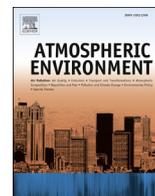




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Precipitation chemistry and wet deposition in a remote wet savanna site in West Africa: Djougou (Benin)



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HIGHLIGHTS

- We provide a background study of the rain chemistry of a rural wet savanna site.
- The frequency distribution of pH of rainwater at Djougou (Benin) is computed.
- We estimate the nitrogenous compound emitted monthly by different sources.
- We compute the distribution of monthly means of the wet deposition of major ions.
- We estimate the sources contributions to the rain chemical content in West Africa.

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ABSTRACT

In the framework of the IDAF (IGAC/DEBITS/Africa) international program, this study aims to study the chemical composition of precipitation and associated wet deposition at the rural site of Djougou in Benin, representative of a West and Central African wet savanna. Five hundred and thirty rainfall samples were collected at Djougou, Benin, from July 2005 to December 2009 to provide a unique database. The chemical composition of precipitation was analyzed for inorganic (Ca^{2+} , Mg^{2+} , Na^+ , NH_4^+ , K^+ , NO_3^- , Cl^- , SO_4^{2-}) and organic (HCOO^- , CH_3COO^- , $\text{C}_2\text{H}_5\text{COO}^-$, $\text{C}_2\text{O}_4^{2-}$) ions, using ion chromatography. The 530 collected rain events represent a total of 5706.1 mm of rainfall compared to the measured pluviometry 6138.9 mm, indicating that the collection efficiency is about 93%. The order of total annual loading rates for soluble cations is $\text{NH}_4^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$. For soluble anions the order of loading is carbonates $> \text{HCOO}^- > \text{NO}_3^- > \text{CH}_3\text{COO}^- > \text{SO}_4^{2-} > \text{Cl}^- > \text{C}_2\text{O}_4^{2-} > \text{C}_2\text{H}_5\text{COO}^-$. In the wet savanna of Djougou, 86% of the measured pH values range between 4.7 and 5.7 with a median pH of 5.19, corresponding to a VWM (Volume Weighed Mean) H^+ concentration of $6.46 \mu\text{eq} \cdot \text{L}^{-1}$. This acidity results from a mixture of mineral and organic acids. The annual sea salt contribution was computed for K^+ , Mg^{2+} , Ca^{2+} and SO_4^{2-} and represents 4.2% of K^+ , 41% of Mg^{2+} , 1.3% of Ca^{2+} , and 7.4% of SO_4^{2-} . These results show that K^+ , Ca^{2+} , SO_4^{2-} , and Mg^{2+} were mainly of non-marine origin. The marine contribution is estimated at 9%. The results of the chemical composition of rainwater of Djougou indicates that, except for the carbonates, ammonium has the highest VWM concentration ($14.3 \mu\text{eq} \cdot \text{L}^{-1}$) and nitrate concentration is $8.2 \mu\text{eq} \cdot \text{L}^{-1}$. The distribution of monthly VWM concentration for all ions is computed and shows the highest values during the dry season, comparing to the wet season. Identified nitrogenous compound sources (NO_x and NH_3) are domestic animals, natural emissions from savanna soils, biomass burning and biofuel combustions. The second highest contribution is the calcium ion ($13.3 \mu\text{eq} \cdot \text{L}^{-1}$), characteristic of dust aerosols from terrigenous sources, Calcium contributes up to 46% of the precipitation chemistry in Djougou. Finally, these results are compared to those obtained for other selected African sites representative of other main natural ecosystems: dry savanna and forest. The study of the African ecosystem transect indicates a pH gradient with more acidic pH in the forested ecosystem. Nitrogenous contribution

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to the chemical composition of rain in Lamto, wet savanna, (24%) is equivalent to the one estimated in Djougou (24%). The last contribution concerns organic acidity, which represents 7% of total ionic content of precipitation at Djougou. The relative particulate contribution PC and the relative gaseous contribution GC are calculated using the mean chemical composition measured in Djougou for the studied period. The comparison with other African sites gives 40% and 43% PC in wet savannas of Lamto (Côte d'Ivoire) and Djougou (Benin) respectively, 20% PC in the equatorial forest of Zoetele (Cameroon) and 80% PC in dry savanna of Banizoumbou (Niger). The results shown here indicate the existence of a North-South gradients of organic, marine, terrigenous and nitrogenous contributions along the transect in West and Central Africa.

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1. Introduction

Atmosphere–biosphere interactions are important to understand the biogeochemical cycles of atmospheric species that modulate the atmospheric composition. Anthropogenic emissions and climate change play important roles in modifying atmospheric processes. In this context, wet and dry-deposition of chemical species on the earth's surface play a significant role in controlling the concentration of gases and aerosols in the atmosphere. The chemical composition of atmospheric deposition is the product of several interacting atmospheric physical and chemical processes such as: emission and source strengths; transport processes and dynamics of the atmosphere; atmospheric chemical reactions and removal processes among others. Future changes in atmospheric composition require information on past and present atmospheric composition. In a special issue of the Atmospheric Environment journal, three overview papers dealing with atmospheric composition changes emphasized that trace atmospheric constituents are changing the earth's climate (IPCC, 2007), the global biodiversity (Millennium Ecosystem Assessment, 2005) and the biogeochemical cycle of key atmospheric components such as nitrogen, carbon, and sulfur (Laj et al., 2009; Monks et al., 2009; Fowler et al., 2009). Moreover, these papers focused on the need to optimize observing systems coordinated from regional to global scale to analyze and predict future atmospheric composition. The study of deposition processes and their quantification thus allows for identifying the spatial and temporal evolution of atmospheric chemistry and is an important way for distinguishing between natural and anthropogenic influences. In regions where biogeochemical cycles are disturbed by human activities, atmospheric deposition can either be a source of toxic substances or a source of nutrients for the ecosystems. Having an understanding of chemical deposition fluxes is therefore an essential aspect of a global interdisciplinary approach in order to develop a predictive capacity for the functioning ecosystems and determining the impacts on biogeochemical cycles (Brimblecombe et al., 2007; Bobbink et al., 2010; Vitousek et al., 1997; Whelpdale and Kaiser, 1996; Pienaar, 2005).

Since the last three decades rainwater chemistry is subject of intensive research in many countries and in different ecosystems. In 1995, the first WMO global precipitation chemistry assessment provided a critical review of worldwide acidic atmospheric deposition (Whelpdale et al., 1996). In the framework of WMO/GAW (World Meteorological Organization/Global Atmospheric Watch), a recent assessment has presented a global overview of worldwide precipitation chemistry and deposition by using quality assured measurements to complement and validate available global models (Vet et al., 2014). The assessment presents precipitation chemistry and deposition measurements obtained from several regional and 22 national monitoring networks for North America, South America, Europe, Africa, Asia Oceania, and the oceans. This report demonstrates that deposition data computed from quality assured

measurements were limited in many regions, especially in the tropics. The IDAF project has contributed to this work and has been recognized by WMO/GAW to provide a unique deposition database for some African sites. DEBITS (Deposition of Biogeochemically Trace species), a task of IGAC (International Global Atmospheric Chemistry) since 2005, represents one of these regional networks dedicated to study atmospheric deposition in the tropics (Pienaar, 2005). In the framework of DEBITS, the IDAF (IGAC/DEBITS/AFRICA) project started in 1994 and aims to study dry and wet deposition fluxes in Africa. The goal of IDAF program is to provide a long-term measuring network to study atmospheric composition and wet and dry atmospheric processes and fluxes. During the Long Observation Phase of the AMMA (African Monsoon Multidisciplinary Analysis) program, IDAF took an active part in investigating rainwater chemistry and in determining aerosols and gas concentrations in the atmosphere over West/Central Africa (AMMA/LOP, Lebel et al., 2009; Mougouin et al., 2009; Mari et al., 2010).

The measuring network of the IDAF project includes 10 monitoring sites covering three types of ecosystems over West and Central Africa: dry Savanna (Banizoumbou in Niger, Katibougou and Agoufou in Mali, Louis – Trichardt, Amersfoort and Cape Point in South Africa), wet savanna (Lamto in Ivory Coast and Djougou in Benin) and equatorial forest (Zoetele in Cameroon and Bomassa in Congo).

Among studies performed in Africa, the works on precipitation chemistry done by Lacaux et al., 1992; Sigha-Nkamdjou et al., 2003; Yoboué et al., 2005; Galy-Lacaux et al., 2009, Laouali et al., 2012, Mphepya et al., 2004, 2006 represent some synthesis papers on wet deposition fluxes representative at the scale of main African ecosystems. In the present investigation, we show wet only sampling and analysis of a 4 year database of rainwater chemistry, at a regional representative wet savanna site in the area of Djougou in Benin. This work complements the previous work of Yoboué et al., 2005 in the wet savanna of Lamto in Côte d'Ivoire.

The objectives of this work are (1) to provide a background study of rainwater chemistry in Benin with samples collected from 2005 to 2009, (2) to provide a better understanding of the source types that contribute to the precipitation content at the scale of the year and the season, (3) to analyze the inter-annual variability of rainwater composition and associated wet deposition fluxes for all the different ionic species. Finally, results are compared to the results obtained for other African sites of the IDAF project representative of wet, dry savannas and forest. Results presented in this paper allow establishing a baseline record against which possible changes in rainwater chemistry due to the changing of emissions. This study should be considered as a new contribution to answer to the WMO/GAW recommendations that emphasize the scarcity of deposition measurements at the scale of the African continent where a strong population growth, an industrial development or agriculture intensification are observed.

2. Study area

Djougou is a village situated in Northwest Benin. The IDAF site is located in Nangatchori (9°65'N, 1°74'E) near Djougou, approximately 460 km from Cotonou. The average altitude is 430 m. Nangatchori belongs to the wet savanna region of Benin (Fig. 1). Fig. 1 shows the 10 IDAF sites, operating in 2014, on a vegetation map of Africa (Mayaux et al., 2004).

The climate of Djougou is sub - Sudanese with a mean annual rainfall of 1190 mm, measured over 50 years (Le Barbe et al., 2002; Le Lay and Galle, 2005). It is characterized by a wet season from April to October, and a dry season from November to March. These seasons are schematically determined by the position of the Intertropical Convergence Zone (ITCZ), the surface formed by the convergence of Saharan and oceanic air masses. The wet season starts when the position of the Intertropical Front reaches rather high latitudes. It allows the south air masses, loaded with moisture of the Atlantic Ocean, to move northward the Saharan hot and dry air masses. This moisture transport is a key factor for the monsoon system in West Africa (Lebel et al., 2009). The daily mean temperatures vary from 25 °C in August to 31 °C in March. Daily amplitude of temperatures achieves 20 °C during the Harmattan period (January) with minimum values from 16 °C to 19 °C to maxima are about 36 °C–39 °C. In August, the daily amplitude of temperatures is less marked with an order of magnitude around 5 °C.

Approximately 70% of the population of this region dedicates itself to agricultural activities (<http://www.gouv.bj/>). The main cultures are yam, corn, sorghum, mil, groundnut, cowpea and cotton. The relief is little bumped and represents a plateau strewn with some hills by place. It is also necessary to notify that this region is just in the South of the Atakora mountain, thus explaining that the rainfall amount is higher compared to more Eastern zones in Benin.

Vegetation is composed of a mosaic of dry forests and savannah, with dense and tall herbaceous strata, mainly composed of perennial grasses, and more or less dense woody strata. In the Global Land Cover Classification, our site is classified as deciduous open woodland (Mayaux et al., 2004; Adon et al., 2010). Ninety-five percent of the area of the Sudanian site is on tropical ferruginous soil (Seghieri et al., 2009; Kamagaté et al., 2007). Most of the landscape is undergoing hydric erosion.

We assume that the IDAF site of Djougou is rural and representative of a remote site of African wet savanna.

3. Material and methods

3.1. Rain sampling

Rainwater samples at Djougou were collected using an automatic precipitation collector designed for the IDAF network. The principle of functioning is as follows:

- The first rain droplets order the rain detector to open the lid of the collector
- To collect rainwater, polyethylene single-use bags are used. In order to avoid any contamination by aerosols and insects, the rain collector remains closed before and after the rain.
- Rain samples are immediately collected by a local observer after the rain event.
- Samples are stored in 50 ml Greiner tubes of 50 ml in a freezer –18 °C (WMO-GAW report n°160, 2004).
- After collection, samples are sent for analysis to the Laboratoire d'Aérodologie in Toulouse in the strict respect of the cold chain, where they are stored in a freezer until analysis.

During all the sampling period, an automatic pluviometer has registered all rain events with a time resolution from 5 min to 1 h at the Djougou site. In addition, during the long-term observation period of the AMMA program (2005–2007) 3 other rain gauges of the same type were settled at the site in the framework of a hydrological project (Depraetere et al., 2009). All equipments were in good agreement and provided rain event depth with a maximum uncertainty of 1/10 mm.

Table 1 shows the seasonal and annual precipitation (mm) at Djougou site for the 2005–2009 period. Annual precipitation varies from a minimum of 1143.5 mm in 2006 to a maximum of 1537.2 mm in 2009. Le Barbé et al., 2002 and Le Lay and Galle, 2005 have measured a mean annual rainfall of 1190 mm (over 50 years) at Djougou in the framework of the upper Ouémé catchment study. In the present study, the mean annual precipitation measured at Djougou from 2005 to 2009 exceeds this value with a mean annual value P_t of 1338.7 mm. The dry season, defined from November to March, represents $4 \pm 3\%$ (23.2–126 mm) of the total annual precipitation. The wet season, from April to October, represents $96 \pm 3\%$ (1088.3–1499.7 mm) of the total annual precipitation.

Table 2 presents the annual total precipitation (P_t) in mm, the percent total precipitation (%TP) in percent and the interannual

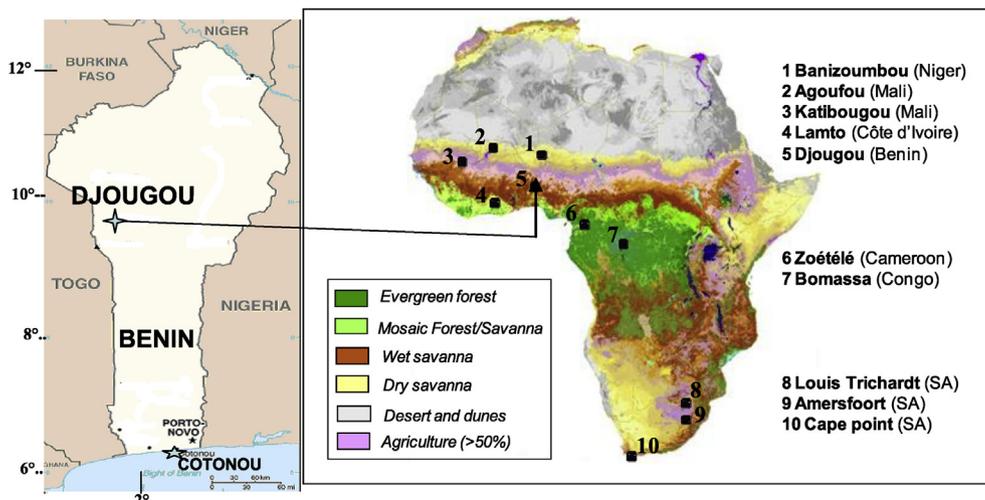


Fig. 1. Situation of the IDAF Djougou site, vegetation and localization map of the 10 measurement stations of the IDAF network.

4. Results and discussions

4.1. Annual volume – weighted mean precipitation concentrations and wet deposition

The annual volume-weighted mean concentrations (VWM) of ionic constituents in Djougou rainwater have been calculated using:

$$\text{VMW} (\mu\text{eq}\cdot\text{L}^{-1}) = \frac{\sum_{i=1}^N C_i P_i}{\sum_{i=1}^N P_i} \quad (4)$$

Where, C_i is the ionic concentration for each element in $\mu\text{eq}\cdot\text{L}^{-1}$, P_i the precipitation amount for each rainy event in mm, and N the total number of rain events. Concentrations of H^+ were calculated from measured pH values. The annual wet deposition (WD) expressed in $\text{kg}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$ is calculated by multiplying the VWM in $\text{mg}\cdot\text{L}^{-1}$ concentrations by the annual average rainfall amount (Pt in mm) according to equation (5).

$$\text{WD} (\text{kg}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}) = \text{VWM} (\text{mg}\cdot\text{L}^{-1}) * \frac{P_t}{100} \quad (5)$$

VWM concentration ($\mu\text{eq}\cdot\text{L}^{-1}$) and annual WD in precipitation over the five-year period (2005–2009) at the wet savanna site of Djougou are displayed in Table 3. In 2005, samples have been collected since July (after the beginning of the rainy season, May and June have not been sampled). Table 2 indicates that collected rains represent only 53% of the 2005 pluviometry. For this reason, the year 2005 is excluded to calculate the mean characteristics of the chemical composition of rain over the study period. Table 3 presents the mean VWM and WD with associated standard deviations during the 2006–2009 period. As a matter of fact, collected samples in July, August September and October 2005 have a very good representativity with an efficiency of collection comprised between 79 and 99% for these four months of the wet season.

The most important ions in Djougou rainwater samples are carbonates ions, NH_4^+ and Ca^{2+} . NH_4^+ and Ca^{2+} VWM

concentrations represent 66% of the total cations VWM concentrations. The carbonates and HCOO^- VWM concentrations represent 53.6% of the total anions VWM concentrations. Afterward, in decreasing order, we find NO_3^- , HCOO^- , CH_3COO^- , H^+ , SO_4^{2-} , Na^+ , Cl^- , Mg^{2+} , K^+ , and $\text{C}_2\text{H}_5\text{COO}^-$. The concentration of cations follows a general pattern $\text{NH}_4^+ > \text{Ca}^{2+} > \text{Na}^+ > \text{Mg}^{2+} > \text{K}^+$, while concentration of anions follows a general pattern Carbonates $> \text{HCOO}^- > \text{NO}_3^- > \text{CH}_3\text{COO}^- > \text{SO}_4^{2-} > \text{Cl}^- > \text{C}_2\text{O}_4^{2-} > \text{C}_2\text{H}_5\text{COO}^-$.

4.1.1. Marine and terrigenous contributions

In order to identify the origin of elements in rainwater, sea salt contribution and corresponding enrichment factors have been calculated according to the method suggested by many authors (Keene et al., 1986; Chao and Wong, 2002; Quiterio et al., 2004) using equations (6) and (7).

Enrichment factors (EF) were calculated using equation (6).

$$(\text{EF})_x = \left[\frac{X/\text{Na}^+}{\text{rain}} \right] / \left[\frac{X/\text{Na}^+}{\text{seawater}} \right] \quad (6)$$

where, EF_x is the enrichment factor of the species X, Na^+ is used as the marine reference, $(X/\text{Na}^+)_{\text{rain}}$ is the ratio of the X ion amount to Na^+ in rain, and $(X/\text{Na}^+)_{\text{seawater}}$ is the ratio of species X to Na^+ in seawater. Reference values $[X/\text{Na}]_{\text{seawater}}$ for the different ions are taken from Keene et al. (1986) to compute EF for marine contribution. EF for marine contributions are calculated from mean VWM of K^+ , Cl^- , Mg^{2+} , SO_4^{2-} , Ca^{2+} (Table 3). The sea-salt fraction (SSF) for some selected ionic components X of rainwater is calculated considering the ionic proportion to Na^+ in seawater and suggesting that Na^+ concentration represents the marine reference using equation (7) (Keene et al., 1986; Singh and Mondal, 2008; Pauliquevis et al., 2012).

$$[X]_{\text{ss}} = \left[\frac{X/\text{Na}^+}{\text{seawater}} \right] \times [\text{Na}^+]_{\text{rainwater}} \quad (7)$$

In addition, a correlation analysis between the different ionic species has been performed using the Spearman Method for the 476 rain events in agreement with the WMO criteria (Table 4). High

Table 3
Annual Volume Weighted Mean (VWM) concentrations in $\mu\text{eq}\cdot\text{L}^{-1}$ and Wet Deposition (WD) expressed in $\text{kg}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$ at Djougou during the period 2005–2009.

	VWM		WD		VWM		WD		VWM		WD		VWM		WD	
	2005	2006	2006	2007	2007	2008	2008	2009	2009	Mean (06–09)	Mean (06–09)	σ_{VWM}	σ_{WD}	Mean (06–09)	σ_{WD}	
H^+	9.87	0.14	8.92	0.1		4.54	0.06	7.01	0.11	6.46	± 2.19	0.09	± 0.02			
Na^+	4.8	1.54	5.5	1.44	3.4	0.98	4.2	1.32	2.15	3.8	± 1.4	1.13	± 0.31			
NH_4^+	8.4	2.11	17.3	3.58	12.2	2.75	13.4	3.31	14.3	3.97	± 2.2	3.40	± 0.51			
N-NH_4^+		1.64		2.78		2.14		2.57		3.09		2.64	± 0.40			
K^+	1.8	0.96	2.4	1.10	1.9	0.92	2.2	1.16	1.5	0.92	± 0.4	1.02	± 0.12			
Ca^{2+}	9.6	2.68	13.8	3.15	13.9	3.47	14.2	3.89	11.5	3.53	± 1.2	3.51	± 0.30			
Mg^{2+}	1.2	0.21	2.1	0.30	2.0	0.30	2.5	0.42	1.8	0.33	± 0.3	0.34	± 0.06			
NO_3^-	6.1	5.27	8.0	5.65	8.0	6.21	7.9	6.73	9.0	8.6	± 0.5	6.8	± 1.28			
N-NO_3^-		0.95		1.01		1.11		1.21		1.54		1.22	± 0.23			
Cl^-	4.2	2.06	3.7	1.52	3.7	1.65	3.8	1.86	2.3	1.27	± 0.7	1.58	± 0.25			
SO_4^{2-}	6.9	4.63	7.3	4.04	5.9	3.53	6.1	4.03	5.6	4.13	± 0.8	3.93	± 0.27			
S-SO_4^{2-}		1.54		1.35		1.18		1.34		1.38		1.31	± 0.09			
HCOO^- ($\text{HCOO}^{-\text{a}}$)	14.2 (13.4)	8.91	9.5 (9.0)	4.87			5.0 (4.3)	3.09	11.3 (10.7)	7.81	± 3.2	5.27	± 1.95			
CH_3COO^- ($\text{CH}_3\text{COO}^{-\text{a}}$)			8.8 (6.1)	5.93			3.7 (3.0)	3.04	7.7 (5.4)	7.01	± 2.6	5.33	± 3.15			
$\text{C}_2\text{H}_5\text{COO}^-$ ($\text{C}_2\text{H}_5\text{COO}^{-\text{a}}$)			0.4 (0.3)	0.37			0.3 (0.2)	0.32	0.5 (0.3)	0.53	± 0.08	0.41	± 0.11			
$\text{C}_2\text{O}_4^{2-}$ ($\text{C}_2\text{O}_4^{2-\text{a}}$)	0.8 (0.7)	0.51	1.3 (1.2)	0.81			1.1 (0.9)	0.68	1.4 (1.3)	0.87	± 0.2	0.59	± 0.10			
Carbonates			13.2	9.20	27.5	20.93	25.8	21.63	21.2	19.89	± 6.4	17.91	± 5.85			
pH	5.01		5.05				5.34		5.15			5.19 ^b				
Pt in mm	1393.7 (838.9) ^c		1143.5		1246.8		1372.4		1537.2			1325 ^d				

σ_{VWM} and σ_{WD} are the standard deviation of VWM and WD respectively.

^a In brackets dissolved part for organic acids.

^b Median pH.

^c Total precipitation during collection period in yr. 2005.

^d Mean Annual Precipitation.

Table 4

Correlation coefficients between ions in rainwater (2005–2009). The “Spearman” method was used with a 1% confidence level.

Variables	H ⁺	Na ⁺	NH ₄ ⁺	K ⁺	Ca ²⁺	Mg ²⁺	NO ₃ ⁻	Cl ⁻	SO ₄ ²⁻	HCOO ⁻	CH ₃ COO ⁻	C ₂ H ₅ COO ⁻	C ₂ O ₄ ²⁻
H ⁺	1												
Na ⁺	-0.20	1											
NH ₄ ⁺	-0.03	0.73	1										
K ⁺	-0.17	0.89	0.79	1									
Ca ²⁺	-0.39	0.73	0.73	0.70	1								
Mg ²⁺	-0.33	0.84	0.81	0.82	0.93	1							
NO ₃ ⁻	-0.03	0.68	0.85	0.71	0.75	0.81	1						
Cl ⁻	-0.24	0.93	0.74	0.87	0.75	0.83	0.74	1					
SO ₄ ²⁻	-0.05	0.73	0.82	0.70	0.77	0.79	0.77	0.72	1				
HCOO ⁻	0.42	0.40	0.60	0.40	0.43	0.43	0.52	0.32	0.54	1			
CH ₃ COO ⁻	0.31	0.38	0.63	0.42	0.38	0.41	0.51	0.32	0.49	0.80	1		
C ₂ H ₅ COO ⁻	0.24	0.32	0.55	0.37	0.33	0.36	0.45	0.28	0.42	0.69	0.93	1	
C ₂ O ₄ ²⁻	0.24	0.51	0.74	0.55	0.49	0.55	0.66	0.49	0.65	0.81	0.78	0.71	1

correlation could indicate that concerned ions have the same origins or participate in a same chemical reaction. Results of sea salt fractions and enrichment factors for K⁺, Cl⁻, Mg²⁺, SO₄²⁻, Ca²⁺ ions are given in Table 5. The SSF for K⁺, Mg²⁺, Ca²⁺ and SO₄²⁻ are estimated to be around 4.2%, 41%, 1.3% and 7.4% respectively. EF_{marine} for Cl⁻ is lower than 1 showing that Cl⁻ was almost 100% marine assuming that all the sodium is from marine source (Cao et al., 2009). The high correlation between Na⁺ and Cl⁻ (r = 0.93) suggests that both have mainly a marine origin. K⁺ and Mg²⁺ are highly correlated with Na⁺ (r = 0.89, and r = 0.84, respectively) and with Cl⁻ (r = 0.87, and r = 0.83, respectively) showing that they also have a marine origin. K⁺, Mg²⁺ and SO₄²⁻ are also correlated with Ca²⁺ (r = 0.70, r = 0.93, r = 0.77 respectively) emphasizing the contribution of the crustal source. Ouafo et al., (personal communication 2014) have recently studied the chemical composition of the aerosols collected at Djougou from 2005 to 2009. This work indicates that during the wet season, the Particulate Organic Matter is predominant, followed by dust and Elemental Carbon in both sizes (PM_{2.5} and PM₁₀). These results point out the importance of biofuel combustion used for cooking, and biogenic emissions during the wet season. This combustion source certainly explains one part of the potassium signature measured in rains. The positive relationship between K⁺, Mg²⁺, SO₄²⁻ and Ca²⁺ confirms the importance of particles coming from the desert and semiarid regions in the chemical composition of rainfall. The North African desert areas (Sahel and Sahara) are probably the most important mineral aerosol source (Kaufman et al., 2005; Marticorena et al., 2010). Due to the partial dissolution of soil dust terrigenous components, rain in the wet savanna of Benin is loaded with dissolved calcium and carbonates (calcite), which may account for a large part of the ionic concentrations of rainwater. In addition to calcite, dolomite, and gypsum, the dissolution of other key minerals such as illite, smectite, palygorskite that compose African dusts, explains the enrichment of Mg²⁺, SO₄²⁻ and K⁺ (Avila et al., 1997). This result is similar to that obtained in other African ecosystems and regions of the world such as in Asia (Löye-Pilot et al., 1986; Sigha-Nkamdjou et al., 2003; Galy-Lacaux et al., 2009; Laouali et al., 2012; Kandler

Table 5Comparison of sea water ratios with rain water components at Djougou. EF_{Marine} = Enrichment Factor, SSF% = Sea-Salt Fraction NSSF = Non Sea-Salt Fraction.

	Cl ⁻ /Na ⁺	SO ₄ ²⁻ /Na ⁺	K ⁺ /Na ⁺	Ca ²⁺ /Na ⁺	Mg ²⁺ /Na ⁺
Sea water ratios (Keene et al., 1986)	1.167	0.121	0.022	0.044	0.227
Ratios in rain	0.896	1.638	0.527	3.449	0.554
EF _{MARINE}	0.8	13.5	24.2	79.7	2.4
SSF (%)	100%	7.4%	4.2%	1.3%	41%
NSSF (%)	0	92.6%	95.8%	98.7%	59%

and Schutz, 2007; Celle-Jeanton et al., 2009; Desboeufs et al., 2010; Kulshrestha et al., 2009).

4.1.2. Nitrogenous compounds

The chemical composition of rainwater at Djougou indicates that nitrogenous compound concentrations represent an important contribution, about 23% of the total ionic charge. Ammonium has the highest VWM concentration with $14.3 \pm 2.2 \mu\text{eq}\cdot\text{L}^{-1}$. Nitrate concentration is $8.2 \pm 0.5 \mu\text{eq}\cdot\text{L}^{-1}$ (Table 3). These results are in accordance with data obtained at the wet savanna site of Lamto where NH₄⁺ and NO₃⁻ are $16.8 \mu\text{eq}\cdot\text{L}^{-1}$ and $8.9 \mu\text{eq}\cdot\text{L}^{-1}$, respectively (Yoboué et al., 2005). NH₄⁺ is also the main nitrogenous ion found in the rain samples at the three dry savannas sites: Agoufou ($25.2 \mu\text{eq}\cdot\text{L}^{-1}$), Banizoumbou ($17.9 \mu\text{eq}\cdot\text{L}^{-1}$), Katibougou ($19.1 \mu\text{eq}\cdot\text{L}^{-1}$) (Laouali et al., 2012). Note that atmospheric monthly NH₃ surface concentrations (3.9 ± 1.2 ppb) measured using passive sampling (Adon et al., 2010) are also higher than NO₂ (1.1 ± 0.1 ppb) at the Djougou site.

Sigha-Nkamdjou et al., 2003 and Yoboué et al., 2005 suggested that ammonium content in precipitation results from the inclusion of gaseous ammonia and particles contained in clouds and rainwater. These inclusions are due to the prevailing emission sources around the studied site. Major sources of NH₃ include bacterial decomposition of urea in animal excreta and emission by natural or fertilized soils (Schlesinger and Hartley, 1992; Galy-Lacaux and Modi, 1998). Biomass burning during the dry season, domestic combustions and incomplete traffic sources all along the year are the other principal sources of NH₃ (Delmas et al., 1995; Brocard et al., 1996; Galy-Lacaux and Modi, 1998; Laouali et al., 2012). To explain nitrate and ammonium concentration in rains, we assume that nitrogenous gaseous compounds such as NO_x and NH₃ are related to main sources such as biomass burning, biogenic NO emissions from soils, NH₃ volatilization and biofuel and fossil fuel combustions (Junker and Liousse, 2008; Delon et al., 2012; Galy-Lacaux and Delon, 2014; Liousse et al., 2014).

Figure 2 presents the relative contributions of each source, i.e. Biogenic NO, biofuel and incomplete traffic (BF), biomass burning (BB) and volatilization processes (Vol.). Fluxes are calculated at a spatial resolution of 5° by 5° around the Djougou site from 2002 to 2007 with a monthly resolution. These calculations use both satellite data and simulation results, following the methodology developed by Delon et al. (2012), and by Galy-Lacaux and Delon, 2014. Biogenic NO emissions from soils have been simulated using a parameterization developed in Delon et al., 2007. The contribution of domestic fires and incomplete traffic to NO_x and NH₃ emissions is estimated according to the work of Junker and Liousse, 2008 and Liousse et al. (2014) based on African fuel

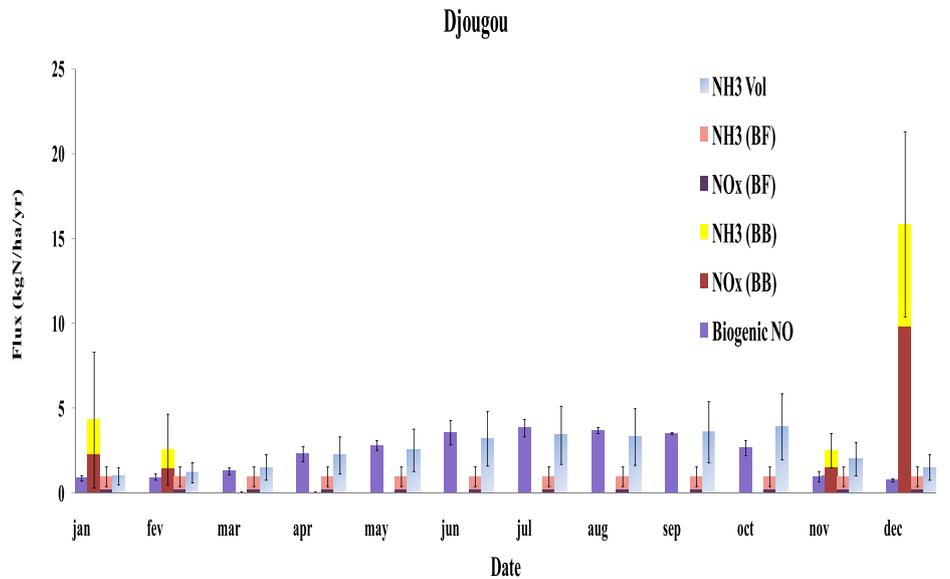


Fig. 2. Mean monthly distribution of nitrogen compounds emissions and associated uncertainties in $\text{kg N} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$. BB = Biomass Burning, vol = volatilization, BF = Bio Fuel, for the Djougou site (2002–2007).

consumption and specific emission factors. The contribution of biomass burning fires is estimated according to Lioussé et al., 2010, based on L3JRC burnt area satellite product, Global Land Cover (GLC) vegetation map and data on burning efficiencies and emission factors. No industrial sources are found in the area of Djougou. NH_3 volatilization is computed from the N input by organic fertilization. Synthetic fertilization in West Africa is considered as negligible (Delon et al., 2012). N input by organic fertilization is the product of N release by livestock (in $\text{kgN} \cdot \text{animal}^{-1} \cdot \text{yr}^{-1}$), by the animal population in Benin (Food and Agriculture Organization, FAO, (2009) (<http://kids.fao.org/glipha>)). For Djougou, this N input is estimated to be $8 \text{ kgN} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$. 30% of this value volatilized as NH_3 . The remaining 70% N stay in the soil and contribute to NO biogenic emission (Delon et al., 2010; Delon et al., 2012; Galy-Lacaux and Delon, 2014). Uncertainties in the estimation of NH_3 volatilization is 50%, as described in Galy-Lacaux and Delon, 2014 and reaches 60% for NH_3 and NO_x biofuel emissions.

As a result, we can notice that NO in the wet savanna of Djougou is mainly produced by soil emission and biomass burning (Fig. 2). NO is oxidized into NO_2 and HNO_3 by photochemical reactions. HNO_3 is further scavenged by clouds. Simulations of biogenic NO soil emission at the Djougou site during the 2002–2007 period shows mean rates of $3.2 \pm 0.6 \text{ kgN} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$ during the wet season and $2.3 \pm 1.2 \text{ kgN} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$ as yearly mean (Fig. 2). Biogenic NO fluxes from soils strongly depend on soil humidity and are lower during the dry season, when microbial activity at the origin of N formation in the soil is less active (Yienger and Levy, 1995; Meixner et al., 1997; Hudman et al., 2012). NH_3 is mainly produced by volatilization processes, biofuel and biomass burning at the Djougou site.

In terms of nitrogenous particulate content in precipitation, gaseous ammonia is transformed into particulate ammonium in the atmosphere and is associated with various anions to form $(\text{NH}_4)_2\text{SO}_4$, NH_4Cl , and NH_4NO_3 . NH_4NO_3 is formed by the reaction of HNO_3 with NH_3 on moist soil surfaces, partly because of the formation of un-dissociated NH_4NO_3 when relative humidity is more than 62% (Singh and Mondal 2008; Saxena et al., 1996). Nitrate in rainwater might be the result of homogenous and heterogeneous gas-phase transformations of NO_x to HNO_3 ,

followed by reaction with NH_3 to form NH_4NO_3 . Dominance of NH_4NO_3 has been reported in rainwater by many authors and reflects the influence of biodegradation and agricultural activities. In this study, correlations between NH_4^+ and SO_4^{2-} ($r = 0.82$), NH_4^+ and Cl^- ($r = 0.74$), and between NH_4^+ and NO_3^- ($r = 0.86$) confirm that ammonium is associated in multiphase reactions.

4.1.3. Acid contribution

The measured pH values in rainwater samples collected from 2005 to 2009 are between 3.96 and 7.47. 86% of rain samples pH range between 4.7 and 5.7. Fig. 3 shows the pH distribution frequency. The median pH is 5.19 and corresponds to a mean VWM H^+ concentration of $6.46 \pm 2.19 \mu\text{eq} \cdot \text{L}^{-1}$. During the studied period (2005–2009), 82% of rainy events had pH values less than 5.60. 5.60 represents the pH value resulting from the equilibrium between atmospheric CO_2 and pure distilled water. This result confirms that the majority of rainy events collected in African wet savannas are acidic (Lacaux et al., 1992; Galy-Lacaux et al., 2009, Yoboué et al., 2005, Sigha-Nkamdjou et al., 2003). The highest pH values superior to 5.9 are essentially found in rain samples with high concentration of calcium, carbonates and magnesium. This demonstrates the associated basic contribution of dust present in rain composition.

Annual acetic, formic, propionic and oxalic volume weighed mean concentrations were calculated for the 2005–2009 period excluding data of 2007 because organic ions VWM could not be measured for this year. Measured VWM concentrations of organic acids are relatively high. Mean HCOO^- (formic) and CH_3COO^- (acetic) concentrations are 8.6 and $6.70 \mu\text{eq} \cdot \text{L}^{-1}$, respectively. VWM concentrations of $\text{C}_2\text{O}_4^{2-}$ and $\text{C}_2\text{H}_5\text{COO}^-$ are lower by a factor of 7 and 15 respectively. HCOO^- and CH_3COO^- VWM concentrations are comparable to those measured at the Lamto wet savanna site, and higher than in Congo (Dimonika Forest, Lacaux et al., 1992). These concentrations represent about half of organic acids VWM concentrations measured in big cities of the world such as Singapore or Sao Paulo (Vet et al., 2014).

In terms of concentration, the more important acids in the atmosphere are acetic and formic acids generally derived from the

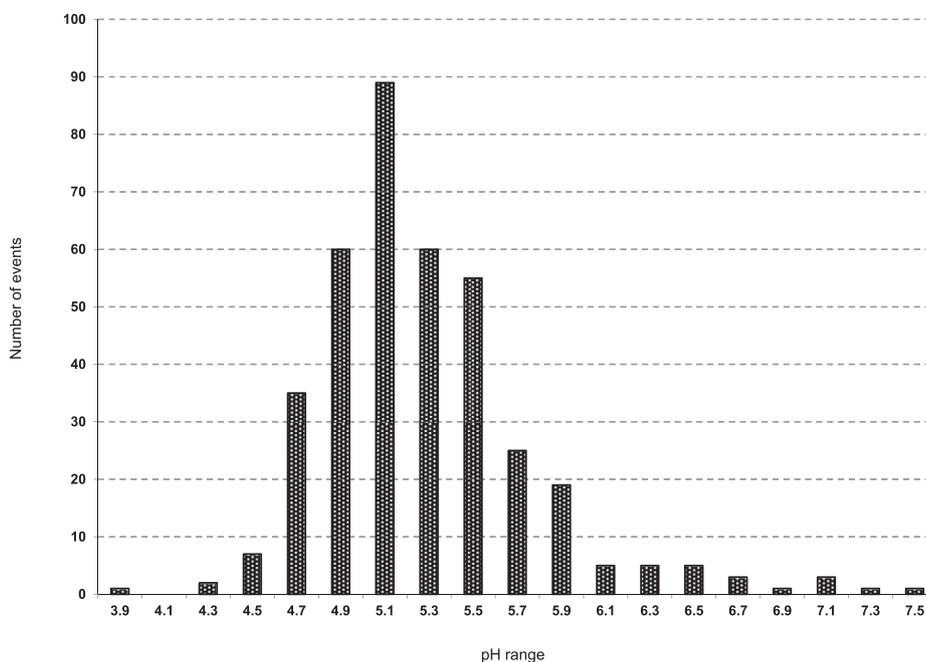


Fig. 3. Frequency distribution of pH.

following sources: vegetation, biomass burning and bio fuel, fossil fuel, agricultural emissions and soils (Paulot et al., 2011). Wet deposition is one of the major sinks of organic acids. Therefore, at Djougou, the rain composition with high organic acidity could be mainly explained by two strong sources: BVOC (Biogenic Volatile Organic carbon) from vegetation and VOC from combustions. Saxton et al. (2007) and Murphy et al. (2010), have performed BVOC measurements during the AMMA 2006 wet season at Djougou and have shown that BVOC levels are high, especially for isoprene and monoterpene. For some specific species, levels in Benin are higher than VOC measurements performed in a forest of the North Congo (Serça et al., 1998). On the other hand, the Djougou site is also influenced by VOC emissions from combustions. Ouafo et al., 2014 (personal communication) and Lioussé et al., 2010 demonstrate that if biomass burning remains the major source of organic aerosols during the dry season in Benin, domestic fires using fuelwood, charcoal and animal waste are also important sources which remain stable all over the year and thus important during the wet season.

To evaluate the acidic contribution to the rain, we consider SO_4^{2-} , NO_3^- and HCOO^- , CH_3COO^- , $\text{C}_2\text{O}_4^{2-}$ and $\text{C}_2\text{H}_5\text{COO}^-$ as the main acidifying components of rains, for mineral and organic acidity respectively. We define the potential acidity (pA) as the sum of nitrate, sulfate, formate and acetate VWM concentrations, supposing that all ions are associated with H^+ (equation (8)).

$$PA = \sum \text{anions} = [\text{SO}_4^{2-}] + [\text{NO}_3^-] + [\text{HCOO}^-] + [\text{CH}_3\text{COO}^-] + [\text{C}_2\text{H}_5\text{COO}^-] + [\text{C}_2\text{O}_4^{2-}] \quad (8)$$

Using pA calculations, we also calculate the Fractional Acidity FA (Balasubramanian et al., 2001; Cao et al., 2009; Cheng et al., 2011) according to equation (9).

$$\sum FA = \frac{[\text{H}^+]}{([\text{SO}_4^{2-}] + [\text{NO}_3^-] + [\text{HCOO}^-] + [\text{CH}_3\text{COO}^-] + [\text{C}_2\text{H}_5\text{COO}^-] + [\text{C}_2\text{O}_4^{2-}])} \quad (9)$$

According to Balasubramanian et al. (2001), if FA equals to 1, the acidity generated by acids is not neutralized at all. In Djougou precipitations, the annual average of FA is 0.23 indicating that about 77% of the rain acidity is neutralized by alkaline ions. The evaluation of the relative contribution of each anion to the Potential Free Acidity (PFA) of precipitation was determined using the following formula (10) (Dos Santos et al., 2007):

$$PFA = \frac{[X]}{\sum \text{anions}} \quad (10)$$

where, [X] is the individual VWM concentration ($\mu\text{eq}\cdot\text{L}^{-1}$) of the concerned anion. Relative contributions of each organic and inorganic acid to the Potential Free Acidity in Djougou rainwater are presented in Table 6. Relative contributions of organic and inorganic acids are 49.6% and 50.4% respectively. Assuming that all

Table 6
Relative contribution of organic and mineral acidity to the total acidity measured at Djougou.

Potential acidity	Concentration ($\mu\text{e L}^{-1}$)	Potential free acidity (%)
Organic		
HCOO ⁻	8.0	28
CH ₃ COO ⁻	4.8	16.8
C ₂ H ₅ COO ⁻	0.3	1.0
C ₂ O ₄ ²⁻	1.1	3.8
Total 1	14.2	49.6
Mineral		
NO ₃ ⁻	8.2	28.7
SO ₄ ²⁻	6.2	21.7
Total 2	14.4	50.4
Total pA	28.6	
H ⁺ measured	6.5	

$$NFx_i = \frac{[x_i]}{[NO_3^-] + [SO_4^{2-}] + [HCOO^-] + [CH_3COO^-] + [C_2O_4^{2-}] + [C_2H_5COO^-]} \quad (11)$$

major organic and inorganic anions (NO_3^- , Cl^- , SO_4^{2-} , $HCOO^-$, CH_3COO^- and $C_2O_4^{2-}$) measured in rainwater composition could be in the form of free acids, the pA is estimated to be $28.6 \mu\text{eq}\cdot\text{L}^{-1}$, leading to a pH of 4.5. This pH is lower than the measured pH of 5.19. That means that a fraction of the acidity is neutralized, especially by alkaline species such as Ca^{2+} , NH_4^+ .

Neutralization Factor NF has also been calculated to appreciate the neutralization of rainwater by different alkaline ions NH_4^+ , Ca^{2+} , Mg^{2+} , and K^+ (Rastogi and Sarin, 2005; Celle-Jeanton et al., 2009). In this study, considering the significant VWM values of CH_3COO^- and $HCOO^-$, the Neutralization Factor was calculated using equation (11):

Where x_i are cations of interest, and all ionic concentrations are expressed in $\mu\text{eq}\cdot\text{L}^{-1}$.

The NF values for NH_4^+ , Ca^{2+} , Mg^{2+} , and K^+ are 0.499, 0.464, 0.074 and 0.070 respectively. These values represent 45%, 42%, 7% and 6% of the contribution to the neutralization process

respectively. These results show that NH_4^+ and Ca^{2+} are the main neutralization ions in rainwater. The analysis of correlation coefficient shows that the acidity (H^+) is not correlated to mineral acids (NO_3^- and SO_4^{2-}) (Table 4). In addition, the good correlation between Ca^{2+} and NO_3^- ($r = 0.75$) indicates the presence of heterogeneous chemistry processes of neutralization between alkaline dust particles and gaseous nitric acid. Galy-Lacaux et al., 2001 have shown that this capture could be complete and could explain to a large extent the neutralization processes of the rain potential acidity. This result has been widely emphasized in other parts of the world where desert soil dust emissions influence rain chemistry, as for example in Spain or in the Mediterranean basin (Avila et al., 1997; Avila et al., 1998; Herut et al., 2000), in Asia (Kulshrestha et al., 2003, 2005; Hu et al., 2003). H^+ is only slightly correlated with $HCOO^-$, CH_3COO^- , $C_2H_5COO^-$ and $C_2O_4^{2-}$ (Table 4). One part of the organic acidity is neutralized by dissolved gases such as ammonia, explaining the low remaining acidity ($6.5 \mu\text{eq}\cdot\text{L}^{-1}$) compared to the pA ($28.6 \mu\text{eq}\cdot\text{L}^{-1}$). This result is illustrated by the

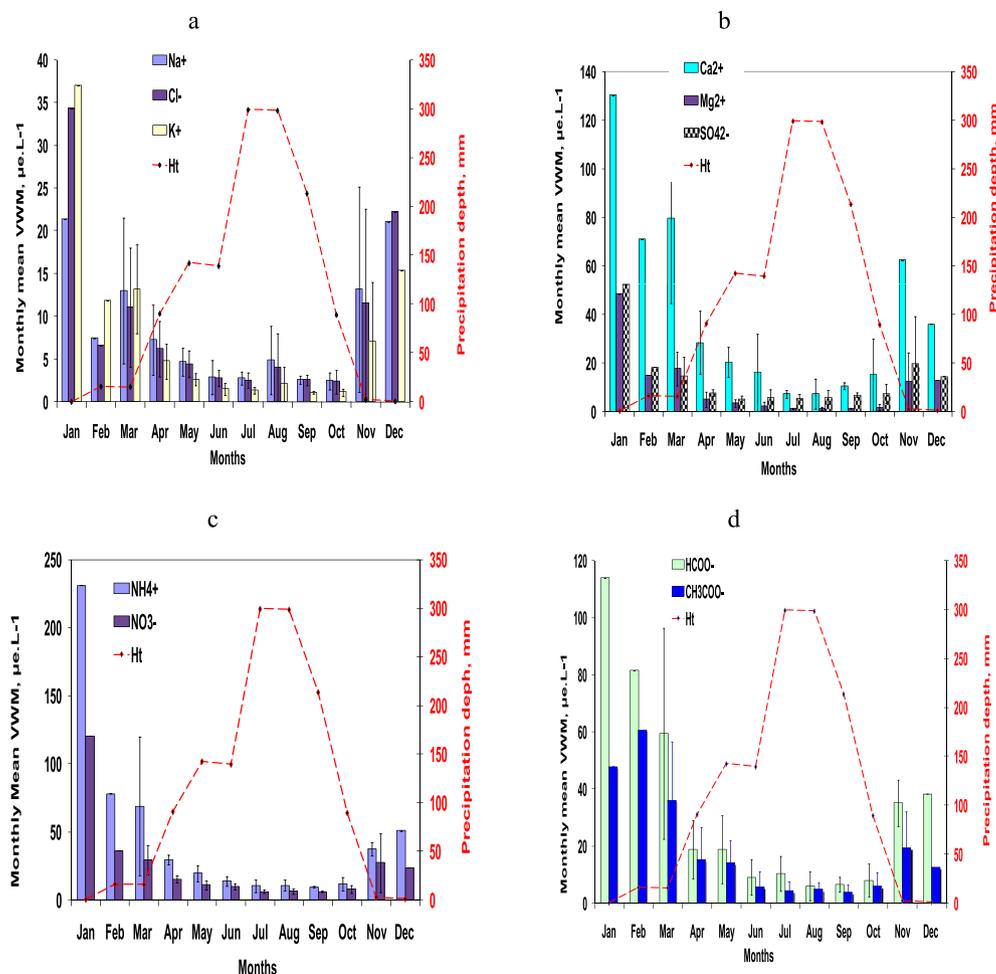


Fig. 4. Distribution of monthly means VWM of major ions in rainwater ($\mu\text{eq}\cdot\text{L}^{-1}$) and mean monthly precipitation depth (mm) 4- a for Na^+ , Cl^- and K^+ ; 4-b for Ca^{2+} , Mg^{2+} and SO_4^{2-} , 4-c for NH_4^+ and NO_3^- ; 4-d for $HCOO^-$ and CH_3COOH for the Djougou site (2005–2009). Vertical bars represent the standard deviation around each monthly mean.

correlation coefficients between NH_4^+ and all organic ions (r varies from 0.55 to 0.74).

4.2. Monthly variation of concentrations and wet deposition of chemical constituents at the wet savanna site of Djougou

Mean monthly distribution of VWM concentrations are presented in Fig. 4a–d, for the main chemical constituents grouped by sources contribution along the year, i.e.: marine (4a), terrigenous (4b), nitrogenous (4c) and organic (4d). Vertical bars indicate the standard deviation while the mean monthly rain depth is superimposed on the monthly VWM ion concentrations. Uncertainty bars for December, January and February are not plotted because of a too low number of rains for these months (Table 1).

Results show the large monthly difference in VWM concentrations for the main chemical constituents in rainwater during the dry season compared to wet season. The first (January to March) and last (November to December) rainfall event of a year presents very high monthly VWM concentrations for the four groups of rain components. These high VWM concentration values obtained during the dry season are due to dust particles in the atmosphere coming from Harmattan winds and to gases emitted by biomass burning (Fig. 2).

In the core of the wet season (April to September), measured VWM concentrations are 2–20 times lower. Monthly NH_4^+ VWM varies from 230.9 in January to $9.4 \mu\text{eq}\cdot\text{L}^{-1}$ during the wet season. Monthly Ca^{2+} VWM concentrations range from 130.5 to $7.2 \mu\text{eq}\cdot\text{L}^{-1}$; NO_3^- from 120.6 to $6.1 \mu\text{eq}\cdot\text{L}^{-1}$ and HCOO^- , CH_3COO^- , SO_4^{2-} , K^+ , Mg^{2+} , Cl^- and Na^+ monthly VWM concentrations vary respectively from 114 to $6.0 \mu\text{eq}\cdot\text{L}^{-1}$, from 47.8 to $3.8 \mu\text{eq}\cdot\text{L}^{-1}$, from 52.4 to $5.4 \mu\text{eq}\cdot\text{L}^{-1}$, from 37.1 to $1.1 \mu\text{eq}\cdot\text{L}^{-1}$, from 48.5 to $1.2 \mu\text{eq}\cdot\text{L}^{-1}$, from 34.4 to $2.4 \mu\text{eq}\cdot\text{L}^{-1}$ and from 21.4 to $2.5 \mu\text{eq}\cdot\text{L}^{-1}$. Seasonal VWM concentrations were calculated. Results indicates that VWM concentration of major ions in Djougou rainwater are on average 5 ± 2 higher in the dry season (November–March) than in the wet season (April–October). The impact of the high VWM concentrations during the dry season on the annual VWM concentrations has been calculated, and shows that results are species dependent. Mg^{2+} , NH_4^+ , Ca^{2+} , K^+ , NO_3^- and CH_3COO^- VWM concentrations during the dry season represent 15%, 11%, 11%, 10%, 7% and 8% of the mean annual VWM concentration, respectively. It represents only 2% or 3% for Na^+ , Cl^- , SO_4^{2-} and carbonates. These proportions show that dry season rains, representing only 4% of the total annual rain depth contributes to about 10% of the total

measured chemical composition of precipitation. Equation (5) is used to compute mean monthly WD for the period (Fig. 5). Results suggest an opposite picture compared to monthly VWM repartition. WD is maximum during the wet season from July to September and increases proportionally to the rain depth amount. Maximum occurs in July and August.

4.3. Inter-annual variability of rain chemistry

At the IDAF site of Djougou, the total annual precipitation varies from 1144 mm to 1539 mm during the sampling period (2005–2009), with a mean of 1325 mm. The variability of the precipitation annual amount corresponds to $\pm 16\%$. pH values range from 3.96 to 7.47 and the annual mean pH is 5.19 with a maximum deviation of ± 0.15 . To investigate the inter-annual variability of the rain chemical composition, the variation around the mean VWM concentrations has been calculated for groups of ionic components, representative of the different contributions identified in previous sections. For the marine contribution, VWM concentrations of Na^+ , Cl^- , ssCa^{2+} , ssMg^{2+} , ssSO_4^{2-} and ssK^+ are summed. For the nitrogenous and the terrigenous contribution, of the sum of NO_3^- and NH_4^+ and carbonate ions, nssCa^{2+} , nssMg^{2+} , nssK^+ and nssSO_4^{2-} VWM concentrations are considered, respectively. Finally, the group representing the organic contribution is composed of organic ions, HCOO^- , CH_3COO^- , $\text{C}_2\text{O}_4^{2-}$ and $\text{C}_2\text{H}_5\text{COO}^-$. For the acidic contribution H^+ VWM concentration is used, calculated from pH values. Results show that the marine contribution varies from 5.4 to $11.5 \mu\text{eq}\cdot\text{L}^{-1}$ with a mean value of $8.8 \pm 2.56 \mu\text{eq}\cdot\text{L}^{-1}$. The nitrogenous contributions vary from 20.3 to $25.3 \mu\text{eq}\cdot\text{L}^{-1}$ with a mean value of $22.5 \pm 2.2 \mu\text{eq}\cdot\text{L}^{-1}$. The terrigenous contribution ranges from 36.7 to $49.8 \mu\text{eq}\cdot\text{L}^{-1}$ with a mean value of $44.0 \pm 6.4 \mu\text{eq}\cdot\text{L}^{-1}$. The VWM concentration related to the organic source varies from 8.3 to $17.7 \mu\text{eq}\cdot\text{L}^{-1}$ with a mean value of $14.2 \pm 5.1 \mu\text{eq}\cdot\text{L}^{-1}$. Ion H^+ VWM concentrations range from 4.5 to $8.9 \mu\text{eq}\cdot\text{L}^{-1}$ with a mean value of $6.46 \mu\text{eq}\cdot\text{L}^{-1}$. At Djougou, the inter-annual variation of rain chemical composition, through the analysis of the different sources contribution, indicates that the marine, the nitrogenous, the organic and the terrigenous contributions vary around 29%, 10%, 36% and 15% respectively around the mean calculated for the period 2005–2009. The mean total ionic charge of rain samples is between 93.0 and $98.9 \mu\text{eq}\cdot\text{L}^{-1}$. Even if differences in the total ionic charge are measured, with a minimum in 2007, wet deposition increases from 2006 to 2009 and follows the same pattern as the rainfall gradient. The total mean annual WD for this period is

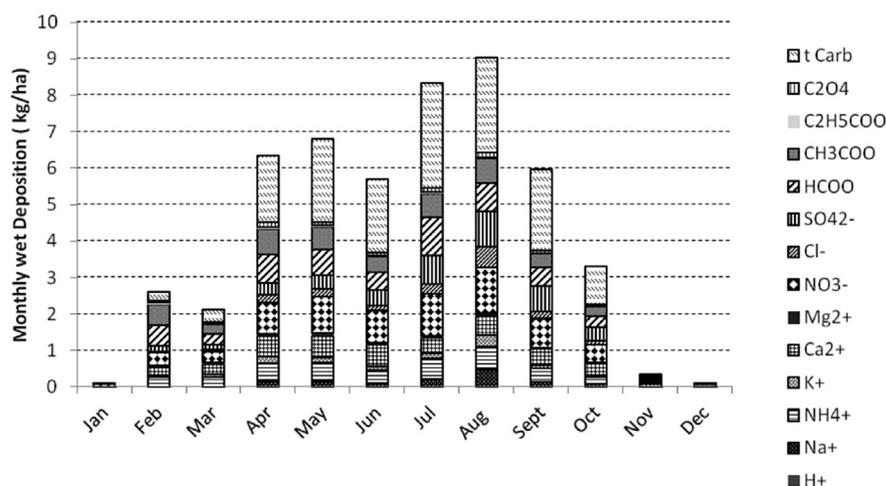


Fig. 5. Distribution of monthly mean Wet Deposition of major ions in the wet savanna site of Djougou (2005–2009).

51.3 kg·ha⁻¹·yr⁻¹. During the experimental period, the WD varied from 42 kg·ha⁻¹·yr⁻¹ in 2006 to 59.7 kg·ha⁻¹·yr⁻¹ in 2009. The total mean WD does not take into account data from 2007 because organic ions VWM could not be measured for this year. S deposition is calculated from SO₄²⁻, and N deposition from NO₃⁻ and NH₄⁺ (Table 3). The results show that sulfur wet deposition, in kg·ha⁻¹·yr⁻¹ varies from 1.28 to 1.38, with a mean value of 1.31. Nitrogen wet deposition ranges from 3.4 to 4.6 kg·ha⁻¹·yr⁻¹, with a mean value of 3.9 ± 0.6 kg·ha⁻¹·yr⁻¹. The computation of standard deviation on VWM and WD from 2006 to 2009 indicates that concentration and deposition variations never exceed 20%. WD interannual variability for dry and wet season has been computed. During the dry season, Mg²⁺, NH₄⁺, Ca²⁺, K⁺ and NO₃⁻ present a variation of 21%, 13%, 15%, 17% and 10% respectively. Cl⁻, SO₄²⁻, HCOO⁻, CH₃COO⁻, C₂H₅COO⁻, C₂O₄²⁻ and carbonates vary within 9%, 7%, 15%, 14%, 13%, 16% and 4% respectively during the period 2005–2009. Overall, wet deposition during the dry season months represents an average of 8% of the total annual wet deposition. That means that 92% of deposition fluxes occur from April to October. However, the results show that the wet deposition measured at Djougou during the dry season accounts for up to 20% of the annual wet deposition for some species, namely magnesium and organic acids, which is not negligible. We assume that biomass burning during the dry season months affects significantly rain chemistry of the first rainy events with emissions of organic compounds.

5. Discussion and conclusions

The results and analysis examined in the previous sections allow us to comment on several aspects of rainwater chemistry in the wet savanna site of Djougou, and to make a comparison with other sites on the transect dry savanna-wet savanna and forest in West and Central Africa.

The mean pH value of 5.19 measured in Djougou precipitation is close to results obtained in the wet savanna site of Lamto in Côte d'Ivoire (5.16, Yoboué et al., 2005). The acidity in the wet savanna of Djougou is the result of a mixture of inorganic and organic acids, where the organic acids (HCOOH, CH₃COOH, C₂H₅COOH and H₂C₂O₄) are responsible for 49% of the potential acidity. NH₄⁺ and Ca²⁺ are identified as the main neutralization ions for the acidity of rainwater in Djougou. The variation of these compounds and their chemical association regulate the acidity which increases from dry savanna to forest. Higher pH are measured in dry savannas at Banizoumbou in Niger (5.75), at Katibougou and Agoufou in Mali (5.54) and (6.28), respectively (Laouali et al., 2012). In the equatorial forest at Zoetele in Cameroon, acidic pH is measured (pH = 4.92), (Sigha-Nkamdjou et al., 2003). This pH is comparable to low values of pH measured in the dry savannas sites of South Africa (Louis Trischardt: 4.91 and Amersfoort: 4.32) (Mphepya et al., 2004, 2006) affected by anthropogenic sources. To compare the mean chemical characteristics of precipitation in the wet savanna of Djougou with

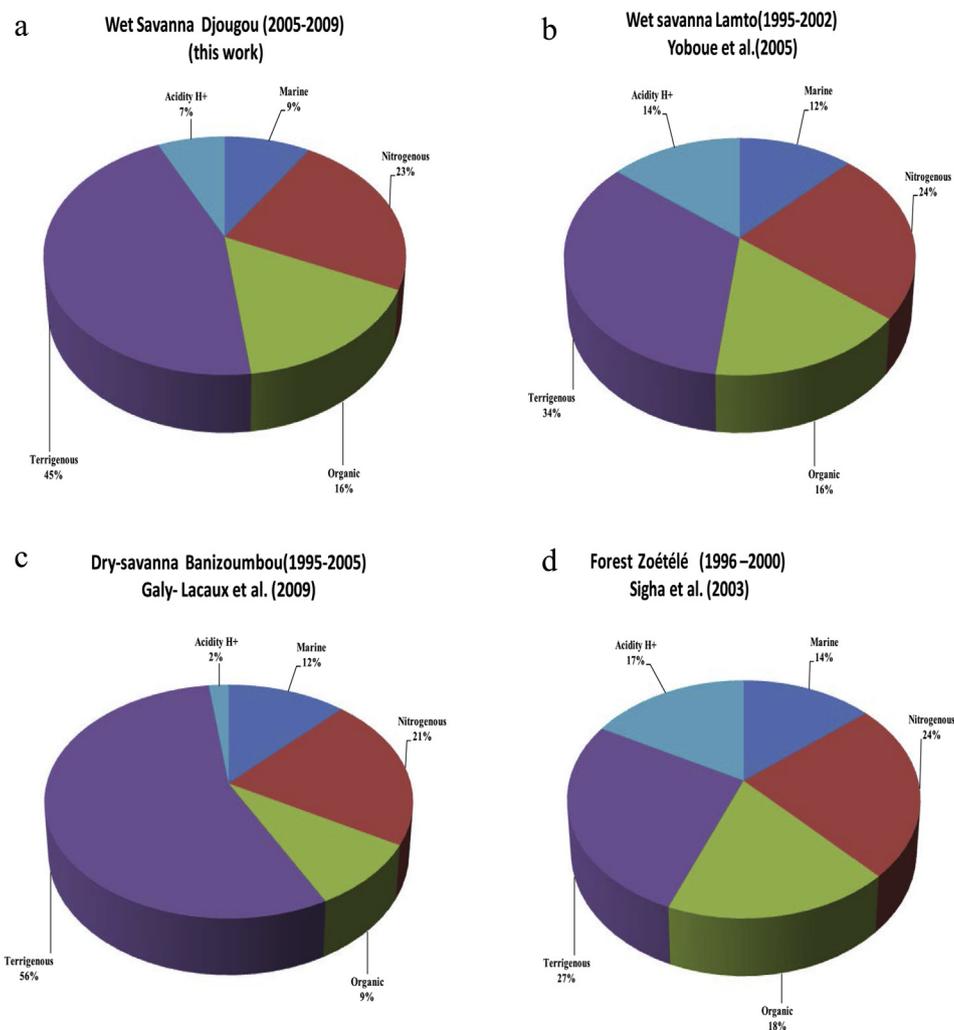


Fig. 6. Estimation of the marine, the nitrogenous, the organic, the acidity and the terrigenous contributions to the rain chemical content along West and Central African ecosystems.

other IDAF sites, we have calculated the mean contribution of marine, nitrogenous, terrigenous and acidic species for all the sites over the studied period. This calculation is done according to results published for dry savannas by Galy-Lacaux et al. (2009), Laouali et al. (2012), for the wet savanna of Lamto by Yoboué et al., 2005 and for the forest by Sigha-Nkamdjou et al., 2003. These papers present studies of rain data collection and associated chemical analysis integrated over 4–10 years. Fig. 6 (a, b, c, d) presents the contributions of groups of species in % for the wet savanna of Djougou in Benin (Fig. 6a) and Lamto in Ivory Coast (Fig. 6b), the dry savanna of Banizoumbou in Niger (Fig. 6c) and the forest of Zoetele (Fig. 6d). The terrigenous contribution represents 55% of the total composition at the dry savanna site of Banizoumbou whereas it represents 46% in Djougou and 34% in Lamto. Nitrogenous contribution in Lamto is 24%, 23% in Djougou, 24% in Zoetele and 21% in Banizoumbou. To investigate the relative contribution of particles and gases in rainwater, we applied the methodology proposed by Yoboué et al., 2005 to our study. We calculate the relative particulate contribution (PC) and the relative gaseous contribution (GC) using the mean chemical composition measured in Djougou for the period 2006–2009. Mean GC is 57% and mean PC is 43% in Djougou precipitation. For the wet savanna of Lamto, Yoboué et al., 2005 indicates a GC of 58% and a PC of 42%. In the dry savanna site of Banizoumbou, results give 30% for GC and 70% for PC (Galy-Lacaux et al., 2009) and for the forest of Zoetele Sigha-Nkamdjou et al., 2003 report 50% of GC and 50% of PC. These results show that the gaseous contribution in rainwater is more important in wet savanna and forest ecosystems than in dry savanna, where particulate contributions dominates the chemical composition of rain. The sources of nitrogenous compounds have been identified in this study as significant at Djougou all year. The main nitrogenous sources are the biomass burning and soils during the dry season and vegetation and soil sources during the wet season. The analysis of the identified contributions suggests that the precipitation chemistry at Djougou is influenced by a combination of sources. Four main contributions have been identified. It includes the terrigenous contribution (soil and dust), the nitrogenous contribution (biomass burning, livestock, biofuel and biogenic emissions), the marine and the organic contributions. The computation of the inter-annual variability of wet deposition at Djougou (2005–2009) is in the range of $20 \pm 7\%$ for marine, terrigenous, organic, nitrogenous and acidic contributions respectively. The largest uncertainties concern the concentrations of organic acids due to difficulties in sample preservation. The seasonal analysis of the wet deposition (WD) shows that its value during the wet season represents an average of 92% of the wet annual deposition. This seasonal analysis has also shown that rainy events during the dry season months are strongly affected by biomass and biofuel combustion sources and charged in organic acidity, explaining 20% of the organic acids measured in annual chemical composition of precipitation.

To conclude, this study describes 4–5 years of continuous measurement of rain chemistry in the wet savanna site of Djougou in Benin. The rainwater chemistry presented in this work may be considered as background estimation for Benin and responds to concerns of climate change in a tropical region where limited databases are available. These data provide an ideal baseline against which changes in rainwater chemistry as a result of local and regional land use may occur. In this way, the IDAF project based on a long term monitoring of atmospheric deposition should help to document possible trends in Africa, a continent where demographic pressure, land use change and atmospheric emissions could strongly evolve in the future.

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