also, the leaching of the atmosphere by precipitation greatly reduces the concentration of PM_{10} .

The variation of $PM_{2.5}$ concentration is more consistent than that of PM_{10} . These concentrations depend on the concentrations of the gases in the atmosphere and the weather conditions that favor the processes of their oxidation, nucleation and condensation. These include solar radiation, relative humidity and the stability of the atmosphere. Some of these conditions seem to be satisfied in March, June and August, when $PM_{2.5}$ peaks are observed. The concentration of $PM_{2.5}$ higher than that of PM_{10} during June and August (Figure-1) confirms this hypothesis. In the wet savanna of Djougou: Figure-1b shows a coherent variation in the concentration of $PM_{2.5}$ and PM_{10} at Djougou. This situation indicates a slight variation of meteorological parameters over the time in this region. The dry season with high concentration (November - March) and the wet season with low concentration of aerosols (April-October) are clearly remarkable. This could signal the seasonality of the emission sources of aerosol precursor (gases) and condensation nuclei, which are mainly carbon soot (emitted by biomass fires and domestic fires), marine particles (transported by the monsoon during the wet season) and terrigenous particles (transported from the Sahara and the Sahel by Harmattan during the dry season)¹¹.

Monthly mean concentrations of ionic species in $PM_{2.5}$ and PM_{10} at two stations: In the dry savanna of Banizoumbou: Figure-2a presenting the variation in monthly mean concentrations of ionic species in $PM_{2.5}$ shows that their soluble part is dominated by Ca^{2+} , NO_3^- , SO_4^{2-} and K^+ in this order during the dry season and NO_3^- , NH_4^+ and SO_4^{2-} in the wet season. The peak of concentrations of ionic species in $PM_{2.5}$ at Banizoumbou is obtained in March, June and August. It should be noted that during the rainy season, the concentration of $NO_3^$ and NH_4^+ increased considerably, in agreement with significant NO_x and NH_3 emissions from wet soils²⁰.



Figure-1 (a, b): (a) Variation in PM concentration at Banizoumbou, and (b) at Djougou.



Figure-2(a-d): (a, b) Variation of monthly mean concentrations of ionic species in $PM_{2.5}$ and PM_{10} at Banizoumbou and (c,d), at Djougou.

Figure-2b presenting the variation in the average concentration of the ionic species in PM_{10} shows that their soluble part is dominated by the Ca^{2+} , SO_4^{2-} and NO_3^- in this order in the dry season and NO_3^- , Ca^{2+} and NH_4^+ in the wet season. The dominant ions during the dry season show the signature of the terrigenous source due to wind erosion (Harmattan) and biomass fires which are absent or weakened during the wet season¹¹. The emissions of NO_x , SO_2 , and NH_3 from fertilized soils, decomposition of urea and animal excreta and vegetation debris show the signature of the biogenic source during the wet season. These gases are subjected to photochemical or liquid-phase oxidation in the atmosphere.

The analysis of Figures-2a and 2b also shows that when the concentration of the ionic species is high in the $PM_{2.5}$, it is then low in PM_{10} and vice versa. This situation could be explained by the fact that the formation of $PM_{2.5}$ requires a high concentration of NO_x , SO_2 , NH_3 , oxidizing agents, relatively high humidity, low temperature and atmospheric stability. This is why we have found high concentrations of NO_3^- , NH_4^+ in the $PM_{2.5}$ during the wet season in which period significant quantities of NO_x and NH_3 are emitted into the atmosphere.

The formation of PM_{10} is favored by a high concentration of terrigenous and marine species (Ca²⁺, Mg²⁺, Na⁺, Cl⁻) suspended in the atmosphere. The processes leading to the formation of PM_{10} would be the capture of gases by terrigenous particles and soot carbon, condensation and coagulation of even smaller particles (PM_{2.5}) obtained by nucleation.

In the wet savanna of Djougou: Figures-2c and 2d presenting the variation of the concentration of the ionic species of the soluble part of PM_{2.5} and PM₁₀ show that during the dry season the dominant ions Ca²⁺, NO₃, SO₄²⁻ and K⁺ given in this order are the same for PM_{25} and PM_{10} . As at Banizoumbou, these ions bear witness the signature of the terrigenous source due to wind erosion (Harmattan) and biomass fires. During the wet season, $SO_4^{2^-}$, (NH_4^+, NO_3^-) and K^+ are in this order the ions which dominate the chemical composition of the soluble part of PM_{2.5} and PM₁₀. These ions come from gaseous emissions of wet soils, fertilizer use and vegetation. The crustal contribution (Ca²⁺) is considerably weakened by monsoon, leaching by precipitation and moisture. The dry season (November - March) is the period of high concentration of PM_{2.5} and PM₁₀. Although during this period rainfall is rare, relative humidity and atmospheric stability allow the nucleation and gas condensation processes on pre-existing particles leading to PM_{2.5} formation. The diffusion and coagulation of these small particles increases their size and leads to the formation of PM_{10} .

Seasonal mean concentrations of ionic species of $PM_{2.5}$ and PM_{10} at the two stations: The evolution of the seasonal average concentration of the ionic species of the aerosols at Banizoumbou and Djougou makes possible the deduction of the existing seasonal behavior or not of their sources and the physicochemical processes that engage them in the formation of

 $PM_{2,5}$ and PM_{10} . Figures-3 (a-d) shows the seasonal evolution of the concentrations of the ionic species in these particles.

Figure-3a presenting the variation of ionic species in $PM_{2.5}$ shows that $SO_4^{2^-}$ and Ca^{2^+} have higher concentrations during the dry season, whereas NO_3^- and NH_4^+ have very high concentrations in the wet season. In PM_{10} (Figure-3b), only NO_3^- has higher concentration during wet season than in dry season. Mg^{2+} and NH_4^+ have approximately the same concentrations during both seasons.

Figure-3c giving the evolution of the concentrations of ionic species in the $PM_{2.5}$ at Djougou, shows that the concentrations of SO_4^{2-} and NH_4^+ during the dry season are higher than those in the wet season. As for PM_{10} , it is found that only the concentration of NH_4^+ during wet season is greater than that in the dry season.

These results explain the seasonality of the terrigenous source (Ca^{2+}) and the more intense biomass sources $(NO_3^-, SO_4^{2-} \text{ and } NH_4^+)$ during the dry season. The concentration of NH_4^+ and NO_3^- is enhanced by the high emission of NH_3 and NO_x from soils, hydrolyze of animal excreta and vegetation during the wet season.

Figure-3 (a-d) explains the alkalinity $(Ca^{2+} + NH_4^+)$ and the acidity $(NO_3^- + SO_4^{2-})$ due to the particles in the atmosphere at both sites²¹. The acidity of $PM_{2.5}$ at Banizoumbou during the wet season is mainly due to the NO_3^- and the alkalinity to Ca^{2+} and NH_4^+ whereas for PM_{10} the major alkaline species is Ca^{2+} . This result partially explains why the rainfall is alkaline (pH > 5.6) at Banizoumbou⁸. During the dry season, the acidity is due to NO_3^- and SO_4^{2-} and alkalinity to strong suspension of terrigenous dust transported from the Sahara and the Sahel by the Harmattan.

At Djougou, for both seasons and for $PM_{2.5}$ and PM_{10} , the acidity would be due to NO_3^- and SO_4^{-2-} while the alkalinity is dominated by Ca^{2+} during the dry season although it is of low concentration in this region. This alkalinity is weakly due only to the NH_4^+ during wet season because the terrigenous source is strongly weakened. This fact clearly explains why precipitation at Djougou is acidic (pH < 5.6)⁹. Potassium (K⁺) and sodium (Na⁺) contribute significantly to the alkalinity of the particles in the atmosphere at Djougou, but also organic acids are responsible for a non-negligible acidity. These results are consigned in table 1 giving the ratio "dry season concentration divided by wet season concentration" and table 2 of the percentages of cations and anions taken separately.

Annual mean concentrations of ionic species in $PM_{2.5}$ and PM_{10} at the two sites: Figure-4(a, b) shows a comparison of concentrations of the ionic species in $PM_{2.5}$ and PM_{10} collected at Banizoumbou and Djougou. Thus, it is clear that concentrations of SO_4^{2-} , NH_4^+ and K^+ are higher in PM_{10} at Djougou than at Banizoumbou, while Ca^{2+} is higher at Banizoumbou than at Djougou.

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This demonstrates the influence of the amount of biomass burned at Djougou and the strong presence of wind erosion at Banizoumbou. For PM_{2.5}, the concentration of all ionic species (except for Mg²⁺) is much higher at Banizoumbou than at Djougou. Thus, we deduce that there is more PM_{2.5} suspended in dry savanna than in wet savanna but approximately the same concentrations of PM₁₀. In sum, the atmosphere appears to be more charged with particles in dry savanna than in wet savanna. This large number of fine particles contributes considerably to the formation of small droplets of water which evaporate most of the time before reaching the soil and significantly reduce the intensity of precipitations in dry savanna. An average number of large particles lead to rapid condensation of water vapor and form large droplets capable to reach the soil¹⁸. The hygroscopicity of these particles also depends on the chemical species composing them.



Figure-3(a-d):(a, b) Variation of seasonal mean concentration of ionic species in the PM at Banizoumbou and (c, d) at Djougou.



Study of the sources of ionic species in $PM_{2.5}$ and PM_{10} at **Banizoumbou and Djougou**: Table-2 gives the cationic and anionic percentages of the ionic species. It is possible to identify the major cations and anions in $PM_{2.5}$ and PM_{10} during dry season and wet seasons.

The cations: Primary or directly suspended species in the atmosphere come mainly from soil erosion (Ca²⁺, Mg²⁺, Na⁺), biomass fires and vegetation (NO3, K⁺, C2O4²⁻) or transported from the sea towards the continent by the monsoon (Na⁺, Cl⁻). Ca^{2+} is the major cation found in the PM₁₀atBanizoumbou (70.14%) and Djougou (63.70%) during the dry season. This is due to the influence of the Harmattan which causes large amounts of dust moving from the north-east to the south-west during this period. NH_4^+ (49.60%) is the major cation found in PM_{2.5} at Banizoumboubutat Djougouin PM_{2.5} and PM₁₀ during the wet season with 48.58% and 46.73% respectively. The NH_4^+ comes mainly from the dissolved ammonia NH₃ volatilized in the atmosphere. Volatilization of ammonia is greater during the wet season when crop fertilizer use is permanent and moisture promotes bacterial decomposition of urea and animal and plant debris. In particular, Ca²⁺has non-negligible quantities in all the particles during the wet season (Table-1). This situation could be explained by the existence of meteorological disturbances such as grain lines which are accompanied by strong winds capable to suspend large quantities of dust. Mg²⁺, K⁺ and Na⁺ are almost equivalent to PM2.5 and PM10 formation in both ecosystems (dry savanna and wet savanna). Ca^{2+} and NH_4^+ are the major cations that play an important role in the neutralization of atmospheric acidity²³

The anions: NO_3^- is most important in $PM_{2.5}$ and PM_{10} at Banizoumbou during the wet season and at Djougou during the

dry season. This ion comes from bacterial nitrification in soils and oxidation of NO_x emitted by moistened soils during the rainy season. In the dry season, NO_3^- is obtained by the oxidation of NO_x from biomass fires. SO_4^{2-} is more important in PM_{2.5} and PM₁₀ during the dry season at Banizoumbou and during the wet season at Djougou. In the dry savanna of Banizoumbou, this ion comes from a small amount of burnt biomass and soil. At Djougou during the wet season, SO_4^{2-} is derived from marine contribution, phytoplankton activity emitting sulfidic organic compounds such as Dimethylsulfite (DMS), biomass fires during the dry season, domestic fires, emissions of the southern hemisphere biomass fires carried by the monsoon. We also notice that the predominant anion is NO_3^{-1} in PM_{2.5} and PM₁₀ at Banizoumbou during all the two seasons (exception of PM2,5 in dry season), whereas at Djougou it is only during the dry season. SO_4^{2-} is the predominant anion at Djougou during the wet season. Minor anions such as carboxylate ion (soil, fires and vegetation emission) and chloride ion (marine and fires emission) have a relatively higher contribution during the dry season in both ecosystems.

Degrees of oxidation of sulfur and nitrogen: DOS and DON: DOS, defined as $SO_2 / (SO_2 + SO_4^{2^-})$, expresses the Degree of Oxidation of Sulfur to $SO_4^{2^-}$ and DON, defined as $NO_2 / (NO_2 + NO_3^-)$, expresses the Degree of Oxidation of Nitrogen in NO_3^- . DON and DOS indicate the importance of secondary aerosol formation processes. The high DON and DOS values assume that oxidation of gases is possible and several forms of secondary aerosols may exist in the atmosphere. Earlier studies^{24,25} have reported that in the primary pollutant the value of DOS is lower than 0.10. Ohta and Okita²⁶ reported that when the ratio was greater than 0.10, photochemical oxidation of SO₂ would occur in the atmosphere.

Percentages of ions in PM		Banizo	oumbou		Djougou				
	PM	I _{2.5}	PN	I ₁₀	PM	I _{2.5}	PM ₁₀		
Cations (%)	Dry season	Wet season	Dry season	Wet season	Dry season	Dry season Wet season		Wet season	
Na ⁺	13.71	11.76	10.49	11.47	12.03	13.49	10.86	12.35	
NH4 ⁺	12.49	49.60	5.74	15.94	9.52	48.58	6.82	46.73	
K+	14.47	10.31	8.78	7.46	18.57	16.09	13.77	12.18	
Mg ²⁺	2.95	3.12	4.85	9.93	4.59	1.99	4.85	3.32	
Ca ²⁺	56.38	25.21	70.14	55.21	55.29	19.85	63.70	25.41	
Anions (%)									
Cl	7.53	3.914	5.73	3.18	4.78	3.91	4.77	2.86	
NO ₃ ⁻	36.60	76.77	46.63	75.09	40.08	23.59	41.96	40.88	
SO4 ²⁻	36.87	11.25	34.12	10.24	38.77	57.87	38.01	46.16	
*R-COO	19.00	8.06	13.52	11.49	16.37	14.62	15.26	10.10	

Table-1: Percentages of ions in PM_{2.5} and PM₁₀ at Banizoumbou and Djougou.

*R-COO⁻: organic compounds.

Figure-5 (a, b) indicates that the DON peaks in February and March explain oxidation of NO_x on the surface of the terrigenous particles due to intensity of Harmattan and solar radiation. This phenomenon is observable for $PM_{2.5}$ and PM_{10} levels. In August and September (for $PM_{2.5}$) and July (for PM_{10}), the peaks of DON indicate NO_x oxidation in the liquid phase due to high relative humidity and high concentration of atmospheric oxidants such as OH⁻, HO₂, RO₂ and O₃¹¹. This is more remarkable for the $PM_{2.5}$ level. Throughout the dry season, DOS is higher than DON. This is due to the availability of SO₂ during the dry season than the wet season.

At Djougou Figure-5 (c, d), from January to June, DON and DOS have approximately very similar values. The DOS has two peaks, in July and November for $PM_{2.5}$ and PM_{10} . These peaks correspond to the transport of southern biomass fire emissions and the beginning of the dry season.DON shows slight fluctuations from July to December for $PM_{2.5}$ and PM_{10} and below DOS (except for September and October for PM_{10}). This allows us to deduce that the sources of NO_x and NO_3^- are permanent or at least complementary. These sources include biomass fires, domestic fires, bacterial nitrification an denitrification of organic matter at ground level but also solar radiation and relative humidity which determine the physicochemical processes of PM transformations.

Physicochemical processes of $PM_{2.5}$ and $PM_{2.5 - 10}$ particles formation at Banizoumbou and Djougou: Neutralization of particles acidity: The investigation of these physicochemical processes that affect the pollutants in the atmosphere allows us to deduce the forms of molecules that remain isolated or that agglomerate and modify the size and the physical properties of the aerosols. Tables-3a and 3b give the coefficients of correlation between anions and cations and thus reflect the physicochemical processes of $PM_{2.5}$ and $PM_{2.5} - 10$ (particle which diameter ranges between 2.5 and 10µm) formation.

Tables-2(a, b) show strong correlation coefficients between cations and anions for $PM_{2.5}$ and $PM_{2.5-10}$ (difference between PM_{10} and $PM_{2.5}$). While some coefficients of correlation reflect the provenance of chemical species from the same source¹¹, most of them express the multiple physicochemical processes that engage them in the formation of atmospheric aerosols.

The preponderant process showed by these results is the neutralization of the acidity of particles characterized mainly by the adsorption of gases such as sulfuric acid (H_2SO_4) , nitric acid (HNO₃), hydrochloric acid (HCl) on pre-existing particles. This process is called heterogeneous nucleation. However, under specific meteorological conditions, the formation of purely secondary fine particles such as (NH₄)₂SO₄, NH₄HSO₄ and NH₄NO₃ obtained principally by oxidation and homogenous nucleation of the gaseous precursor is also observed. The formation of these aerosols can also become easier when they are carried out in aqueous phase, and therefore under a high relative humidity. In the atmosphere, ammonia occurs at (NH₄)₂SO₄, NH₄HSO₄, NH₄Cl, and NH₄NO₃form. NH₄NO₃ is formed by the reaction of HNO₃ with NH₃ on moist soil surfaces, partly because of the formation of un-dissociated NH_4NO_3 when relative humidity is more than $62\%^{23}$.

There is more good correlation between cations and anions of $PM_{2.5}$ and $PM_{2.5-10}$ at Djougou than at Banizoumbou. This state of fact could be explained by multiphasic processes (solid-liquid-gas) of chemical species at Djougoubecause the relative humidity is higher there and the atmosphere is more stable.

For both sites, Ca^{2+} and NH_4^+ constitute the two major cations which play a predominant role in the process of the neutralization of particles acidity. From table 3 showing the neutralization factors relative to each of the cations, we deduce that Ca^{2+} is the predominant alkaline at Banizoumbou for $PM_{2.5}$ during the dry season and for PM_{10} during both seasons. At Djougou during the dry season, Ca^{2+} is the predominant alkaline for $PM_{2,5}$ and PM_{10} . The influence of the neutralization of the particles acidity due to the NH_4^+ is only sensitive during the wet season. The other cations (K⁺, Mg^{2+} , Na^+) have low but relatively higher neutralization factors during the dry season. In sum, it can be deduced that the molecules formed are salts of sulfates, nitrates, chlorides or carboxylate. We notice that the neutralization factor is calculated using the equation as follow:

$$NF(X) = [X] / ([SO_4^{2^-}] + [NO_3^-])$$
(2)
where X is one of the five cations.



Figure-5 (a-d): Variation of DOS and DON for PM2,5 and PM10 at Banizoumbou (a, b) and Djougou (c, d).

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Banizoumbou			PM _{2.5}			PM _{2.5-10}				
Dry season	Na ⁺	K^+	Mg ²⁺	Ca ²⁺	$\mathrm{NH_4}^+$	Na ⁺	K^+	Mg ²⁺	Ca ²⁺	$\mathrm{NH_4}^+$
Cl	0.87	0.31	0.56	0.72	-0.15	0.70	0.51	0.62	0.54	0.44
SO4 ²⁻	0.82	0.36	0.66	0.85	-0.03	0.81	0.55	0.72	0.83	0.50
NO ₃	0.15	0.05	0.27	0.26	0.87	0.35	0.23	0.70	0.31	0.64
HCOO ⁻	0.23	-0.03	0.06	0.25	-0.08	0.21	0.33	0.38	0.18	0.19
CH ₃ COO ⁻	0.68	0.20	0.50	0.75	-0.13	0.55	0.45	0.61	0.46	0.28
C ₂ O ₄ ²⁻	0.84	0.41	0.77	0.94	-0.01	0.54	0.56	0.70	0.49	0.51
Wet season										
Cl	0.89	0.38	0.72	0.88	-0.01	0.62	0.32	0.16	0.27	0.11
SO4 ²⁻	0.76	0.39	0.91	0.81	-0.05	0.54	0.42	0.34	0.42	0.08
NO ₃	-0.10	0.78	-0.01	-0.06	0.94	0.07	0.90	0.40	0.42	0.92
HCOO ⁻	-0.21	0.33	-0.21	-0.31	0.49	0.37	0.07	0.54	0.50	0.27
CH ₃ COO ⁻	0.17	-0.46	0.07	0.06	0.58	0.13	-0.13	0.30	0.36	-0.11
C ₂ O ₄ ²⁻	0.79	0.46	0.72	0.69	0.13	0.44	0.51	0.47	0.60	0.21

Table-2a: Cations and anions correlation coefficients for PM_{2.5} and PM_{2.5-10} at Banizoumbou.

Table-2b: Cations and anions correlation coefficients for $PM_{2.5}$ and $PM_{2.5-10}$ at Djougou.

Djougou			PM _{2.5}			PM _{2.5-10}				
Dry season	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	$\mathrm{NH_4}^+$	Na^+	K^+	Mg ²⁺	Ca ²⁺	$\mathrm{NH_4}^+$
Cl	0.84	0.74	0.80	0.80	0.83	0.60	0.71	0.59	0.57	0.51
SO4 ²⁻	0.86	0.90	0.79	0.77	0.49	0.36	0.89	0.33	0.22	0.88
NO ₃ ⁻	0.56	0.63	0.62	0.53	0.63	0.52	0.63	0.57	0.42	0.65
HCOO ⁻	0.44	0.55	0.46	0.47	0.63	0.53	0.58	0.64	0.51	0.62
CH ₃ COO ⁻	0.61	0.70	0.64	0.59	0.62	0.64	0.77	0.68	0.57	0.65
$C_2 O_4^{2-}$	0.69	0.90	0.67	0.62	0.59	0.50	0.86	0.50	0.39	0.76
Wet season										
Cl	0.42	0.15	0.37	0.50	0.14	0.70	0.60	0.64	0.68	0.59
SO4 ²⁻	0.91	0.98	0.80	0.49	0.94	0.86	0.95	0.88	0.60	0.22
NO ₃ ⁻	0.67	0.57	0.60	0.56	0.70	0.38	0.30	0.44	0.52	0.41
HCOO ⁻	0.94	0.92	0.73	0.41	0.80	0.52	0.50	0.48	0.56	0.51
CH ₃ COO ⁻	0.89	0.81	0.71	0.56	0.74	0.78	0.67	0.80	0.90	0.67
$C_2O_4^{2-}$	0.94	0.99	0.82	0.49	0.90	0.90	0.96	0.94	0.73	0.37

Neutralization Factors		Banizo	oumbou		Djougou				
	PM	I _{2.5}	PM_{10}		PM	I _{2.5}	PM_{10}		
Cations	Dry season	Wet season	Dry season	Wet season	Dry season	Wet season	Dry season	Wet season	
Na ⁺	0.32	0.16	0.38	0.20	0.39	0.21	0.45	0.19	
$\mathrm{NH_4}^+$	0.38	0.87	0.27	0.36	0.40	0.95	0.36	0.94	
K+	0.20	0.08	0.19	0.08	0.36	0.15	0.33	0.11	
Mg ²⁺	0.13	0.08	0.34	0.34	0.29	0.06	0.38	0.10	
Ca ²⁺	1.53	0.4	2.93	1.13	2.06	0.35	3.02	0.46	

Table-3: Neutralization factors for cations of PM at Banizoumbou and Djougou.

Diffusion and coagulation between large and small particles: The aerosols formed during primary physicochemical processes such as nucleation and condensation adapt different behaviors depending on the meteorological conditions of the atmosphere and the nature of the chemical species composing them. The temperature plays an important role in the gas / particle distribution of the various products formed but also in the reaction schemes^{27,28}. Under the influence of thermal or Brownian agitation, the diffusion of the small particles to the largest one leads to their coagulation which consequently reduces the number of particles, increases their size and modifies their optical and hygroscopic properties. A coherent set of molecular is formed. This multiphasic process would be at the origin of the multiple correlations obtained between the preponderant species for PM_{2.5} and PM_{2.5-10}. Figures 6 (a-f) and 7 (a-f) clearly illustrate these processes. These figures presenting the linear regression equations of groups of inorganic acids $(NO_3^- + SO_4^{2-} + Cl^-)$ and organic acids $(HCOO^- +$ $CH_3COO^- + C_2O_4^{2-}$) to alkaline groups $(Ca^{2+} + NH_4^+)$, $(NH_4^+ + C_2O_4^{2-})$ $K^+ + Mg^{2+}$ and $(Na^+ + K^+ + Mg^{2+})$ respectively show very important results. The correlation coefficients between these groups are significant. This result highlights the processes of condensation of gases on the surface of particles and especially the coagulation between them, gathering more and more large number of chemical species together.

Thus it becomes important to mention that, apart from the neutralization of particle acidity, the role played by terrigenous species in the process of cloud formation. The hygroscopicity of the dust depends on the condensation or coagulation of the soluble secondary aerosols. Most inorganic salts present in aerosols are hygroscopic and condensation-cloud-nuclei - active at 100nm diameters and typical cloud super-saturations²⁹. Mineral dust populations can also indirectly affect condensation-cloud-nuclei number populations through physical processes³⁰.

Aerosols increase the radiation absorbed in their layer of residence, resulting in a local warming of the air modifying the vertical temperature profile on which the formation of clouds depends³¹. At the local level, aerosols affect the fauna and flora.

The deposition of the particles on the surface of the plants can for example limit their photosynthesis³². This situation is accompanied by a renewal of the foliage after the period of high influence of the Harmattan which is characterized by a high concentration of aerosols in dry savanna.

Conclusion

The characterization of the chemical composition of PM_{2.5} and PM₁₀ provides information on the presence of secondary organic and inorganic compounds and monthly, annual and seasonal trends in the concentrations of these chemical compounds. Our results show the influence of meteorological conditions and changing seasons on the emission process of aerosols. The processes leading to the formation of PM₁₀ would be the capture of gases by terrigenous particles, condensation and coagulation of even smaller particles (PM_{2.5}) obtained by nucleation. Analysis of the seasonal variation in ionic species concentration in the PM at Banizoumbou and Djougou shows seasonality of the terrigenous source (Ca^{2+}) and the more intense biomass fires $(NO_3^-, SO_4^{2-} \text{ and } NH_4^+)$ during the dry season. The concentration of NH₄⁺ and NO₃⁻ is enhanced by the high emission of NH₃ and NO_x from soils and vegetation during the wet season. Concentrations of $SO_4^{2^2}$, NH_4^+ and K^+ are higher in PM₁₀ at Djougou than at Banizoumbou, while Ca²⁺ is higher at Banizoumbou than at Djougou. In PM2.5, the concentration of each ionic species (except for Mg²⁺) is much higher at Banizoumbou than at Djougou. Thus, we deduce that there is more PM_{2.5} suspended in the atmosphere in dry savanna than in wet savanna but the PM₁₀ concentrations are similar in both ecosystems. The significant coefficients of correlation between cations (Ca²⁺, NH₄⁺, K⁺, Na⁺, K⁺) and anions (NO₃⁻, SO₄²⁻, Cl⁻, organic acids) responsible for particle acidity not only express the belonging of two chemical species to the same source but also the physicochemical processes that engage them in the formation of aerosols. The main process is the neutralization of the acidity of particles which passes through oxidation, homogeneous nucleation in the case of purely secondary aerosols (NH₄)₂SO₄, NH₄NO₃, NH₄HNO₃), heterogeneous nucleation, condensation and coagulation. These are multiphasic processes that depend heavily on weather conditions in the atmosphere.

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Figure-6(a-f): Correlation coefficient of acid group to alkaline groups for Banizoumbou (PM).

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Figure-7(a-f): Correlation coefficient of acid groups to alkaline groups for Djougou (PM).

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