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The purpose of this study is to analyze a long term database of the chemical composition of precipitation at three African dry savanna sites in the Sahel. The precipitation samples were collected during the monsoon season at Agoufou (15°20′N, 01°29′W, Mali) from 2004 to 2006, Banizoumbou (13°31′N, 02°38′E, Niger) from 1994 to 2009 and Katibougou (12°56′N, 07°32′ W, Mali) from 1997 to 2008. pH and major inorganic and organic ions in precipitation were analyzed by ionic chromatography. A characterization of mean precipitation chemistry with the associated wet deposition fluxes for each species is presented. The first important result is that interannual variability of all volume-weighted mean (VWM) concentrations is low, ranging between ±5% and ±25%. Acidity in dry savannas is low and indicates the strong alkaline nature of the precipitation. The average annual pH at Agoufou is 6.28, 5.75 at Banizoumbou and 5.54 at Katibougou. This result is correlated with the important terrigenous contribution measured in the chemical content of precipitation, implying acidity neutralization by mineral species such as Ca^{2+} and NH_4^+. Mg^{2+} and K^+ are found to play a minor role in neutralization. Enrichment factor calculations for Ca^{2+}, SO_4^-, K^+ and Mg^{2+} with respect to the sea reference reveal a significant influence of Saharan and Sahelian crustal sources. VWM concentrations of these species dominate the composition of measured precipitation. An estimation of the potential particulate and gas contribution to the total precipitation composition is given for each site: At Agoufou, the mean relative contribution in rainwater is 80% for particles and 20% for gases, while at the Banizoumbou and Katibougou sites, results indicate 70% for particles and 30% for gases. The high particulate phase contribution to precipitation emphasizes the importance of multiphase processes between gases and particles in the atmospheric chemistry typical of African semi-arid savanna ecosystems. The second highest contribution is nitrogenous, with high VWM concentrations of NO_3^- and NH_4^+ measured at the three sites. Monthly evolution of NO_3^- and NH_4^+ concentrations are studied in relation to gaseous emission sources in the Sahelian region, i.e. biogenic soil emission and ammonia sources from animals. The calculated wet nitrogen deposition flux presents a regular increase throughout the wet season at the three sites. Results suggest total mean nitrogen deposition fluxes of 1.80 kg N ha^{-1} yr^{-1} at Agoufou, 2.10 kg N ha^{-1} yr^{-1} at Banizoumbou, and 3.30 kg N ha^{-1} yr^{-1} at Katibougou. The marine contribution is lower, 23% at Agoufou, 17% at Banizoumbou and 13% at Katibougou. The last contribution concerns organic acidity, which ranges from 5% at Agoufou, 10% at Banizoumbou to 14% at Katibougou. Terrigenous and marine contributions present a negative gradient, whereas nitrogenous and organic contributions a positive gradient along the Sahelian transect defined by Agoufou–Banizoumbou–Katibougou.

1. Introduction

In arid and semi-arid regions desertification is a land degradation problem of major importance resulting from various factors including climatic variations and human activities i.e. soil erosion

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caused by wind and/or water, deterioration of soil properties and natural vegetation. High demographic growth and rapid development of economic activities has resulted in an agricultural intensification process to increase food production complicating the situation of desertification. The arid and semi-arid regions, because of their particular climate, where wind erosion frequently exceeds water erosion, are the principal sources of atmospheric dust transported over great distances from eroded soils (Orange et al., 1993; Gomes et al., 2003). Soil erosion is a major global environmental and agricultural problem, which has intensified in recent years. In the tropics, the atmosphere has a high dust load throughout the year as a result of the common occurrence of "dust devils" (Saxena et al., 1996). Dust devils are local convective circulations that occur particularly in arid and semi-arid environments. In recent years, multidisciplinary research has received considerable attention, mainly within arid and semi-arid regions where ecosystems are characterized by low, discrete rainfall, high temperatures, periodic droughts and little vegetation cover (Estell et al., 2006).

Various sources from natural and anthropogenic activities influence the chemical composition of precipitation. Chemical species in rainfall may differ from those originally emitted e.g. emission of alkaline (dust particles and gaseous NH_3) can significantly influence precipitation acidity by neutralizing a certain fraction of the acids (Placet and Streets, 1987; Khemani et al., 1993). The mineral acidity in precipitation is mainly related to the acids HNO_3 and H_2SO_4 formed from NO_x and SO_2 gaseous precursors.

In Africa, the IDAF (IGAC/DEBITS/AFRICA) program started in 1994. The IDAF network is the French contribution to the international IGAC (International Global Atmospheric Chemistry)/DEBITS (Deposition of Biogeochemically Important Trace Species) program. The IDAF program is associated with the African Monsoon Mutidisciplinary Analysis/Long Observing Period (AMMA/LOP, Lebel et al., 2010) over West/Central Africa and with the South Africa Climate Change Air Pollution-PICS (SACCLAP) project in southern Africa. The main objectives of IDAF are to measure wet and dry deposition fluxes and identify the relative contribution of natural and anthropogenic sources. The IDAF activity is based on high quality measurements of atmospheric chemistry (rainwater, aerosol and gaseous chemical composition) on the multi-year scale. 10 measurement sites exist covering three types of African ecosystems: dry savanna (Niger, Mali and South Africa), wet savanna (Ivory Coast and Benin) and equatorial forest (Cameroon and Congo) (Fig. 1). Data from the measuring sites at Agoufou (Mali), Banizoumbou (Niger) and Katibougou (Mali), which represent the Sahelian dry savanna sites, are analyzed here.

Wet and dry deposition play an essential role in controlling the concentration of biogeochemical elements in the atmosphere. The chemical content of precipitation integrates numerous physical and chemical mechanisms. Therefore, the study of precipitation composition and associated wet deposition is linked to the temporal and spatial evolution of atmospheric chemistry. Moreover, the identification of chemical and physical characteristics of rainwater helps to evaluate the influence of different sources and enhances the understanding of the local and regional dispersion of gases and particles as well as their potential impacts on ecosystems. Incorporation of S and N oxides in wet deposition is particularly important as they are precursors of major acids H_2SO_4 and HNO_3 (Ro et al., 1988; Minoura and Iwasaka, 1996; Voldner et al., 1986; Dikaiakos et al., 1990).

Precipitation influences the removal of particulate matter and gaseous pollutants in the atmosphere. The physico-chemical characterization of precipitation continues to be investigated due to the increased atmospheric input of substances and their effects upon terrestrial ecosystems, surface waters, vegetation and materials (Bravo et al., 2000).

Recent studies of precipitation chemistry in African ecosystems have been published as part of the IDAF network, e.g. Galy-Lacaux and Modi (1998); Galy-Lacaux et al., 2001; Al-ourabi and Lacaux (2002); Lacaux et al. (1993, 2003); Yoboué et al. (2005); Sigha-Nkamdjou et al. (2003); Mphepya at al. (2004, 2005); Galy-Lacaux et al. (2009).

The present work complements these studies on precipitation content at other African sites. The main objectives of this study are to:

- provide the main precipitation chemistry characteristics and a quantification of wet deposition fluxes representative of dry African savanna ecosystems;

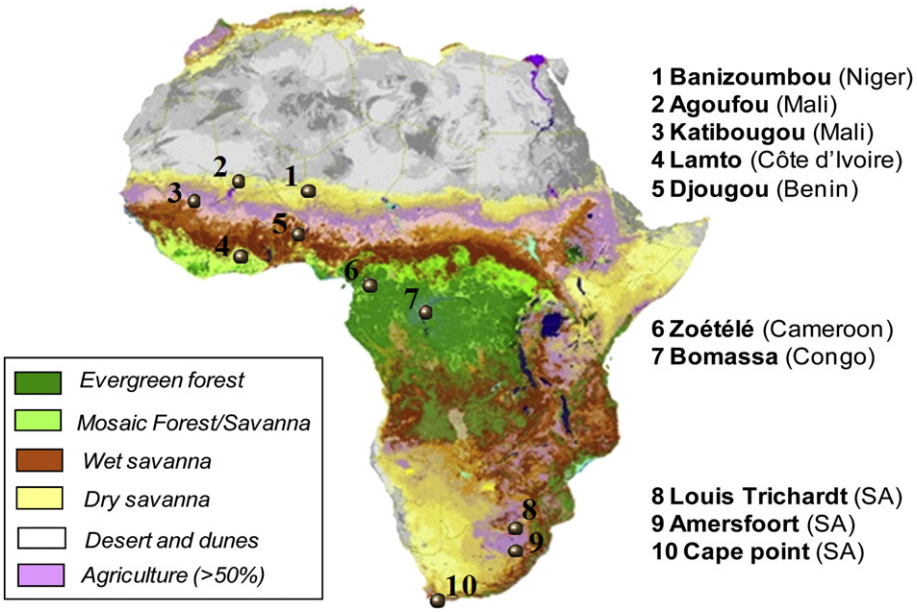

Fig. 1. Vegetation and location map of the 10 measurement stations of the IDAF network.

- study the temporal and spatial trends of the chemical composition of rainwater and associated wet deposition fluxes during the monsoon season;
- compare the results between the three dry savanna sites as well as with the other IDAF sites representative of semi-arid savanna in South Africa, wet savanna in Lamto (Ivory Coast) and equatorial forest in Zoetele (Cameroon);
- investigate the variability of the main atmospheric sources of nitrogenous species in the gas phase that influence ammonium and nitrate content in precipitation.

2. Materials and methods

2.1. Sampling sites

Fig. 1 presents the vegetation map and location of the 10 IDAF measurement stations. Sites are displayed on the land cover map of Africa from Mayaux et al. (2004). We focus on the three Sahelian sites, Katibougou, Agoufou and Banizoumbou, situated in Mali and Niger. Rainfall samples were collected at Agoufou (Mali) from 2004 to 2006, at Banizoumbou (Niger) from 1994 to 2009 and at Katibougou (Mali) from 1997 to 2008. Galy-Lacaux et al. (2009) have published a long term synthesis of precipitation chemistry at Banizoumbou (Niger) using data from 1994 to 2005. The three sites used here are representative of rural and agro-pastoral sites in Western African dry savannas ecosystems. Measurements of rainwater, aerosol chemical composition and surface gaseous concentrations were made at all three sites (Adon et al., 2010). The Agoufou site was incorporated into the IDAF network in the framework of the AMMA (African Monsoon Multidisciplinary Analysis) program in 2004. Activity at this site stopped in 2006 in terms of rainfall observations but measurements of gaseous concentrations continue.

Rainfall in the Sahel is governed by the West African monsoon system. The Western African climate is largely determined by the position of the Inter-Tropical Convergence Zone (ITCZ), which separates the hot and dry continental air coming from the Sahara desert (Harmattan) from the cooler, humid maritime air masses (Monsoon) originating from the equatorial Atlantic Ocean. In the Sahel, 80% of the total rainfall is associated with mesoscale convective systems during the summer monsoon in June and July (Mohr et al., 2009). Mesoscale convective systems (MCS) are also responsible for the major fraction of annual, local wind erosion and hence for most of the Sahelian dust emissions (Janicot et al., 2008). The three stations investigated have a semi-arid climate, with a dry season from October to May and a wet season from June to September. The sites are located along a latitudinal gradient and are briefly described in Table 1. Agoufou is situated towards the northern limit of the area reached by the West African monsoon and is part of the Malian Gourma mesocale site of the AMMA CATCH program (Couplage de L'Atmosphère Tropicale et du Cycle Hydrologique) (Mougin et al., 2009). Mean annual rainfall over the three-year study period was 321 mm (Table 1). Banizoumbou is situated about 60 km east of Niamey in a rural and agro-pastoral area of the Sahelian region of Niger. Annual average rainfall over the 15-year study period was 509 mm (Table 1). More detailed information for these two sites is available in Galy-Lacaux and Modi (1998) and Galy-Lacaux et al. (2009). Katibougou is located in the Koulikoro region, at the IPR center (Institut Polytechnique Rural) approximately 60 km northeast of Bamako. This site represents a rural site in the Sudano-Sahelian zone with some extended agricultural practices nearby. Annual precipitation varied from a minimum of 585 mm in 2000 to a maximum 1039 mm in 1999. Mean annual rainfall for the 1997 to 2008 period was 804 mm (Table 1).

2.2. Rain collection

An automatic precipitation collector specially designed for the IDAF network was located in the three IDAF sites (Galy-Lacaux et al., 2009). The automatic instrument is designed to collect only wet deposition. It collects precipitation with a high degree of cleanliness in a single-use polyethylene bag, avoiding aerosol deposit before the onset of rain. A precipitation detector automatically controls the aperture of the cover, which hermetically closes the polyethylene bag. The surface of rain collection is 225 cm^2. After each precipitation event, 50 cm^3 of the collected precipitation is sampled in 50 ml Greiner tubes. The preservation of the rainwater samples is an important problem because microbial degradation can modify the chemical composition of rainwater. For this study all samples were stored in a deep freeze environment from collection to analysis.

A total of 61 precipitation events were collected at Agoufou, 358 at Banizoumbou and 510 at Katibougou, representing total collected rainfall amounts of 764, 6880 and 8337 mm, respectively. Table 1 presents the calculated mean efficiency of collection (EC) for each site. These values indicate a good representativity of the dataset in accordance with the precipitation completeness quality criteria given by the Global Atmospheric Watch (GAW) Program of the World Meteorological Organization (WMO, 2004).

2.3. Analytical procedure and data quality control of rain samples

Precipitation-dissolved content was determined at the Laboratory of Aerology (LA), Toulouse, France. Inorganic and organic ions were determined by ion chromatography (IC). All details of analytical procedures are described by Galy-Lacaux et al. (2009). The quality of measurements depends not only on the samples but also on the analysis and the standardized and accredited procedures. Since 1996, the Laboratory of Aerology has participated in the quality control inter-comparison program organized twice a year by the WMO GAW. Fig. 2 summarizes the results from last five tests (2005–2009) from the laboratory of Aerology WMO intercomparison. According to the results of the quality assurance program, analytical precision is estimated to be 5% or better for all ions, well within the uncertainties of all measured values presented here.

pH is measured with an ATI Orion 350 instrument with a combined electrode (ATI Orion model 9252) filled with KCl (4 M) and saturated with AgCl. Two standard solutions (WTW) at pH 4.01 and 7.00 are used for its calibration. H^+ ion concentrations are

Table 1
Geographic characteristics and rainwater collection at the three dry savannas sites. Mean Annual rainfall (H in mm ± SD Standard Deviation), mean collected rainfall depth Hc in mm and mean Efficiency Collection (EC) in %.

Station	Country	Latitude	Longitude	Elevation m^{-1}	H (mm) ± SD	Hc (mm)	EC (%)
Agoufou (2004–2006)	Mali	15°20′ N	01°29′ W	300	321 ± 19	254	78
Banizoumbou (1994–2009)	Niger	13°31′ N	02°38′ E	220	509 ± 34	459	89
Katibougou (1997–2008)	Mali	12°56′ N	07°32′ W	290	804 ± 31	695	89

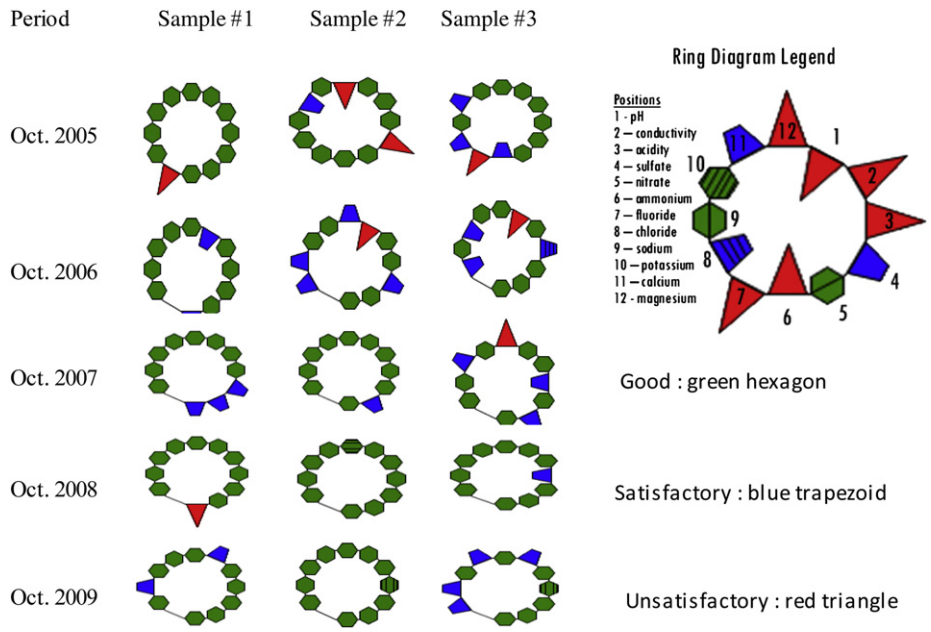

Fig. 2. The last five participations (2005–2009) of the laboratory of Aerologie to the WMO inter-comparison tests. According the ring diagram representation, this result shows the analysis of 3 blind samples analyzed by the laboratory of Aerologie and compared to WMO referenced values.

calculated from the pH. Precision is 0.01 pH units. To improve the quality of the IDAF dataset further, the WMO quality criteria based on the ionic balance were applied to all the IDAF precipitation samples (WMO, 2004). A calculation of the ion difference (ID) for each sample is performed to consider the ionic balance with the following equation:

$$\text{Ion Difference } (\%) = 100 \times ([\text{CE} - \text{AE}]/[\text{CE} + \text{AE}]) \quad (1)$$

where AE is the anion sum in μeq l^{-1} and CE is the cation sum in μeq l^{-1}. Acceptable ID according to the total sample ionic charge is given by the WMO GAW manual report, 2004. 91, 94 and 92% of all samples at Agoufou, Banizoumbou and Katibougou, respectively, were within the WMO acceptance range. Only these samples have been used in the calculations presented in this paper.

2.4. Calculation of annual volume-weighted mean concentration and wet deposition

The annual volume-weighted mean concentration (VWM) of each ion was calculated using the following relationship:

$$\text{VMW}\left(\mu\text{eq } 1^{-1}\right) = \sum_{i=1}^{N} c_i p_i / \sum_{i=1}^{N} p_i \quad (2)$$

where C_i is the ion concentration for each element in μeq l^{-1}, P_i the precipitation amount for each rainfall event in mm, and N the total number of samples. To calculate the mean VWM concentration of each ion over the period 2004–2006 at Agoufou, 1994–2009 at Banizoumbou and 1997–2008 at Katibougou, N is considered equal to 61, 358, 510, respectively.

The annual wet deposition (WD) expressed in mmol m^{-2} yr^{-1} is calculated by multiplying the VWM concentrations by the annual average rainfall amount. From the VWM concentrations of the components in mg L^{-1}, o the wet deposition in kg ha^{-1} yr^{-1} can be obtained. The Efficiency Collection (EC%) that represents the completeness of precipitation depth associated with valid chemical composition analysis is between 80 and 90% for all sites. The analytical precision is estimated to be 5% or better for all ions.

A principal component analysis (PCA) was applied to all the rainwater measurements. The correlation coefficients between the different chemical parameters are examined in order to determine the potential sources that influence rainwater composition. High correlation indicates that chemical compounds may have the same origin and/or are affected by advection of the same air masses.

To estimate the contribution of the sea salt component to the measured precipitation composition, excess concentrations of sulphate, chloride, potassium, calcium and magnesium with respect to sea salt are calculated using Na^+ reference (Keene et al., 1986). The sea salt fraction of any particular species, X, is given by:

$$\text{ssF}_X = \left[\text{Na}^{2+}_{\text{rain}}\right]\left[\text{X}/\text{Na}^{2+}\right]_{\text{seawater}}, \quad (3)$$

Similarly, the non-sea salt fraction of X can also be given by:

$$\text{nssF}_X = [\text{X}_{\text{rain}}] - \left[\left\{\text{Na}^{2+}_{\text{rain}}\right\} * \left\{\text{X}/\text{Na}^{2+}\right\}_{\text{seawater}}\right] \quad (4)$$

where X_{rain} is the concentration of species X in rainwater. The corresponding enrichment factor (EF) of different components with respect to Na^+ are calculated using equation (5):

$$(\text{EF})_X = (\text{X}/\text{Na}^+)_{\text{rain}}/(\text{X}/\text{Na}^+)_{\text{seawater}}, \quad (5)$$

where $(EF)_X$ is the enrichment factor of species X, Na^+ is a reference element for the sea, (X/Na^+)rain is the ratio of the amount of species X to that of species Na^+ in the rain, and (X/Na^+) seawater is the ratio of species X to species Na^+ in the seawater (Chao and Wong, 2002; Quiterio et al., 2004).

3. Results and discussion

In this section we study the mean monthly and annual chemical composition of precipitation, as well as the wet deposition fluxes estimated at the three measurement sites. Table 2 presents the calculated annual VWM concentrations and the annual mean WD for all data. The entire database is used to study the temporal and spatial trends of the chemical composition of rainwater and

Table 2
Volume-Weighted Mean concentration VWM (μeq l^{-1}) and Wet Deposition WD (kg ha^{-1} yr^{-1}) measured at the three Sahelian savannas.

Species	Agoufou (2004–2006)		Banizoumbou (1994–2009)		Katibougou (1997–2008)	
	VWM (μeq l^{-1})	WD (kg ha^{-1} yr^{-1})	VWM (μeq l^{-1})	WD (kg ha^{-1} yr^{-1})	VWM (μeq l^{-1})	WD (kg ha^{-1} yr^{-1})
H^+	0.5 (±0.2)	0.002 (±0.001)	1.8 (±0.5)	0.009 (±0.003)	3.0 (±1.0)	0.024 (±0.007)
pH	6.28 (±0.15)	–	5.75 (±0.14)	–	5.54 (±0.14)	–
Na^+	18.8 (±1.2)	1.36 (±0.32)	9.9 (±2.9)	1.17 (±0.47)	6.3 (±1.8)	1.16 (±0.41)
NH_4^+[a]	25.2 (±2.0)	1.12 (±0.26)	17.9 (±3.5)	1.29 (±0.37)	19.1 (±3.7)	2.13 (±0.50)
K^+	12.4 (±0.7)	1.55 (±0.39)	8.1 (±2.9)	1.66 (±0.77)	3.7 (±1.0)	0.12 (±0.04)
Ca^{2+}	32.3 (±1.5)	2.09 (±0.56)	27.0 (±4.8)	2.75 (±0.62)	22.9 (±2.7)	3.65 (±0.60)
Mg^{2+}	16.5 (±2.9)	0.67 (±0.23)	7.3 (±2.0)	0.46 (±0.17)	4.5 (±1.3)	0.43 (±0.12)
NO_3^-[a]	14.6 (±0.8)	0.66 (±0.19)	10.8 (±2.5)	0.77 (±0.20)	10.4 (±2.0)	1.16 (±0.28)
Cl^-	20.2 (±0.1)	2.30 (±0.60)	9.9 (±3.0)	1.82 (±0.81)	6.5 (±1.8)	1.86 (±0.66)
SO_4^{2-}[b]	14.3 (±3.3)	0.70 (±0.13)	9.7 (±1.6)	0.80 (±0.23)	7.3 (±1.1)	0.94 (±0.20)
tCarb[c]	39.6 (±1.7)	7.77 (±2.10)	28.5 (±6.4)	8.82 (±2.14)	19.1 (±5.8)	9.35 (±3.21)
$HCOO^-$	4.5 (±1.1)	0.67 (±0.26)	6.6 (±2.2)	0.82 (±0.46)	10.3 (±3.1)	3.71 (±1.08)
CH_3COO^-	3.9 (±1.1)	0.74 (±0.28)	6.6 (±2.2)	0.68 (±0.36)	5.2 (±1.7)	2.44 (±0.74)
$C_2H_5COO^-$	0.2 (±0.1)	0.04 (±0.01)	0.3 (±0.3)	0.05 (±0.05)	0.1 (±0.1)	0.09 (±0.07)
$C_2O_4^{2-}$	2.2 (±0.8)	0.15 (±0.06)	1.8 (±0.6)	0.05 (±0.02)	1.8 (±0.9)	0.35 (±0.12)

[a] NH_4^+ and NO_3^- in kg N ha^{-1} yr^{-1}.
[b] SO_4^{2-} in kg S ha^{-1} yr^{-1}.
[c] tcarb: is total carbonates.

associated wet deposition during the measurement period. Special focus is placed on the investigation of the concentration and wet deposition of nitrogenous compounds. We investigate the variability of the main gas phase atmospheric sources that influence ammonium and nitrate precipitation content. We also quantify and study the seasonal evolution of nitrogen wet deposition fluxes, which are key in terms of natural input to soils and vegetation in semi-arid regions in developing nations.

3.1. Chemical composition of precipitation and wet deposition fluxes

Table 2 presents the mean annual VWM concentrations and wet deposition fluxes as well as the associated standard deviations for all species measured at the three IDAF sites. All standard deviations are low, never exceeding ±6.4%. These values are therefore representative of a mean characterization of the rainfall chemical content and the associated fluxes for the reported time periods.

Correlation coefficients between the different ionic species using the Spearman method (with a 1% confidence level) are calculated for all individual events.

3.1.1. Marine contribution

According to the method described in Section 2.4, marine and non-marine contributions of the different ionic species in precipitation and the corresponding Enrichment Factors (EF) were estimated. Table 3 shows the ratio of Ca^{2+}, SO_4^{2+}, Mg^{2+} and K^+ with respect to Na^+ in rainwater and seawater, as well as their enrichment factors (EF). Na^+ and Cl^- ions are highly correlated ($r = 0.78$, 0.76 and 0.92, at Agoufou, Banizoumbou and Katibougou, respectively). These mean annual ratios of these two ions are 1.074, 1.000 and 1.032, at the three sites respectively; values which are close to the sea-water ratio of 1.167 (Keene et al., 1986), and which correspond to the same EF value close between 0.9 and 1. The ratios of SO_4^{2-}/Na^+, K^+/Na^+, Ca^{2+}/Na^+ and Mg^{2+}/Na^+ in rainwater at the three sites were found to be higher than the seawater ratios. In addition to the marine contribution of these species, high ratios of SO_4^{2-}, K^+, Ca^{2+} and Mg^{2+} suggest a non-marine origin for these species. Similar results were found by Khemani et al. (1993) and Kulshrestha et al. (2003, 2005, 2009) for Indian sites. These elevated values indicate a contribution from crustal sources. The values of the sea salt fraction (ssF) and non-sea salt fraction (nssF) support this observation (Table 4). Crustal sources contribute between 84 and 90% SO_4^{2-}, 96-96% K^+, 98–99% Ca^{2+} and 68–74% Mg^{2+} at the three sites.

Fig. 4 gives an example of a marine episode as it occurs generally during the wet season in the Sahel. Back trajectory analyzes, were calculated using the NOAA HYSPLIT MODEL (Draxler and Rolph, 2003), at the three dry savanna sites for the monsoon season at a constant altitude of 500 m. Results clearly indicate that the monsoonal air masses coming from the Guinean Gulf are rich in sea salt aerosols and influence the three Sahelian sites, despite their distance from the sea. The marine contributions for Mg^{2+}, SO_4^{2-}, K^+, Ca^{2+} are estimated to be around 26%, 16%, 3% and 2%, respectively, at Agoufou, 31%, 12%, 3% and 1% at Banizoumbou and 32%, 10%, 4% and 1% at Katibougou. Contribution of the Mg^{2+} content in rain is estimated for the three sites and ranges from 26 to 32% and from 68 to 74% for marine and terrigenous sources, respectively. In Africa, convective rainfall includes marine elements from the boundary layer and terrigenous elements from atmospheric levels above the boundary layer which are affected by continental air masses. We clearly retrieve these two chemical signatures during the monsoon season along the Sahelian transect investigated.

3.1.2. Terrigenous contribution

Measured total carbonates and calcium ions are the most abundant species with concentrations of 32.3, 27.0 and 22.9 μeq l^{-1}, at Agoufou, Banizoumbou and Katibougou, respectively. Ca^{2+} was

Table 3
Comparison of seawater ratios with rainwater components at the three IDAF savanna sites.

Sea water rain		1.16	0.121	0.022	0.044	0.227
Ratios in rain	Agoufou (2004–2006); this work.	0.681	0.404	0.435	1.276	0.430
	Banizoumbou (2006–2007); this work.	1.000	0.815	1.105	2.277	0.805
	Katibougou (1997–2008); this work.	1.035	1.281	0.632	4.719	0.789
Enrichment factor	Agoufou (2004–2006); this work.	0.6	3.3	19.8	29.0	1.9
	Banizoumbou (2006–2007); this work.	0.9	6.7	50.2	51.8	3.5
	Katibougou (1997–2008); this work.	0.9	10.2	27.6	78.6	3.2

Table 4
Non-sea salt (nss) and sea salt (ss) of rainwater components at the three dry savannas.

Ion	Agoufou (μeq l^{-1})	Banizoumbou (μeq l^{-1})	Katibougou (μeq l^{-1})
$nssCa^{2+}$	31.5	26.6	22.6
$ssCa^{2+}$	0.8	0.4	0.3
$nssSO_4^{2-}$	12.0	8.5	6.5
$ssSO_4^{2-}$	2.3	1.2	0.8
$nssMg^{2+}$	12.2	5.1	3.1
$ssMg^{2+}$	4.3	2.2	1.4
$nssK^{+}$	12.0	7.9	3.6
ssK^{+}	0.4	0.2	0.1

significantly correlated with SO_4^{2-} (r = 0.83; 0.67; 0.87), Mg^{2+} (r = 0.82; 0.79; 0.93) and K^{+} (0.62; 0.56; 0.79). These correlations indicate that the main terrigenous ions are associated with the formation of eolian particles, including gypsum ($CaSO_4$), calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$) (Bohn et al., 1985; Loÿe-Pilot et al., 1986; Galy-Lacaux and Modi, 1998) as well as illite [$K(Al,Mg)_3SiA_{10}(OH)$] (Pitts and Pitts, 1986; Parmar et al., 2001; Nair et al., 2006; Kumar et al., 2007; Kulshrestha et al., 2009; Anatolaki and Tsitouridou, 2009). The North African desert areas (Sahel and Sahara) are probably the most important mineral aerosol source globally (Kaufman et al., 2005). Due to the partial dissolution of terrigenous soil dust components, rain in the Sahelian region is loaded with dissolved calcium and carbonates (calcite), which may account for the major fraction of the ionic concentrations of rainwater (Orange et al., 1993; Galy-Lacaux et al., 2009). The origin of potassium ions in rainwater is from washout of mineral dust and from biomass burning aerosols (Yoboué, 1991; Andreae et al., 1988; Crozat et al., 1978).

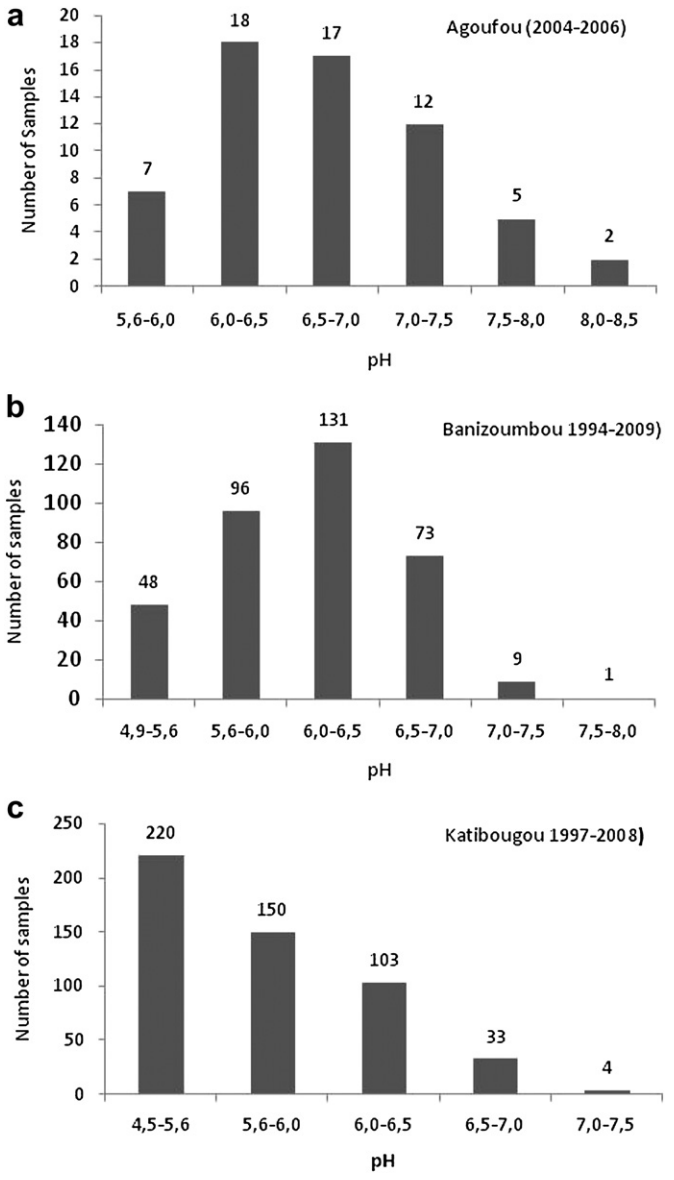

Fig. 3. Frequency distribution of rainfall pH values at the three dry savanna sites.

The study of the VWM concentrations of terrigenous species along the West African transect Agoufou–Banizoumbou–Katibougou shows a negative gradient from north to south (Table 2). Non-sea salt calcium concentrations, associated with dust emission, vary from 31.5 μeq l^{-1} at Agoufou, to 26.6 μeq l^{-1} at both Banizoumbou and Katibougou. Non-sea salt sulphate, potassium and magnesium concentrations show a similar gradient (Table 4).

The sum of the potential terrigenous species defined by $Ca^{2+} + Mg^{2+} + SO_4^{2-} + K^{+}$ + carbonates equals 115.1 μeq l^{-1} and corresponds to 56% of the total ionic content at Agoufou; to 80.6 μeq l^{-1}, or 56% of the total ionic content at Banizoumbou and to 53.8 μeq l^{-1}, or 45% of the total ionic content at Katibougou. This high terrigenous contribution emphasizes the direct influence of soil dust on rainfall of the Sahelian region. This terrigenous contribution involves highest wet deposition for Ca^{2+}: 2.09 ± 0.56; 2.75 ± 0.62 and 3.65 ± 0.60 kg ha^{-1} yr^{-1} at Agoufou, Banizoumbou and Katibougou, respectively (Table 2). Two South African IDAF sites, Louis Trichardt and Amersfoort, both in semi-arid savanna (and Amersfoort near industrial sites as well) present wet deposition of Ca^{2+} of the same order of magnitude: 1.8 and 2.8 kg ha^{-1} yr^{-1} at the two sites respectively (Mphepya et al., 2005).

3.1.3. Nitrogenous contribution

NO_x and NH_3 are the main nitrogenous gases emitted in the tropics and are removed in precipitation and aerosol as nitrate (NO_3^-) and ammonium (NH_4^+).

NH_4^+ is the main nitrogenous ion found in the rain samples at all three sites. The annual VWM concentration of NH_4^+ is 25.2 μeq l^{-1}, 17.9 μeq l^{-1} and 19.1 μeq l^{-1} at Agoufou, Banizoumbou and Katibougou respectively (Table 2). These values are comparable to those obtained at Kollo, Niger (NH_4^+ = 19.1 μeq l^{-1}, Modi et al., 1995) and at Banizoumbou (NH_4^+ = 18.1 μeq l^{-1}, Galy-Lacaux et al., 2009). The VWM concentrations calculated at the South African semi-arid savanna sites of Louis Trichardt and Skukuza are 9.0 and 9.7 μeq l^{-1}, respectively (Mphepya et al., 2005, 2006).

NH_4^+ content in precipitation results from the incorporation of gaseous ammonia and particles containing NH_4^+ in clouds and rainwater. NH_3 originates largely from bacterial decomposition of urea in animal excreta, and from emission by natural or fertilized soils (Schlesinger and Hartley, 1992; Galy-Lacaux and Modi, 1998). Domestic and wild animals also lead to volatilization of ammonia in tropical pastures (Galbally and Gillet, 1988; Schlesinger and Hartley, 1992). Another significant source of ammonia is savanna fires and domestic fuel wood burning (Lobert et al., 1990; Delmas et al., 1995; Brocard et al., 1996). Seinfeld (1986) reported that ammonia generally occurs in the atmosphere as $(NH_4)_2SO_4$, but is also found in the form of NH_4NO_3 (Parmar et al., 2000). During the wet season in the Sahelian region the burning of savanna is improbable and the main source of ammonia is likely the hydrolysis of urea from animal urine deposited in grazing areas. High densities of domestic animals are concentrated on the fresh natural pastures which turn green during the rainy season. McCalley and Sparks (2008) measured NO and NH_3 emission from the desertic Mojave soils and indicate that seasonal changes in temperature and

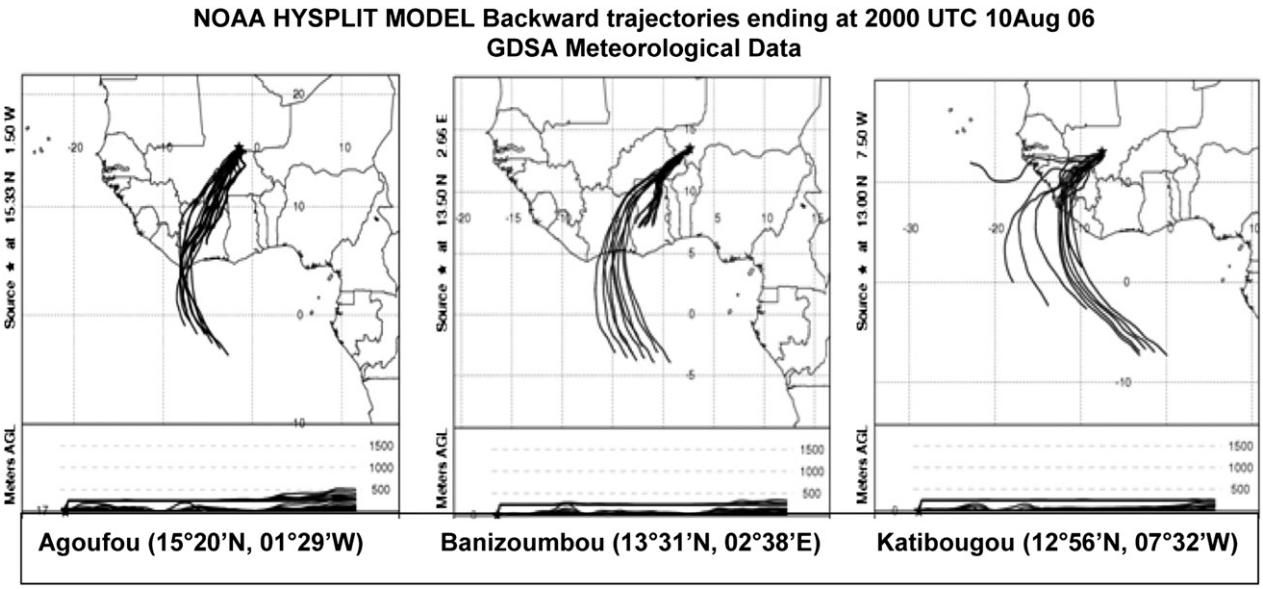

Fig. 4. Back trajectories obtained by means of the NOAA Hysplit Model, giving the direction of the monsoonal air mass during the wet season.

precipitation drive emissions, with maximum deposition fluxes in the wet season ranging 0.9–10 ng N m^{-2} s^{-1} (from 0.3 to 3 kg N ha^{-1} yr^{-1}). Wet deposition of ammonium of up to 0.88 kg N ha^{-1} yr^{-1} at Banizoumbou confirms the intense source of ammonia in this semi-arid savanna region (Galy-Lacaux and Modi, 1998). Atmospheric ammonia fluxes have been estimated in the Sahel and more generally in Africa (Schlecht et al., 1998; Bouwman et al., 2002). In the Sahelian zone, agro-pastoralism appears to be very important, representing 25–30% of GDP (Gross Production Product). For example, pastoralism contributes 10–15% of the GDP of both Mali and Niger. Recently, Delon et al. (2010) developed a specific NH_3 emission inventory for 23 West African countries. This inventory takes into account the volatilization of NH_3 from cattle dung. NH_3 volatilization from synthetic fertilizer is negligible in this region (Bouwman et al., 2002). The quantity of nitrogen released by livestock is calculated from Schlecht et al. (1998), in g N $head^{-1}$ day^{-1}, for cows, sheep and goats. This estimate is multiplied by the number of animals per km^2 in each region of each country concerned, using information from the FAO (Food and Agriculture Organization) and GLiPHA (Global Livestock Production and Health Atlas) database. The mean total nitrogen input from animal manure is estimated to be 23 kg N ha^{-1} yr^{-1} at Agoufou, 25 kg N ha^{-1} yr^{-1} at Banizoumbou and 11 kg N ha^{-1} yr^{-1} at Katibougou, with approximately 30% of this input released into the atmosphere (Delon et al., 2010). In the Sahel region favorable conditions are encountered for NH_3 volatilization, i.e. high temperatures, low soil moisture and bare soils surfaces. Thus, we assume that gaseous NH_3 is a significant contributor to the ammonium content of Sahelian precipitation.

In the present study, an intra-annual variation of NH_3 volatilization has been added, with higher emissions during the wet season. Indeed, similar to NO production from nitrification, rates of NH_3 volatilization should be sensitive to soil conditions that influence NH_4^+ concentrations and turnover in the soil (McCalley and Sparks, 2008). The increase in soil moisture at the beginning of the wet season is correlated to the increase of NO and NH_3 concentrations at the dry savanna sites (Adon et al., 2010).

Furthermore, the excreta quantity is not constant throughout the year, and presents a maximum at the beginning of the dry season at both Agoufou and Banizoumbou (Hiernaux et al., 1998, 2002; Schlecht et al., 1998). Due to a lack of data in Katibougou, we have supposed that the processes are similar to those at the two other sites. The quantity of N released from animal excreta is therefore maximum in October and November. The combination of these two processes (increased soil moisture at the beginning of the wet season and increased excreta at the beginning of the dry season) gives a monthly evolution of the NH_3 volatilization as shown in Fig. 6.

Nitrate contributes the second largest fraction to the nitrogenous content of precipitation at the 3 measurement sites. Concentrations of 14.6 μeq l^{-1}, 10.8 μeq l^{-1} and 10.4 μeq l^{-1} were measured at Agoufou, Banizoumbou and Katibougou, respectively. These values are in the same range of those measured at the South African semi-arid savanna sites of Louis Trichardt and Skukuza (8.0 and 8.17 μeq l^{-1}, respectively) (Mphepya, 2005, 2006), the rural Indian site of Iqbalpur (8.6 μeq l^{-1}) (Monika et al., 2000), the wet savanna site of Lamto (7.7 μeq l^{-1}) (Yoboué et al., 2005) as well as at the equatorial forest site of Zoetele (6.9 μeq l^{-1}) (Sigha-Nkamdjou et al., 2003). The concentrations measured at the 3 sites investigated here are lower than those at Amersfoort, South Africa (dry savanna site located near industrial areas; 25.0 μeq l^{-1}) (Mphepya et al., 2005).

In the Sahel, microbial processes in tropical savanna soils leads to the production of nitric oxide (NO) (Parsons et al., 1996; Levine et al., 1996; Serca et al., 1994, 1998), the major oxygenated nitrogen compound released from savanna soils. Over the infertile soils of the semi-arid savanna regions of South Africa Parsons et al. (1996) measured emission fluxes of 1.1 kg N ha^{-1} yr^{-1}, the same order of magnitude in size as the deposition fluxes measured in the Sahel. Original measurements of NO emission in the Sahelian savanna at Banizoumbou, where natural emissions are perturbed by grazing activities, indicate rates of 1.9 ± 0.8 kg N ha^{-1} yr^{-1} (Serça et al., 1998). Correlations between Mg^{2+} and NO_3^-, and between Ca^{2+} and NO_3^-, are around 0.68 at Agoufou, 0.76 at Banizoumbou and 0.83 at Katibougou, indicating potential heterogenous and multiphase chemical processes occurring between alkaline dust and gaseous nitric acid (Dentener et al., 1996; Galy-Lacaux et al., 2001).

Fig. 5(a–c) show the mean monthly variability of NO_3^- and NH_4^+ VWM and Fig. 5(d–f) mean monthly wet deposition flux of NO_3^-

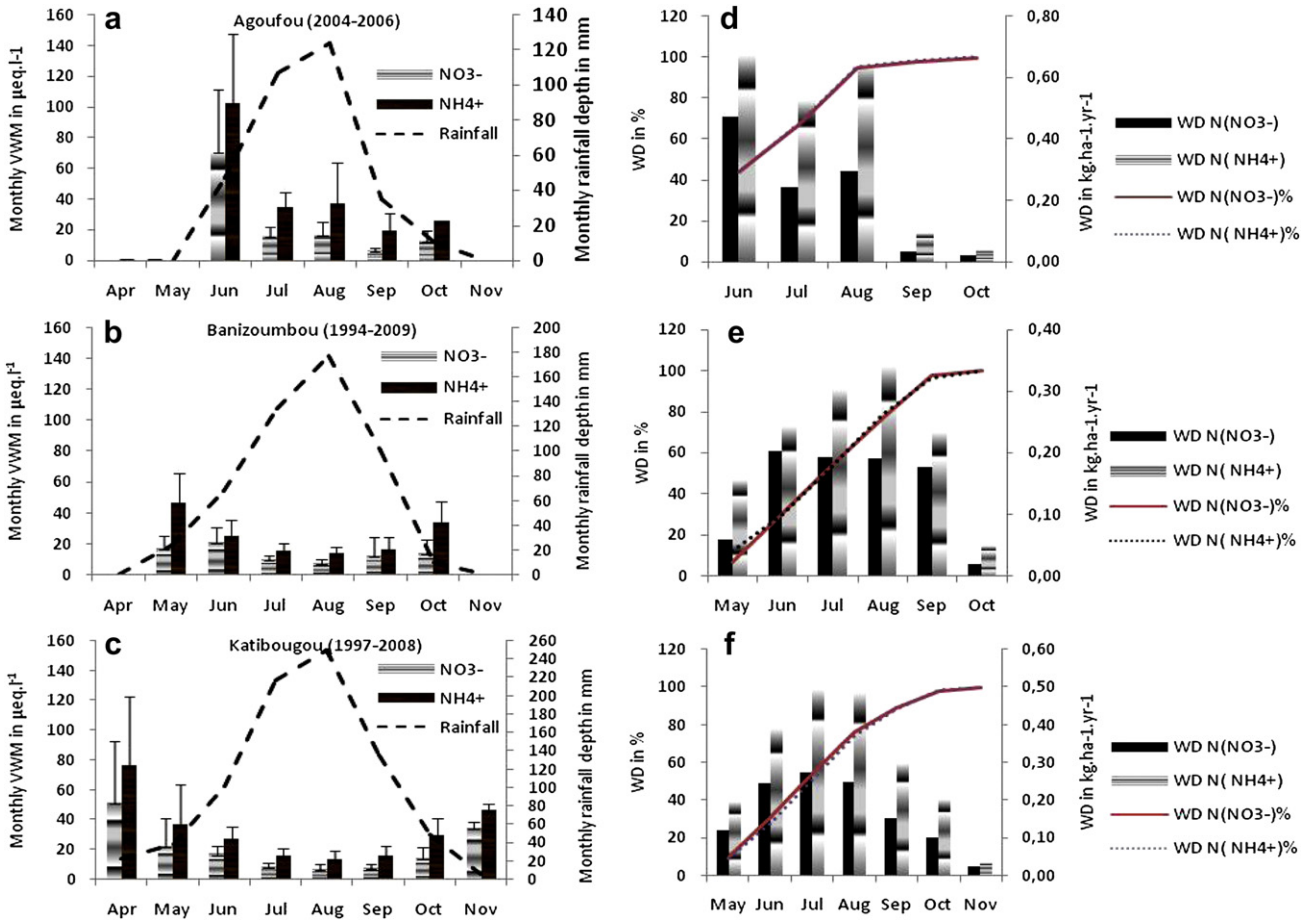

Fig. 5. (a–c)Mean monthly VWM concentrations of NO_3^- and NH_4^+ in µeq l^{-1} and mean monthly rainfall depth at the three dry savanna sites. Vertical bars represent the standard deviation around each monthly mean. (d–f): Mean monthly wet deposition flux in kg N ha^{-1} yr^{-1} and cumulative % of total N deposition calculated from monthly mean over all the studied periods.

and NH_4^+ as well as the cumulative wet deposition for the study period. Vertical bars indicate the standard deviation while the mean monthly precipitation depth is superimposed upon the monthly VWM concentrations. The range of NO_3^- and NH_4^+ concentrations in rain are shown in Fig. 5(a–c). Monthly NO_3^- and NH_4^+ VWM concentrations begin to increase significantly just after the first rains at the beginning of the wet season (Fig. 5a–c). Wet deposition fluxes increase throughout the wet season at all three sites. At Agoufou the wet deposition fluxes of ammonia is 1.20 kg N ha^{-1} yr^{-1} at the beginning of the wet season and reaches up to 3.10 kg N ha^{-1} yr^{-1} by the end of the wet season. Similar patterns are exhibited at Banizoumbou and Katibougou (Fig. 5d–f).

Using the methodology presented by Delon et al. (2010), Fig. 6(a–c) present the monthly mean distribution of N emission fluxes (i.e. NO_x from biomass burning (BB), biogenic NO from soils, NH_3 from BB and NH_3 from volatilization) from April to November. Uncertainty bars for each contribution are also shown. The emission flux is dominated firstly by the volatilization of ammonia, and secondly by the biogenic fraction during the wet season at Agoufou and Banizoumbou. At Katibougou, where livestock is less numerous, contributions of biogenic NO and volatilized NH_3 are comparable. The release of ammonia from animal urine and excreta is estimated to be approximately 7.2 ± 3.7 kg N ha^{-1} yr^{-1} at Agoufou, 8.1 ± 4.2 kg N ha^{-1} yr^{-1} at Banizoumbou and 3.9±2 kg N ha^{-1} yr^{-1} at Katibougou (Delon et al., 2010) (Fig. 6(a–c)). NH_3 emission from BB represents only 4% compared to NH_3 volatilization.

Fig. 5(a–f) and 6(a–c) can be used to interpret the nitrate and ammonium VWM concentrations measured in precipitation as well as to understand their monthly evolution. At each site (Fig. 5(a–c)) the highest concentration occurs with the first rains, whereas the highest biogenic emission occurs 2–3 months later (Fig. 6(a–c)) when the wet deposition fluxes of NH_4^+ and NO_3^- are maximum (Fig. 5(d–f)). Indeed, the first rains are more loaded in NH_4^+ and NO_3^- due to the scavenging in the lower atmosphere by these first rains, leading to very high concentrations in the precipitation but to relatively low deposition rates. The maximum biogenic emission of NO from soils, occurs in the heart of the wet season, whereas the highest concentrations are found in the beginning of the season (Adon et al., 2010). This is the result of traditional agricultural practices, such as grazing, manure application and decomposition of crop residues, followed by rain on the sandy soils of this area (Jaegle et al., 2004). In fact, the first rains that occur in April–May activate bacterial nitrification, leading to nitrogen consumption and consequently to the release of large pulses of NO (Davidson, 1992; Laville et al., 2005; Ludwig et al., 2001; Williams et al., 1992; Yienger and Levy, 1995). NO is immediately converted into NO_2 in the atmosphere through oxidative processes. After the consumption of the excess nitrogen, wet season NO biogenic emissions decrease but remain at relatively high levels compared to the dry season (Serça et al., 1998). Significant correlations are found between NH_4^+ and NO_3^- ($r = 0.69$ at Agoufou, 0.75 at Banizoumbou and 0.88 at Katibougou), indicating that the above particles originate from similar processes.

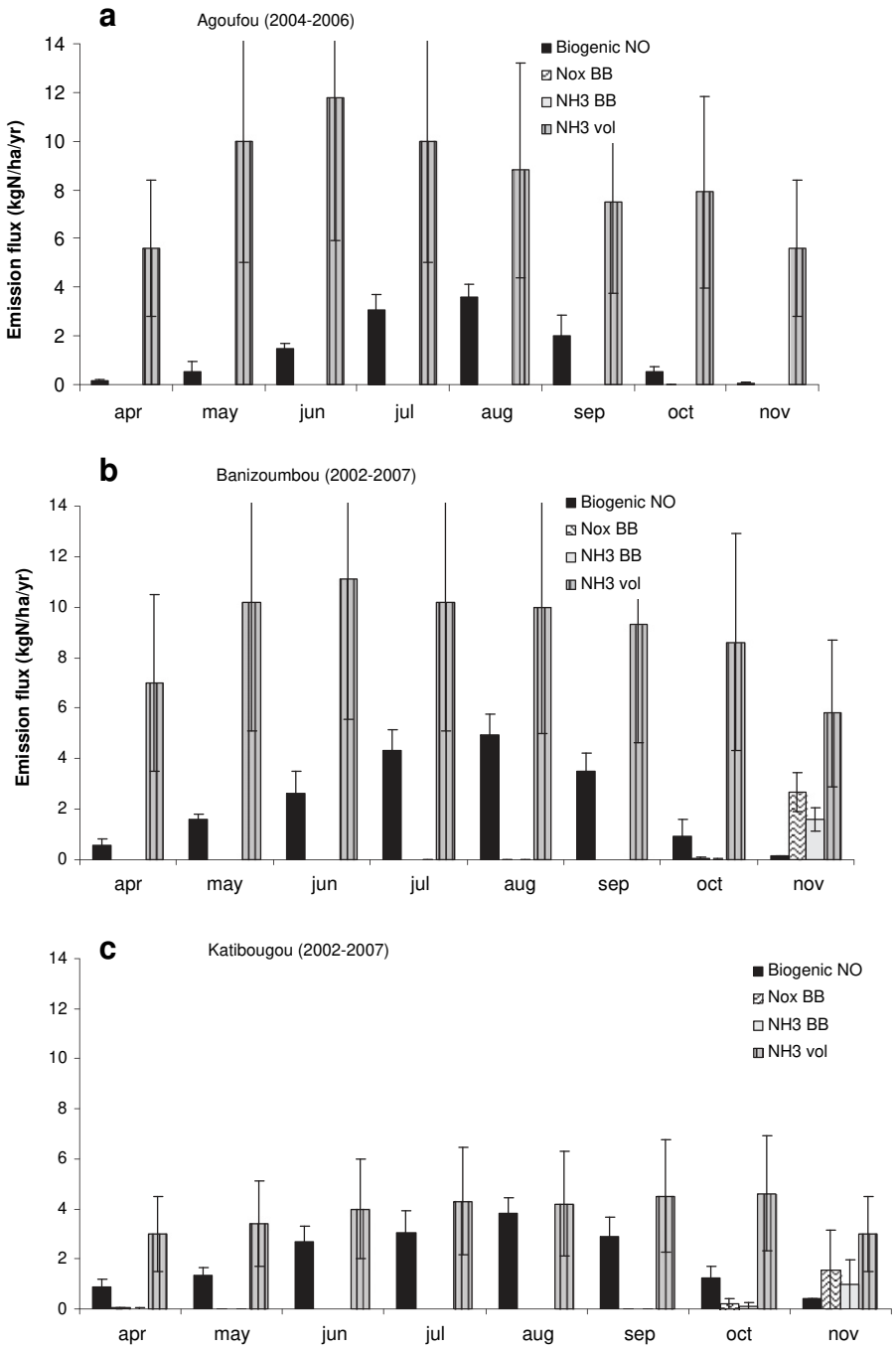

Fig. 6. (a–c)Monthly mean distribution of N emission fluxes and associated uncertainties in kg N ha^{-1} yr^{-1} for NO_x from biomass burning (BB), biogenic NO from soils, NH_3 from BB and NH_3 from volatilization at the three dry savanna sites.

Indeed, the potential presence of NH_4, NO_3 may explain these correlations.

A second maximum occurs at the beginning of the dry season in November at Katibougou. This appears to be associated with biomass burning sources in the Northern Hemisphere during this period (Jaegle et al., 2004), which likely influence the nitrate content of precipitation measured at the end of the monsoon season. At Agoufou and Banizoumbou a second maximum is observed in September. For these sites, we assume that this second peak is likely related to rain events occurring after several dry days, and producing slight pulses of NO from soils. Biomass burning emissions in the region of these sites is very low because of the low quantity of biomass available. In July, when the wet season is well established, 60% of the total N wet deposition flux is reached at Agoufou and 50% at both Banizoumbou and Katibougou. In August, in the heart of the wet season, 90% of the total flux is reached at Agoufou and 80% at Banizoumbou and Katibougou.

3.1.4. pH and acidity

Gaseous atmospheric species (NO_x, SO_2, NH_3) and water-soluble constituents of the ambient aerosols derived from sea-salts, crustal

dust and/or anthropogenic or biogenic emissions play a dominant role in the chemical characterization of rainwater on a regional scale. Depending upon their relative contribution, an individual precipitation event can be acidic or alkaline in nature.

Mean pH measurements for the three Sahelian savanna sites are given in Table 2 while Fig. 3 presents the pH frequency distribution for the three study sites. The mean pH is 6.28, 5.75 and 5.54 at Agoufou, Banizoumbou and Katibougou, respectively. The average acidity in the precipitation samples in the three dry savanna sites is weak, with hydrogen ion VWM concentrations equal to 0.5; 1.8 and 3.0 μeq l^{-1} at Agoufou, Banizoumbou and Katibougou, respectively. The pH values are significantly higher than those reported at the South African semi-arid savanna sites of Amersfoort (pH = 4.35) and Louis Trichard (pH = 4.91) (Mphepya et al., 2005); but comparable to several other arid and semi-arid rural sites of India (Norman et al., 2001; Pillai et al., 2001; Kulshrestha et al., 2003). Rain acidity at the South African dry-savanna sites is higher because of the greater influence by NO_x and SO_x industrial emissions from the Highveld region, which are recirculated around the country (Turner et al., 1996; Mphepya et al., 2005, 2006).

Results show that 100% of the 61 events collected at Agoufou present an alkaline pH higher than 5.6 (pH = 5.6 being the equilibrium of atmospheric CO_2 and cloud water). At Banizoumbou and Katibougou, 87% of the 358 and 57% of the 510 rainfall samples, respectively, are also in the alkaline range. The observed alkalinity of rainwater is due to the high loading of particulate matter in the atmosphere common to semi-arid region conditions. Dust is rich in calcium bicarbonate/carbonate representing a major buffering agent for acidity generated by sulphuric, nitric and organic acids (Galy-Lacaux et al., 2001; Khemani et al., 1993; Kulshrestha et al., 2003). We observe a latitudinal geographical gradient of the mean pH, with highest pH at the most northerly site (Agoufou) and lowest pH at the southerly site (Katibougou). Our database clearly demonstrates that the pH gradient is correlated to the calcium gradient measured in rain, which ranges from 32.3 μeq l^{-1} at Agoufou to 27.0 μeq l^{-1} at Banizoumbou and 22.9 μeq l^{-1} at Katibougou.

In spite of the weak acidity found in the precipitation measurements at these three dry savanna sites, the calculated potential contribution of organic acidity (formate, acetate, propionate and oxalate) is 27% at Agoufou, 39% at Banizoumbou and 50% at Katibougou. The potential contribution of mineral acidity, mainly related to the incorporation of H_2SO_4 and HNO_3, is equal to 73%, 61% and 50%, at the three sites, respectively. These contributions are comparable to measurements made in other African ecosystems. In wet savanna (Lamto) the potential acidity contribution by organic acids is equal to 56% and the contribution of mineral acids is 44% (Yoboué et al., 2005). At Amersfoort, an industrial site in a dry savanna ecosystem (South Africa), organic acids contribute only 16% of the total acidity (Mphepya et al., 2004). The contribution of organic acids (40–60%) in African forests is equivalent to that of mineral acids (40–60%). According the modeling work of Galy-Lacaux et al. (2001), we can assume that almost all the nitric acid available is neutralized by alkaline solid dust particles. Sulfuric acid, a strong acid, is also rapidly captured by alkaline particles. We suppose that the remaining acidity in rain samples is related to organic compounds.

If we define the acidity potential (pA) as the sum of the potential acidic compounds in the form of nitric or sulphuric acids and organic acids, pA is found equal to 39.7 μeq l^{-1} at Agoufou, 33.5 μeq l^{-1} at Banizoumbou and 35.1 μeq l^{-1} at Katibougou. The measured acidity (mA) is low and equal to 0.5 μeq l^{-1}, 1.8 μeq l^{-1} and 3.0 μeq l^{-1} at Agoufou, Banizoumbou and Katibougou, respectively. Therefore 39.2, 31.7 and 32.1 μeq l^{-1} of H^+ is neutralized, at the three dry savanna stations respectively. Evidence for the neutralization of rainwater at the Sahelian sites is provided by good correlations between major anions (NO_3^- and SO_4^{2-}) and major terrigenous cations (Ca^{2+}, NH_4^+, Mg^{2+}) with coefficients ranging between 0.64 and 0.91. According to Orange et al. (1993), Dentener et al. (1996), Galy-Lacaux and Modi (1998), Galy-Lacaux et al. (2001), Sigha-Nkamdjou et al. (2003), Yoboué et al. (2005), a large fraction of terrigenous particles in tropical Africa are dominated by $CaCO_3$. This alkaline compound can neutralize gaseous HNO_3 to form solid calcium nitrate. The high calcium content can explain 82% of the neutralized acidity at Agoufou, 85% at Banizoumbou and 71% at Katibougou. Other heterogeneous mechanisms suggest that alkaline particles, containing Mg^{2+} and K^+, amongst others, may also contribute to neutralization of acid rain at these three sites. Neutralization of sulfuric and/or nitric acids by bases such as anions (oxides, carbonates or bicarbonates, etc.) associated with base cations such as Ca^{2+}, NH_4^+, Mg^{2+}, etc., can be evaluated by calculating the neutralization factors (NF) using the following equation (Possanzini et al., 1988):

$$NF_X = X/\left(NO_3^- + SO_4^{2-}\right) \quad (6)$$

where X is the chemical component of interest (Ca^{2+}, NH_4^+, Mg^{2+}, etc). Table 5 presents the NF calculation for the three measurement sites. NF values for Ca^{2+} are around 1.1 to 1.3 depending on the site. NH_4^+ and Mg^{2+} show lower NF values, varying between 0.9–1 and 0.25–0.57, respectively. As a result, Ca^{2+} appears to be the major ion that neutralizes the strong acids, followed by NH_4^+.

Table 5
Neutralization Factors (NF) of rainwater calculated at the three dry savannas sites.

Ecosystem	Station	pH	NF_{Ca}^{2+}	$NF_{NH_4}^{+}$	NF_{Mg}^{2+}
Dry Savannas	Agoufou (2004–2006)	6.28	1.12	0.87	0.57
	Banizoumbou (2006–2009)	5.75	1.32	0.87	0.36
	Katibougou (1997–2008)	5.54	1.29	1.08	0.25

In this study, the annual mean VWM of formate at Agoufou is 4.5 μeq l^{-1}, 3.9 μeq l^{-1} for acetate and 2.2 μeq l^{-1} for oxalate. At Banizoumbou formate also dominates with concentrations of 6.6 μeq l^{-1} and concentrations of 4.3 and 1.8 μeq l^{-1} for acetate and oxalate, respectively. Katibougou presents higher organic ions concentrations with 10.3 μeq l^{-1}, 5.2 and 1.8 μeq l^{-1} for formate, acetate and oxalate, respectively. The organic acidity measured during the monsoon season is significantly higher at Katibougou than at the two other sites. The origin of the high organic acidity at Katibougou can be explained by the presence of a denser vegetation at the site. Indeed, Galy-Lacaux and Modi (1998) as well Guenther et al. (2006) mainly attributed the organic acidity contribution in precipitation composition to the vegetation source of volatile organic carbon. It is hypothesized that the organic acidity measured in the precipitation is related to the vegetation cycle in the Sahel. Fig. 7 presents the values of leaf area index (LAI) from MODIS (Moderate resolution Imaging Spectroradiometer) satellite measurements. Mean LAI is given for three years 2004, 2005 and 2006 at a spatial resolution of 0.1° × 0.1° around each site, and illustrates the intensity of vegetation coverage and the seasonal cycle of vegetation growth. The vegetation at Katibougou, which is characterized by a Soudano-Sahel climate, is considerably more dense than at the two other sites of Agoufou and Banizoumbou. This vegetation produces biogenic volatile organic compounds (BVOC), as mentioned by Murphy et al. (2010), Reeves et al. (2010), Ferreira et al. (2010). In contrast, north of 12°N, no BVOC are emitted because of the low vegetation density as seen in Fig. 7. The precipitation is also an important parameter and annual rainfall

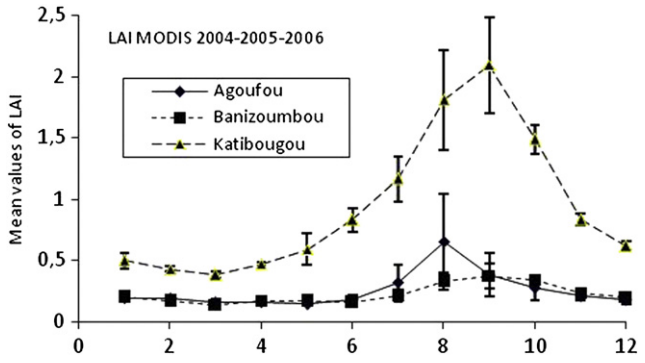

Fig. 7. Values of MODIS Leaf Area Index (LAI) giving the vegetation amplitudes for the years of survey common to the three sites 2004, 2005 and 2006.

measured at Katibougou is higher by a factor of two to three compared to the two other sites. In the Sahel, the seasonal dynamics of the vegetation is strongly determined by rainfall during the monsoon season (Tracol, 2004) (Figs. 8 and 9).

3.2. Interannual variability of VWM concentrations and wet deposition fluxes

Annual VWM concentrations and wet deposition fluxes of ionic species are calculated from all data. The results are analyzed to investigate the interannual variability of the major compounds at the three dry savanna sites. The variability can be evaluated as a function of the importance of the main sources and the precipitation intensity at all three sites.

From year to year, the dominant species are the same over the study period. Except for carbonates, the VWM mean concentrations of the four dominant ions in rainfall followed the order: $Ca^{2+} > NH_4^+ > Cl^- > NO_3^-$ at Agoufou and Banizoumbou, and $Ca^{2+} > NH_4^+ > NO_3^- > HCOO^-$ at Katibougou. The two most dominant ions, Ca^{2+} and NH_4^+, vary in concentration from 31.3 to 34.1 μeq l^{-1} and 22.8–26.3 μeq l^{-1}, respectively, at Agoufou; from 20.5 to 36.3 μeq l^{-1} and 12.9–26.5 μeq l^{-1} at Banizoumbou and from 16.4 to 27.0 μeq l^{-1} and 13.2–23.9 eq l^{-1}, respectively, at Katibougou. At Agoufou the sum of the species calculated for each year is: 204.9 μeq l^{-1} in 2004, 204.3 μeq l^{-1} in 2005, 206.1 μeq l^{-1} in 2006 (with corresponding mean for the three years is 205.2 μeq l^{-1}), thus indicating virtually no interannual variability. This is not the case at the two other sites. Over the 15-year study period at Banizoumbou, the annual sum of species or annual ionic charge varies from a minimum of 111.9 μeq l^{-1} in 1999 to a maximum of 162.2 μeq l^{-1} in 2008, with a mean of 143.9 μeq l^{-1}. At Katibougou, over the 12-year study period, the annual sum ranges from a minimum of 89.7 μeq l^{-1} in 1999 to a maximum of 148.1 μeq l^{-1} in 2000, with a mean of 120.2 μeq l^{-1}. The total ionic charge in precipitation measured at Banizoumbou and Katibougou shows the same variation in terms of magnitude and direction with a maximum variability of ±25%.

Na^+ and Cl^- ions are identified as major marine compounds, $nssCa^{2+}$, $nssMg^{2+}$ and $nssSO_4^{2-}$ represent the terrigenous contribution, NO_3^- and NH_4^+ the nitrogenous contribution, formate and acetate the vegetation source. VWM fluctuations for all groups of elements are very low at Agoufou with a variability of ±5%. They are relatively high at Banizoumbou and Katibougou with a similar variability for the terrigenous compounds (±25%) and ±15% to ±20% for the nitrogenous and vegetation groups, respectively. The global tendency of the total deposition for all chemical species follows the same trend as that observed for the chemical concentrations from year to year.

To investigate the wet deposition fluxes, it is important to note that fluxes are directly linked to the rainfall gradient between the three different dry savanna sites. Except for carbonates, the wet deposition flux of ammonium is highest. Recently, results of wet atmospheric nitrogen deposition over Africa have revealed that it is dominated by NH_4^+, which accounts for about 60% of the total N flux (IGAC, 2003). For nitrate deposition, fluxes of 0.66 kg N ha^{-1} yr^{-1}, 0.77 kg N ha^{-1} yr^{-1} and 1.16 kg N ha^{-1} yr^{-1} were measured at Agoufou, Banizoumbou and Katibougou, respectively. These values are within the range of those of the semi-arid savanna site of Louis Trichardt (0.8 kg N ha^{-1} yr^{-1}), the wet savanna site of Lamto (1.3 kg N ha^{-1} yr^{-1}) and the forest site of Zoetele (2.0 kg N ha^{-1} yr^{-1}). Agoufou presents higher wet deposition of the marine compounds Na^+, and Cl^- (Table 2). The organic ion wet deposition flux at Katibougou is the highest of all three sites while lower fluxes are found at Agoufou and Banizoumbou. H^+ deposition fluxes on the three sahelian sites are very low (0.002 kg ha^{-1} yr^{-1} to 0.024 kg ha^{-1} yr^{-1}). This gradient of acidity is correlated to the nitrate and the organic ions deposition gradients. Wet deposition fluxes of H^+ are more important in wet savannas (e.g. at Lamto 0.083 kg ha^{-1} yr^{-1}) and in equatorial forest (e.g. at Zoetele 0.243 kg ha^{-1} yr^{-1}). The above results highlight the importance of acidity sources in African wet savanna and forest ecosystems compared to Sahelian dry savannas.

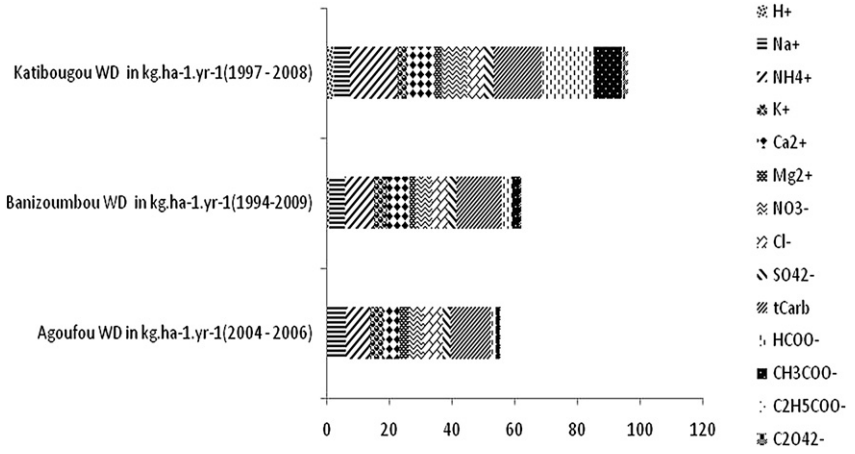

Fig. 8. Mean annual Wet Deposition WD (kg ha^{-1} yr^{-1}) fluxes over the three African dry savannas calculated from all database.

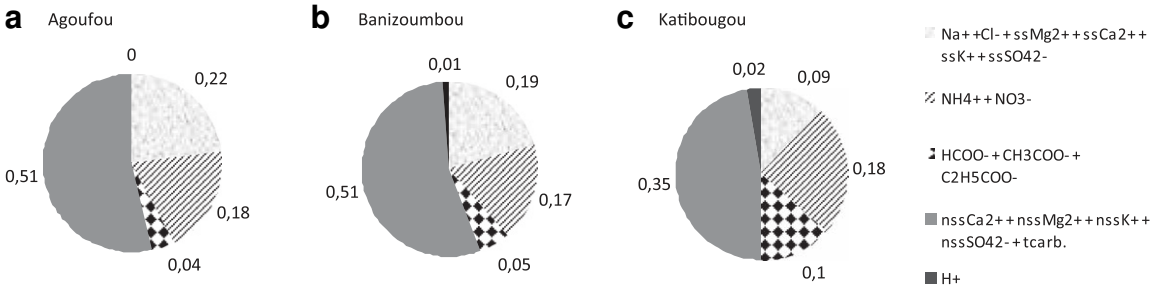

Fig. 9. (a–c) Estimation of the marine, the nitrogenous, the organic, the acidity and the terrigenous contribution to the rain chemical content measured at the three sahelian dry savannas.

4. Conclusions

We present the first long-term analysis of the chemical content of precipitation at three Sahelian dry savanna sites: Agoufou (2004–2006), Banizoumbou (1994–2009) and Katibougou (1997–2008). We compare the global precipitation characteristics for the three study sites to other African ecosystems (i.e. wet savanna and forest) and we present a synthesis and a calculation of the different atmospheric source contributions to the precipitation chemical content along the Sahelian transect.

The mean total chemical charge of precipitation for each site is calculated from the volume-weighted mean (VWM) precipitation concentrations (Table 2). Mean total ionic charges present significant negative gradient along the transect Agoufou, Banizoumbou, Katibougou (from 205 to 120 μeq l^{-1}). In contrast, a clear positive gradient of total wet deposition flux is measured, corresponding to the precipitation gradient.

For the years for which rainfall chemistry measurements are available at all three sites (i.e. 2004–2006), the analysis of the mean total chemical charge indicates similar values and the same negative concentration gradient from Agoufou to Katibougou. The site of Zoetele in the equatorial forest of Cameroon has been studied from 1998 to 2000 and the wet savanna site of Lamto in Ivory Coast from 1996 to 2002 (Sigha-Nkamdjou et al., 2003; Yoboué et al., 2005). The total chemistry charges at these sites are lower compared to the three dry savannas studied in this paper (100.2 and 86.6 μeq l^{-1} at Lamto and Zoetele, respectively). The relative global contribution of particles and gases in rainwater is determined using the concept proposed by Yoboué et al. (2005). Results indicate that at Agoufou and Banizoumbou the relative contribution of gases and particles to the chemical content of rain is 80% and 20% respectively. For Katibougou, particles and gases contribute 70% and 30% of the total, respectively. The particle contribution decreases from 70 to 80% in the Sahelian dry savannas, to 40% in wet savannas and 20% in forests. This is consistent with the high dust emissions from the Sahel, and progressive washout of particles along the transect: dry savannas–wet savanna–equatorial forest.

This study gives a first estimation of the potential contribution of different atmospheric sources identified in the precipitation composition analysis for three sahelian savannas sites. This estimation is done according to groups of sources presented in Section 3.1 and calculated from the mean total charge of each ecosystem for the study period. The main conclusions are:

- terrigenous species are the most abundant compounds, contributing between 46 and 53% of the total;
- the nitrogenous contribution at the three sites is relatively high and accounts for between 19 and 25% of the total;
- the marine contribution is lower, contributing between 13 and 23% of the total;
- finally, organic acidity contibutes between 5 and 14% of the total at each site.

Terrigenous and marine contributions present a negative gradient whereas there is a positive gradient in nitrogenous and organic contributions along the Sahelian transect defined by Agoufou–Banizoumbou–Katibougou. The average rainwater pH decreases from Agoufou (6.28), to Banizoumbou (5.75) and to Katibougou (5.54). The pH evolution along this latitudinal gradient is certainly correlated to the negative gradient of the major terrigenous species concentrations along the transect which creates a gradient of potential neutralizing agents for the acidity of precipitation. In the near future, a study of total deposition from the long-term series will allow the analysis of the temporal trends of atmospheric deposition including both wet and dry processes, linked to climate variability and anthropogenic activities in semi-arid African ecosystems.

Acknowledgments

This work is part of the IDAF (IGAC/DEBITS/AFRICA) project. It has been supported by the "Institut National des Sciences de L'Univers" within the framework of the ORE programme (Observatoire de Recherche en Environnement). Based upon a French initiative, the AMMA project is now supported by an international scientific group including a large number of agencies, especially from France, the United Kingdom, the United States and Africa. It has been the beneficiary of a major financial contribution from the European Community's Sixth Framework Research Programme (FP6), see www.amma-internatio-nal.org<http://-www.amma-international.org>. The authors thank A.I. Modi from the University of Niamey, who started the IDAF Banizoumbou site in Niger (in 1994) and the IRD (Institut de Recherche pour le Developpement) in Niamey for logistical support. We thank Drissa Diallo from the University of Bamako who initiated the involvement of the meteorological station of Katibougou at the IPR (Institut Polytechnique Rural) in 1994 with the IRD. We thank Robert Rosset (Laboratoire d'Aérologie, Toulouse) for back trajectory analysis calculations and Pierre Hiernaux (Geoscience Environnement Toulouse) for his personal contribution to the nitrogen section. Finally, we are also grateful to Fiona Tummon for editing the manuscript and all the field technicians of the IDAF network: Alfari Zakou for Banizoumbou in Niger, Hama Maïga for Agoufou in Mali and Kanoute Cheick for Katibougou in Mali.

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