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ABSTRACT

Experimental data on precipitation chemistry were collected at a semi-arid savanna in Senegal (Dahra) in 2013, 2014 and 2017. The chemical composition of precipitation was analyzed for inorganic and organic ions, using ionic chromatography. The pH values of precipitation range from 4.50 to 8.50 with 89% of the samples having basic pH. The composition of precipitation was controlled by four source contributions: marine, terrigenous, biogenic, and organic acids emissions from vegetation. The terrigenous contribution was the highest accounting for 42% of the total annual Volume Weighted Mean ionic concentrations, due to the proximity of the Saharan desert, followed by the marine source representing 36%, due to the location of Dahra close to the Atlantic Ocean. Nitrogenous (N) contribution represents 16% of the mean annual total ionic charge, from biogenic sources and livestock crossing the site all year round. Finally, the lowest contribution is from organic acidity (5%), due to the low density of vegetation especially during the dry season. Wet deposition fluxes in Dahra for all compounds show larger values than at other Sahelian savanna sites. Dry N deposition in Dahra was also estimated by inferential method using gas concentration measurements and modeled dry deposition velocities. The total N deposition fluxes (wet plus dry) range from 3.80 to 4.81 kgN ha^{-1} yr^{-1}, comparable to fluxes at other semi-arid savannas in Niger and Mali. Wet deposition contributed with 37–53% of the total N flux, suggesting that wet N deposition is equally important to dry deposition fluxes for direct N loading to savanna ecosystems in the Sahel, with a large contribution of reduced compounds. This study shows that Dahra presents a precipitation chemistry composition with characteristics close to those from other Sahelian sites, with however the specificity of being more influenced by the proximity of the Atlantic ocean and the presence of livestock year round.

1. Introduction

Studying the transport and exchanges of chemical compounds between the surface and the atmosphere improves our global understanding of environmental conditions related to quality of air, soil, water, and climate change. Concentrations of chemical compounds in the atmosphere are controlled by emissions and deposition processes (both wet and dry). Studying the chemical content of precipitation gives an insight in compounds origin, in their source magnitude and further atmospheric transport, in chemical reactions in air masses and removal processes, at the regional scale (Galy-Lacaux et al., 2009; Laouali et al., 2012; Vet et al., 2014). The study of chemical and dynamic characteristics of precipitations reveals the different sources of pollutants encountered by air masses through their trajectories, and helps to understand how gases and particles are displayed regionally, and how they may affect ecosystem ecology. Anthropogenic and biogenic influences are identified through the study of deposition processes and their quantification, and through temporal and spatial evolution of precipitation chemistry (Akpo et al., 2015).

If the surfaces crossed by air masses during their transfer are

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influenced by anthropogenic activity, atmospheric deposition can be either a source of toxic substances or a source of nutrients for the ecosystems (Galy-Lacaux et al., 2009). Investigating the chemical content of precipitation and wet deposition fluxes is therefore an interdisciplinary approach between chemistry, physics and biology, focusing on ecosystem services and biogeochemical cycles. Indeed, it has been shown that acidic compounds contained in wet deposition cause damages on soil, vegetation, coastal waters and continental waters (Bravo et al., 2000), because of anthropogenic emissions of sulfur (S) and nitrogen (N) compounds due to energy production, transport, industry and agriculture (Conradie et al., 2016), which leads to the formation of the major sulfuric (H_2SO_4) and nitric (HNO_3) acids (Ro et al., 1988; Minoura and Iwasaka, 1996; Voldner et al., 1986; Dikaiakos et al., 1990).

In arid and semi-arid regions, wind erosion frequently exceeds water erosion, and atmospheric dusts from these surfaces are transported over great distances (Orange et al., 1993; Gomes et al., 2003). The short rainy season occurring in these regions induces sudden and strong local emission processes from natural soils, especially of nitrogenous compounds. Pastoralism is highly developed semi arid regions, it participates to local economy and influences land use management. These local sources will influence the atmospheric chemical composition in the same way as the transport of air masses from larger distance, in which chemical transformations of compounds will confer a specific character to the precipitation events.

Monitoring wet and dry deposition processes on a long term basis is essential to determine potential trends of chemical compound content in precipitation and air. Therefore, the variation in natural and anthropogenic sources should be assessed, and related to land use and climate change.

The aim of this study is to increase the knowledge on precipitation chemistry for semi-arid savanna ecosystems, where annual monitoring with high quality measurements are not developed. The main objectives are to: (1) study the temporal variations of the chemical composition of precipitation and associated wet deposition fluxes in situ at the Dahra field site in Senegal, representative of semi-arid savanna ecosystems of the Sahel region, (2) assess the major sources of ionic species determining the chemical composition of precipitation, (3) quantifying the nitrogenous wet and dry deposition fluxes at the monthly scale, and ecosystem-scale nitrogen compound emissions, and (4) study the spatial variation of the chemical composition of precipitation and associated wet deposition fluxes by comparing fluxes at the Dahra site with three Sahelian semi-arid savanna sites in Mali and Niger, as well as other sites representative of West African ecosystems. The novelty of this study lies in the assessment of monthly and annual variation of wet deposition fluxes for a large range of chemical compounds in a region where few measurements are available, together with a determination of the importance of different sources along an East-West gradient. Furthermore, a recent and complete atmospheric nitrogen deposition budget is presented highlighting the importance of nitrogenous compounds in this region of the world where anthropogenic influence is weak and limited to livestock presence.

2. Site description

This study is embedded in the International Network to study Deposition and Atmospheric composition in Africa (INDAAF, https://indaaf.obs-mip.fr/) network, a program dedicated to the long-term monitoring of atmospheric composition and wet and dry deposition fluxes in Africa with high quality measurements of atmospheric chemical data.

The Dahra field site (15°24′10"N, 15°25′56"W, elevation 40 m) is located about 7 km north-east of the town of Dahra, and 8 km far from the Zootechnical Research Center (CRZ) of the Senegalese Institute of Agricultural Research (ISRA), the institutional host of the site. The Dahra field site is in the Ferlo sylvo-pastoral region of Senegal within the Sahelian ecoclimatic zone (Fig. 1). The sylvo pastoral area of the Ferlo (SPA) appears to be homogenous and the land is relatively flat, with small dune formations oriented from East to West and interspersed by shallow valleys. The soils of the SPA can be classified into three major units: (i) isohumic hydromorphic soils in the Ferlo valley; (ii) sandy clay soils; (iii) gravelly soils with lateritic outcrops (CSE, ANACIM and FAO, 2017).The geographical characteristics of the Dahra site, compared with three other Sahelian sites of the INDAAF network, are presented in

Table 1
Geographic characteristics and rainwater collection at four dry savannas sites of the INDAAF network: Mean Annual rainfall (H in mm ± SD Standard Deviation). *: Laouali et al. (2012). **: this work.

Station	Country	Latitude	Longitude	Elevation (m)	H (mm) ± SD
Dahra (1959–2017)**	Senegal	15°24′ N	15°26′ W	40	356 ± 120
Agoufou (2004–2006)*	Mali	15°20′ N	1°29′ W	300	321 ± 19
Banizoumbou (1994–2009)*	Niger	13°31′ N	2°38′ W	220	509 ± 34
Katibougou (1997–2008)*	Mali	12°56′ N	7°32′ W	290	804 ± 31

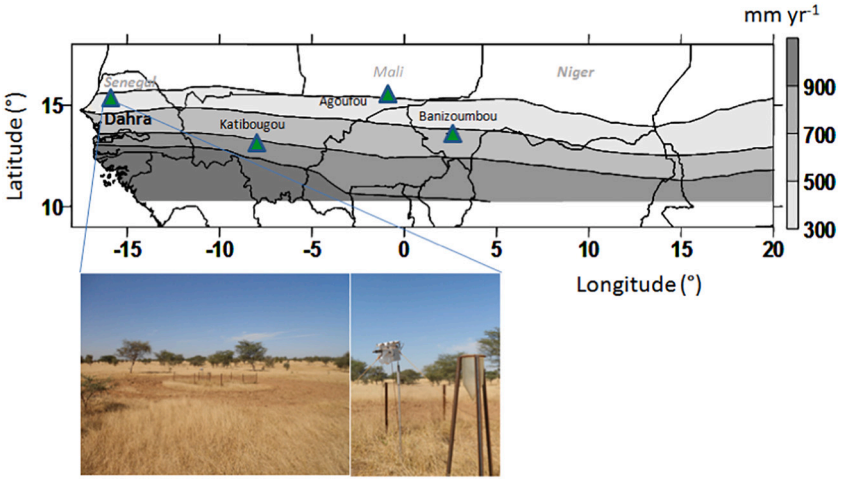

Fig. 1. Location of the Dahra site in West Africa, with 3 other Sahelian sites (Agoufou and Katibougou in Mali, Banizoumbou in Niger) and isohyets (Figure adapted from Lebel et al., 2009). Photos show the site, the rain collector and the rain gauge.

Table 1. Dahra is located in a predominantly pastoral zone containing nearly 15% of the national livestock in Tropical Livestock Unit (TLU) in 2013 (CSE, 2015). Livestock is generally extensively farmed and use natural pastures consisting of grass cover dominated by annual herbaceous (Ndiaye et al., 2014), scattered with trees and shrubs (Tagesson et al., 2015).

The wet season is relatively short and occurs from mid-July to mid-October approximately (Rasmussen et al., 2011),grass and straw cover homogeneously the soil from end of July to mid December, followed by bare soil the rest of the year. Pastures are usually not managed by fires.

The general precipitation characteristics at the Dahra site were assessed following the Annual Intervariability Index (AII) concept, calculated using Eq. (1) (Sarr, 2009):

$$\mathrm{AII} = \frac{P_i - P_m}{\sigma} \quad (1)$$

where Pi (mm) is the cumulative precipitation for a year i; Pm (mm) and σ (mm) are the mean and standard deviation of annual precipitation observed for a given series, respectively. According to Sarr (2009), the degree of drought is a function of the AII of precipitation. If AII > 2, the humidity is extreme, and AII < −2 represents extreme drought. The intermediate values of the index are 1 < AII < 2, 0 < AII <1, −1 < AII < 0 and − 2 < AII < −1 corresponding to high humidity, moderate humidity, moderate drought and strong drought, respectively.

The AII was calculated in Dahra for the period 1959–2017 from historical data available at the CRZ and never published before, collected by local investigators with a manual rain gauge by direct reading (Fig. S1). This figure confirms the significance of the droughts in the seventies and early eighties representing the main climatic events of the 20th century in the Sahel, as reported by many authors (Nicholson, 1981; Folland et al., 1986; Le Barbé and Lebel, 1997; Lebel et al., 2009).

During the period 1959–2017, average annual precipitation is 358.7 mm and annual precipitation ranges between 107.8 mm in 1983 and 775.2 mm in 1969 indicating that Dahra experiences a typical Sahelian climate defined by the 100 mm and 700 mm isohyets (Prince et al., 1995). The AII is marked by an alternation of dry years (58%) and wet years (42%) with years of extreme rainfall (1969 and 2010), and extreme drought (1983).

3. Material and methods

3.1. Meteorological data

A meteorological station was installed at the Dahra site in 2002, providing data on precipitation, wind speed, relative humidity, air temperature, at different heights, soil temperature and soil moisture at different depths. All devices and equipment are fully detailed in Tagesson et al. (2015) and Delon et al. (2017, 2019). In 2017, precipitation data from the meteorological station were not available during a short period due to a power break, and the data set was completed by precipitation measured from a nearby manual rain gauge with direct reading. This rain gauge was installed in the frame of INDAAF network. The gauge is set up one meter above soil according to the World Meteorological Organization (WMO) recommendations. It is graduated from 0 to 150 mm, with a minimum resolution of 0.25 mm. Reading is done every day at 8:00 AM by a local collaborator.

3.2. Precipitation collection for chemical analysis

A semi-automatic precipitation collector specially designed for the INDAAF network was installed and used in Dahra during 2013, 2014 and 2017. This collector is the same as the ones installed at the three other INDAAF sites of the Sahelian belt, Agoufou, Banizoumbou and Katibougou (Laouali et al., 2012). The semi-automatic instrument is a “wet-deposition only” collector. Precipitation is collected with a high degree of cleanliness in a single-use polyethylene bag. The bag is covered, avoiding deposit of aerosols before the onset of precipitation. A precipitation detector automatically controls the aperture of the cover when the rain begins. The surface of rain collection is 225 cm^2. At the end of each rain event, a local site operator collects water from each precipitation event in a 50 ml Greiner tube, changes the bag and closes the cover. Samples are immediately frozen in a deep freezer (−18 °C). Preserving the rainwater samples from contamination is important since microbial activity could modify its chemical composition. After collection, frozen samples were sent to the Laboratoire d’Aerologie in Toulouse for analysis.

The percentage of Total Precipitation (%TP, Table 2) is calculated as the ratio between the total annual precipitation Pt (precipitation really falling at the site, measured by the automatic meteorological station in 2013 and 2014, and by the manual rain gauge in 2017 as detailed in section 3.1) and the collected precipitation Pc by the semi automatic collector (collected samples are sometimes missing, and collected precipitation is often less than real precipitation) (WMO-GAW, 2004). From June 2013 to October 2014, and June to October 2017, a total collected precipitation amount Pc of 986.2 mm was sampled, whereas the total precipitation amount Pt was 1082.3 mm during the three-year monitoring period. The %TP for each of the sampling years was >80% (Table 2) which is considered to be a good score for collection efficiency and gives confidence in the representativeness of rain samples in reference to the total precipitation (WMO, 2004). Inter-annual variability of precipitation at the Dahra site, calculated as the deviation from to the mean annual precipitation of the 2012–2017 period (370 mm), ranges from −10 to 7% for the three years of sampling (Table 2), whereas it is ±24% for the period 2012–2017 (Fig. 2).

3.3. Chemical analyses and data quality of rain samples

The chemical composition of rain was determined at Laboratoire d’Aérologie (Toulouse, France) for the major inorganic (Na^+, $NH4^+$, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO^{3-}, SO_4^{2-}, NO_2^-) and organic ions ($HCOO^-$, $CH3COO^-$, $C_2H_5COO^-$, $C_2O_4^{2-}$) using Ionic Chromatography (IC) as described in Galy-Lacaux and Modi (1998) and Akpo et al. (2015). The IC analyses are performed using ICS5000+ and ICS1100 ionic chromatographs with two automatic samplers (AS50). The eluents for anions and cations are NaOH and MSA, respectively. Certified ionic standards are used for IC calibration. 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. The precision is 0.01pH unit.

According to prior results and through the bi annual participation of the Laboratoire d’Aérologie (reference 700,106) since 1996 to the inter-laboratory comparison study (LIS) of WMO-GAW precipitation quality assurance program, analytical precision is estimated at 5% or better for all ions. All uncertainties from measurements and calculations combined, the uncertainty of the wet deposition fluxes is around 10%. Data quality is further ensured by calculating the Ion Difference for each sample to consider the ionic balance (WMO, 2004). WMO quality criteria were applied to all 65 precipitation samples, based on the

Table 2
Annual Total Precipitation Pt (in mm); Inter-annual variability of precipitation in %; Annual Collected Precipitation Pc (in mm); percent Total Precipitation (in %TP) and number of collected samples for the three years of sampling (2013, 2014 and 2017) in Dahra.

Year	2013	2014	2017
Pt (mm)	355.1	331.7	395.5
Interannual variability (%)	-4	-10	7
Pc (mm)	321.2	269.5	395.5
% TP	90	81	100
Number of collected samples	26	17	19

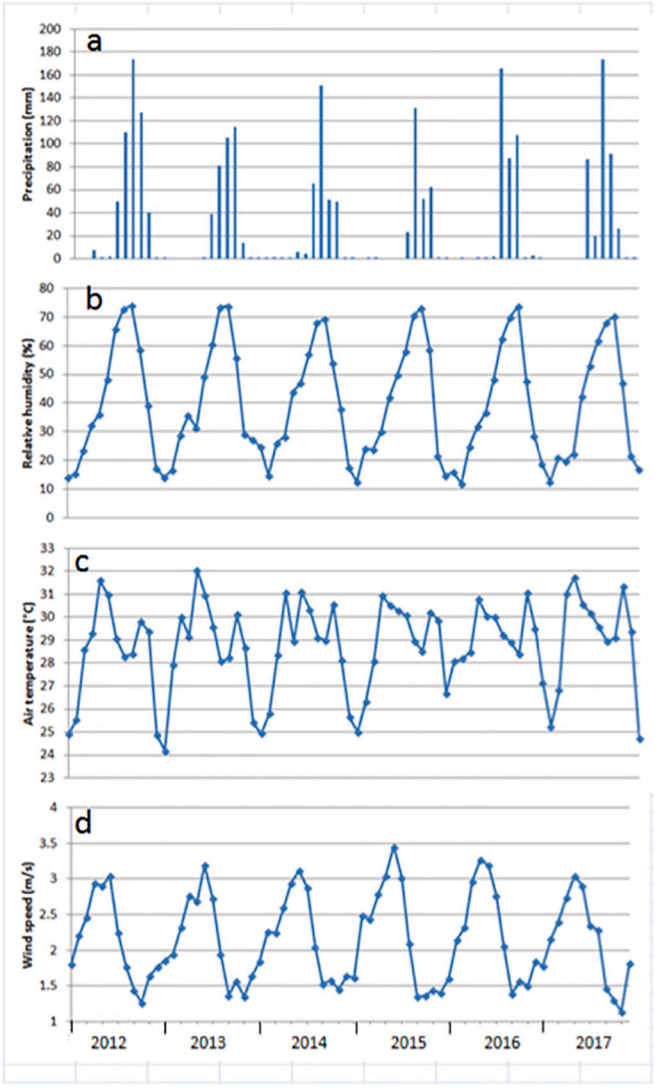

Fig. 2. (a) Monthly precipitation (mm), (b) relative humidity (%), (c) air temperature at 2 m (°C), and (d) wind speed at 2 m (m s^{-1}) at Dahra from 2012 to 2017. In (d) black vertical dashes correspond to the months of January for each year.

verification of the ionic balance (ratio between ion difference and ion sum) by calculating the ion difference (difference between the sum of cation concentrations and the sum of anion concentrations) and the ion sum (sum of all ion concentrations). Equations are fully detailed in Akpo et al. (2015). 95% of the collected samples (62 of the samples) were within the WMO acceptance range and the three remaining samples were rejected. Considering Pc (986.2 mm) and Pt (1082.3 mm), the collection efficiency corresponding to the 62 samples is 91% for the three-year period of monitoring.

3.4. Annual volume-weighted mean (VWM) and wet deposition (WD) fluxes

The volume-weighted mean concentrations of ionic constituents in rainwater (VWM, μeq L^{-1}) were calculated:

$$\mathrm{VWM} = \frac{\sum_{i=1}^{N} C_i \cdot P_i}{\sum_{i=1}^{N} P_i} \quad (2)$$

where, C_i is the ionic concentration for each species in μeq L^{-1}, P_i the precipitation amount for each rainy event in mm, and N the total number of rain events (Yoboué et al., 2005). Concentrations of H^+ were calculated from measured pH values. The annual wet deposition (WD, kg ha^{-1} yr^{-1}) is calculated by multiplying the VWM concentrations in μeq L^{-1} by the annual precipitation amount (Pt in mm) and the molar mass of each species (*Mi,* g mol^{-1}) and dividing by the ionic charge c_i (c_i is 2 for Ca^{2+}, Mg^{2+}, SO_4^{2-} and $C_2O_4^{2-}$, and 1 for all other species):

$$\mathrm{WD} = (\mathrm{VWM}/c_i{*}\mathrm{Pt}{*}\mathrm{Mi})/100000 \quad (3)$$

3.5. Analysis of source contributions

Four different source contributions in the precipitation chemical content were identified: organic/acidic, marine, terrigenous, and nitrogenous (Fig. 3). These different source contributions in Dahra are compared with source contributions in other dry savanna sites in West Africa, with results for Agoufou, Banizoumbou and Katibougou taken from Laouali et al. (2012), (Fig. 3). The Spearman method is used (with XLSTAT software) to determine the correlation between the different ionic species of the 62 rain samples. A high correlation between ions is an indication on the potential same origins of concerned ions or on their participation in the same chemical reaction (Table S1).

The sea-salt fraction (ssF) for some selected ions X in precipitation is calculated using Eq. (4), considering the ionic proportion to Na^+ in seawater, Na^+ concentration representing the marine reference (Keene et al., 1986; Singh and Mondal, 2008; Pauliquevis et al., 2012).

$$\mathrm{ssF_X} = [\mathrm{X}/\mathrm{Na^+}]_{\mathrm{seawater}} \times [\mathrm{Na^+}]_{\mathrm{rain}} \quad (4)$$

where $\mathrm{ssF_X}$ is the sea salt contribution of X in μeq L^{-1}, $[Na^+]_{rain}$ is the concentration of Na^+ in rain (μeq L^{-1}) and $[X/Na+]_{seawater}$ is the ratio of species X to Na^+ in seawater (Keene et al., 1986).

Similarly, the non-sea salt fraction of X is:

$$\mathrm{nssF_X} = [\mathrm{X}]_{\mathrm{rain}} - \mathrm{ssF_X} \quad (5)$$

where $[X]_{rain}$ is the concentration of species X in rainwater, and $\mathrm{nssF_X}$ is the non-sea salt fraction of species X in μeq L^{-1}.

Enrichment factors (EF) were used to study the origin of elements in the atmosphere, precipitation or seawater. Ion Na^+ is chosen herein as the index element of the sea source. $(EF)_{sea}$ value approaching one indicates that the element derives from the sea source. The value of $(EF)_{sea}$ over one indicates that the element derives from another contributing source. Enrichment factors were calculated by:

$$(\mathrm{EF})_{\mathrm{X}} = [\mathrm{X}/\mathrm{Na^+}]_{\mathrm{rain}} / (\mathrm{X}/\mathrm{Na^+}]_{\mathrm{seawater}} \quad (6)$$

where $(EF)_X$ is the enrichment factor of the species VWM concentration of X species, Na^+ is used as the seawater reference,$[X/Na^+]_{rain}$ is the ratio of the X ion amount to Na^+ in rain.

The neutralization factor (NF) is an indicator of the potential of bases (e.g. Mg^{2+}, Ca^{2+}, NH_4^+ and HCO_3^-) to neutralize sulfur and nitric acids and was calculated by:

$$\mathrm{NF_X} = [X]/([\mathrm{NO_3^-}] + [\mathrm{SO_4^{2-}}]) \quad (7)$$

where [X] is the concentration of the corresponding base, $[NO_3^-]$ the nitrate VWM concentration and $[SO_4^{2-}]$ the sulfate VWM concentration in rain (Laouali et al., 2012; Possanzini et al., 1988).

The potential acidity (pA) is the sum of inorganic (nitrate and sulfate) and organic (HCOOH, CH_3COOH, C_2H_5COOH, $C_2O_4H_2$) ions considering that all ions are associated with H^+ (Sigha-Nkamdjou et al., 2003). Assuming that all major organic and inorganic anions measured in precipitation could be in the form of free acids, pA corresponds to a theoretical pH. If this theoretical pH is lower than the measured pH, a fraction of the acidity is neutralized, especially by alkaline species such as Ca^{2+}, NH_4^+. Neutralization Factor (NF) of sulfuric and/or nitric acids

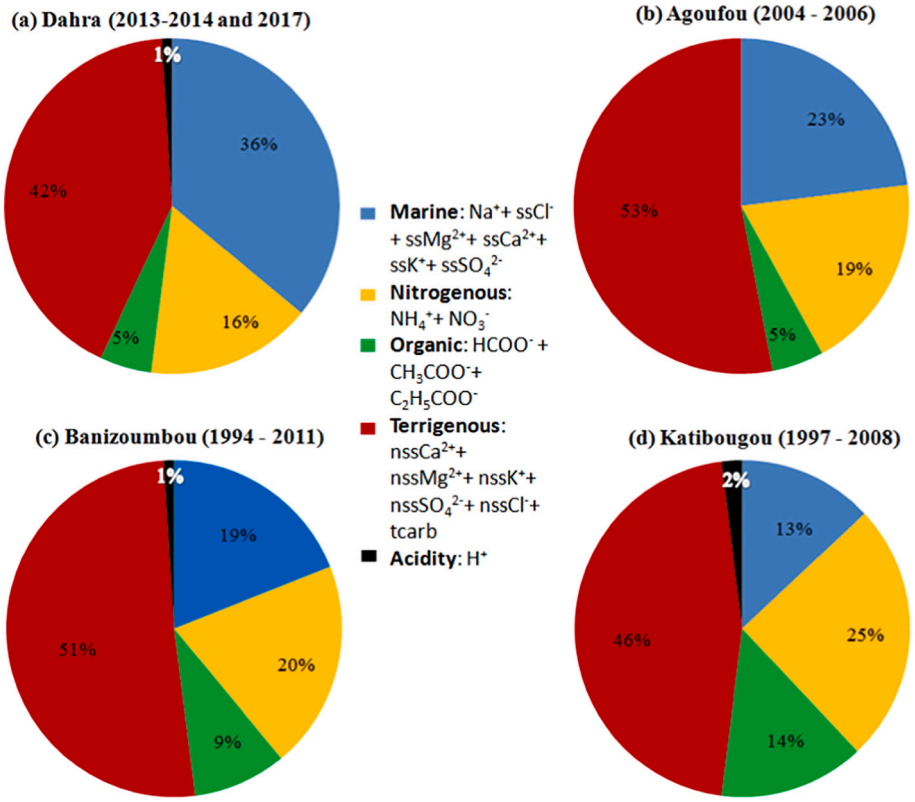

Fig. 3. (a-d): Estimation of the marine, nitrogenous, organic, acidity and terrigenous contributions to the rain chemical content measured at four Sahelian dry savanna sites of the INDAAF network.

by bases such as anions (oxides, carbonates or bicarbonates, etc.) associated with base cations such as Ca^{2+}, NH_4^+, Mg^{2+}, K^+ can be evaluated using Eq. (7).

3.6. Atmospheric nitrogen gaseous concentrations and dry deposition fluxes

Atmospheric concentrations of NO_2, HNO_3 and NH_3 were measured using passive samplers on a monthly basis from May 2012 to December 2017. The samplers were exposed in pairs at 1.5 m height above the ground. The sampling procedure and chemical analysis of samples, as well as the validation method and detection limit were described in detail in Adon et al. (2010).

Dry deposition fluxes were estimated using the inferential method, with gaseous concentration measurements (NO_2, HNO_3, NH_3) and modeled deposition velocities. The big-leaf dry deposition model of Zhang et al. (2003), adapted by Adon et al. (2013) to West African ecosystems was used to calculate dry deposition velocities, except for NH_3 bidirectional exchange which was calculated from Zhang et al. (2010). Meteorological data used for these calculations were provided by the meteorological station installed at the Dahra site.

4. Results and discussions

4.1. Meteorological conditions

Meteorological parameters measured at the Dahra site show a strong seasonal variation, but weak interannual variability during January 2012 to December 2017 (Fig. 2a-d). Monthly precipitation ranges between 2 and 174 mm (Fig. 2a). Air temperature and relative humidity at 2 m vary respectively from 28.0 to 31.3 °C (average 29.6 °C) and from 47% to 74% (average 61%) in the wet season, whereas in the dry season, air temperature and relative humidity range respectively between 24 °C and 32 °C (average 28 °C) and between 12% and 44% (average 25%, Fig. 2b and c). Wind speed at 2 m remains low and range from 1.1 to 3.4 m s^{-1} during all the study period (2012 to 2017) (Fig. 2d). Soil moisture at 5 cm varies between 2 and 9% (figure not shown). During the studied period, the annual precipitation was 355.1 mm in 2013, 331.7 mm in 2014, and 395.5 mm in 2017 (Table 2).

4.2. Inter annual and monthly variation of VWM ionic concentrations and WD fluxes in Dahra

Annual VWM concentrations and WD fluxes for the three-year sampling period (Table 4) are analyzed to investigate the inter-annual variability of the major compounds in the dry savanna precipitation. The results show clearly significant variability during the period of study, depending on the annual precipitation, meteorological parameters, atmospheric particulate and gas sources. In 2013 and 2014, except tcarbonates, Na^+ is the most abundant ion in Dahra precipitation (44.2 μeq L^{-1} in 2013, 64.5 μeq L^{-1} in 2014). The second most dominant ion is Cl^- (40.4 μeq L^{-1} in 2013, and 48.9 μeq L^{-1} in 2014) followed in decreasing order by Ca^{2+}, NH_4^+, SO_4^{2-}, NO_3^-, K^+, Mg^{2+}, $HCOO^-$, CH_3COO^-, $C_2O_4^{2-}$, H^+, and $C_2H_5COO^-$ (Table 4). In 2017, Ca^{2+} (34.2 μeq L^{-1}) is the most abundant. The second most dominant ion is NH_4^+ (29.3 μeq L^{-1}) followed in decreasing order by Cl^-, Na^+, SO_4^{2-}, NO_3^-, Mg^{2+}, CH_3COO^-, $HCOO^-$, $C_2O_4^{2-}$, H^+, and $C_2H_5COO^-$ (Table 4). The annual ionic charge is defined as the sum of the VWM concentrations for one year. The annual total ionic charge is 279.7 μeq L^{-1} in 2013 with 355.1 mm of rain, 341.3 μeq L^{-1} in 2014 with 331.7 mm or rain, and 278.2 μeq L^{-1} in 2017 with 395.5 mm of rain, showing a slight anti correlation between the precipitation chemical load and the annual precipitation amount ($R^2 = 0.6$).

The fluctuation of the chemical load in precipitation for 2013, 2014 and 2017 varies from −7 to 14% relatively to the mean. At the Dahra site, the maximum variability of the precipitation annual amount

corresponds to ±10% (for the 3 years of study, Table 2, whereas it is ±24% from 2012 to 2017). pH values range from 5.70 to 6.35 and the annual mean pH is 5.89, with a maximum deviation of ±9%. The inter-annual variations around the mean (2013–2014 and 2017), calculated for groups of elements representative of the different sources identified previously, are further analyzed. The VWM of marine species ranges from 7.7 to 64.4 μeq L^{-1} with maximum deviation around the annual VWM concentrations between ±20% and ± 46%. The contribution of terrigenous species ranges from 10.4 to 36.6 μeq L^{-1} with deviation between ±15% and ± 25%. The nitrogenous contribution ranges between 12.9 and 36.5 μeq L^{-1}. The VWM concentrations of the organic group vary from 2.2 to 7.2 μeq L^{-1}. The nitrogenous and organic compounds vary by ±15% around the mean. The total ionic content of the precipitation depends on the strength of atmospheric gases and particles sources, and on the precipitation annual amount and distribution. The variation of the annual precipitation and the variation of precipitation regimes clearly impact the inter-annual variability of the total ionic content of rain, as well as the discrete aspect of the Sahelian precipitation which affects wet deposition fluxes of nutrients. However, in addition to rain physical characteristics, the variability of the rain chemical content may be impacted by the potential variation of the intensity of gas and particles sources.

Monthly evolution of VWM ionic concentrations and WD fluxes show that the highest VWM ionic concentrations occur during the least humid months, and the highest WD fluxes occur during the wettest months at all the four Sahelian sites (Fig. 4). Heavy rains lead to low ionic concentrations of VWM confirming the cleaning of the atmosphere by these rains. Therefore the ionic concentration is the highest at the start and end of the rainy season while the wet deposition is at the minimum during these periods, clearly apparent in Fig. 4 for the three sites Dahra (Fig. 4a), Banizoumbou (Fig. 4c), and Katibougou (Fig. 4d). It should be noted that in Katibougou the leaching phenomenon is much greater than at the three other sites, due to the higher precipitation amount received at this site.

4.3. Contribution of sources

In the sections presented below, results obtained from the analysis of the Dahra site database are systematically compared to results published in Laouali et al. (2012) for three other Sahelian sites, i.e. Banizoumbou (Niger), Agoufou (Mali) and Katibougou (Mali). The comparison is also extended further south to other West African ecosystems, wet savannas and forests, with appropriate references.

4.3.1. Organic and acid contribution

The pH values of precipitation samples range from 4.5 to 8.5 in Dahra (Fig. 5b). The reference pH of rainwater is 5.6, considered as the acidity of pure water in equilibrium with the atmospheric CO_2 concentration average. 89% of the 62 events collected in Dahra present an alkaline pH (> 5.6). In Agoufou, Banizoumbou and Katibougou, 100% of

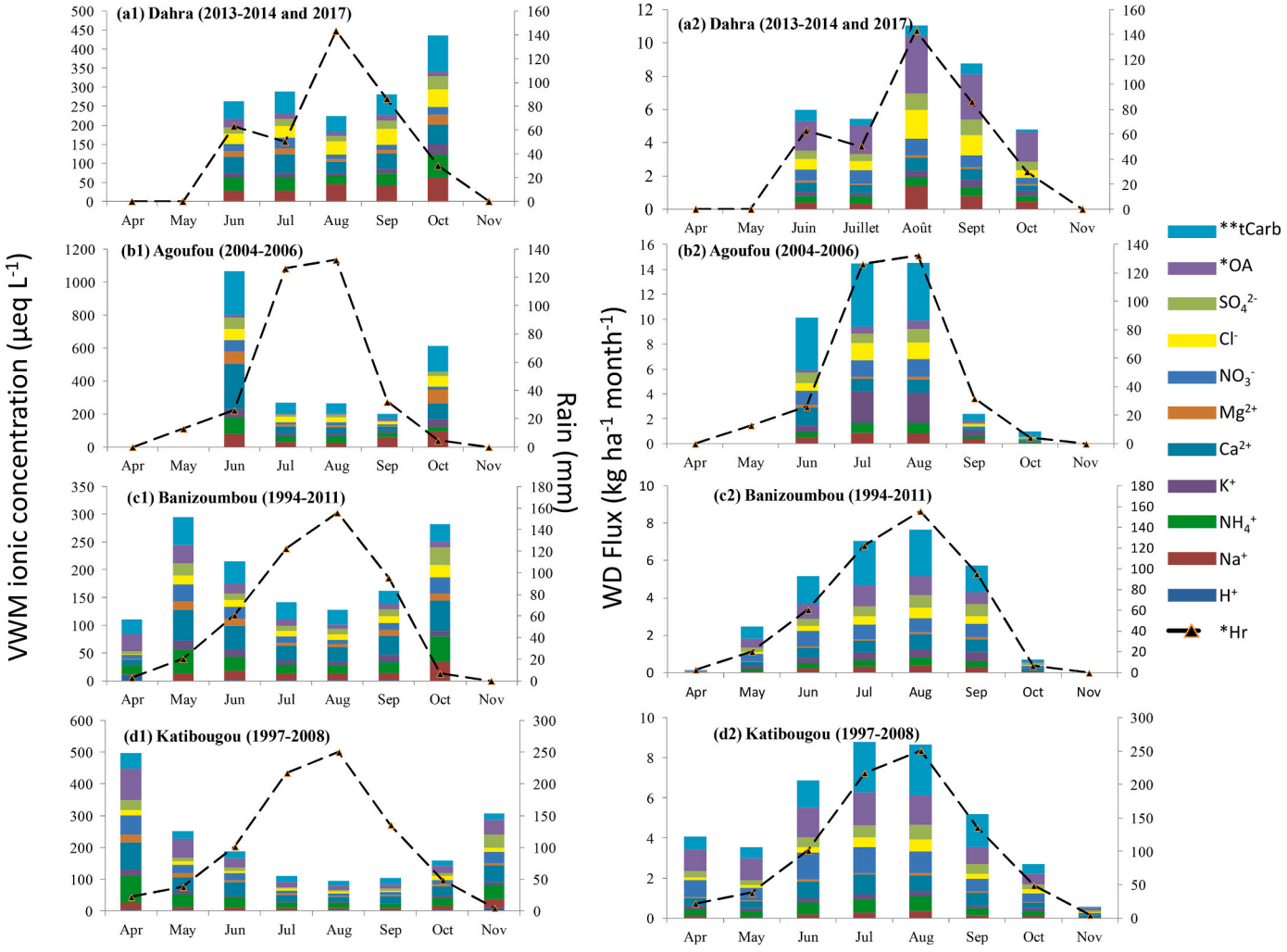

Fig. 4. Monthly variation of VWM ionic concentrations and WD fluxes at the four Sahelian savanna sites of the INDAAF network. Black lines represent monthly rain depths.

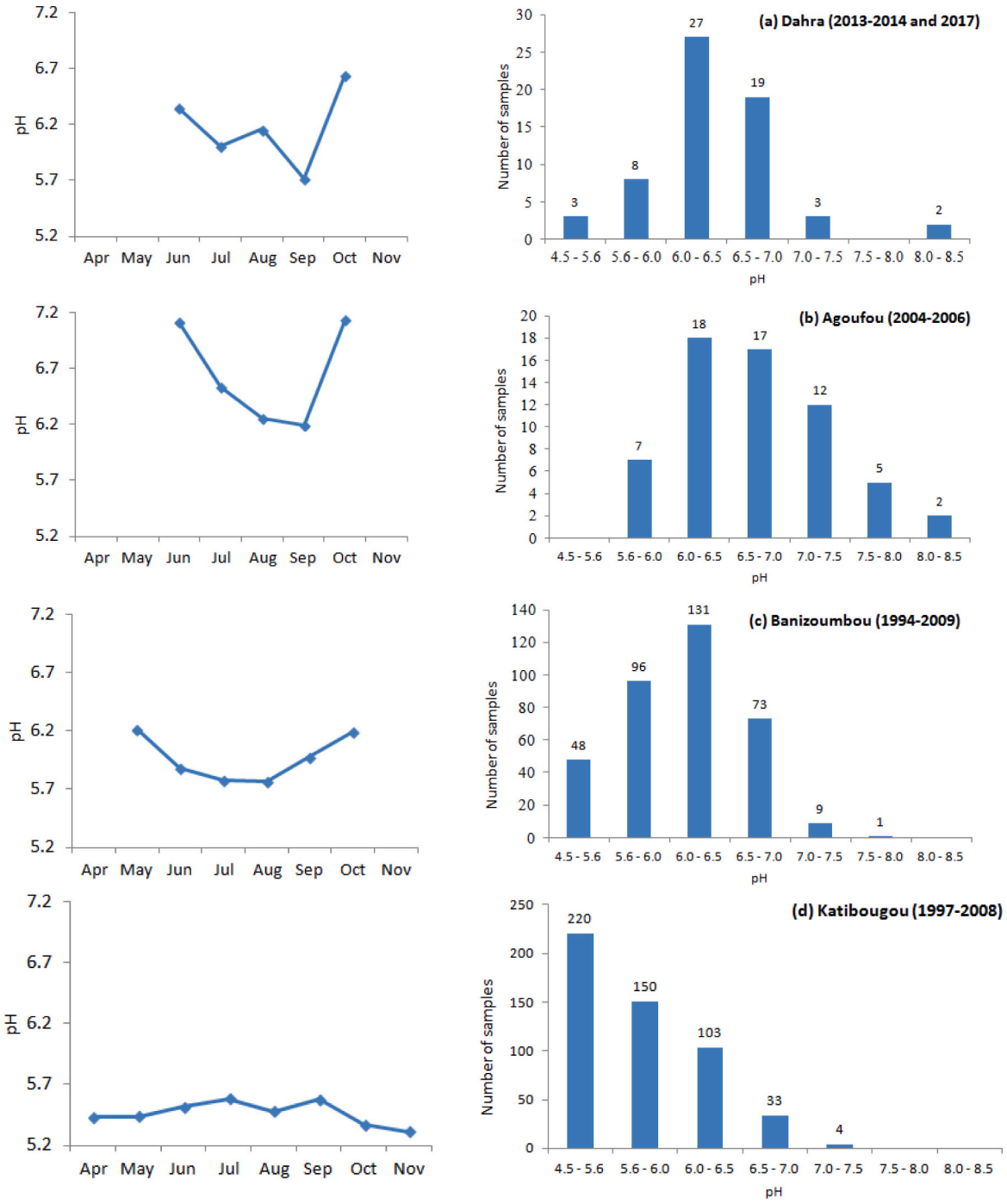

Fig. 5. Left: Temporal variation of pH in rainwater and Right: frequency distribution of pH values at the four Sahelian sites.

the 61, 87% of the 425 and 57% of the 510 precipitation samples also have a pH in the alkaline range, respectively (Fig. 5). In Dahra, the average pH of rainwater, calculated from volume-weighted mean ionic concentration of H^+, equals 6.00. At the four Sahelian sites, pH shows the weakest values in the core of the wet season (around August, except in Katibougou where it deceases at the end of the wet season as well), corresponding to a weaker intensity of the monsoon system, and leading to basic precipitation at the beginning and end of the wet season.

At the four Sahelian dry savanna sites, precipitation presents an alkaline character, due to the high loading of particulate matter, a common feature in semi-arid regions due to the proximity of the Saharan desert. Indeed, dust contains calcium bicarbonate/carbonate, acting as a buffering agent for acidity generated by sulfuric, nitric and organic acids (Galy-Lacaux et al., 2001; Kulshrestha et al., 2003). The average pH value (6.00) in Dahra is close to pH values measured in the three other semi-arid savanna sites of Agoufou (pH = 6.28), Banizoumbou (pH = 5.82), and Katibougou (pH = 5.54), also influenced by desert dust.

The calculated potential contribution of organic acidity (formate, acetate, propionate and oxalate) is 27% and the remaining contribution (73% of mineral acidity) is mainly related to the dissolution of H_2SO_4 and HNO_3 (Table 3). This distribution of organic vs mineral acidity is similar in Agoufou, where the potential acidity contribution by organic acids is 27%, whereas it is 39% in Banizoumbou and 50% in Katibougou, due to the presence of denser vegetation and potential emissions of volatile organic compounds. As a comparison, in the wet savanna of Lamto (Côte d'Ivoire) the potential acidity contribution by organic acids

Table 3
Relative contribution of organic and mineral acidity to the total acidity measured at Dahra (2013–2014 and 2017 period).

Acidity	Concentration in μeq.L^{-1}	Acidity (%)
Organic acidity		
$HCOO^-$	5.7	12
CH_3COO^-	4.5	10
$C_2H_5COO^-$	0.2	0
$C_2O_4^{2-}$	2.6	5
Total 1	13.0	27
Mineral acidity		
NO_3^-	14.5	31
SO_4^{2-}	19.8	42
Total 2	34.3	73
Total H^+ potential	47.3	
H^+ measured	1.0	

is 56% (Yoboué et al., 2005), whereas it is only 16% at the Amersfoort industrial site, a dry savanna ecosystem in South Africa (Mphepya et al., 2004). Almost all the HNO_3 available is neutralized by alkaline solid dust particles and H_2SO_4 is captured by alkaline particles (Galy-Lacaux et al., 2001). The remaining acidity in precipitation in Dahra may therefore be related to organic compounds. Indeed, nitric and sulfuric acids, considered as strong acids, are completely neutralized in the Sahel by heterogeneous reaction with dust aerosols (Dentener et al., 1996; Galy-Lacaux and Modi, 1998), whereas organic acids, considered as weak acids, are not completely neutralized and thus certainly contribute to a larger part of the free acidity. However, one part of the organic acidity can also be neutralized by alkaline species. It is therefore assumed that measured acidity in rain in Dahra will be mainly explained by organic acids as mineral ones were completely neutralized by alkaline aerosols.

Dahra potential acidity (pA) is 47.3 μeq L^{-1}, corresponding to a pH of 4.33. The measured acidity (mA) is 1.00 μeq L^{-1} (Table 3). Therefore, 46.3 μeq L^{-1} of H^+ has been neutralized. A fraction of the acidity is neutralized by alkaline species such as Ca^{2+}, NH_4^+. NF value for Ca^{2+} is 1.11 and NH_4^+ and Mg^{2+} have lower NF values, 0.91 and 0.35, respectively. As a result, Ca^{2+} appears to be the major ion neutralizing the strong acids, followed by NH_4^+. This result is a common feature of the influence of desert soil dust emissions influencing precipitation chemistry, as mentioned in many other studies (Akpo et al., 2015 and references therein).

The annual VWM concentration of $HCOO^-$, CH_3COO^-, and $C_2O_4^{2-}$ in Dahra are similar to those obtained in Agoufou (Tables 4, 5). At the Katibougou site, organic ions concentrations are larger than in Dahra, which can be explained by the occurrence of biomass burning and the presence of denser vegetation at this site. Indeed, the contribution of organic acidity in precipitation is mainly due to volatile organic carbon (VOC) emissions from the vegetation and to the vegetation cycle in the Sahel (Guenther et al., 2006; Galy-Lacaux et al., 2009). During the monsoon season, the organic acidity is therefore significantly higher in Katibougou than at the three other sites because the growing of the vegetation is driven by the precipitation amount (Tracol, 2004), two times larger in Katibougou.

Dahra, as well as Agoufou located at the same latitude, present the same acidic and organic characteristics, highlighting the influence of the Saharan desert and the low density of vegetation in its rain composition, compared to more southern sites.

4.3.2. *Marine contribution*

Enrichment factors (EF) and sea-salt fraction (ssF) were used to estimate the marine contributions for Ca^{2+}, SO_4^{2-}, Mg^{2+}, K^+, and Cl^-, whereas all the sodium Na^+ is considered to be of marine origin (Eq. (4), Tables S2, 6). The Ratios of Ca^{2+}, SO_4^{2-}, Mg^{2+}, K^-, and Cl^- in relation to the sodium ion Na^+, at the four Sahelian sites are given in Table 6. For all four sites, the Cl^-/Na^+ ratio was close to 1 indicating that the Cl^- ion has a marine origin. The ratios SO_4^{2-}/Na^+, K^+/Na^+, and Ca^{2+}/Na^+ in Dahra were found to be higher than the seawater ratio, whereas the Mg^{2+}/Na^+ ratio (0.27) was relatively similar (Table 6). In addition, there was a strong correlation between Na^+ and Mg^{2+} ($R^2 = 0.91$), and Cl^- and Mg^{2+} ($R^2 = 0.79$) for Dahra (Table S1) while weaker correlations were observed for the three other sites (Laouali et al., 2012). The marine contribution could thereby be considered as the major source of Mg^{2+} at the Dahra site. At Agoufou, Banizoumbou, and Katibougou Sahelian sites all ratios including Mg^{2+}/Na^+**are** higher than those of seawater (Laouali et al., 2012). Similar results were found by Kulshrestha et al. (2003, 2005, 2009) for rural dry Indian sites. The high ratios of Ca^{2+}, SO_4^{2-}, Mg^{2+}, K^+ over Na^+ at the Sahelian sites indicate potential contributions from anthropogenic and crustal sources (Conradie et al., 2016) and not only from marine sources.

The enrichment factor EFs calculated for the Dahra site confirm that the source of Mg^{2+} is mainly from marine origin (EF of Mg^{2+} is 1.2). Other elements, such as Ca^{2+}, K^+, SO_4^{2-} exhibit higher EF confirming that these elements origin from other sources (Table 6).

The marine contributions for Mg^{2+}, SO_4^{2-}, K^+, Ca^{2+} are 84%, 27%, 8%, and 5% at the Dahra site, 26%, 16%, 3% and 2% in Agoufou, 31%, 12%, 3% and 1% in Banizoumbou and 32%, 10%, 4% and 1% in

Table 4
Volume-Weighted Mean Concentration VWM (μeq.L^{-1}) and Wet Deposition WD (kg ha^{-1} yr^{-1}) measured at Dahra.

Species	Dahra (2013)		Dahra (2014)		Dahra (2017)		Dahra (2013–2014 - 2017)	
	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})	VWM (μeq L^{-1})	WD (kg ha^{-1} yr^{-1})
H^+	2.01	0.007	0.46	0.001	0.53	0.002	1.00 (±1.05)	0.004 (± 0.003)
pH	5.70	–	6.33	–	6.27	–	6.10 (±0.35)	–
Na^+	44.18	3.60	64.45	4.77	23.82	2.18	44.15 (±20.31)	3.51 (± 1.30)
NH_4^+	28.07	1.79	36.5	2.11	29.25	2.10	31.27 (±4.57)	2.00 (± 0.18)
N in NH_4^+		1.40		1.64		1.63		1.55 (± 0.14)
K^+	11.39	1.58	17.12	2.15	7.73	1.20	12.08 (±4.73)	1.64 (± 0.48)
Ca^{2+}	38.27	2.71	43.08	2.78	34.20	2.73	38.52 (±4.45)	2.74 (± 0.03)
Mg^{2+}	11.30	0.49	14.57	0.57	9.92	0.48	11.93 (±2.39)	0.51 (± 0.05)
NO_3^-	12.89	2.83	13.63	2.72	17.08	4.21	14.53 (±2.24)	3.25 (± 0.83)
N in NO_3^-		0.64		0.61		0.95		0.73 (± 0.18)
Cl^-	40.39	5.07	48.89	5.57	25.05	3.53	38.11 (±12.08)	4.73 (± 1.06)
SO_4^{2-}	22.27	3.79	22.27	3.44	14.86	2.84	19.80 (±4.28)	3.36 (± 0.48)
S in SO_4^{2-}		2.52		2.29		1.89		2.23 (± 0.32)
*tCarb	53.55	11.56	68.69	13.48	38.26	9.29	53.50 (±15.22)	11.44 (± 2.10)
$HCOO^-$	7.19	1.15	5.23	0.76	4.65	0.83	5.69 (±1.33)	0.91 (± 0.21)
CH_3COO^-	5.14	1.08	3.37	0.64	5.13	1.21	4.55 (±1.02)	0.97 (± 0.30)
$C_2H_5COO^-$	0.22	0.06	0.23	0.05	0.20	0.06	0.22 (±0.02)	0.06 (± 0.00)
$C_2O_4^{2-}$	2.80	0.22	2.64	0.19	2.21	0.19	2.55 (±0.31)	0.20 (± 0.15)

*tCarb = total carbonates, ± refers to standard deviation.

Table 5
Volume Weighted Mean Concentration VWM (μeq L^{-1}) and Wet Deposition WD (kg ha^{-1} yr^{-1}) measured at the four Sahelian savannas.

Species	Dahra (2013–2014 - 2017)		Agoufou (2004–2006)		Banizoumbou (1994–2011)		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})	VWM (μeq L^{-1})	WD (kg ha^{-1} yr^{-1})
H^+	1.00 (±1.05)	0.004 (± 0.003)	0.5 (± 0.2)	0.002 (± 0.001)	1.5 (± 0.6)	0.009 (± 0.004)	3.0 (± 1.0)	0.024 (± 0.007)
pH	6.10 (±0.35)	–	6.28 (± 0.15)	–	5.82 (± 0.20)	–	5.54 (± 0.14)	–
Na^+	44.15 (±20.31)	3.51 (± 1.30)	18.8 (± 1.2)	1.36 (± 0.32)	11.9 (± 3.8)	1.34 (± 0.50)	6.3 (± 1.8)	1.16 (± 0.41)
NH_4^+	31.27 (±4.57)	2.00 (± 0.18)	25.2 (± 2.0)	1.56 (± 0.26)	18.5 (± 4.8)	1.15 (± 0.50)	19.1 (± 3.7)	1.18 (± 0.50)
N in NH_4^+		1.55 (± 0.14)		1.12		0.89		0.92
K^+	12.08 (±4.73)	1.64 (± 0.48)	12.4 (± 0.7)	1.55 (± 0.39)	9.2 (± 3.3)	1.77 (± 0.90)	3.7 (± 1.0)	0.12 (± 0.04)
Ca^{2+}	38.52 (±4.45)	2.74 (± 0.03)	32.3 (± 1.5)	2.09 (± 0.56)	27.8 (± 4.5)	2.73 (± 0.70)	22.9 (± 2.7)	3.65 (± 0.60)
Mg^{2+}	11.93 (±2.39)	0.51 (± 0.05)	16.5 (± 2.9)	0.67 (± 0.23)	7.2 (± 1.9)	0.43 (± 0.17)	4.5 (± 1.3)	0.43 (± 0.12)
NO_3^-	14.53 (±2.24)	3.25 (± 0.83)	14.6 (± 0.8)	3.12 (± 0.19)	10.6 (± 2.1)	2.26 (± 1.00)	10.4 (± 2.0)	2.22 (± 0.28)
N in NO_3^-		0.73 (± 0.18)		0.66		0.51		0.50
Cl^-	38.11 (±12.08)	4.73 (± 1.06)	20.2 (± 0.1)	2.30 (± 0.60)	11.1 (± 3.9)	1.93 (± 0.81)	6.5 (± 1.8)	1.86 (± 0.66)
SO_4^{2-}	19.80 (±4.28)	3.36 (± 0.48)	14.3 (± 3.3)	2.37 (± 0.13)	10.0 (± 1.7)	1.15 (± 0.23)	7.3 (± 0.1)	1.21 (± 0.20)
S in SO_4^{2-}		1.12 (± 0.16)		0.79		0.55		0.40
*tCarb	53.50 (±15.22)	11.44 (± 2.10)	39.6 (± 1.7)	7.77 (± 2.10)	28.5 (± 6.5)	7.75 (± 2.00)	19.1 (± 5.8)	9.35 (± 3.21)
$HCOO^-$	5.69 (±1.33)	0.91 (± 0.21)	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^-	4.55 (±1.02)	0.97 (± 0.30)	3.9 (± 1.1)	0.74 (± 0.28)	6.6 (± 2.2)	0.68 (± 0.36)	5.2 (± 1.7)	2.44 (± 0.74)
$C_2H_5COO^-$	0.22 (±0.02)	0.06 (± 0.00)	0.2 (± 0.1)	0.04 (± 0.01)	0.3 (± 0.03)	0.05 (± 0.05)	0.1 (± 0.1)	0.09 (± 0.07)
$C_2O_4^{2-}$	2.55 (±0.31)	0.20 (± 0.02)	2.2 (± 0.8)	0.11 (± 0.06)	1.8 (± 0.6)	0.05 (± 0.02)	1.8 (± 0.9)	0.35 (± 0.12)

*tCarb = total carbonates, ± refers to standard deviation.

Table 6
Seawater ratios and equivalent ratios of ionic components to Na^+, with corresponding enrichment factors (EF) at the four INDAAF dry savanna sites.

Ion ratios	Seawater	Dahra (2013–2014 and 2017)	Agoufou (2004–2006)	Banizoumbou (1994–2011)	Katibougou (1997–2008)
Ca^{2+}/Na^+	0.044	0.88	1.718	2.336	3.635
$EF^{2+}_{(Ca)}$		19.8	29.0	52.8	78.6
SO_4^{2-}/Na^+	0.121	0.45	0.761	0.840	1.159
$EF(SO_4^{2-})$		3.7	3.3	6.9	10.2
Mg^{2+}/Na^+	0.227	0.27	0.878	0.605	0.714
$EF(Mg^{2+})$		1.2	1.9	2.7	3.2
K^+/Na^+	0.022	0.27	0.660	0.773	0.587
$EF(K^+)$		12.4	19.8	34.9	27.6
Cl^-/Na^+	1.161	0.86	1.074	0.933	1.032
$EF(Cl^-)$		0.7	0.6	0.8	0.9

*Seawater ratios from Keene et al. (1986).

Katibougou, respectively. Marine contribution in relation to the total ionic content at the four sites are 36% in Dahra, 23% in Agoufou, 17% in Banizoumbou, and 13% in Katibougou (Fig. 3). The higher value in Dahra is explained by its proximity to the sea compared to the three other sites. Furthermore, air masses leading to precipitation in Katibougou, Banizoumbou and Agoufou are linked to the monsoon system entering the continent and creating convective squall lines, whereas in Dahra, air masses are directly coming from the Atlantic ocean and are less driven by mesoscale convective systems (Marticorena et al., 2010), conferring a more specific marine character at Dahra site.

4.3.3. Terrigenous compounds contribution

The total ionic charge of the potential terrigenous compounds ($nssCa^{2+}$ + $nssK^+$ + $nssSO_4^{2-}$ + $nssMg^{2+}$ + $nssCl^-$ + tcarbonates, Table S2) is 117.5 μeq L^{-1} and represents 42% of the total ionic content (278.2 μeq L^{-1}) in precipitation at the Dahra site. Terrigenous and marine contributions lead to the highest mean wet deposition fluxes of Ca^{2+} (WD = 5.48 kg ha^{-1} yr^{-1}), total carbonates (11.44 kg ha^{-1} yr^{-1}), Cl^- (4.73 kg ha^{-1} yr^{-1}) and Na^+ (3.51 kg ha^{-1} yr^{-1}) (Table 4).

The annual VWM concentrations of Ca^{2+} (Table 5) present a negative terrigenous gradient from Dahra (38.5 μeq L^{-1}), to Agoufou, Banizoumbou, and Katibougou (Table 5). This terrigenous gradient continues to decrease from North to South towards the wet savanna of Lamto in Côte d'Ivoire (Ca^{2+} = 9.5 μeq L^{-1}, Yoboué et al., 2005), and to the forested ecosystem of Cameroon (Sigha-Nkamdjou et al., 2003) with 8.9 μeq L^{-1}. Lower values, between 12.0 and 18.7 μeq L^{-1}, are found for two South African dry INDAAF sites, Louis Trichardt and Amersfoort (Mphepya et al., 2005).

In Dahra, the ions K^+ and SO_4^{2-} are correlated with Ca^{2+} (R = 0.73, and R = 0.77, respectively, Table S1) emphasizing the contribution of the terrigenous sources, varying between 74 and 95% of the total precipitation chemical load for SO_4^{2-}, 91–97% for K^+, and 95–99% for Ca^{2+} at the four Sahelian sites.

Terrigenous contributions involve the highest mean wet deposition fluxes for Ca^{2+} at the four sites (Table 5). Lower wet deposition fluxes of Ca^{2+} are found in Louis Trichardt and Amersfoort urban sites in South Africa with 1.8 and 2.8 kg ha^{-1} yr^{-1} at the two sites, respectively (Mphepya et al., 2005). The terrigenous contributions to the total ionic content (tcarb+$nssCa^{2+}$+$nssSO_4^{2-}$ + $nssK^+$+$nssCl^-$)/(Total VWM of ionic concentrations) are 42% in Dahra, 53% in Agoufou, 51% in Banizoumbou and 46% in Katibougou, and constitute the highest contribution to the chemical composition of precipitation for West African sites (Fig. 3).

The terrigenous contribution to the chemical composition of precipitation is linked to African soil dust composition, including e.g. calcite, dolomite, gypsum and other key minerals such as illite, smectite and palygorskite (Avila et al., 1997; Galy-Lacaux et al., 2009; Conradie et al., 2016). These high contributions of terrigenous sources in the Sahelian African sites feature the direct influence of soil dust in precipitation over the Sahelian region. The northern Sahel and Sahara are probably the most important mineral aerosol source (Kaufman et al., 2005; Marticorena et al., 2010), which impacts more the Eastern Sahel (Mali, Niger) than the Western Sahel (Senegal) due to the lowest occurrence of convective systems in Senegal and therefore the lowest production of local dust emissions (Marticorena et al., 2017). For this reason, Dahra is impacted by dust due to its proximity to the Sahara

desert, but its western location far from source areas decreases the dust influence compared to sites located more easterly on the continent. Due to the partial dissolution of soil dust terrigenous compounds, precipitation in Dahra is loaded with dissolved calcium and carbonates (calcite), explaining the ionic content, as often mentioned in precipitation chemistry studies performed in other African or Mediterranean ecosystems, or in Asia (Galy-Lacaux et al., 2009; Laouali et al., 2012; Celle-Jeanton and Travi, 2009; Desboeufs et al., 2010; Kulshrestha et al., 2009; Akpo et al., 2015).

4.3.4. *Nitrogenous compounds contribution*

The nitrogenous contribution is in third position after marine and terrigenous contributions in the chemical composition of precipitation collected in Dahra, as shown by the VWM ionic concentrations of nitrate and ammonium measured during the three-year study (Table 4). The concentrations of inorganic nitrogen in precipitation in Dahra are larger than at the three other sahelian sites of Agoufou, Banizoumbou and Katibougou (Table 4). In Dahra, pastoralism is an important activity and livestock herds cross the site all year round, leading to important loads of manure and subsequent N compound emissions, as detailed below. In a lesser extent, this is also the case in Agoufou, located at the same latitude (15°N approximately). Furthermore the four sahelian sites are subject to N compound pulse emissions from natural soils, as detailed below, these pulse emissions being more effective in Dahra and Agoufou due to their higher latitudinal location and drier soils. These results confirm the importance of the nitrogenous contribution in this area (Laouali et al., 2012; Delon et al., 2012) and give an indication on the potential sources of nitrogen from this sylvo-pastoral region in Senegal, linked to soil processes and livestock.

In comparison, South African semi-arid savannas of Louis Trichardt (LT) and Skukuza present lower VWM ionic concentrations of nitrate and ammonium (NO_3^- = 8 to 8.1 μeq L^{-1} and NH_4^+ = 9 to 9.7 μeq L^{-1}, Mphepya et al., 2005, 2006). Mphepya et al. (2005) show that the Amersfoort site presents higher concentrations of nitrate (25.0 μeq L^{-1}) and ammonium (22.3 μeq L^{-1}), related to industrial NOx emissions. VWM concentrations along a transect dry savanna - wet savanna – forest highlight a decreasing gradient of inorganic nitrogen content in precipitations. Annual VWM concentrations of nitrate and ammonium in the wet savanna of Lamto (respectively 7.7 and 17.6 μeq L^{-1}, Yoboué et al., 2005) and in the forest of Zoetele (respectively 6.9 and 10.5μeq L^{-1}, Sigha-Nkamdjou et al., 2003) are lower than those measured in Dahra. As a comparison, in developed regions of the northern hemisphere, N deposition is influenced by the use of synthetic fertilizers in rural regions, and by traffic and industries in urban regions. Generally, N deposition is one order of magnitude larger in regions where the anthropogenic influence is high (Vet et al., 2014).

Wet deposition flux of ammonium measured in Dahra reaches 1.55 kgN ha^{-1} yr^{-1}, and wet deposition flux of nitrates reaches 0.73 kgN ha^{-1} yr^{-1} (Tables 5, 6). Correlation between Ca^{2+} and NO_3^- is around 0.54 in Dahra (Table S1), 0.68 in Agoufou, 0.76 in Banizoumbou and 0.83 in Katibougou. As in the three other Sahelian sites, this correlation indicates potential heterogenous and multiphase chemical processes occurring between alkaline dust and gaseous nitric acid in precipitation in Dahra (Laouali et al., 2012).

The monthly concentrations of NO_2, HNO_3 and NH_3 measured by passive samplers (Fig. 6a) in 2013, 2014 and 2017 gives an indication on the evolution of surface nitrogenous gas concentrations in Dahra and at the Sahelian sites. Monthly mean NO_2 concentrations (Fig. 6a) range

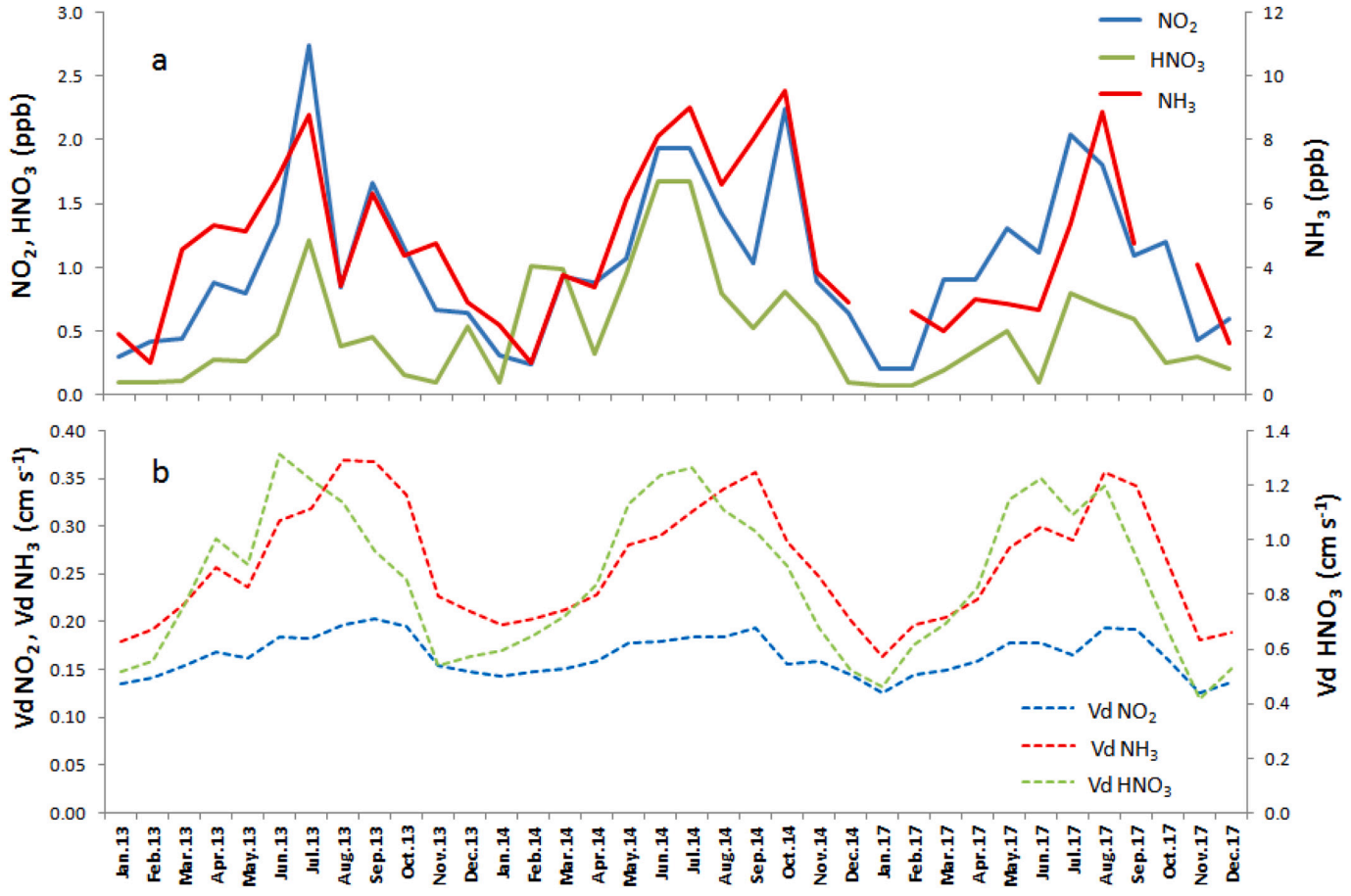

Fig. 6. (a) Monthly average concentrations of NO_2, NH_3 and HNO_3 (ppb) measured by passive samplers at Dahra site and (b) deposition velocities for NO_2, NH_3 and HNO_3 (cm s^{-1}) simulated with Zhang et al. (2003, 2010) model for years 2013, 2014, 2017.

between 0.4 ± 0.1 ppb and 2.7 ± 0.4 ppb at the Dahra site. Monthly concentrations start to increase significantly in May/June before the onset of the monsoon season. A first maximum is observed in June/July with the first rains and corresponds to the emission of biogenic NO emissions from soils, involved by the accumulation of mineral nitrogen during the long dry season. Indeed, when the wet season begins, the first rains activate microbial processes and nitrification, which leads to large pulses of NO from bare soils before the vegetation growth (Delon et al., 2015; Oswald et al., 2013; Hudman et al., 2012). After its release to the atmosphere, NO is rapidly converted into NO_2 through oxidative processes. After these pulses occurring at the beginning of the wet season, NO emissions decrease, and nitrogen from the soil is taken up by plants for their growth. NO_2 concentrations levels remain relatively high compared to the dry season, correlated to NO emissions from soils still occurring during the wet season, but less intense (Serça et al., 1998; Delon et al., 2015). A second maximum in NO_2 concentration occurs at the beginning of the dry season in September-October in Dahra. Dahra is located in a region where vegetation density is rather low, and biomass burning has a limited impact on atmospheric gas concentrations, despite the occurrence of fires in the Northern hemisphere at that period (Jaegle et al., 2004). On the other hand, NO emissions from soils due to the decomposition of organic matter at the end of the wet season may occur, when vegetation does not take up nitrogen from soil anymore, and soil moisture is still sufficient to allow mineralization of organic matter (Delon et al., 2019). The highest NO_2 concentrations are found at the beginning of the wet season (Fig. 6a), as reported in Adon et al. (2010) for other West African sites.

HNO_3 is an end product of nitrogen compounds oxidation in the atmosphere. The HNO_3 concentration annual cycle shows the highest concentrations in June July (Fig. 6a), consistent with NO_2 concentration in air and NO_3^- concentrations in precipitations at the Dahra site.

This is consistent with the monthly evolution of NH_3 concentrations (Fig. 6a). A first peak occurs at the beginning of the wet season in June/July, before the growing of the vegetation, and a second peak occurs at the end of the wet season in September-October (Fig. 6a), corresponding to potential decomposition of organic matter and emission from litter (Delon et al., 2017). In August, the NH_3 atmospheric concentration decreases due to the washout of the atmosphere by precipitation. Furthermore, in the Sahel, the high NH_3 concentrations in air and high ammonium content in precipitations are directly linked to the volatilization of animal manure (Galy-Lacaux and Modi, 1998; Serça et al., 1998; C. Galy-Lacaux et al., 2009; Delon et al., 2012). Indeed, developing countries are responsible for the emissions of 15 TgN, which represents 2/3 of the global emissions from animal manure (Galy – Lacaux & Delon, 2014). NH_3 volatilization is more likely to occur in the Sahel than in other regions of the world because of high temperatures, low soil moisture and bare soil surfaces. Furthermore, the quality and quantity of feed are better at the end of the wet season resulting in more nitrogen in animal manure (Hiernaux et al., 1998; Hiernaux and Turner, 2002; Schlecht and Hiernaux, 2004).

Emissions of nitrogen compounds from soils, taking into account NO biogenic emissions, volatilization of NH_3, and NOx and NH_3 emissions from biomass burning and domestic fires (Fig. 7) (Galy-Lacaux and Delon, 2014) were estimated for Sahelian sites from literature results reported in Delon et al. (2012), for the period 2002–2007. The average annual biogenic NO flux is estimated at 1.14 ± 0.92 kgN ha^{-1} yr^{-1} in Dahra according to Delon et al. (2019) for the years 2012 and 2013. This average value is extrapolated to further years with an uncertainty based on the interannual variability of the rain (±24% from 2012 to 2017 as presented in section 3.2). Domestic fire emissions, estimated for the reference year 2003 (and considering no specific trend) contribute very weakly to this emission budget with 0.08 kgN ha^{-1} yr^{-1}). The contribution of biomass burning for nitrogen compounds emission is also weak (0.006 ± 0.003 kgN ha^{-1} yr^{-1}). The volatilization of ammonia from animal urine and excreta is 7.6 ± 2.7 kg N $ha^{-1}.yr^{-1}$ in Dahra (Fig. 7). Indeed, the livestock density in the Ferlo region of Senegal (Food and Agriculture Organization, FAO, Global Livestock Production and Health Atlas GLiPHA (2009, http://kids.fao.org/glipha/), combined with the N content in animal excreta (Schlecht and Hiernaux, 2004) leads to a N input in the soil of 25.2 kgN ha^{-1} yr^{-1}. 30% of this input is volatilized as NH_3 (Delon et al., 2012). The total N emission reaches 8.8 ± 3.1 kgN ha^{-1} yr^{-1}.

4.4. Annual VWM concentrations and WD fluxes in Sahelian dry savanna sites

The annual chemical load in precipitation (Fig. 8a) is 278.2, 205.2, 146.2 and 120.2 μeq.L^{-1} in Dahra, Agoufou, Banizoumbou, and Katibougou, respectively, showing a clear negative gradient of the total chemical load in precipitation from Northern to Southern dry savanna sites. The WD fluxes (8b) are impacted by the precipitation gradient from North to South, with 356 mm in Dahra, 321 mm in Agoufou, 509 mm in Banizoumbou and 804 mm in Katibougou. Therefore, the large total chemical load in Dahra for all species leads to the largest wet deposition flux compared to the three other sites. Along this transect, the different ionic species were grouped according to their origin previously

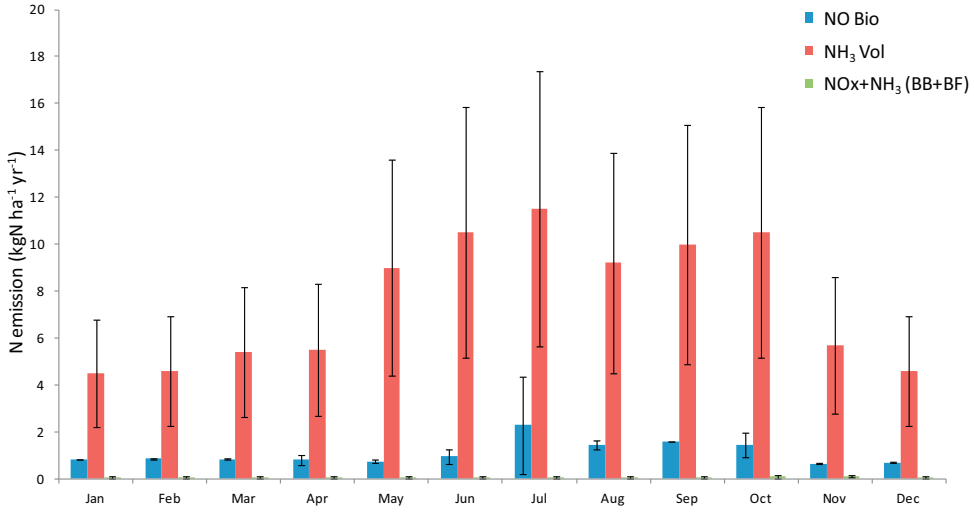

Fig. 7. Mean monthly distribution of nitrogen compound emissions in kgN ha^{-1} yr^{-1}, BB = Biomass Burning, BF=BioFuel, Vol. = Volatilization, NO Bio = Biogenic NO flux. Error bars indicate the standard deviation. These emissions are based on estimations for the period 2002–2007.

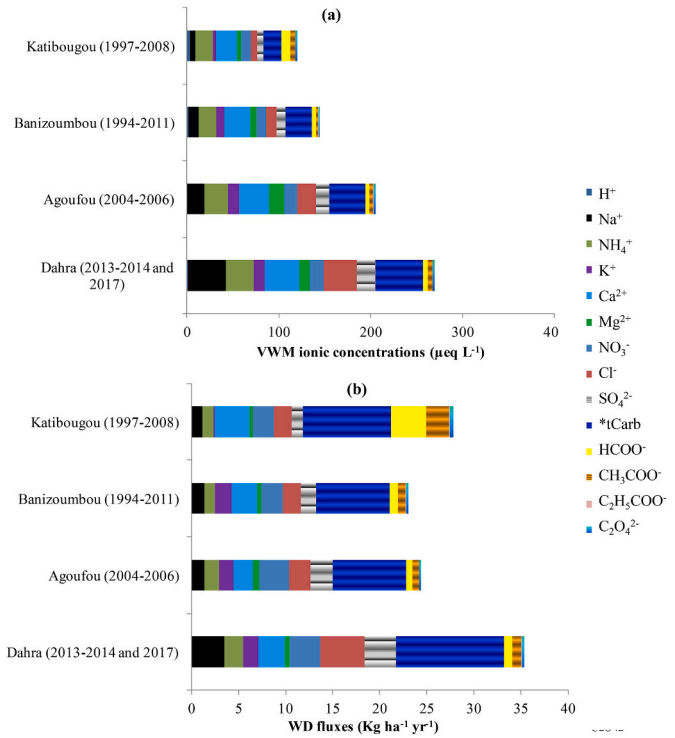

Fig. 8. (a) Annual ionic Volume Weighed Mean (VWM) concentrations (µeq L^{-1}) and (b) Annual average Wet deposition (WD) fluxes (kg ha^{-1} yr^{-1}) at the four African dry savanna sites of the INDAAF network.

identified in section 4.3 (Fig. 4(a-d)). The contribution of the organic component in Dahra is lower (5%) than in Banizoumbou (9%) and Katibougou (14%) but comparable to Agoufou (5%). As vegetation density depends on precipitation, this result is not surprising because vegetation and soil play an important role in semi-arid and arid areas in the contribution of organic compounds. Due to the proximity of the Atlantic Ocean, Dahra has the highest marine contribution among the four semi-arid savanna sites, with 36% of the total content of chemical compounds, against 23% in Agoufou, 19% in Banizoumbou and 13% in Katibougou. A strong contribution of terrigenous compounds is observed at all four semi-arid sites, slightly less important in Dahra (42%), compared to Agoufou (53%), Banizoumbou (51%) and Katibougou (46%), (Fig. 3). A negative gradient of the major terrigenous species concentrations appears from Dahra to Agoufou, Banizoumbou and Katibougou, from north to south, related to source regions of dust and their potential transport. The acidity of precipitation and the concentrations of potential neutralizing agents evolve along this transect of ecosystems. The nitrogenous contribution to the total chemical content of rain is roughly comparable at the four savanna sites and varies between 16% and 25%, with the highest contribution in Dahra and Agoufou due to a larger impact of livestock and biogenic emissions from soils in these northernmost located sites.

4.5. Wet and dry nitrogen deposition in Dahra

4.5.1. Wet deposition of N species

The monthly nitrogen WD flux corresponds to the sum of monthly WD NH_4^+-N and NO_3^- -N fluxes. August 2014, with 150.8 mm of precipitation, has the highest nitrogen WD flux (0.85 kgN ha^{-1} $month^{-1}$) followed by August 2013 (0.41 kgN ha^{-1} $month^{-1}$) with 105.1 mm, and August 2017 (0.58 kgN ha^{-1} $month^{-1}$) with 173.4 mm (Fig. 9).

The annual nitrogen WD flux is defined as the sum of the monthly nitrogen WD for one year. Annual nitrogen WD fluxes range between 1.79 and 2.59 kgN ha^{-1} yr^{-1} during the three years of study at the Dahra site with a mean value of 2.28 ± 0.32 kgN ha^{-1} yr^{-1}. These fluxes are comparable to WD fluxes measured at Agoufou, Banizoumbou and Katibougou, with values between 1.40 and 2.28 kgN ha^{-1} yr^{-1} (Table 5). At all dry savanna sites, N wet deposition is dominated by NH_4^+. This reduced N contribution to the total N wet deposition represents 68%, 63%, 63% and 65% respectively in Dahra, Agoufou, Banizoumbou and Katibougou. This result emphasizes the importance of the animal source at Dahra site, compared to biogenic emissions of oxygenized compounds from soils. In Vet et al. (2014), the combined model-measurements maps of N indicated that modeled wet deposition fluxes were underestimated in the Sahelian region of Mali (0–1 kgN ha^{-1} yr^{-1}). Our measurements at Dahra show that N wet deposition in the Sahelian part of Senegal is about 2 kgN ha^{-1} yr^{-1}, higher by a factor of two than modeled mean values (Vet et al., 2014). The annual nitrogen WD flux measured in Dahra is lower than for wet savanna sites (3.5–5.3 kgN ha^{-1} yr^{-1}) or in the equatorial forest of Zoetele (3.6 kgN ha^{-1} yr^{-1}, Galy-Lacaux and Delon, 2014). Despite the high values of VWM ionic concentrations of NO_3^- and NH_4^+ measured in dry savanna precipitation, the nitrate and ammonium deposition fluxes increase from dry to wet savannas and to the forest ecosystems. Indeed, WD fluxes are driven by the precipitation amount, increasing as well along the transect dry savannas–wet savannas–forest, from 350 to 1550 mm.yr^{-1}.

4.5.2. Dry and total nitrogen deposition fluxes

To give the relative contribution of wet to total nitrogen deposition fluxes, dry deposition fluxes for the same period (2013–2014 and 2017) were calculated from gaseous concentration measurements (NO_2, HNO_3,

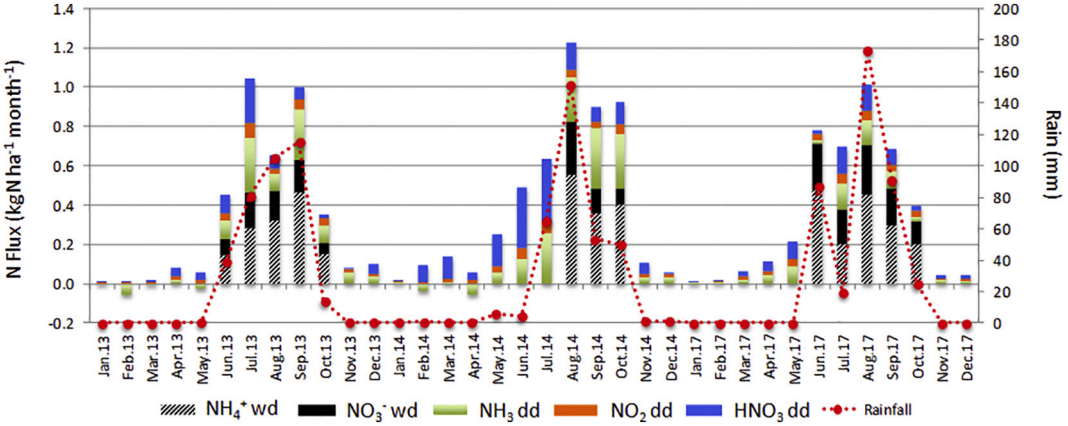

Fig. 9. Monthly nitrogen wet deposition (wd) fluxes of NH_4^+ and NO_3^-, dry deposition (dd) fluxes of NO_2, NH_3 and HNO_3 (kgN ha^{-1} $month^{-1}$), and rainfall (in mm) at Dahra site for years 2013, 2014 and 2017.

NH_3, Fig. 6a) and modeled deposition velocities (Fig. 6b). Dry deposition velocity monthly means range from 0.16 to 0.20 cm s^{-1} for NO_2, from 0.52 to 1.31 cm s^{-1} for HNO_3 and from 0.18 to 0.37 cm s^{-1} for NH_3 for the years 2013, 2014 and 2017 and annual gas concentrations measured in 2013, 2014 and 2017 are 1.03 ± 0.60, 4.63 ± 2.4, 0.49 ± 0.42 ppb in Dahra. These values are of the same order than those reported for the three savanna sites of the INDAAF network (Agoufou, Banizoumbou and Katibougou) reported in Delon et al. (2010) and Adon et al. (2013). Concerning concentration levels, Dahra presents annual comparable HNO_3 concentrations but lower NO_2 and NH_3 concentrations than reported in Adon et al. (2013) for dry savanna sites in Mali and Niger (1.8–2.4 ppb of NO_2 and 6.3 to 7.3 ppb of NH_3).

In Dahra, the monthly dry deposition fluxes range between 0.004 and 0.08 kgN ha^{-1} $month^{-1}$ for NO_2, and between 0.005 and 0.32 kgN ha^{-1} $month^{-1}$ for HNO_3 (Fig. 9). Using the bidirectional exchange for NH_3 flux calculation, contrary to the usual convention, in this figure, a negative sign denotes emission fluxes (contrary to Fig. 7) and a positive sign, deposition fluxes. Thus, the monthly net fluxes of NH_3 range from an emission of −0.06 kgN ha^{-1} $month^{-1}$ in the dry season to a deposition of 0.31 kgN ha^{-1} $month^{-1}$ in the wet season, which is comparable to modeling values obtained by Delon et al. (2019) ranging between 0.02 and 0.21 kgN ha^{-1} $month^{-1}$ from dry to wet seasons. At the annual scale, nitrogen dry deposition fluxes were estimated at 0.32 (±0.02) kgN ha^{-1} yr^{-1} for NO_2, 0.89 (±0.48) kgN ha^{-1} yr^{-1} for HNO_3 and 0.89 (±0.33) kgN ha^{-1} yr^{-1} for NH_3. The total annual N (NO_2 + HNO_3 + NH_3) dry deposition flux at the Dahra site was 1.79 kgN ha^{-1} yr^{-1} in 2013, 3.02 kgN ha^{-1} yr^{-1} in 2014 and 1.49 kgN ha^{-1} yr^{-1} in 2017 with a mean of 2.10 ± 0.81 kgN ha^{-1} yr^{-1} for the three years. These annual N dry deposition estimates are within the range of values estimated at the three INDAAF savanna sites (1.6 to 3.8 kgN.ha^{-1}.yr^{-1}, Adon et al. (2013)), though being in the lower range of previous estimates because they only rely on gaseous dry N deposition excluding particulate dry N deposition. However, particulate nitrate concentrations have been found very low in dry savannas (Delon et al., 2010; Galy-Lacaux and Delon, 2014).

The total (dry + wet) annual N deposition flux is 3.80 kgN ha^{-1} yr^{-1} in 2013, 4.81 kgN ha^{-1} yr^{-1} in 2014 and 4.08 kgN ha^{-1} yr^{-1} in 2017 in Dahra with a mean of 4.23 ± 0.52 kgN ha^{-1} yr^{-1} for the three years. Wet deposition contributes to 53% of the total N deposition flux in 2013, 37% in 2014 and 64% in 2017. These results suggest that the contribution of N wet deposition is as important as N dry deposition for direct N effect on the dry savanna ecosystems. The reduced form (NH_4^+, NH_3) of nitrogen compounds contributes 55% to total N deposition flux for the three years of study, due essentially to the presence of livestock, as stated above. Pulse emissions of oxygenized compounds exert an influence in the N rain content during the short rainy season, whereas the presence of livestock year round will influence both dry and wet N deposition fluxes. The magnitudes of total N deposition fluxes to the Dahra site are comparable to those of dry savanna sites ranging from 3.4 to 7.1 kg N ha^{-1} yr^{-1} (Adon et al., 2013).

5. Conclusion

In this paper, new results from a study on precipitation chemistry at the Dahra site (Senegal), representative of a Sahelian dry savanna are presented and inter-compared with results of Agoufou and Katibougou (Mali), Banizoumbou (Niger), from the INDAAF program over West Africa.

The mean precipitation chemical content in Dahra is computed on inter-annual time scales and for the full 2013–2014 and 2017 period. The five main ions in Dahra precipitation were Na^+, Cl^-, Ca^{2+}, NH_4^+, and SO_4^{2-}, with relatively high concentration levels. The largest source contribution of those compounds is the terrigenous source (proximity of the Saharan desert), followed by marine source (proximity of the Atlantic ocean), nitrogenous source (animals, decomposition of organic matter), and organic source (vegetation, biomass burning). Na^+, representing the marine source, is the most abundant in Dahra as compared to other Sahelian sites. Precipitation concentration of $nssCa^{2+}$, $nssSO_4^{2-}$, and $nssK^+$ are linked to terrigenous sources from wind erosion of Saharan and Sahelian soils. The nitrogenous contribution is also high, with the concentration of NH_4^+ in Dahra being higher than those found at the three other semi-arid sites due to the importance of transhumance of livestock herds at this site.

In Dahra, the total (wet + dry) annual N deposition fluxes range between 3.80 and 4.81 kgN ha^{-1} yr^{-1}. Wet deposition fluxes contribute to 37–64% of the total N flux. In parallel, N emissions were also calculated and reach 8.8 ± 3.1 kgN ha^{-1} yr^{-1}. At the time of the study, total (wet + dry) N deposition flux in Dahra is lower than N estimated emission sources, which indicates that this site is not yet influenced by remote anthropogenic activities. Our annual total N deposition estimates are within the range of values estimated for other dry savanna sites in Mali and Niger, with the specificity of NH_3 volatilization from animal manure contributeing in the largest way to the N total budget, both for N emission and N deposition fluxes in Dahra. This original study of the deposition characterization in a Sahelian region, with several combined influence of sources because of its specific location close to the ocean and the desert, answers a recommendation of the WMO deposition assessment (Vet et al., 2014) to implement more measurements in under sampled arid-regions of Africa. In the future the INDAAF program (long term monitoring of atmospheric deposition) will allow the documentation of spatial and temporal trends of nitrogenous compounds representative of the major ecosystems in Africa, a continent where the anthropogenic pressure due to demographic expansion, and land use, change rapidly and contribute to the increase of pollutant emissions to the atmosphere.

Declaration of Competing Interest

None.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.atmosres.2020.105423.

References

Adon, M., Galy-Lacaux, C., Yoboue, V., Delon, C., Lacaux, J.P., Castera, P., Gardrat, E., Pienaar, J., Al Ourabi, H., Dungall, L., Diop, B., Sigha-Nkamdjou, L., Akpo, A., Lavenu, F., Mougin, E., 2010. Long-term measurements of Sulphur dioxide, nitrogen dioxide, ammonia, nitric acid and ozone in Africa using passive samplers. Atmospheric Chemistry and Physics 10, 7467–7487.

Adon, M., Galy-Lacaux, C., Delon, C., Yoboue, V., Solmon, F., Kaptue Tchuente, A.T., 2013. Dry deposition of nitrogen compounds (NO_2, HNO_3, NH_3), sulfur dioxide and ozone in west and central African ecosystems using the inferential method. Atmospheric Chemistry and Physics 13, 11351–11374. https://doi.org/10.5194/acp-1311351-2013.

Akpo, A.B., Galy-Lacaux, C., Laouali, D., Delon, C., Liousse, C., Adon, M., Gardrat, E., Mariscal, A., Darakpa, C., 2015. Precipitation chemistry and wet deposition in a remote wet savanna site in West Africa: Djougou (Benin). Atmospheric Environment 115, 110–123.

Avila, A., Queralt-Mitjans, I., Alarcon, M., 1997. Mineralogical composition of Africa dust delivered by red rains over northeastern Spain. Journal of Geophysical Research 102 (D18), 21977–21996.
Bravo, H.A., Saavedra, M.I.R., Sanchez, P.A., Torres, R.J., Granada, L.M.M., 2000. Chemical composition of precipitation in a Mexican Maya region. Atmospheric Environment 34, 1197e1204.
Celle-Jeanton, H., Travi, Y., Loye ePilot, M.-D., Huneau, F., Bertrand, G., 2009. Rainwater chemistry at a Mediterranean inland station (Avignon, France). Local Contrib. Versus Long-Range Supply Atmos. Res. 91, 118–126.
Conradie, E.H., Van Zyl, P.G., Pienaar, J.J., Beukes, J.P., Galy-Lacaux, C., Venter, A.D., Mkhatshwa, G.V., 2016. The chemical composition and fluxes of atmospheric wet deposition at four sites in South Africa. Atmospheric Environment 146, 113–131.
CSE, 2015. Actualisation du découpage et de la caractérisation des zones écogéographiques du Sénégal. MEDD., DEEC, Dakar, p. 92.
CSE, ANACIM, FAO, 2017. Diagnostic des menaces, des contraintes et des opportunités liées au changement climatique et aux savoirs endogènes en matière d'adaptation dans la Zone Sylvo-Pastorale, le Bassin arachidier et le Sénégal Oriental, p. 79.
Delon, C., Galy-Lacaux, C., Boone, A., Liousse, C., Serça, D., Adon, M., Diop, B., Akpo, A., Lavenu, F., Mougin, E., Timouk, F., 2010. Atmospheric nitrogen budget in Sahelian dry savannas. Atmospheric Chemistry and Physics 10, 2691–2708.
Delon, C., Galy-Lacaux, C., Adon, M., Liousse, C., Serça, D., Diop, B., Akpo, A., 2012. Nitrogen compounds emission and deposition in West African ecosystems: comparison between wet and dry savanna. Biogeosciences 9, 385–402.
Delon, C., Mougin, E., Serça, D., Grippa, M., Hiernaux, P., Diawara, M., Galy-Lacaux, C., Kergoat, L., 2015. Biogeosciences 12, 3253–3272. https://doi.org/10.5194/bg-12-3253-2015.
Delon, C., Galy-Lacaux, C., Serça, D., Loubet, B., Camara, N., Gardrat, E., Saneh, I., Fensholt, R., Tagesson, T., Le Dantec, V., Sambou, B., Diop, C., Mougin, E., 2017. Soil and vegetation-atmosphere exchange of NO, NH_3, and N_2O from field measurements in a semi arid grazed ecosystem in Senegal. Atmospheric Environment 156, 36–51. https://doi.org/10.1016/j.atmosenv.2017.02.024.
Delon, C., Galy-Lacaux, C., Serça, D., Personne, E., Mougin, E., Adon, M., Dantec, V.L., Loubet, B., Fensholt, R., Tagesson, T., 2019. Modelling land–atmosphere daily exchanges of NO, NH_3, and CO_2 in a semi-arid grazed ecosystem in Senegal. Biogeosciences 16, 2049–2077. https://doi.org/10.5194/bg-16-2049-2019.
Dentener, Frank J., Gregory R., Carmichael, Yang, Zhang, Jos, Lelieveld, Paul J., Crutzen, 1996. Role of mineral aerosol as a reactive surface in the global troposphere. Journal of Geophysical Research 101 (D17), 22,869–22,889.
Desboeufs, K., Journet, E., Rajot, J.-L., Chevaillier, S., Triquet, S., Formenti, P., Zakou, A., 2010. Chemical properties of rain events during the AMMA campaign: an evidence of dust and biogenic influence in the convective systems. Atmospheric Chemistry and Physics 10, 15263–15293.
Dikaiakos, J.G., Tsitouris, C.G., Siskos, P.A., Melissos, D.A., Nastos, P., 1990. Rainwater composition in Athens, Greece. Atmospheric Environment 24B (1), 171–176.
Folland, C.K., Palmer, T.N., Parker, D.E., 1986. Sahel rainfall and wordwide sea Temperature, 1901-1985. Nature 320, 602–607.
Galy-Lacaux, C., Delon, C., 2014. Nitrogen emission and deposition budget in West and Central Africa. Environement Research Letter 9 (125002). https://doi.org/10.1088/1748-9326/9/12/125002.
Galy-Lacaux, C., Modi, A.I., 1998. Precipitation chemistry in the Sahelian savanna of Niger, Africa. Journal of Atmospheric Chemistry 30, 319–343.
Galy-Lacaux, C., Carmichael el, G.R., Song, C.H., Lacaux, J.P., Modi, I., 2001. Heterogenous processes involving nitrogenous compounds and Saharan dust inferred from measurements and model calculations Region. Journal of Geophysical Research 106, 12559–12578.
Galy-Lacaux, C., Laouali, D., Descroix, L., Liousse, C., 2009. Long term precipitation chemistry and wet deposition in a remote dry savanna site in Africa (Niger). Atmospheric Chemistry and Physics 9, 1579–1595.
Galy-Lacaux, C., Modi, A.I, Precipitation chemistry in the sahelian savanna of Nifer, Africa, 1998. Precipitation chemistry in the sahelian savanna of Niger, Africa. Journal of Atmospheric Chemistry 30, 319–343.
Gomes, L., Arrue, J.L., Lopez, M.V., Sterk, G., Richard, D., Gracia, R., Sabre, M., Gaudichet, A., Frangi, J.P., 2003. Wind erosion in a semiarid agricultural area of Spain. Catena 52, 235–256.
Guenther, A., Karl, T., Harley, P., Wiedinmyer, P., Palmer, P.I., Geron, C., 2006. Estimates of global terrestrial isoprene emissions using MEGAN (Model of emissions of gases and Aerosols from Nature). Atmospheric Chemistry and Physics 6, 3181–3210. http://www.atmos-chem-phys.net/6/3181/2006/.
Hiernaux, P., Turner, M.D., 2002. The influence of farmer and pastoralism management practices on desertification processes in the Sahel. In: Reynolds, J.F., Stafford Smith, D.M. (Eds.), Global Desertification: Do Humans Cause Deserts? Dahlem University Press, Berlin, pp. 135–148.
Hiernaux, P., Fernandez-Rivera, S., Schlecht, E., Turner, M.D., Williams, T.O., 1998. Livestock-mediated nutrient transfers in Sahelian agro-ecosystems. In: Renard, G., Neef, A., Becker, K., von Oppen, M. (Eds.), Soil fertility management in West African land use systems, Niamey, Niger, 4–8.03.97. Margraf Verlag, Weikersheim, Germany, pp. 339–347.
Hudman, R.C., Moore, N.E., Mebust, A.K., Martin, R.V., Russell, A.R., Valin, L.C., Cohen, R.C., 2012. Steps towards a mechanistic model of global soil nitric oxide emissions: implementation and space based-constraints. Atmospheric Chemistry and Physics 12, 7779–7795. https://doi.org/10.5194/acp-12-7779-2012.
Jaegle, L., Martin, R.V., Chance, K., Steinberger, L., Kurosu, T.P., Jacob, D.J., Modi, A.I., Yoboué, V., Sigha-Nkamdjou, L., Galy-Lacaux, C., 2004. Satellite mapping of rain-induced nitric oxide emissions from soils. Journal of Geophysical Research 109 (D21310). https://doi.org/10.1029/2004JD004787.
Kaufman, Y.J., Koren, I., Remer, L.A., Tanre, D., Ginoux, P., Fan, S., 2005. Dust transport and deposition observed from the Terra- Moderate resolution Imaging Spectroradiometer (MODIS) spacecraft over the Atlantic Ocean. Journal of Geophysical Research 110 (D24202). https://doi.org/10.1029/2003JD004436.
Keene, W.C., Pszenny, A.A., Galloway, J.N., Hartley, M.E., 1986. Sea-salt corrections and interpretation of constituent ratios in marine precipitation, 1986 corrections and interpretation of constituent ratios in marine precipitation. Journal of Geophysical Research 91, 6647–6658.
Kulshrestha, A., Satsangi, P.G., Masih, J., Taneja, A., 2009. Metal concentration of PM2.5 and PM10 particles and seasonal variations in urban and rural environment of Agra, India. Sci. Total Environ. 407, 6196–6204.
Kulshrestha, U.C., Kulshrestha, Monika J., Sekar, R., Sastry, G.S.R., Vairamani, M., 2003. Chemical characteristics of rainwater at an urban site of south-Central India. Atmospheric Environment 30, 4149–4154.
Kulshrestha, U.C., Granat, L., Engardt, M., Rodhe, H., 2005. Review of precipitation monitoring studies in India-a search for region patterns. Atmospheric Environment 39, 7403–7419.
Laouali, D., Galy-Lacaux, C., Diop, B., Delon, C., Orange, D., Lacaux, J.P., Akpo, A., Lavenu, F., Gardrat, E., Castera, P., 2012. Long term monitoring of the chemical composition of precipitation and wet deposition fluxes over three Sahelian savannas. Atmospheric Environment 50, 314–327.
Le Barbé, L., Lebel, T., 1997. Rainfall climatology of the Hapex-Sahel region during the years 1950–1990. Journal of Hydrology 188–189, 43–73.
Lebel, T., Cappelaere, B., Galle, S., Hanan, N.P., Kergoat, L., Levis, S., Vieux, B., Descroix, L., Gosset, M., Mougin, E., Peugeot, C., Seguis, L., 2009. AMMA-CATCH studies in the Sahelian region of West-Africa: an overview. Journal of Hydrology 375 (1–2).
Marticorena, B., Chatenet, B., Rajot, J.L., Traoré, S., Coulibaly, M., Diallo, A., Koné, I., Maman, A., NDiaye, T., Zakou, A., 2010. Temporal variability of mineral dust concentrations over West Africa: analyses of a pluriannual monitoring from the AMMA Sahelian dust Transect. Atmospheric Chemistry and Physics 10, 8899–8915. https://doi.org/10.5194/acp-10-8899-2010.
Marticorena, B., Chatenet, B., Rajot, J.L., Bergametti, G., Deroubaix, A., Vincent, J., Kouoi, A., Schmechtig, C., Coulibaly, M., Diallo, A., Koné, I., Maman, A., Diaye, T.N., Zakou, A., 2017. Mineral dust over west and Central Sahel: seasonal patterns of dry and wet deposition fluxes from a pluriannual sampling (2006–2012). Journal of Geophysical Research – Atmospheres 122, 1338–1364. https://doi.org/10.1002/2016JD025995.
Minoura, H., Iwasaka, Y., 1996. Rapid change in nitrate and sulphate concentrations observed in early stage of precipitation and their deposition processes. Journal of Atmospheric Chemistry 24, 39–55.
Mphepya, J.N., Pienaar, J.J., Galy-Lacaux, C., Held, G., Turner, C.R., 2004. Precipitation chemistry in semi-arid areas of Southern Africa: a case study of a rural and an industrial site. Journal of Atmospheric Chemistry 47, 1–24.
Mphepya, J.N., Galy-Lacaux, C., Lacaux, J.P., Held, G., Pienaar, J.J., 2005. Precipitation chemistry and wet deposition in Kruger National Park, South Africa. J. Atmos. 13-28.
Mphepya, J.N., Galy-Lacaux, C., Lacaux, J.P., Held, G., Pienaar, J.J., 2006. Precipitation chemistry and wet deposition in Kruger National Park, South Africa. J. Atmos. 53, 169–183.
Ndiaye, O., Diop, A.T., Akpo, L.E., Diène, M., 2014. Dynamique de la teneur en carbone et en azote des sols dans les systèmes d'exploitation du Ferlo: cas du CRZ de Dahra. J. Appl. Biosci. 83, 7554–7569. https://doi.org/10.4314/jab.v83i1.5.
Nicholson, S.E., 1981. Rainfall and atmospheric circulation during drought periods and wetter years in West Africa. Monthly Weather Review 109, 2191–2208.
Orange, D., Gac, J.Y., Diallo, M.I., Diallo, M.I., 1993. Geochemical assessment of atmospheric deposition including Harmattan dust in continental West Africa. In: IAHS Publ. Proceedings of Yokohama Symposium, 215, pp. 303–312.
Oswald, R., Behrendt, T., Ermel, M., Wu, D., Su, H., Cheng, Y., Breuninger, C., Moravek, A., Mougin, E., Delon, C., Loubet, B., Pommerening-Röser, A., Sörgel, M., Pöschl, U., Hoffmann, T., Andreae, M.O., Meixner, F.X., Trebs, I., 2013. HONO emissions from soil bacteria as a major source of atmospheric reactive nitrogen. Science 341, 1233. https://doi.org/10.1126/science.1242266.
Pauliquevis, T., Lara, L.L., Antunes, M.L., Artaxo, P., 2012. Aerosol and precipitation chemistry measurements in a remote site in Central Amazonia: the role of biogenic contribution. Atmospheric Chemistry and Physics 12, 4987–5015.
Possanzini, M., Buttini, P., Di Palo, V., 1988. Characterization of a rural area in terms of dry and wet deposition. Sci. Total Environ. 74, 111.
Prince, S.D., Kerr, Y.H., Goutorbe, J.P., et al., 1995. Geographical, biological and remote sensing aspects of the hydrologic atmospheric pilot experiment in the Sahel (HAPEX-Sahel). Remote Sensing of Environment 51, 215–234.
Rasmussen, M.O., Göttsche, F.M., Diop, D., Mbow, C., Olesen, F.S., Fensholt, R., Sandholt, I., 2011. Tree survey and allometric models for tiger bush in northern Senegal and comparison with tree parameters derived from high resolution satellite data. International Journal of Applied Earth Observation and Geoinformation 13, 517–527.
Ro, C.U., Tang, A.J.S., Chan, W.H., Kirk, R.W., Reid, N.W., Lusis, M.A., 1988. Wet and dry deposition of Sulphur and nitrogen compounds in Ontario. Atmospheric Environment 22 (12), 2763–2772.
Sarr, M.A., 2009. Evolution récente du climat et de la végétation au Sénégal: cas du bassin versant du Ferlo. Thèse de Doctorat en Géographie et aménagement, 3. Université Jean Moulin Lyon, p. 384.
Schlecht, E., Hiernaux, P., 2004. Beyond adding up inputs and outputs: process assessment and upscaling in modelling nutrient flows. Nutr. Cy. Agroecosys. 70, 303–319.
Serça, D., Delmas, R., Le Roux, X., Parsons, D.A.B., Scholes, M.C., Abbadie, L., 1998. Coauthors. Comparison of nitrogen monoxide emissions from several African

tropical ecosystems and influence of season and fire. Glob. Biogeochem. Cy. 12, 637–651.
Sigha-Nkamdjou, L., Galy-Lacaux, C., Pont, V., Richard, S., Sighoumnou, D., Lacaux, J.P., 2003. Rainwater chemistry and wet deposition over the equatorial Forested ecosystem of Zoétélé (Cameroon). Journal of Atmospheric Chemistry 46, 173–198.
Singh, A.K., Mondal, G.C., 2008. Chemical characterization of wet precipitation events and deposition of pollutants in coal mining region. India. J. Atmos. Chem. 59, 1–23.
Tagesson, T., Fensholt, R., Cropley, F., Guiro, I., Horion, S., Ehammer, A., Ardö, J., 2015. Dynamics in carbon exchange fluxes for a grazed semi-arid savanna ecosystem in West Africa. Agriculture, Ecosystems and Environment 205, 15–24.
Tracol, Y., 2004. Etude des variations interannnuelles de la production herbacée des pâturages sahéliens: Exemple du Gourma malien. Université Paul Sabatier, Toulouse, France, Thèse de doctorat.
Vet, R., Artz, R.S., Carou, S., Shaw, M., Ro, C.-U., Aas, W., Baker, A., Bowersox, Van C., Dentener, F., Galy-Lacaux, C., Hou, A., Pienaar, J.J., Gillett, R., Forti, M.C., Gromov, S., Hara, H., Khodzher, T., Mahowald, N.M., Nickovic, S., Rao, P.S.P., Reid, N.W., 2014. A global assessment of precipitation chemistry and sulfiur nitrogen, sea salt, base cations, organic acids a,d pH, and phosphorus. Atmospheric Environment 93, 3–100.
Voldner, E.C., Barrie, L.A., Sirois, A., 1986. A review of dry deposition of Sulphur and nitrogen with emphasis on long range transport modeling in North America. Atmospheric Environment 20, 2101–2123.
WMO, November 2004. Manual for the GAW Precipitation Chemistry Programme Guidelines, Data Quality Objectives and Standard Operating Procedures (WMO TD No. 1251), p. 186.
Yoboué, V., Galy-Lacaux, C., Lacaux, J.P., Silue, S., 2005. Rainwater chemistry and wet deposition over the wet Savanna ecosystem of Lamto (Côte d'Ivoire). Journal of Atmospheric Chemistry 52, 117–141.
Zhang, L., Brook, J.R., Vet, R., 2003. A revised parameterization for gaseous dry deposition in air-quality models. Atmospheric Chemistry and Physics 3, 2067–2082. https://doi.org/10.5194/acp-3-2067-2003.
Zhang, L., Wright, P.L., Asman, W.A.H., 2010. Bi-directional air surface exchange of atmospheric ammonia – a review of measurements and a development of a big-leaf model or applications in regional-scale air-quality models. Journal of Geophysical Research 115, D20310. https://doi.org/10.1029/2009JD013589.