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Characterizing Aerosols Chemistry in the Great African Ecosystems

D. Laouali[a*], O. Moussa[a], C. Galy-Lacaux[b]

[a]*Université Abdou Moumouni, Faculté des Sciences et Techniques, Département de Physique, BP 10662, Niamey, Niger*
[b]*Laboratoire d'Aérologie, 14 Av. Edouard Belin, 31400 Toulouse, France*

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laoualid@yahoo.fr
(D. Laouali)
Tel: +227 90 84 94 09;
Fax: +227 20 31 57 36

Abstract

Within the framework of the IDAF network program (IGAC: International Global Atmospheric Chemistry / DEBITS: Deposition of Biogeochemical Important Traces Species / Africa), we present in this paper a study on aerosol chemistry along the African ecosystem transect: dry savanna - wet savanna - equatorial forest. Once per week, particle samples were collected on the studied sites, and their soluble portion was determined by Ion Chromatography (IC). Inorganic (Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}) and organic ($HCOO^-$, CH_3COO^-, $C_2H_5COO^-$) ions are analysed. The measurements were performed in three IDAF stations for several years: dry savanna of Banizoumbou (1996 - 2004) in Niger, wet savanna of Lamto (1998 - 2005) in Ivory Coast, and equatorial forest of Zoetele (1999 - 2003) in Cameroon. We have found that the ion calcium Ca^{2+} predominates in the chemical composition of the aerosols in dry savanna of Banizoumbou and has a negative gradient of mean annual concentration along the African transect. The values of mean annual concentrations of ion Ca^{2+} are: at Banizoumbou (1.38 µg/m^3), Lamto (0.33 µg/m^3) and Zoetele (0.14 µg/m^3). The terrigenous compounds and particularly the Ca^{2+} play an important role in the neutralisation of the atmospheric acidity. In wet savanna of Lamto and in forest of Zoetele, SO_4^{2-} is the most important ion in the chemical composition of aerosols. The nitrate is also high in these three African ecosystems. The concentrations of sulphate and nitrate are respectively 0.82 and 0.50 µg/m^3 at Banizoumbou, 1.19 and 0.65 µg/m^3 at Lamto, 0.87 and 0.24 µg/m^3 at Zoetele, respectively. The sulfates and nitrates come from many sources (terrigenous, biogenic, marine, biomass burning, anthropogenic). The marine contribution (Cl^-), is more important at Lamto nearest the sea (0.28 µg/m^3). This contribution is reduced by the orographic rainfall at Zoetele (0.03 µg/m^3) and lower at Banizoumbou (0.14 µg/m^3). The chemical composition of the aerosols depends of the seasonal dynamic of the two air masses, Harmattan and monsoon in each ecosystem. The dry deposition fluxes have the same variations as the concentrations of chemicals species.

1. Introduction

The studies of Atmospheric aerosols have been conducted in African tropical ecosystems over national and international programs like DECAFE, SAFARI, ESPRESSO, IDAF. The study of the tropical environment is of particular interest because it is the seat of important biogenic emissions (gases and particles) that can be increased quickly by population pressure (destruction of tropical forests, desertification...) in the next years. The tropics have been recognized by the scientific community as one of the most active regions for atmospheric chemistry [1]. Indeed, ecological changes and land use change are intense there and it results in a change of biosphere -atmosphere interactions and therefore gaseous and particulate emissions. The IDAF program of measuring atmospheric deposition in Africa launched in 1994 in Ivory Coast is part of the program of atmospheric chemistry studies (Emissions, transformations, transports, depositions) in the tropics. As part of this IDAF program, this study focuses on aerosol samples collected in three stations representing the great West and Central African ecosystems. The IDAF network covers ten stations in Africa, each one corresponding to a large African ecosystem at the regional level **(Figure 1)**. During the first half of 2004, a large number of studies on precipitation chemistry have been made in the tropical belt. These works include those made in Africa ecosystems [2-10]. 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 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 are the subject of this work. Our study aims to determine the variability of monthly, seasonal and annual concentrations of aerosols in the main African ecosystems, to identify the major sources of emissions of these particles, to estimate dry deposition flux of important biogeochemical species, and to compare the results obtained in the three major African ecosystems represented by the three sites studied.

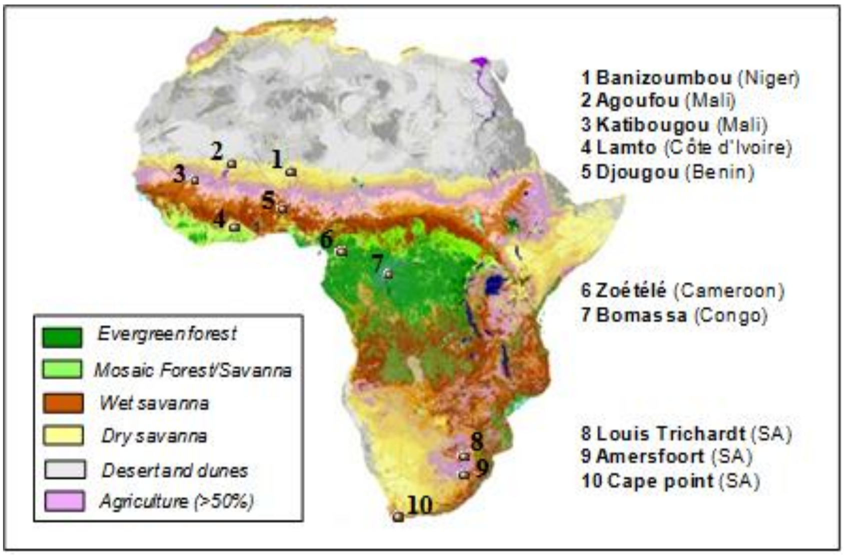

Figure 1: Vegetation Map and location of stations IDAF

2. Materials and Methods

2. 1. Measurement sites and meteorology

Banizoumbou (13° 31'N, 2° 38'E) has a semi-arid climate with a dry season from October to May and a wet season from June to September. The essential rainfall occurs with great regularity between June and September (maximum in August) and with wide variations in space and time. The region is characterized by an average rainfall of 500 mm/year and high temperatures (maximum in April-May during the studied period). These seasons are determined schematically by the change of position in latitude of the Intertropical Convergence Zone (ITCZ) which separates hot and dry air masses coming from the Sahara desert (Harmattan) and more humid maritime air masses coming from the Atlantic Ocean (the monsoon). The ITCZ determines the rainfall areas. It reaches extreme positions at two different times of the year. In January, the ITCZ is almost at 5 °N, corresponding to the dry season in northern savannas of this latitude. For Banizoumbou station, this position corresponds to the dry season. In July, the ITCZ is located at approximately 23 °N and determines the wet season of African savannas in the northern hemisphere.

The Lamto station (6° 13'N, 5° 2'0) is in an ecological reserve located 160 km from Abidjan on the edge of dense forest areas and Guinea Savanna. Lamto, is located in the central zone with forested / wet savanna. The annual rainfall in Lamto is about 1200mm (its variation goes from less than 800 to 1700 mm). These variations in rainfall put the site of Lamto among the least watered areas alongside Bondoukou (1177 mm) and Bouake (1109 mm) site characteristics of forest boundaries / savanna [12]. The Harmattan coming from the Sahara every year reaches the Lamto station in dry season [13]. It can cause frequent haze, greatly reducing atmospheric transmission, and causing a decrease in humidity. Moreover, during the long rainy season of seven months (April to October) the nebulosity is often important and reduces greatly the solar radiation reaching the ground [14].

The IDAF station of Zoetele (Zoetele / Nsimi) is located 120 km south - east of Yaoundé in the equatorial climate field. The distribution of the seasons is generally the result of the movement of atmospheric air masses under the action of the trade winds (northern and southern). In addition to the alternation of the two air masses (Harmattan and monsoon), the site is also influenced by the Indian Ocean air masses forming the Inter Oceanic Confluence (IOC) with the air masses from the Atlantic Ocean. On the action of these air masses is added the recycling of water vapor by vegetation which could explain the abundance and regularity of rainfall throughout the year in this area, thus, the dry season is slightly marked. At Zoetele equatorial forest, the wet season is over 9 months (March to November) and the dry season on the remaining 3 months.

2. 2. Collection and analysis method

2. 2. 1. Sample Collection

The aerosol samples were collected once per week, with Teflon Millipore filters. Sampling was performed with a power autonomous pumping unit. For collecting the particulates, a volume of air is filtered through a Teflon filter nucleopore types (37 mm in diameter and 0.2 µm pore size). The pumping system runs continuously for 24 hours at an average flow rate of 5 L / min. The treated filters are then refrigerated and sent for analysis to the Aerology Laboratory of Toulouse.

2. 2. 2. Method for chemical analysis of samples

The chemical composition of aerosol samples was analyzed by ionic chromatography in aqueous phase using a chromatographe DIONEX model QIC. In the aerosol, the chemical composition of the soluble part is determined. Teflon filter is desorbed in 12 ml of ultrapure water (18 MΩ). As Teflon is hydrophobic, the exposed face is placed up the filter into the desorption vial. The desorption water analysis is then performed by ion chromatography to determine the inorganic and organic ions. Measurement accuracy is of the order of 10%.

2. 2. 3. Calculation of weighted average concentration and dry deposition

For the three IDAF stations concerned by this work, the pumped air volumes have allowed to determine the weighted average concentration of the chemical species present in the collected aerosols. The concentration is calculated by using the following equation 1:

$$C_a = \frac{\sum (C_i \cdot V_i)}{\sum V_i} \qquad (1)$$

C_a is the weighted average concentration in µg/m^3, C_i the concentration of specie i in µg/m^3 and V_i the volume of air pumped in m^3.

Variations of monthly, seasonal and annual weighted mean concentrations of chemical species in the soluble part of the aerosols are displayed for each of three stations studied. These allow us to appreciate monthly, seasonal and inter-annual variability of the chemical composition of aerosols, to evaluate their emission sources and their dry deposition in each ecosystem. The deposit helps to clean the atmosphere from its pollutants but this is not without effect on the state of vegetation, soil, surface water (acidification ...) [15] and the excreta of animals and men [16]. From the deposition rate for each particle, it becomes then possible to calculate the dry deposition using equation 2:

$$D_S = C_X \times V_d \qquad (2)$$

D_S is the dry deposition of chemical species (mg.m^{-2}.yr^{-1}), V_d is the speed of dry deposition (cm/s) and C_x is mean atmospheric concentration of the specie x, expressed in µg/m^3.

We estimated dry deposition of particles by considering the following speed of the deposit:

$V_d = 0.15 \pm 0.05$ cm/s.

This choice is based on the work of Whelpdale [17]. Thus for a year we have:

$$D_S = (0.15 \pm 0.05) \times 10^{-2} \times (365 \times 24 \times 3600) \times C_X \times 10^{-6} = (47.304 \pm 15.768) \times C_X .mg \cdot m^{-2} \cdot an^{-1}.$$

For the rest, we will be only interested on the deposits of mineral chemical species of the aerosols because the organic portion is relatively small.

3. Results and Discussions

3. 1. Monthly average concentrations of aerosols in different ecosystems

Using **figures 2(a-c)** of the variations of monthly mean concentrations we can identify periods of high concentrations and, therefore, deduce the local and distant sources of emission of chemical compounds for each station.

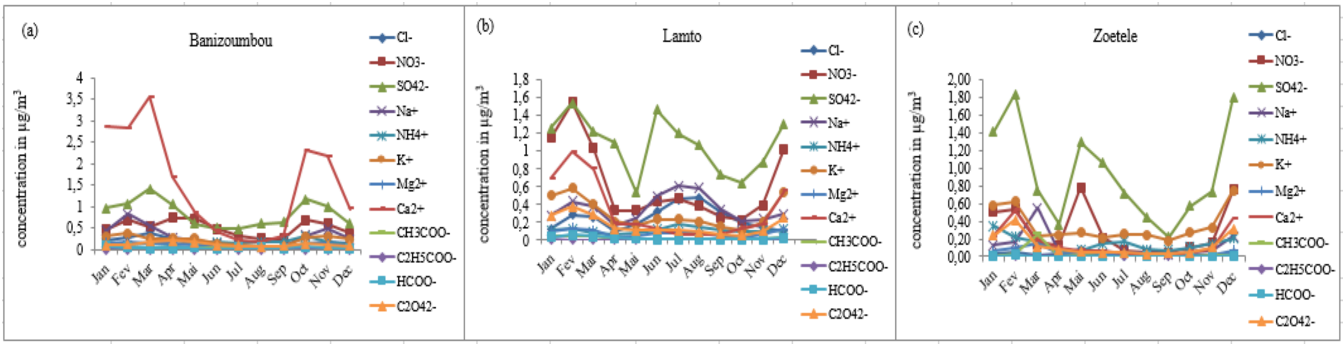

Figure: 2(a-c): Monthly average concentrations of aerosols collected in the three stations

3. 1. 1. Station in dry savanna of Banizoumbou

We notice two periods on this **figure 2a** giving the variations of monthly mean concentrations of aerosols collected at Banizoumbou site. The first period (April to September) during which the aerosol concentrations decrease and become low. During this period terrigenous source is weakened by the low Saharan thermal depression and the ITCZ aspiring the monsoon northwards. The main sources for this period are agriculture, livestock, local biogenic emissions of nitrogenous compounds, sulfur compounds and organic acids emitted by soil and vegetation, the meteorological perturbations like Grain lines in July, August and September for the terrigenous contribution. During this period the Inter -Tropical Front (FIT) is located north of Banizoumbou station. The monsoon which blows on all the southern part of FIT carries marine aerosols. It should also be noticed that during this wet period, leaching of the atmosphere by the precipitations contributes significantly to lower the concentrations of aerosols. Thus, the chemical composition of aerosols is predominated by the following three ions given in descending order of concentration: SO_4^{2-}, Ca^{2+} and NO_3^-. We note that during the second period from October to March the aerosol concentration is relatively high. During this period terrigenous source is activated by the anticyclone of the Azores and the dynamic anticyclone of Libya. The South is overheated; the harmattan transports the desert dust towards south-west and manage to increase the concentration of the aerosols. The beginning of this period coincides with the harvest of agricultural products, during which a considerable amount of animal excreta and plant debris is exposed to mechanical wind action and to bacterial decomposition. During the dry period between February and March, combustion of biomass is important and could explain the increase in atmospheric aerosol emissions. Three chemical species dominate the chemical composition of aerosols during this period. Giving in decreasing order of concentration, these species are: Ca^{2+}, SO_4^{2-} and NO_3^-.

3.1. 2. Station in wet savanna of Lamto

Two periods are also remarkable in **Figure 2b** representing the variations of monthly mean concentrations of aerosols collected in wet savanna of Lamto. The first period which runs from April to October is the period of the rainy season with a short dry season between July and August. During short dry season, the leaching of the atmosphere by precipitations decreases and concentration of aerosols increases then decreases slightly because of the return of heavy rain due to the period of withdrawal of the monsoon in the south. During this wet period, four species dominate the chemical composition of aerosols in wet savanna of Lamto. Giving in decreasing order of concentration, these species are: SO_4^{2-}, Na^+, NO_3^- and Cl^-. The concentration of those ions shows the influence of the biogenic source and the marine source during this period. The second period is observed from November to March during which the concentration of aerosols is high. This period is the dry season in which there is no leaching phenomenon. The distant terrigenous contribution due to Harmattan comes in addition to the local biogenic source. Trees cutting and biomass burning in January-February for agricultural causes, especially accentuate the concentration of sulfates and nitrates. Extensive use of wood or coal as an energy source is also a major source of emission of aerosols in this wet region. The four chemical species that predominate in this period are as followed, in descending order of concentration: $S0_4^{2-}$, NO_3^-, Ca^{2+} and K^+. These ions show the influence of the local biogenic source, of biomass burning and of distant terrigenous source.

3. 1. 3. Station in equatorial forest of Zoetele

The variation of monthly average concentrations of aerosols collected at Zoetele station **(Figure 2c)** is the same as that of Lamto station. But the wet season during which the concentrations are relatively low because of permanent leaching of the atmosphere and the weakening of terrigenous source goes from March to November with a peak of aerosol concentrations in May corresponding to the timely withdrawal of rainfall. December to February (dry season), the concentration of aerosols is important because the leaching of the atmosphere by precipitation is very low. The major ions in the wet season are given in descending order of concentration as follow: SO_4^{2-}, K^+, NH_4^+ and NO_3^-. These ions are local biogenic emissions from soil and vegetation. The marine ions, which had to be important during this period are mostly eliminated by the almost permanent rains and especially by orographic rainfalls due to the uplands located about 100 Km between Atlantic Ocean and Zoetele site [6]. During the dry season, SO_4^{2-}, K^+, Ca^{2+} and NO_3^- are, in this order of decreasing concentration, and represent the major species in this site. During this dry period, distant terrigenous source is added to the local biogenic sources of soil and vegetation.

3. 2. Seasonal average concentrations of aerosols in different ecosystems

The values of the seasonal average concentrations allow us to deduce the seasonality of emissions of chemical species entering in the chemical composition of aerosols in the atmosphere. Those values also allow us to highlight the importance of leaching of the atmosphere by precipitation. The variations in terms of seasonal average concentrations are given in **Figures 3(a-c)**.

From the **Figures 3(a-c)**, we notice that at the dry savanna of Banizoumbou **(Figure 3a)**, the average concentration of chemical species during the dry season is higher than that obtained during the wet season. This is due to the weakness of terrigenous source and leaching of the atmosphere by rain during the wet season. The same situation is observed at the wet savanna of Lamto **(Figure 3b)** except that the strong influence of the monsoon reversed the trend for marine compounds (Na^+ and Cl^-).

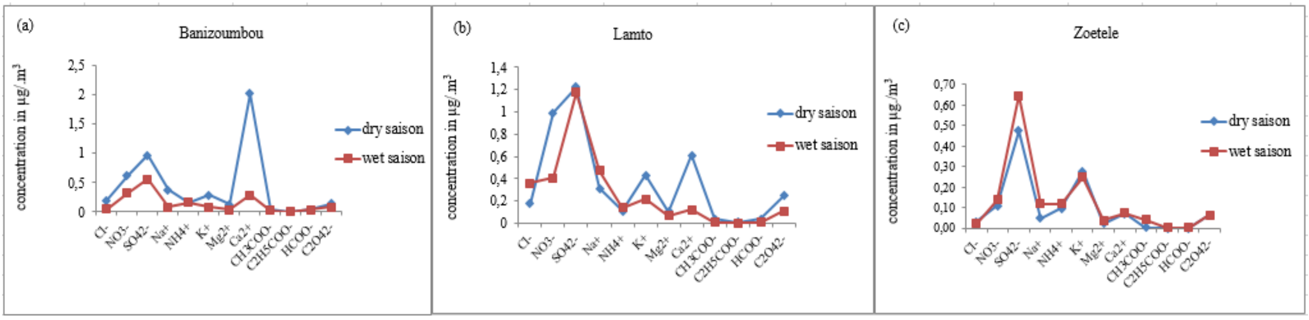

Figure: 3(a, c): seasonal average concentrations of aerosols collected in three stations.

At the equatorial forest of Zoetele **(Figure 3c)**, the concentration of biogenic species (NO_3^-, SO_4^{2-}, K^+, NH_4^+) and marine (Cl^- and Na^+) during the wet season is higher than that during the dry season. This situation can be attributed to the long duration of the rainy season (9 months), permanent rainfall, vegetation density and high humidity. In all study sites, concentrations of NH_4^+ and Mg^{2+}remained approximately constant despite changing seasons.

The assumption that emissions of nitrogenous compounds across the bacterial nitrification, decomposition of animal excreta, crop residue, are activated by the moisture is warranted by the results of Stewart [18] who noticed during the AMMA (Multidisciplinary Analysis African monsoon) campaign, emissions of nitrogen monoxide NO like large puffs on the soils of the west African Sahel freshly dampened after a drought event. By using satellite data, Jaeglé [19] showed that the emissions of NO by the humid soil can significantly increase concentrations of NOx in West Africa. For sulfates, their emissions are accentuated by the development of phytoplankton and algae.

3. 3. Annual weighted average concentrations in different ecosystems

The determination of the weighted average annual concentrations of chemical species allows to identify the high important compounds in the chemical composition of atmospheric aerosols of each ecosystem and to deduce their probable sources. The **figures 4(a-c)** show the variations in annual average concentrations of chemical species constituting the soluble portion of aerosols.

The **figure 4a** presenting variation of annual mean concentrations of aerosols at Banizoumbou station has a very large peak in calcium Ca^{2+}. Its concentration changes from 0.36 µg/m^3 in 1999 to 2.73 µg/m^3 in 2000. This peak of concentration confirms the predominance of the terrigenous source in the dry savanna region. After the calcium, the others chemical species measured at Banizoumbou are classified in the following descending order: SO_4^{2-}, NO_3^- , K^+, NH_4^+, Na^+, Cl^-, $C_2O_4^{2-}$ and Mg^{2+}. The concentrations of acetate, propionate and formate are relatively low.

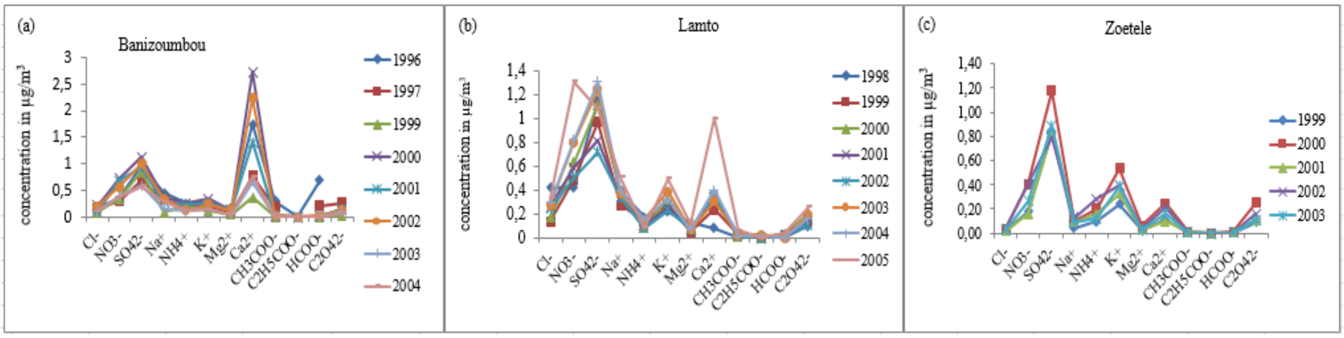

Figure: 4(a-c): average annual concentrations of aerosols collected in three stations.

Considering the structure of soils of the savanna region constituting the environment of this station and also its geographical position in relation to the desert gateway, it may be noted that SO_4^{2-}, K^+, Mg^{2+} and NO_3^- have non negligible terrigenous contributions. The correlation coefficients of these ions with the calcium at Banizoumbou are: 0.81; 0.75; 0.86, 0.60 respectively **(Table 1)**

Indeed, the soil of this savanna region of the Sahara and Sahel are constituted primarily of gypsum ($CaSO_4$), calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$) [2, 20]. Also, we must remember that these savanna areas are excellent agro-pastoral areas with a very high density of the animal population. The bacterial nitrification and denitrification of urea, animal's excreta, plant debris, and the use of nitrogenous and potassium fertilizers explain the importance of the concentration of nitrogenous compounds (NO_3^- and NH_4^+) [21-23] and potassium K^+. Biological processes in soils represent a significant source of nitric oxides NOx [24] and so of nitrogenous compounds (NO_3^- and NH_4^+) in the atmosphere. The biomass burning is also an important source of nitrogenous and sulfur compounds [21; 22]. Indeed, nitrogen is combined to the oxygen at relatively high temperatures to form nitrogen oxides NOx which may, in suspension, undergo chemical and photochemical reactions and lead to the formation of nitric acid (HNO_3). The same process can occur with sulfur dioxide SO_2 from the combustion of fossil fuels and biomass combustion leading to the formation of sulfuric acid (H_2SO_4). These acidic gases can diffuse on the large preexisting particles such as desert dust grains (Ca^{2+}, Mg^{2+}, K^+, Na^+) in suspension and leading thus to more important sizes of particles [13]. Consequently, terrigenous particles play an important role in neutralizing atmospheric acidity.

Table 1: Correlation coefficients between species in the aerosols at Banizoumbou

Banizoumbou	Cl^-	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	CH_3COO^-	$HCOO^-$	$C_2O_4^{2-}$
Cl^-	1.00										
NO_3^-	0.55	1.00									
SO_4^{2-}	0.83	0.74	1.00								
Na^+	0.76	0.65	0.73	1.00							
NH_4^+	0.30	0.65	0.62	0.40	1.00						
K^+	0.65	0.82	0.73	0.76	0.60	1.00					
Mg^{2+}	0.69	0.80	0.79	0.79	0.57	0.91	1.00				
Ca^{2+}	0.79	0.60	0.81	0.26	0.40	0.75	0.86	1.00			
CH_3COO^-	0.17	0.23	0.14	0.26	0.18	0.21	0.16	0.06	1.00		
$HCOO^-$	0.13	0.06	0.09	0.14	0.04	0.10	0.10	0.08	0.70	1.00	
$C_2O_4^{2-}$	0.43	0.74	0.59	0.48	0.49	0.60	0.56	0.42	0.49	0.33	1.00

The terrigenous source is the result of the erosion of arid soils or fragmented by farming and exposed to mechanical wind action. This aerosol has an atmospheric cycle which has an important role in tropospheric chemistry, primarily for the neutralization of air acidity [25]. This important role of the terrigenous compounds explains the strong correlation between SO_4^{2-}, NO_3^- and between large particles mainly terrigenous and marine (Table 1). For examples of these reactions, we can write the following:

- neutralization of nitric acid and sulfuric acid by $CaCO_3$:

$$CaCO_3 + 2HNO_3 \rightarrow Ca(NO_3)_2 + H_2O + CO_2 \qquad (3)$$

$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2O + CO_2 \qquad (4)$$

Similar reactions can happen with potassium carbonate (K_2CO_3), and magnesium carbonate ($MgCO_3$).

- The neutralization of sulfuric acid and nitric acid by ammonia:

$$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4 \qquad (5)$$

$$NH_3 + HNO_3 \rightarrow NH_4NO_3 \qquad (6)$$

It is these various emission sources and physicochemical processes of transformation that explain the correlation between these ions.

Na^+ and Cl^- are marine contributions transported by the monsoon. The concentration of these ions is relatively low because Banizoumbou station is far from the sea. These ions also participate to the physical processes of clouds formation because they represent condensation nuclei. So they are easily eliminated by wet deposition in aqueous clouds phase [26]. They also participate in the same aging process as Ca^{2+}, K^+, Mg^{2+}, SO_4^{2-} as evidenced by their high correlation coefficients **(Tables 1)**. The high concentration of SO_4^{2-} results from the combination of several sources as shown by his correlation coefficients with the terrigenous source ion tracer (Ca^{2+}), the marine source ion tracer (Cl^-), the bushfires ion tracer ($C_2O_4^{2-}$) and anthropogenic emissions **(Table 1)**. Its concentration changes from 0.59 µg/m^3 in 2003 to 1.13µg/m^3 in 2000 at Banizoumbou site.

The **figure 4b** presenting the variations of annual average concentrations of aerosols in wet savanna of Lamto shows that SO_4^{2-} corresponds to the largest peak of concentration. This peak noticed during all the years of measurement, shows the importance of the density of the biomass burned and the extent of phytoplankton training which is much more developed in wet savanna and in forest. The sea closer to the Lamto station (100km), is a great source of sulfur compounds. The high correlation of this ion with Ca^{2+} (terrigenous source), Cl^- (marine source) $C_2O_4^{2-}$ (biomass burning), NO_3^- (biogenic), K^+ (vegetation) **(Table 2)**, clearly confirm the provenance of the sulfate from these different sources. Its concentration changes from 0.72 µg/m^3 in 2002 to 1.31 µg/m^3 in 2004. After SO_4^{2-}, the others chemical species measured at Lamto are ranked in following descending order concentration: NO_3^-, Ca^{2+}, Na^+, K^+, Cl^-, $C_2O_4^{2-}$, NH_4^+, and Mg^{2+}. The concentration of particulate NH_4^+ is low in wet savanna of Lamto. The work of Yoboué [9] on the chemical composition of the precipitation collected in the wet savanna of Lamto showed that NH_4^+ is the dominant ion. In fact, nitrogenous compounds (NO_3^-, and NH_4^+) must have significant concentrations in this wooded wetland ecosystem due to the importance of biomass but also due to importance of biomass burning and bacterial decomposition of organic matter which follows deforestation in the wet savanna. The almost permanent moisture also increases the emission of nitrogenous compounds by bacterial nitrification and denitrification of animal's excreta and plant debris. Fertilizer use is also an important source of nitrogenous compounds. Constituting a condensation nucleus, NH_4^+ is easily removed from the atmosphere by wet deposition, hence its low concentration in the aerosol.

Table 2: Correlation coefficients between species in the aerosols at Lamto

Lamto	Cl^-	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	CH_3COO^-	$HCOO^-$	$C_2O_4^{2-}$
Cl^-	1.00										
NO_3^-	0.48	1.00									
SO_4^{2-}	0.59	0.70	1.00								
Na^+	0.86	0.65	0.80	1.00							
NH_4^+	0.59	0.39	0.79	0.63	1.00						
K^+	0.59	0.82	0.78	0.60	0.54	1.00					
Mg^{2+}	0.39	0.75	0.60	0.73	0.52	0.72	1.00				
Ca^{2+}	0.59	0.88	0.53	0.49	0.16	0.73	0.66	1.00			
CH_3COO^-	0.36	0.68	0.44	0.38	0.26	0.77	0.57	0.70	1.00		
$HCOO^-$	0.16	0.54	0.40	0.33	0.24	0.66	0.52	0.60	0.69	1.00	
$C_2O_4^{2-}$	0.39	0.87	0.76	0.58	0.46	0.93	0.75	0.82	0.76	0.71	1.00

Na^+ and Cl^- concentrations were relatively high compared to the concentrations calculated in dry savanna. The proximity of the sea could explain the increase in the concentration of these ions along the transect: dry savanna - wet savanna. Indeed, monsoon comes with humidity and marine compounds during its crossing of the Atlantic Ocean and transports them to the mainland. The importance of the average concentration of these marine ions (coarse) and the high relative humidity in this ecosystem make that the precipitations become very important. The Ca^{2+} reflects the influence of terrigenous source transported from Sahara and Sahel by the harmattan and the meteorological perturbations like grain lines during the rainy season, the AEJ and the TEJ. The low concentration of this ion certifies that the terrigenous source in wet savanna of Lamto is weakened by the density of vegetation and high humidity. The correlation coefficient between Ca^{2+} and Cl^- ($R = 0.59$) shows that there is also a weak marine contribution of this ion **(Table 2)**. The concentration of K^+, higher at Lamto than at Banizoumbou explains the importance of vegetation density in wet savanna of Lamto and so the importance of biomass burning. This ion is strongly correlated with oxalate as fire tracer ($R = 0.93$), NO_3^- ($R = 0.82$) and SO_4^{2-} ($R = 0.78$) **(Table 2)**.

Figure 4c presenting variations of aerosol concentrations in the equatorial forest of Zoetele has the same shape as that obtained at the wet savanna of Lamto. We can then deduce from **Table 3** that the aerosols emitted to both types of ecosystems (wet savanna and forest) are approximately the same. SO_4^{2-} has the largest peak of concentration. Its concentration varies from 0.79 µg/m^3 in 2002 to 1.18 µg/m^3 in 2000. After this ion, come in descending order: K^+, NO_3^-, NH_4^+, Ca^{2+}, $C_2O_4^{2-}$, Na^+, Mg^{2+}, Cl^-. However, we notice a decreased concentration of the majority of the chemical species in going from Lamto to Zoetele. This fact may be attributed to leaching of the atmosphere by the almost continuous rainfall in equatorial forest of Zoetele. The orographic rainfall due to the highland that is situated between Zoetele and the Atlantic Ocean is the raison of the low concentration of marine aerosols in this site located just 200 km from the Atlantic Ocean. The duration of the rainy season, most important in the equatorial forest (9 months) than in wet savanna (7 months) is also another cause of weak concentrations of the particles. The concentration of K^+ increased slightly from the wet savanna of Lamto to equatorial forest of Zoetele. This increase in the concentration of K^+ and its high correlation with $C_2O_4^{2-}$ shows the importance of vegetation density in equatorial forest and that biomass burning is an important source of aerosols.

Table 3: Correlation coefficients between species in the aerosols at Zoetele

Zoetele	Cl^-	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	CH_3COO^-	$HCOO^-$	$C_2O_4^{2-}$
Cl^-	1.00										
NO_3^-	0.98	1.00									
SO_4^{2-}	0.41	0.48	1.00								
Na^+	0.74	0.75	0.13	1.00							
NH_4^+	0.72	0.78	0.05	0.88	1.00						
K^+	0.76	0.80	0.80	0.68	0.53	1.00					
Mg^{2+}	0.70	0.78	0.89	0.50	0.49	0.94	1.00				
Ca^{2+}	0.96	0.98	0.61	0.71	0.69	0.88	0.86	1.00			
CH_3COO^-	0.24	0.37	0.91	0.23	0.18	0.77	0.86	0.48	1.00		
$HCOO^-$	0.45	0.55	0.97	0.17	0.18	0.80	0.93	0.66	0.91	1.00	
$C_2O_4^{2-}$	0.71	0.81	0.84	0.55	0.58	0.92	0.99	0.87	0.83	0.90	1.00

The annual average concentration of aerosols is dominated in order of importance as follows:

- terrigenous compounds (37%), sulfates (22%), and nitrogenous compounds (17%) in dry savanna of Banizoumbou;
- sulfates (30%), nitrogenous compounds (23%) and marine compounds (18%) in wet savanna of Lamto;
- sulfates (41%), nitrogenous compounds (20%), and potassium (17%) in equatorial forest of Zoetele.

Figure 5 (a-c) show that the terrigenous contribution is the 4th in the chemical composition of the aerosols found at wet savanna of Lamto (13%) and at equatorial forest of Zoetele (10%).

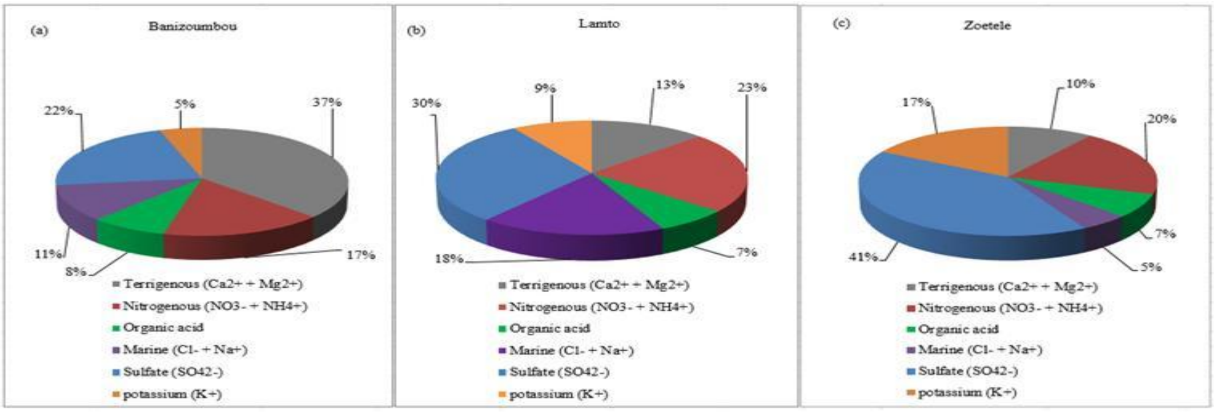

Figure: 5(a-c): Chemical composition of the aerosols in the different ecosystems

3. 4. Annual particles mean dry deposition in different ecosystems

Figure 6 shows the values of the average annual deposits for each chemical species entering the chemical composition of atmospheric aerosols of the three major African ecosystems. The formula for computing the particulate dry deposit shows that it is proportional to the concentration in the atmosphere of the chemical species considered. Therefore, the order of importance of dry deposition of particles is the same as that of their mean concentrations in each ecosystem. The order of importance of dry annual average deposition of the major chemical species in each of the three studied IDAF stations is as follows:

- for dry savanna of Banizoumbou, we found this order: $Ca^{2+} > SO_4^{2-} > NO_3^- > Na^+ > K^+ > NH_4^+ > Cl^- > Mg^{2+}$. This classification indicates the predominance of terrigenous source followed by biogenic source due to soil, biomass burning, agriculture and livestock;
- for wet savanna of Lamto we found $SO_4^{2-} > NO_3^- > Ca^{2+} > Na^+ > K^+ > Cl^- > NH_4^+ > Mg^{2+}$. This order indicates the predominance of local biogenic source due to vegetation, soil, biomass burning, humidity and agriculture. This source is followed by the distant terrigenous source and the marine source;
- for equatorial forest of Zoetele we found $SO_4^{2-} > K^+ > NO_3^- > NH_4^+ > Ca^{2+} > Na^+ > Mg^{2+} > Cl^-$. This order shows that the sources are the same as in Lamto with little influence of marine source due to orographic rainfall.

We notice that the fluxes of dry particulate deposition of ammonium (NH_4^+) and magnesium (Mg^{2+}) do not show major differences between the different ecosystems.

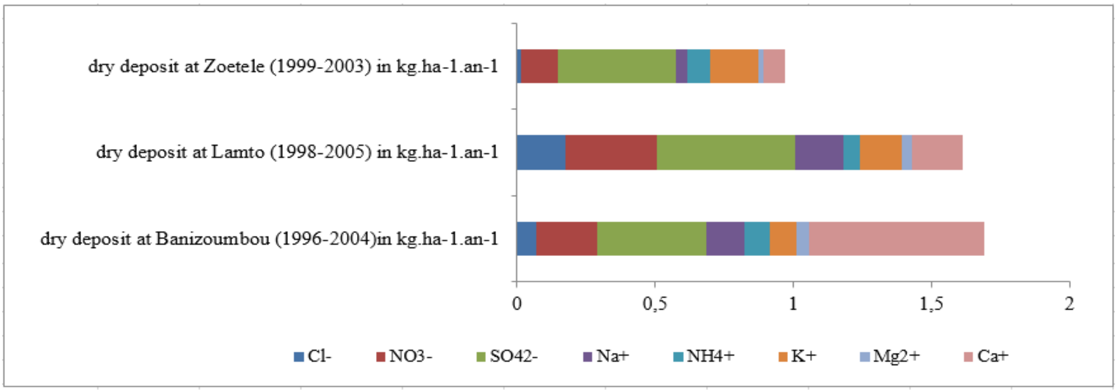

Figure: 6: Annual average dry deposition in kg. ha^{-1}.an^{-1}

The aerosols containing Ca^{2+} species; NO$_3^-$; SO$_4^{2-}$ and NH$_4^+$ have a strong influence on the status of ecosystems, human health, and overall climate. It is then important to evaluate mass flow of calcium, nitrogen and sulfur related to deposits of those chemical species.

Conclusion

In the dry savanna, terrigenous source is the most important of all. Livestock, agriculture and biomass burning are important sources of emissions of nitrogenous and sulfur compounds. In wet savanna and forest, the density of the biomass burned, the high humidity and increasing agricultural activity are the causes that make the concentration of nitrogenous and sulfur compounds higher.

The influence of the changing seasons on the particulate emission process has been highlighted. Thus, it was established that:

- the terrigenous source predominates during the dry season in dry savanna because of the strong influence of wind erosion. The desert dust is transported by Harmattan from the north-east to the south-west of the continent. This explains the negative gradient of concentration of Ca^{2+} (terrigenous contribution tracer), along the transect dry savanna - wet savanna – equatorial forest;
- the marine contribution depends on the importance of the monsoon on the continent and the geographic location of the site compared to the sea. It is important progressively from north to the south;
- because of their multiple sources, nitrates are relatively important in the different ecosystems;
- the sulfates is the chemical species that predominate in the chemical composition of aerosols in wet savanna and forest. The concentration of SO$_4^{2-}$ is also important in dry savanna. The sulfur compounds are mainly emitted by biomass burning taking place in all ecosystems during the dry season after the clearing or after deforestation in the wet savanna and forest;
- the wet savanna and the equatorial forest have a marine additional source of sulfur compounds due to the development of phytoplankton, algae and especially of the sea proximity;
- the concentration of potassium and organic acids, mainly depend on the vegetation cover density of each ecosystem. In the chemical composition of the aerosols, the following proportions are obtained for the organic acids: 10.40% at Banizoumbou, 14.47% at Lamto and 23.69% at Zoetele.

This study also highlights the key role played by terrigenous particles in the process of neutralization of atmospheric acidity and the leaching of the atmosphere by rainfall which can lead to a considerable decrease of the concentration of aerosols.

The annual average deposits were calculated from weighted average annual concentrations. The calcium, nitrogenous compounds and sulfates present the more important dry depositions in the three study sites. The evolution of their concentrations requires scientific community's special attention due to their impacts on climate and human health.

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