International Journal of Environment and Climate Change

Volume 14, Issue 10, Page 674-690, 2024; Article no.IJECC.124588
ISSN: 2581-8627
(Past name: British Journal of Environment & Climate Change, Past ISSN: 2231–4784)

Long-Term Estimation of Rainfall Acidity in Major African Ecosystems

Yayé Abassa [a], Moussa Ouma [b*], Bonkaney Abdou Latif [b] and Dungall Laouali [a]

[a] Université Abdou Moumouni de Niamey, Faculté des Sciences et Techniques, Département de Physique, BP 10662, Niamey, Niger.
[b] Université Abdou Moumouni de Niamey, Ecole Normale Supérieure, Département de Physique, BP 10963, Niamey, Niger.

Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

Article Information

DOI: https://doi.org/10.9734/ijecc/2024/v14i104516

Open Peer Review History:
This journal follows the Advanced Open Peer Review policy. Identity of the Reviewers, Editor(s) and additional Reviewers, peer review comments, different versions of the manuscript, comments of the editors, etc are available here: https://www.sdiarticle5.com/review-history/124588

Original Research Article

Received: 01/08/2024
Accepted: 03/10/2024
Published: 15/10/2024

ABSTRACT

The paper examines the acidity of precipitation in three major ecosystems in Western and Central Africa, using data from 413 rainfall samples in the dry savanna of Banizoumbou, Niger; 1,056 samples in the wet savanna of Lamto, Ivory Coast; and 578 samples in the equatorial forest of Zoetele, Cameroon. Analyzed at the Toulouse Aerology Laboratory, the findings indicate that rain in Banizoumbou is alkaline (mean pH 6.19), while at Lamto and Zoetele it is acidic (mean pH 5.24 and 5.45, respectively). Despite significant potential acidity, actual acidity (measured by H^+ ion concentration) remains low across all sites. The study highlights the importance of a multiphasic process in rainwater neutralization, involving the capture of acidic gases by mineral dust and gas-particle interactions primarily influenced by ammonia (NH_3). Notably, the relationship between pH and the ratio of cations to anions varies: in Banizoumbou, they move inversely, whereas in Lamto

**Corresponding author: E-mail: moussaoumat@gmail.com;*

Cite as: *Abassa, Yayé, Moussa Ouma, Bonkaney Abdou Latif, and Dungall Laouali. 2024. "Long-Term Estimation of Rainfall Acidity in Major African Ecosystems". International Journal of Environment and Climate Change 14 (10):674-90. https://doi.org/10.9734/ijecc/2024/v14i104516.*

and Zoetele, they change in the same direction. This suggests that terrestrial dust influences dominate in the dry savanna, while gas-particle conversion processes are more prominent in the wet savanna and equatorial forest.

Keywords: Rain samples; african ecosystems; dry savanna; wet savanna; equatorial forest; acidity; alkalinity.

1. INTRODUCTION

This study is carried out within the framework of the IDAF program (IGAC-DEBITS-AFRICA) which started in 1994. This program has set up 10 measurement sites covering three types of ecosystems: dry savannas (Niger, Mali, South Africa), wet savannas (Ivory Coast, Benin) and equatorial forests (Cameroon, Congo). It is in this context that, data from the Banizoumbou, Lamto and Zoetele stations representing the African ecosystems of dry savanna, wet savanna and equatorial forest respectively, are studied in this work. It is important to notify that multidisciplinary research has recently received particular attention, mainly in arid and semi-arid environments where ecosystems are characterized by low and discontinuous precipitations, high temperatures, periodic droughts with little vegetation. Several studies on the chemical composition of precipitations have been carried out in tropical areas of America Asia and Australia [1-6] and in tropical and equatorial areas of Africa [7-20]. These studies, on the scale of Africa, highlight, on one hand, the existence and the influence of terrigenous, marine, biogenic and anthropogenic sources and, on the other hand, quantify the flow of wet and dry depositions, in relation to gas and particle sources [21].

To complement these works, long-term experimental data on rainwater collected in three large African ecosystems are presented in this study. This aims to:

- study the evolution of the acidity of precipitations in West and Central African ecosystems;
- analyze the relative acidic contribution of mineral and gas phases in precipitations in order to highlight the role of heterogeneous processes;
- compare the degree of acidity of precipitations along the three African ecosystems: dry savanna-wet savanna-equatorial forest.

After the description of the measurement sites and the exposition of the data collection and chemical analysis procedure, the results obtained in this work are presented.

2. MATERIALS AND METHODS

2.1 Presentation of Measurement Sites

The three IDAF study sites considered in this work are: Banizoumbou in Niger (dry savanna), Lamto in Ivory Coast (wet savanna) and Zoetele in Cameroon (equatorial forest). They represent a transect of african ecosystems. The geographic, ecological and climatic characteristics of these sites are presented in Table 1. The dry savanna is characterized by a short rainy season extending from June to September, while for the wet savanna and equatorial forest, the wet season extends respectively from April to October and March to November. A detailed description of IDAF monitoring stations can be found in Adon et al. [14].

These sites are located in undisturbed (rural) ecosystems dominated by gases and atmospheric particles emission sources from biogenic degradation, terrigenous dust, biomass fires or animal and plant debris. The sources of dry savanna are mainly terrigenous chemical compounds and nitrogen compounds, linked to soil emissions and biogenic emissions from domestic animal waste. In wet savanna, the main emissions come from biomass fires, soils, vegetation and domestic animals. For forest ecosystem, the main sources come from vegetation and soils. The long-term measurements carried out on the three sites complete the IDAF database allow the study of the impacts of environmental evolution in the broad sense (climate, biogeochemical cycle, hydrology, health, etc.).

2.2 Collection and Chemical Analysis Procedure

2.2.1 Rainwater collection procedure

An automatic precipitation collector, specially designed for the IDAF network, is installed in the three sites in West and Central Africa. The latter collects precipitation with a high degree of cleanliness in a single-use polyethylene bag, avoiding the deposition of aerosol before the start of the rain. A precipitation sensor automatically controls the opening of the lid, which seals the polyethylene bag. The surface area of the rain collection is 225 cm^2.

After each precipitation event, 50 cm^3 of the collected precipitation is sampled into 50 ml Greiner tubes. Preservation of rainwater samples is an important issue due to microbial degradation that could change its chemical composition. Rain samples containing 15 mg of biocide of thymol are kept in the refrigerator before being transferred to the Toulouse Aerology Laboratory for analysis. More details on sample conservation procedures are described by Gillett and Ayers [22].

2.2.2 Chemical analysis

The inorganic (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, SO_4^{2-}) and organic ($HCOO^-$, CH_3COO^-, $C_2H_5COO^-$, $C_2O_4^{2-}$) ions contained in the rain samples are determined by ion chromatography in aqueous phase. pH is measured with an ATI Orion 350 instrument in combination with an electrode (ATI Orion model 9252) filled with KCl (4M) and saturated with AgCl. Two standard solutions (WTW) at pH 4.01 and 7.00 are used for its calibration leading to an accuracy of 0.01pH. More details on the analytical procedures are described by Galy-Lacaux et al. [10] and Adon et al. [14].

The quality of measurements depends not only on sampling, but also on analysis and standardized procedures. Since 1996, the Aerology Laboratory has participated in the quality control comparison program organized twice a year by the World Meteorological Organization (WMO). According to the results of the quality assurance program, the analytical precision is estimated to be 5% or better for all ions, well below the uncertainties of all measured values presented here.

2.2.3 Methods of calculation

Seasonal volume-weighted mean (VWM) concentrations of ionic constituents in rainwater were calculated using the following equation 1:

$$M\ (\mu eq.L^{-1}) = \frac{\sum_{i=1}^{N} C_i \cdot P_i}{\sum_{i=1}^{N} P_i} \qquad (1)$$

Where C_i is the ionic concentration for each element in $\mu eq.L^{-1}$, P_i the quantity of precipitation for each rain event in mm, and N the total number of samples.

The values of monthly mean concentrations obtained for each ionic species made it possible to examine their variation with the pH and to deduce the main causes of the acidic or basic nature of rainwater in the three major African ecosystems: dry savanna (Banizoumbou), wet savanna (Lamto) and equatorial forest (Zoetele).

Table 1. Geographic, ecological and climatic characteristics of sites in West and Central Africa

Ecosystem	Sitte	Location Latitude, Longitude	Climate	Country
Dry savanna	Banizoumbou	13°31′N, 02°38′E	Sahelian Dry season: October - May Wet season: June - September	Niger
Wet savanna	Lamto	06°13′N, 05°02′W	Guinean Dry season: November - March Wet season: April - October	Ivory Coast
Forest	Zoetele	03°15′N, 11°53′E	Equatorial Dry season: December - February Wet season: March - Novamber	Cameroon

3. RESULTS AND DISCUSSION

Fig. 1 shows the pH frequency distribution for the three study sites. The results show that 84% of the samples analyzed for Banizoumbou have an alkaline pH greater than 5.6 (pH = 5.6 being the balance of atmospheric CO_2 in rainwater). On the other hand, 84% and 58% of the rainwater samples analyzed for Lamto and Zoetele respectively are in the acidity range. These rates are in agreement with the average pH values calculated for rainwater from these three sites. So, in Banizoumbou, the rains are alkaline with a mean pH of 6.19. The mean pH values in Lamto and Zoetele are respectively 5.24 and 5.45, reflecting the acidic nature of rainwater in these two sites where the density of vegetation is high.

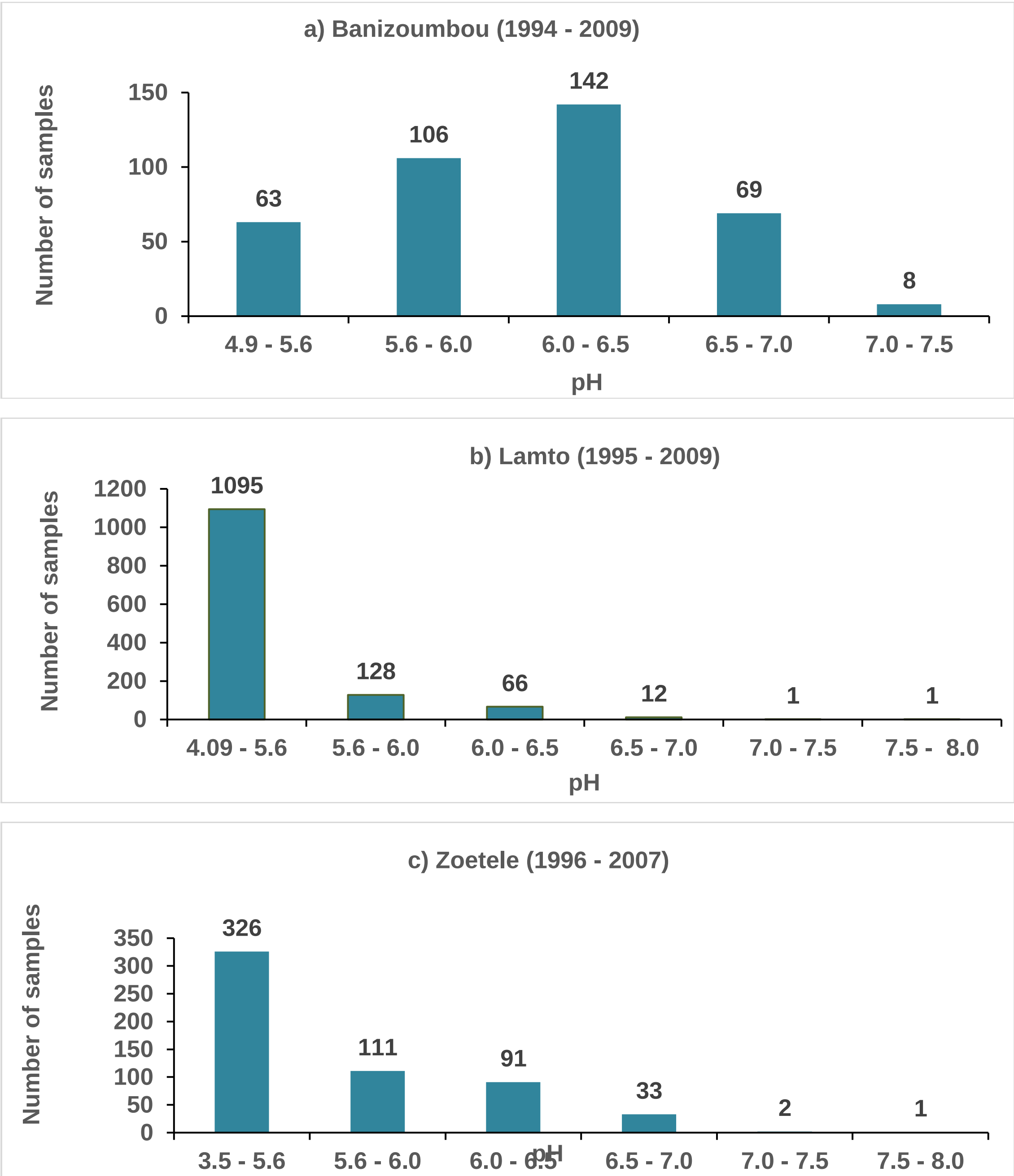


Fig. 1. Distribution of rainwater pH values frequency at the three sites (a. Banizoumbou, b. Lamto and c. Zoetele)

These pH values are significantly higher than those reported for the semi-arid South Africa savanna sites of Amersfoort (pH = 4.35) and Louis Trichard (pH = 4.91) [7]; but comparable to several other arid and semi-arid rural sites in India [23-25]. Rainwater acidity at dry savanna sites in South Africa is high due to the greater influence of industrial NO_x and SO_x emissions from the Highveld region [7-8].

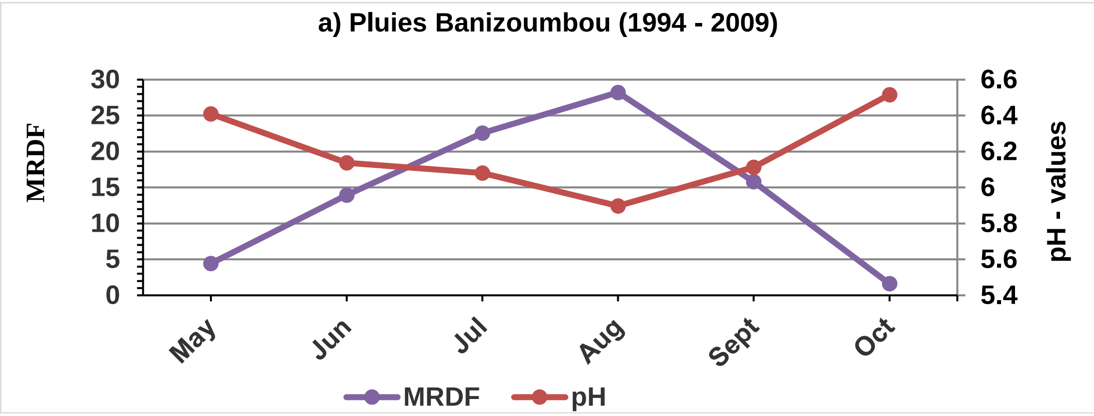
3.1 Variation of Monthly Average pH and Rainy Days Frequency (MRDF)

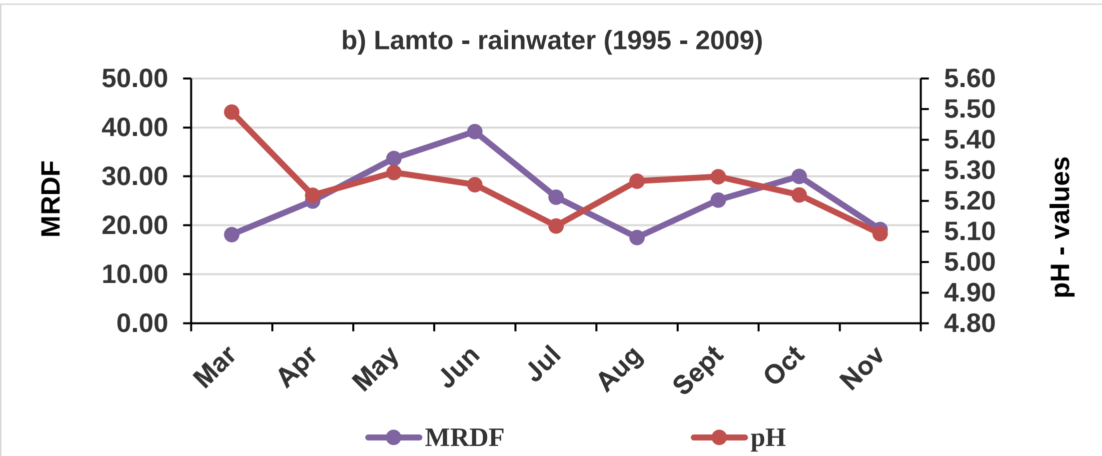
Fig. 2 depicts the seasonal variation of the monthly average pH of rainwater and the monthly rainy days frequency (MRDF) for the sites of Banizoumbou, Lamto and Zoetele.

The higher pH values reflecting the alkalinity are obtained during the months marking the end of the dry season for which the MRDF are very low. These are May (pH = 6.41) at Banizoumbou, March (pH = 5.49) at Lamto and pH = 5.40 at Zoetele during February. Also, the short dry season around August is characterized by a high pH value at the two sites Lamto (pH = 5.26) and Zoetele (pH = 5.79) compared to the other rainy months. Particularly, the highest pH at Banizoumbou (pH = 6.52) is obtained in October at the end of the rainy season. This is due to the fact that during these periods, the concentration of terrigenous species (Ca^{2+}, Mg^{2+}) in the atmosphere is very high and neutralized the acidic compounds [26].

The lowest value of pH is obtained in August (pH = 5.90) at Banizoumbou. Indeed, this month is characterized by a significant rainy days frequency, which contribute to gases (NH_3, NO_2, SO_2) emission, low concentration of terrigenous particles and then causing the pH to decrease [27,28].

However, in Lamto and Zoétélé, the lowest pH is obtained respectively in December (pH = 4.81) and June (pH = 5.16). In fact, these months are characterized by low rainy days frequency which is favorable to significant emissions of gases (NO_2 and SO_2) precursors of strong acids (HNO_3, H_2SO_4), ammonia (NH_3) represented by the weak acid (NH_4^+) in rainwater but also volatile organic compounds precursors of organic acids (RCOOH) [29].





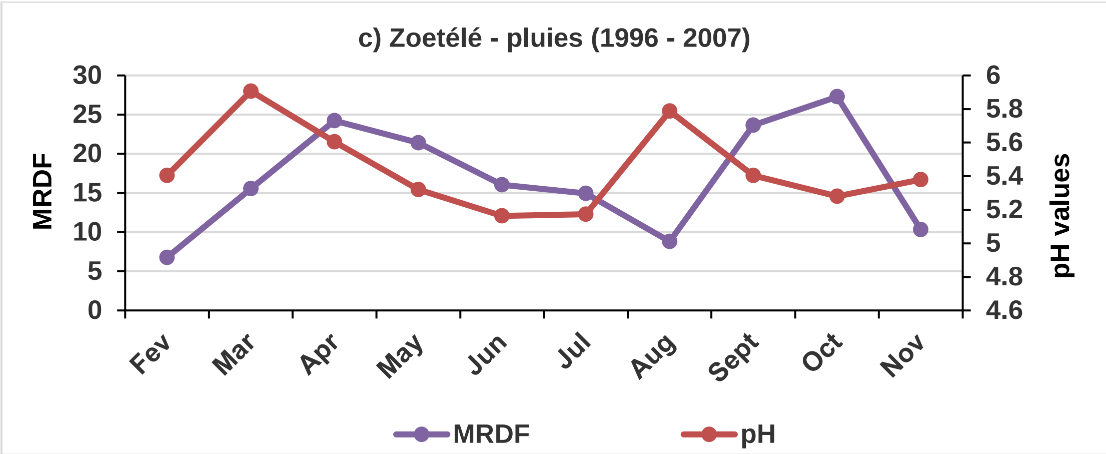


Fig. 2. Covariation of monthly mean pH and monthly rainy days frequency (MRDF) for the three sites (a. Banizoumbou, b. Lamto and c. Zoetele)

Thus, the variation in the pH of rainwater seems to be controlled by the interaction between alkaline load and acid load through heterogeneous particle-gas-water vapor processes [10,28]. A study of the correlation of the major ionic species contained in rainwater and the variation of the pH with their concentrations shows this result more explicitly.

3.2 Correlation between Cations and Anions Contained in Rainwater

Table 2 presents the correlation coefficients between the cations and anions contained in rainwater collected at the three sites: Banizoumbou, Lamto and Zoetele.

Over the three ecosystems, the process of cloud formation leading to rainfall events requires the pre-existence of water vapor condensation nuclei. This multiphase process which involves particles, gases and water vapor is influenced by the meteorological conditions of the ecosystem but also by the chemical properties of the substances concerned. The gaseous acids HNO_3, H_2SO_4 are known to be hygroscopic as are their salts such as NH_4Cl, $(NH_4)_2SO_4$, NH_4HSO_4, NH_4NO_3. These chemical products are obtained by gas condensation or gas-particle conversion. Also, ions from of inorganic particles (Ca^{2+}, K^+, Mg^{2+}, Na^+) coming from terrigenous dust and water vapor [12,26], lead to the formation of non-volatile salts such as $NaNO_3$, KCl, $CaSO_4$, NH_4Cl, $(NH_4)_2SO_4$, NH_4HSO_4, NH_4NO_3. These particle – gas – water vapor interactions leading to the formation of clouds are the main cause of the strong correlations observed between anions (representatives of acidic forms in water: HNO_3/NO_3^-; H_2SO_4/SO_4^{2-}; organic acids: $RCOOH/RCOO^-$) and alkaline cations (Ca^{2+}, K^+, Mg^{2+}, Na^+ and the weak acid NH_4^+ representing NH_3). This multiphase process is strengthened by low temperature and high relative humidity [29].

Depending on the weather conditions of the ecosystem and the availability of suspended chemical substances in the atmosphere, the following dominant alkaline species in order of high correlation coefficients (Table 2) are: in Banizoumbou $Ca^{2+} > NH_4^+ > Na^+$), in Lamto ($NH_4^+ > Ca^{2+} > Na^+$) and in Zoetele ($NH_4^+ > Ca^{2+} > Na^+$). $Mg^{2+}$is not given despite its strong correlation coefficient because Mg^{2+} is associated with Ca^2 since both ions come from the same substance, the dolomite $CaMg(CO_3)_2$ [30]. From this result, it can be deduced that($Ca^{2+} + NH_4^+$) is an indicator for the alkaline nature of rainwater collected over the three sites.

However, NH_4^+ is a weak acid tending to lower the pH value when its concentration is very high. Ca^{2+} (terrigenous source) is therefore a cause of the alkaline character of rainwater at Banizoumbou in dry savanna and NH_4^+ (gaseous emission of NH_3) the cause of their acidic character at Lamto in wet savanna [9] and at Zoetele in the equatorial forest [5]. The role of these two major cations is the neutralization of acidic species [10,31].

Table 2. Correlation coefficients between cations and anions contained in rainwater collected at Banizoumbou (1994 to 2009), Lamto (1995 to 2009) and Zoetele (1996 to 2007)

Correlation coefficients between anions and cations															
Stations	Banizoumbou					Lamto					Zoetele				
Ions	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}
NO_3^-	0.02	0.61	0.18	0.85	0.84	0.14	0.80	0.78	0.74	0.75	0.82	0.86	0.53	0.57	0.44
Cl^-	0.75	0.73	0.93	0.25	0.42	0.92	0.44	0.45	0.13	0.46	0.93	0.74	0.71	0.73	0.58
SO_4^{2-}	0.95	0.77	0.47	0.72	0.73	0.43	0.85	0.87	0.73	0.84	0.62	0.61	0.71	0.50	0.33
$HCOO^-$	-0.16	0.50	0.06	0.75	0.70	-0.09	0.93	0.73	0.91	0.76	0.74	0.94	0.08	0.36	0.40
CH_3COO^-	0.04	0.68	0.42	0.77	0.84	0.02	0.95	0.82	0.95	0.84	0.73	0.49	0.33	0.68	0.02
$C_2H_5COO^-$	-0.36	-0.02	0.16	-0.42	-0.46	-0.03	0.41	0.44	0.62	0.62	-0.09	-0.12	-0.19	-0.14	-0.40
$C_2O_4^{2-}$	-0.16	0.52	0.29	0.61	0.67	0.06	0.91	0.65	0.72	0.72	0.60	0.96	0.12	0.17	0.53
tCarbonates	0.95	0.56	0.36	0.43	0.41	0.16	0.76	0.93	0.90	0.90	-0.01	-0.14	0.73	0.31	0.52

Horizontal reading of Table 2 shows that the anionic species representing the neutralized acids are given in order of strong correlation coefficients: in Banizoumbou (SO_4^{2-} > NO_3^- > Cl^- > CH_3COO^-), in Lamto ($HCOO^-$ > SO_4^{2-} > NO_3^- > CH_3COO^-) and at Zoetele (NO_3^- > SO_4^{2-} > $HCOO^-$ > Cl^-). By considering Cl^- as transported from the sea by water vapor [10], one can deduce that the acidifying species coming mainly from ecosystem conditions are SO_4^{2-}, NO_3^- with a significant influence of the organic acids RCOOH at Lamto in wet savanna and Zoetele in equatorial forest. Thus, the sum (SO_4^{2-} + NO_3^-) is an indicator for the acidic nature of rainwater collected in Banizoumbou, Lamto and Zoetele [27].

In addition, these results are even more remarkable through the values of the neutralization factors of the cationic species and the values of the acidification capacities of the anionic species given by Tables 3, 4 and 5.

3.3 Neutralization Factor and Acidification Capacity

The values of the neutralization factors (NF) and the acidification capacities (AC) are determined by using the following formulas:

$$NF(X^{p+}) = \frac{p[X^{p+}]}{[NO_3^-]+2[SO_4^{2-}]+[HCOO^-]+[CH_3COO^-]+[C_2H_5COO^-]+2[C_2O_4^{2-}]} \quad (2)$$

$$AC(Y^{n-}) = \frac{n[Y^{n-}]}{[NO_3^-]+2[SO_4^{2-}]+[HCOO^-]+[CH_3COO^-]+[C_2H_5COO^-]+2[C_2O_4^{2-}]} \quad (3)$$

with X^{p+} one of the cations Ca^{2+}, K^+, Mg^{2+}, Na^+ et NH_4^+, Y^{n-} one of the anions SO_4^{2-}, NO_3^-,

$HCOO^-$, CH_3COO^-, $C_2H_5COO^-$, et $C_2O_4^{2-}$ and $[X] = \frac{VWM(X)\ in\ \mu eq/L}{molair\ mass\ of\ X}$

The mean values of the neutralization factors and acidification capacity are consistent to the results obtained from the correlation coefficients concerning the species indicating the alkalinity (Ca^{2+} and NH_4^+) and the acidity (NO_3^- and SO_4^{2-}) of the rainwater at the three sites with a higher influence of organic acids at Lamto and Zoetele (Tables 3, 4 and 5).

These values suggest:

- The formation in solid phase of substances such as Na_2SO_4, $NaHSO_4$, NaCl, NH_4Cl, NH_4NO_3, $(NH_4)_2SO_4$, NH_4HSO_4, $(NH_4)_3H(SO_4)_2$ KCl, K_2SO_4, $KHSO_4$, KNO_3, $CaCl_2$, $CaSO_4$, $Ca(NO_3)_2$, $MgCl_2$, $MgSO_4$, $Mg(NO_3)_2$
- The transition of the these substances to the ionic form during the condensation of water vapor on their surfaces,
- And the formation of clouds.

For ammonia (NH_3) and organic acids (RCOOH), the dissolution in the liquid phase in clouds is partial (weak base and weak acids respectively) and therefore these chemicals species exist in rainwater in their molecular form. Furthermore, it should be noted that the average pH, calculated from the concentration of H^+, in the dry savanna of Banizoumbou, in the wet savanna of Lamto and in the equatorial forest of Zoetele is 5.93, 5.09, and 5.16 corresponding respectively to a VWM (H^+) of 1.17, 8.05 and 6.84 µeq.L^{-1}. Despite the low acidity observed in precipitation at these three African sites, the potential contribution of organic acidity (formate, acetate, propionate and oxalate) calculated is high and equal to 28% at Banizoumbou, 53% at Lamto and 43% in Zoetele (Table 6). These organic compounds result from the oxidation of volatile organic carbon (VOC) to aldehyde and carboxylic acid [32]. Volatile organic carbon is emitted by vegetation and by savanna fire during the dry season. The potential contribution of mineral acidity, mainly linked to the incorporation of mineral acids (H_2SO_4 and HNO_3), is respectively equal to 72%, 47% and 57% at the three sites (Table 6). These findings are different from those obtained in The

Table 3. Cations neutralization factors and anions acidification capacities for rainwater collected at Banizoumbou (1994 to 2009)

Banizoumbou	Neutralisation Factors					Acidification Capacities					
Months	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}	NO_3^-	SO_4^{2-}	$HCOO^-$	CH_3COO^-	$C_2H_5COO^-$	$C_2O_4^{2-}$
May	0.96	1.23	0.28	2.22	1.02	0.35	0.37	0.15	0.07	0.00	0.05
June	0.64	1.54	0.27	2.36	1.00	0.40	0.27	0.20	0.09	0.00	0.05
July	0.80	2.11	0.37	2.37	0.80	0.34	0.30	0.20	0.09	0.01	0.05
August	0.91	2.13	0.37	2.69	0.92	0.28	0.37	0.17	0.10	0.01	0.07
September	1.60	264	0.74	2.25	1.12	024	0.47	0.12	0.10	0.01	0.05
October	222	2.28	0.42	2.88	1.10	0.16	0.70	0.08	0.06	0.00	0.00
Mean	1.19	204	0.41	2.46	0.99	0.30	0.41	0.16	0.09	0.01	0.05

Table 4. Cations neutralization factors and anions acidification capacities contained in rainwater collected in Lamto (1995 à 2009)

Lamto	Neutralisation Factors					Acidification Capacities					
Months	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}	NO_3^-	SO_4^{2-}	$HCOO^-$	CH_3COO^-	$C_2H_5COO^-$	$C_2O_4^{2-}$
January	0.31	1.54	0.14	0.72	0.37	0.28	0.20	0.34	0.14	0.00	0.04
February	0.36	1.63	0.20	1.26	0.62	0.23	0.19	0.35	0.17	0.01	0.05
March	0.26	1.60	0.12	0.98	0.38	0.18	0.16	0.42	0.16	0.01	0.07
April	0.27	1.34	0.10	0.85	0.33	0.19	0.16	0.42	0.16	0.01	0.06
May	0.50	1.47	0.13	1.02	0.38	0.20	0.22	0.34	0.17	0.01	0.06
June	0.76	1.33	0.19	0.80	0.65	0.21	0.31	0.25	0.14	0.03	0.06
July	0.96	1.43	0.21	0.50	0.54	0.23	0.30	0.25	0.14	0.01	0.07
August	0.94	1.76	0.18	0.46	0.48	0.20	0.33	0.24	0.16	0.01	0.06
September	0.76	1.63	0.16	0.71	0.40	0.20	0.26	0.31	0.18	0.01	0.04
October	0.61	1.14	0.20	1.12	0.39	0.18	0.24	0.32	0.19	0.02	0.05
November	0.36	1.07	0.15	0.74	0.31	0.22	0.22	0.35	0.16	0.01	0.05
December	0.28	1.20	0.13	0.81	0.37	0.33	0.21	0.20	0.11	0.01	0.04
Mean	0.53	1.43	0.16	0.83	0.43	0.22	0.23	0.32	0.16	0.01	0.05

Table 5. Cations neutralization factors and anions acidification capacities contained in rainwater collected in Zoetele (1996 à 2007)

Zoetele	Neutralisation Factors					Acidification Capacities					
Months	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}	NO_3^-	SO_4^{2-}	$HCOO^-$	CH_3COO^-	$C_2H_5COO^-$	$C_2O_4^{2-}$
January	0.60	1.57	0.36	1.87	0.88	0.42	0.36	0.26	0.20	0.00	0.04
February	0.67	4.39	0.25	1.05	1.90	0.49	0.33	0.74	0.15	0.00	0.16
March	0.62	0.71	0.23	1.93	0.99	0.30	0.26	0.33	0.14	0.00	0.05
April	0.48	0.77	0.25	1.13	0.52	0.13	0.21	0.17	0.09	0.00	0.03
May	0.26	0.60	0.13	0.77	0.22	0.13	0.21	0.21	0.11	0.00	0.03
June	0.25	1.05	0.23	0.62	0.25	0.20	0.29	0.20	0.12	0.00	0.05
July	0.34	1.23	0.33	0.30	0.36	0.25	0.30	0.16	0.10	0.00	0.05
August	0.26	1.18	0.33	0.79	2.32	0.13	0.21	0.06	0.06	0.00	0.04
September	0.22	0.59	0.12	0.49	0.28	0.10	0.09	0.12	0.08	0.00	0.03
October	0.36	0.49	0.15	0.56	0.29	0.11	0.15	0.17	0.11	0.00	0.03
November	0.29	0.87	0.26	0.51	0.36	0.17	0.21	0.15	0.09	0.00	0.02
Mean	0.39	1.31	0.25	0.91	0.76	0.22	0.24	0.23	0.11	0.00	0.05

Amazonian forest where the organics acids are dominant, representing 80 to 90%. Moreover, the results are also different from those obtained in Amersfoort, an industrial site in dry savanna (South Africa), where organic acids contribute only to 16% of the total acidity [6].

Furthermore, in agreement with the work of Galy-Lacaux et al. [33], our findings showed that all mineral acidity (NO_3^- + SO_4^{2-}) is neutralized by solid alkaline dust particles (Ca^{2+}) and ammonia NH_3 (ammonium ion (NH_4^+ in water). Indeed, the neutralization factor of (Ca^{2+} + NH_4^+) is much greater than the acidification capacity of (NO_3^- + SO_4^{2-}) for the rainwater collected at the three sites. Also, it should be noted that the negative gradient of mineral acidity (NO_3^- + SO_4^{2-}) is associated with the negative alkalinity gradient (Ca^{2+} + NH_4^+). This result reveals that the remaining acidity in the rainwater samples is linked to undissociated organic acid molecules (more important in Lamto and Zoetele) and to the excess NH_4^+ in the rainwater (Table 6).

3.4 Variation of Rainwater pH with (Ca^{2+} + NH_4^+), (NO_3^- + SO_4^{2-}) and $RCOO^-$

The influence of mineral acids (NO_3^- + SO_4^{2-}), organic acids ($RCOO^-$ ($HCOO^-$, CH_3COO^-, $C_2H_5COO^-$, $C_2O_4^{2-}$) and alkaline species (Ca^{2+} + NH_4^+) on pH values are shown in Fig. 3.

From this figure, it is clearly observed that the pH variation is consistent with that of the alkaline combination (Ca^{2+} + NH_4^+), acidic mineral (NO_3^- + SO_4^{2-}) and organic acids ($HCOO^-$, CH_3COO^-, $C_2H_5COO^-$, $C_2O_4^{2-}$) in Banizoumbou and Zoetele. However, in Lamto, two distinct features are observed in two different periods:

- From January to March the variation of pH is not consistent with that of alkaline and acidic combinations;
- Then, from April to December where pH and concentrations of species vary in an opposite direction

Indeed, in Banizoumbou, the dominant combination is (Ca^{2+} + NH_4^+) followed by (NO_3^- + SO_4^{2-}) and then by organic acids ($RCOO^-$). Consequently, higher pH values are obtained due to the fact that the alkaline combination (Ca^{2+} + NH_4^+) is well above the quantity of neutralizable mineral acidity. This situation could be explained by the fact that the onset and cessation of rainfall in the dry savanna of Banizoumbou, the terrigenous source is activated by the dust uprisings which accompany a thunderstorm that are mainly of squall line type [26]. This terrigenous source is weakened during the rainy season (August) due to the permanent humidity. Also, gaseous emissions of ammonia NH_3 (NH_4^+- H_2O), SO_2 (H_2SO_4/SO_4^{2-} - H_2O) and NO_2 (HNO_3/NO_3^- - H_2O) become significant [28] during this period. These aspects explain the lowest pH values obtained in August due to abundant rainfall derived from stratiform or shower rainfall events.

At Lamto, the onset (March) is marked by higher pH value due to high value of (Ca^{2+} + NH_4^+). Indeed, during this period, the harmattan transports terrigenous species to the sea coast and increases Ca^{2+} concentration, contributing to the neutralization of acidic compounds. But, because of higher gases emissions (NH_3, NO_2, SO_2…) from soil and vegetation, the monthly mean pH values remained below 5.6 (acid nature of the rainwater). Hence, it can be deduced that the acidity of rainwater in wet savanna is due to the strong influence of organic acids emitted by vegetation and to the excess of NH_4^+ resulting from the dissolution of ammonia NH_3 that comes from bacterial nitrification of organic matter [27]. However, due to constant atmosphere leaching by precipitations, the value of pH decreases sharply from April to November. The lowest pH value obtained in July is due to the very low concentration of terrigenous species (Ca^{2+}) weakened by high humidity [26].

At Zoetele, from February to March pH rises from 5.40 (acid) to 5.90 (alkaline) while the concentration of chemical species in the atmosphere decreases. This is also due to the leaching of the atmosphere, causing the rapid decrease in pH as well as (Ca^{2+} + NH_4^+), (NO_3^- + SO_4^{2-}) and $RCOO^-$. On the other hand, because of the low rainy days in August, the pH and (Ca^{2+} + NH_4^+) increase.

3.5 Influence of Heterogeneous Process

Potential Acidity (pA) is defined by the sum of the concentrations of nitrate, sulfate, formate, acetate, propionate and oxalate, considering that all these ions are associated with H^+ ion [5].

The pA values obtained are respectively 57.03 $\mu eq.L^{-1}$, 50.4 $\mu eq.L^{-1}$, 40.17 $\mu eq.L^{-1}$ for Banizoumbou, Lamto and Zoetele (table 4). By determining the difference between the potential acidity (pA) and the measured acidity (mA = H^+ concentration), we find that 49.23; 48.98; 33.33 $\mu eq.L^{-1}$ of H^+ were neutralized in Banizoumbou, Lamto and Zoetele respectively. According to recent studies on rain chemistry in West and

Central Africa, one of the main neutralization mechanisms is the adsorption of gases strong acids by soil dust particles [33]. Our results obviously show the influence of this heterogeneous multiphasic process. Indeed, at Banizoumbou in Niger, Ca^{2+} corresponds to a neutralization of 92.12% of the potential acidity, while it only explains 33.33% and 42.20% of the acidity neutralized at Lamto and Zoetele respectively. This result is in agreement with EXPRESSO measurements in the wet savanna of the Central Africa Republic [33].

In the three sites, our results highlight the influence of the heterogeneous process between mineral aerosols and nitrogen compounds. Direct adsorption of ammonia NH_3 by water droplets in clouds and raindrops can explain the remaining acidity in the three sites because the ammonium ion NH_4^+ that derived from its dissolution is acidic in nature. Indeed, ammonia NH_3 contributes to reduce the H^+ ion content in rainwater through the reaction:

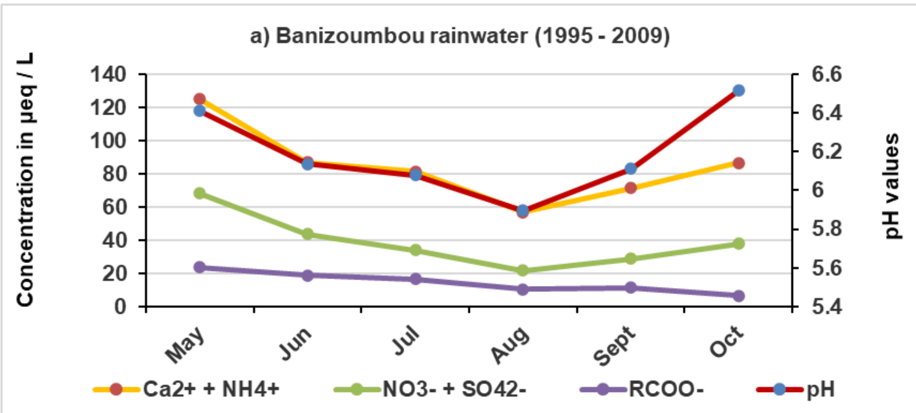
$$NH_3 + H^+ \rightarrow {NH_4}^+$$

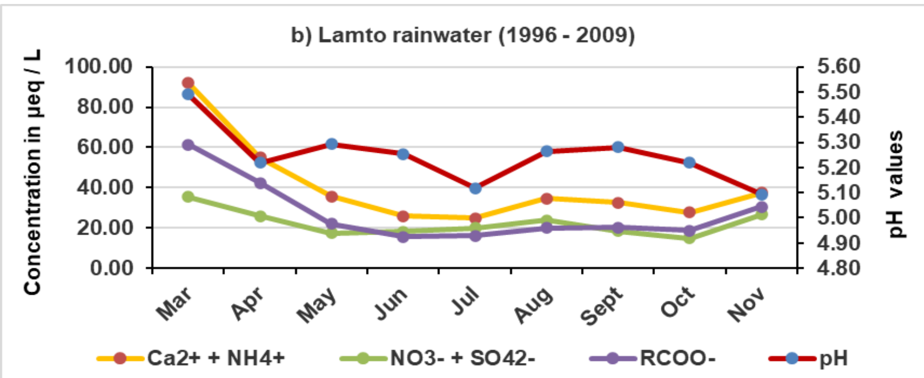
And that of organic acid molecules through the reaction:

$RCOOH + NH_3 \longrightarrow RCOO^- + {NH_4}^+$ [34, 35].

Table 6. Alkaline and acidic influences of ionic species in rainwater from the three sites

Sites		Banizoumbou		Lamto		Zoetele	
	Ions or groups of ions	Concentrations (μeq.L^{-1})	Rates	Concentrations (μeq.L^{-1})	Rates	Concentrations (μéq.L^{-1})	Rates
Alkalinity	Ca^{2+}	46.43	92.13	18.95	33.23	16.95	42.21
	NH_4^+	34.25	67.96	28.69	50.31	21.12	52.58
	$Ca^{2+} + NH_4^+$	80.68	160.09	47.65	83.55	38.07	94.78
Mineral acidity	NO_3^-	18.23	36.17	15.59	27.33	12.40	30.86
	SO_4^{2-}	18.05	35.80	11.32	19.85	10.30	25.64
	$NO_3^- + SO_4^{2-}$	36.27	71.97	26.91	47.18	22.70	56.50
Organic acidity	$RCOO^- = HCOO^- + CH_3COO^- + C_2H_5COO^- + C_2O_4^{2-}$	14.12	28.03	30.12	52.82	17.47	43.50
Potential acidity	$NO_3^- + SO_4^{2-} + HCOO^- + CH_3COO^- + C_2H_5COO^- + C_2O_4^{2-}$	50.40	100.00	57.03	100.00	40.17	100.00





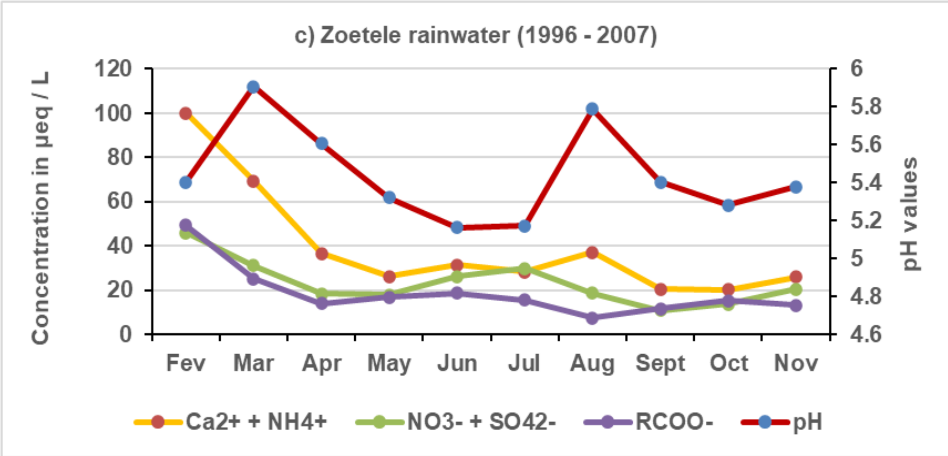
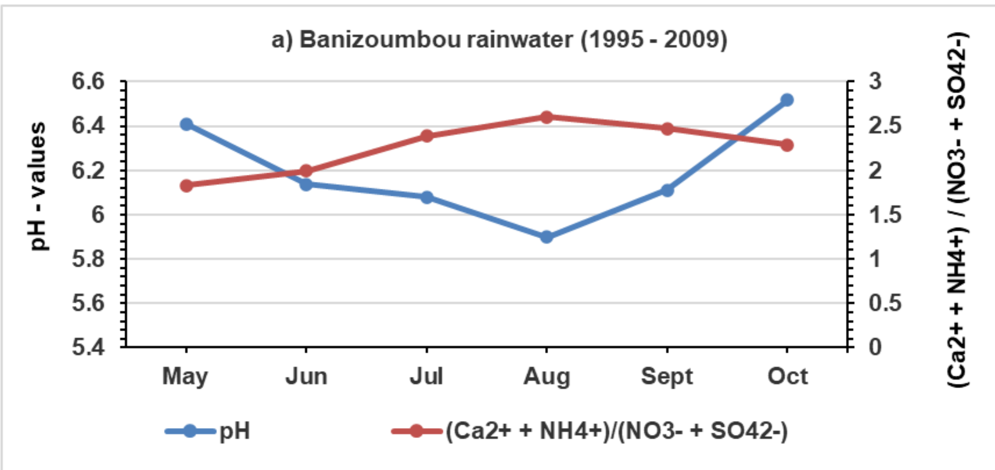


Fig. 3. Variation of pH with the determining groups of chemical species in the three sites (a. Banizoumbou, b. Lamto and c. Zoetele)

These transformations do not completely neutralize the acidic character but weaken it due to the acidic character of NH_4^+ obtained and the remaining molecules of organic acids. This affirmation is confirmed by the high NH_4^+ concentration values found in rainwater samples collected at these three sites (34.25, 28.69 and 21.12 µeq. L^{-1} in Banizoumbou, Lamto and Zoetele, respectively). Thus, the process of neutralization of the acidity of rainwater is dominated by primary particles of terrigenous origin (Ca^{2+}) in dry savanna (Banizoumbou in Niger) and by the gas – particle conversion process controlled by ammonia (NH_3) in wet savanna (Lamto in Ivory Coast) and equatorial forest (Zoetele in Cameroon). This result is fortify by Fig. 4 presenting the variation of pH and that of the ratio (Ca^{2+} + NH_4^+) / (NO_3^- + SO_4^{2-}) which show that:

At Banizoumbou, the variation of pH is opposite to that of the ratio (Ca^{2+} + NH_4^+) / (NO_3^- + SO_4^{2-}). This reflects the predominance of the terrigenous source (Ca^{2+}) which has a purely alkaline character and neutralizes almost all the mineral acidity. Also, the incorporation of abundant ammonia during the wet period tends to lower the pH via NH_4^+ (weak acid) on the one hand and the organic acids RCOOH on the other hand.

At Lamto and Zoetele, the variation of pH values are consistent with that of the ratio (Ca^{2+} + NH_4^+) / (NO_3^- + SO_4^{2-}), reflecting the predominance of the gas – particle conversion process. This highlights the ammonia reactions with mineral acids (H_2SO_4 and HNO_3) and organic acids (RCOOH) witch lead to NH_4^+ formation. The regression lines and the correlation coefficients given in Fig. 5 confirm this result. Furthermore, this heterogeneous process also involves alkaline particles such as Mg^{2+}, K^+ and contributes to the neutralization of the acidity of rainwater in the three study sites.



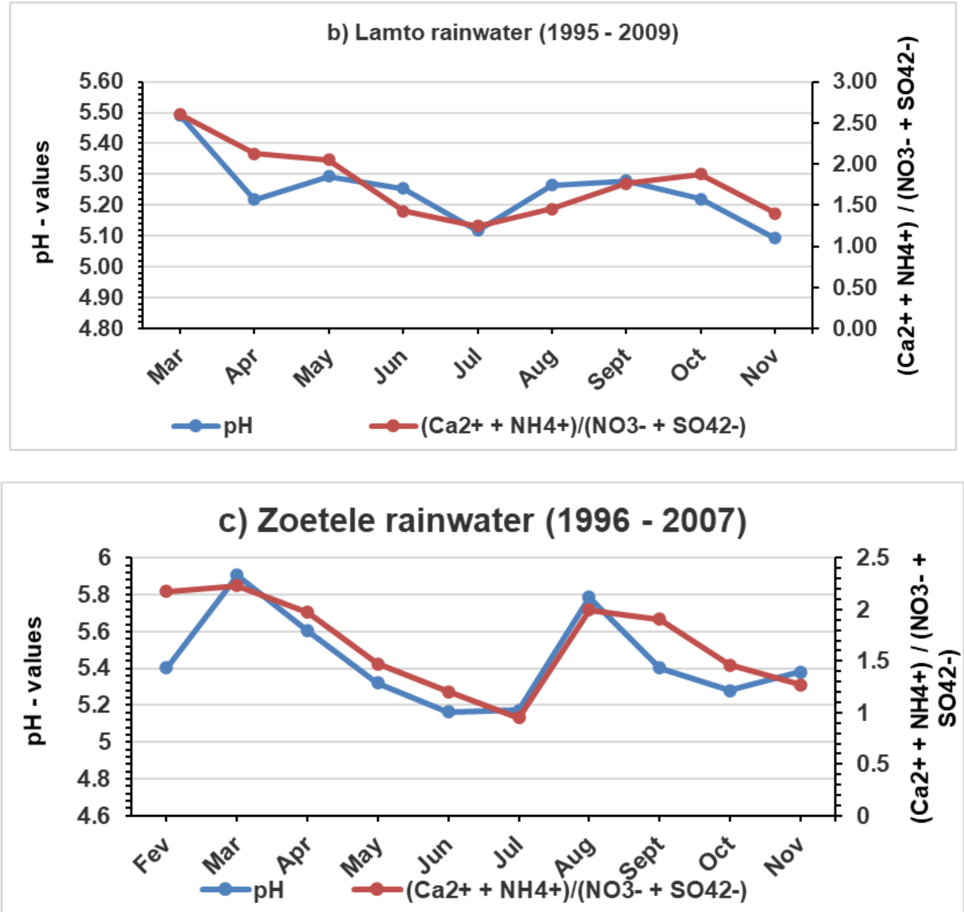
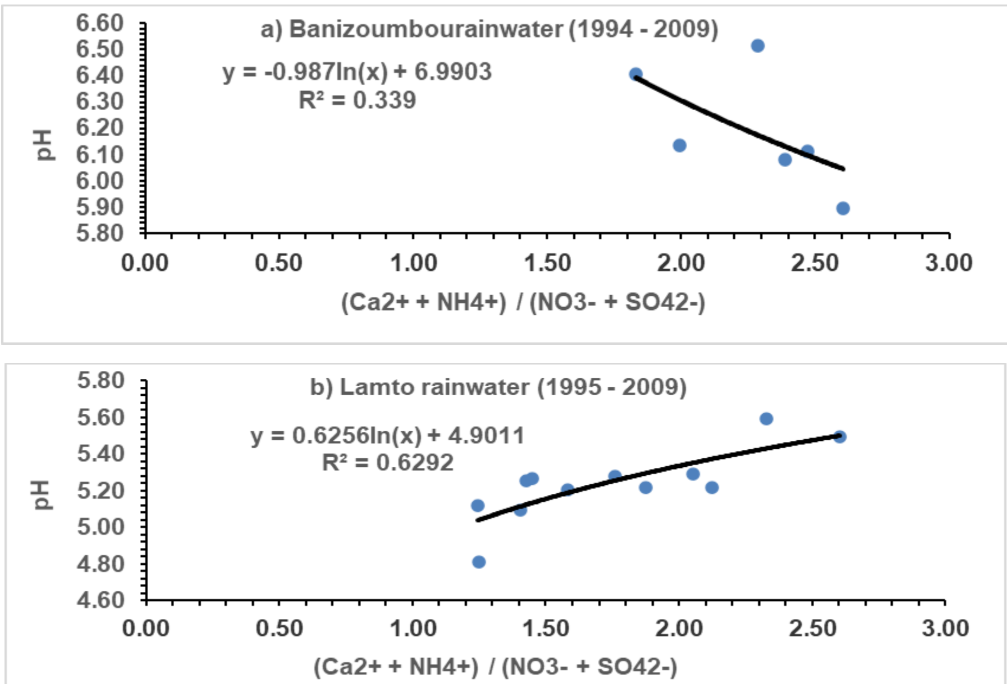


Fig. 4. Variation of pH with the ratio (Ca^{2+} + NH_4^+) / (NO_3^- + SO_4^{2-}) for the three sites (a. Banizoumbou, b. Lamto and c. Zoetele)



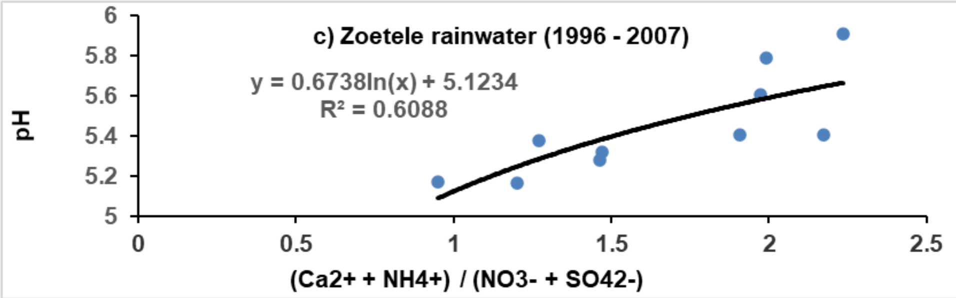


Fig. 5. Variation of pH as a function of the ratio (Ca^{2+} + NH_4^+) / (NO_3^- + SO_4^{2-}): (a. Banizoumbou, b. Lamto and c. Zoétélé)

The equations giving the pH as a function of the ratio (Ca^{2+} + NH_4^+) / (NO_3^- + SO_4^{2-}) displayed in Fig. 5 show that when this ratio takes the unity value (ln1 = 0), rainwater are strongly alkaline (pH_0 = 6.9903) in dry savanna and strongly acidic in wet savanna (pH_0 = 4.9011) and equatorial forest (pH_0 = 5.1234) in comparison to the limit value (pH_0 = 5. 6) for rainwater buffered by carbonates.

4. CONCLUSION

This study, which is part of the IDAF monitoring network, reveals that the $RCOO^-$ organic signature in dry savanna of Banizoumbou is weak compared to that measured in wet savanna (Lamto) and in equatorial forest (Zoetele). Indeed, the potential contribution of organic acidity (formate, acetate, propionate and oxalate) calculated is equal to 28% in Banizoumbou, 53% in Lamto and 43% in Zoetele.

A negative concentration gradient of the alkaline combination (Ca^{2+} + NH_4^+) from dry savanna to equatorial forest is observed. Specifically, the alkaline concentration along the transect are 80.68 µeq.L^{-1}, 47.65 µeq.L^{-1}, 38.07 µeq.L^{-1} for dry savanna, wet savanna and the equatorial forest respectively.

Similarly, a negative gradient of mineral acidity (NO_3^- + SO_4^{2-}) is also observed along the same transect. The values obtained are 36.27 µeq.l^{-1}, 26.91 µeq.L^{-1} and 22.70 µeq.L^{-1} in Banizoumbou, Lamto and Zoetele respectively.

Furthermore, the results also show a negative neutralized acidity gradient due to Multiphasic heterogeneous process which is the main reason of this neutralization. Indeed, the neutralization of the acidity is dominated by the capture of acid gases (HNO_3 and H_2SO_4) by terrigenous species (Ca^{2+}) in the dry savanna and by the gas – particle conversion controlled mainly by the reactions of ammonia with acidic species (HNO_3 and H_2SO_4, RCOOH) in wet savanna and equatorial forest. To sum up, it can be concluded that in dry savanna, the rainwater is alkaline with a mean pH value of 6.19 while in wet savanna and equatorial forest it is acidic with mean pH values of 5.24 and 5.45 respectively. These findings can be interpreted by the fact that the variation of pH during the rainy season is opposite to that of the ratio (Ca^{2+} + NH_4^+) / (NO_2^- + SO_4^{2-}) at Banizoumbou (dry savanna) while that variation is consistent at Lamto (wet savanna) and Zoetele (equatorial forest).

This work provides a solid background of the rainwater chemistry for three major African ecosystems which can be used to address the climate change concerns in tropical region where there is limited dataset. The data obtained could provide a strong baseline for rainwater acidity in West and Central Africa. In this regard, further studies on source intensity and dynamic transport of atmospheric compounds are necessary to understand the inter-annual variability of acid rain in Africa, a continent where population pressure and atmospheric emissions could rapidly evolve in the future.

DISCLAIMER (ARTIFICIAL INTELLIGENCE)

Authors hereby declare that no generative AI technologies such as Large Language Models (ChatGPT, COPILOT, etc) and text-to-image generators have been used during the writing or editing of the manuscript.

AKNOWLEDGEMENTS

This work is part of the IDAF project, and was funded by INSU / CNRS 'National Institute of Universe Sciences / National Center for Scientific Research'. The authors thank the main researchers of the IDAF network, the field technician of the African stations and the IRD (Institute of Research for Development) for their logistical support.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Lacaux JP, Tathy JP, Sigha L. Acid wet deposition in the tropics: two case studies using DEBITS measurements, IGAC activities Newsletter of the International Global Atmospheric Chemistry Project, DEBITS Special Issue. 2003;2:13 –18.
2. Pienaar JJ. Proposal of a new IGAC II task: DEBITS II. (Deposition of Biogeochemically Important Trace Species); 2005. Available:http: //www.igac.noaa.gov/ DEBITS.php.
3. Bates T, Scholes M, Doherty S, Young B. IGAC Science Plan and Implementation Strategy IGBP Report 56, IGBP Secretariat, Stockholm, Sweden. 2006;44.
4. Estell RE, Fredrickson EL, Peters DPC. Introduction to special issue – Landscape linkages and cross scale interactions in arid and semiarid ecosystems, J. Arid Environ. 2006;65(2):193–195.
5. Sigha-Nkamdjou L, Galy-Lacaux C, Pont V, Richard S, Sighoumnou D, Lacaux JP. Rainwater chemistry and wet deposition over the equatorial forested ecosystem of Zoétélé/Cameroon, J. Atmos. Chem. 2003; 46:173–198.
6. Ayers GP, Yeung KK, A. Acid Deposition in Hong Kong. Atmospheric Environment Vol. 30, Nos. 10/11, pp. 1581-1587, 1996 Copyright © 1996 Elsevier Science Ltd, Printed in Great Britain. All rights reserved, 1352-2310/96 $15.00 + 0.00CID
7. Mphepya JN, Pienaar JJ, Galy-Lacaux C, Held G, Turner CR. Precipitation Chemistry in Semi-Arid Areas of Southern Africa: A Case Study of a Rural and an industrial Site, J. Atmos. Chem. 2004; 47:1–24.
8. Mphepya JN, Galy-Lacaux C, Lacaux JP, Held G, Pienaar JJ. Precipitation chemistry and wet deposition in Kruger National Park, south Africa. J. Atmos. 2005:13-28.
9. Mphepya JN, Galy-Lacaux C, Lacaux JP, Held G, Pienaar JJ. Precipitation Chemistry and Wet Deposition in Kruger National Park, South Africa, J. Atmos. Chem. 2006;53:169–183.
10. Yoboué V, Galy-Lacaux C, Lacaux JP, Silué S. Rainwater Chemistry and Wet Deposition over the Wet Savanna Ecosystem of Lamto (Côte d'Ivoire), J. Atm. Chem. 2005;52:117–141.
11. Galy-Lacaux C, Laouali D, Descroix L. Gobron N, Liousse C. Long term precipitation chemistry and wet deposition in a remote dry savanna site in Africa (Niger), Atmos. Chem. Phys. 2009;9: 1579-1595.
12. Galy-Lacaux C, Delon C. Nitrogen emission and deposition budget in West and Central. Environ. Res. 2014;Lett. 9:(125002).Available:http://dx.doi.org/10.1088/1748-9326/9/12/125002.
13. Laouali D, Galy-Lacaux C, Diop B, Delon C, Orange D, Lacaux JP, Akpo A, Lavenu F, Gardrat E, Castera P. Long term monitoring of the chemical composition of precipitation and wet deposition fluxes over three Sahelian savannas. Atmos. Environ. 2012;50:314-327.
14. Akpo AB, Galy-Lacaux C, Laouali D, Delon C, Liousse CM, Adon ME, Gardrat, Mariscal A, Darakpa, C. Precipitation chemistry and wet deposition in a remote wet savanna site in West Africa: Djougou (Benin). Atmos. Environ. 2015;115:110–123.
15. Adon M, Galy-Lacaux C, Yoboué V, Delon C, Lacaux JP, Castera P, Gardrat E, Pienaar J, Al Ourabi H, Dungall L, Diop B, Sigha L, Akpo A, Lavenu F, Mougin E. Long term measurements of sulphur dioxide, nitrogen dioxide, ammonia, nitric acid, and ozone in Africa using passive samplers: Atmos. Chem. Phys. 2010;10:7467-7487.
16. Desboeufs K, Journet E, Rajot JL, Chevaillier S, Triquet S, Formenti P, Zakou A. Chemistry of rain events in West Africa: evidence of dust and biogenic influence in convective systems, Atmos. Chem. Phys. 2010;10 :9283-9293.
17. Marticorena BB, Chatenet JL, Rajot S, Traoré M, Coulibaly A, Diallo I, Koné A, Maman T. NDiaye and A. Zakou, Temporal variability of mineral dust concentrations over West Africa: analyses of a pluriannual monitoring from the AMMA Sahelian Dust Transect, Atmos. Chem. Phys. 2010;10: 8899-8915.
18. Pierre CG, Bergametti B. Marticorena, E. Mougin, C. Bouet and C. Schmechtig, Impact of vegetation and soil moisture seasonal dynamics on dust emissions over the Sahel, J. Geophys. Res. 2012; 117:D06114. DOI:10.1029/2011JD016950,

19. Laouali D, Galy–Lacaux C, Yoboué V. Bulletin d'Informations de la Société Ouest Africaine de Chimie, Caractérisations chimiques des Précipitations en région semi-aride du Niger. 2009 ;N° 06;47-63.
20. Liousse C, Guillaume B, Grégoire JM, Mallet M, Galy C, Pont V, Akpo A, Bedou M, Castéra P, Dungall L, Gardrat E, Granier C, Konaré A, Malavelle F, Mariscal A, Mieville A, Rosset R, Serça D, Solmon F, Tummon F, Assamoi E, Yoboué V, Van Velthoven P. Updated African biomass burning emission inventories in the framework of the AMMA-IDAF program, with an evaluation of combustion aerosols, Atmos. Chem. Phys. 10 :9631-9646. DOI:10.5194/acp-10-9631-2010, 2010.
21. Mayaux P, Bartholome EE, Fritz S, Belward A. A new land cover map of Africa for the year 2000. J. Biogeogr. 2004; 31:861-877.
22. Gilett RW, Ayers GP. The use of thymol as a biocide in rainwater samples, Atm. Env. 1991;254A:2677–2681.
23. Norman M, Das SN, Pillai AG, Granat L, Rodhe H. Influence of air mass trajectories on the chemical composition of precipitation in India. Atmos. Environ. 2001;35:4223-4235.
24. Pillai AG, Naik MS, Momin GA, Rao PD, Safai PD, Ali K, Rodhe H, Granat L. Studies of wet deposition and dustfall at Pune: India Water Air Soil Pollut. 2001;130:475-480.
25. Kulshrestha UC, Granat L, Engardt M, Rodhe H. Review of precipitation monitoring studies in India-a search for region patterns. Atmos. Environ. 2005;39: 7403-7419.
26. Laouali D, Moussa O, Galy-Lacaux C. Characterizing Aerosols Chemistry in the Great African Ecosystems. J. Mater. Environ. Sci. 2017;8(5P):1644-1653.
27. Moussa O, Laouali D, Adon M. Measurement of atmospheric gases in the West and Central African ecosystems J. Mater. Environ. Sci. 2018a;9(10):2812-2821.
28. Moussa O, Laouali D, Akpo AB. Chemical caracterization of $PM_{2.5}$ and PM_{10} collected in dry savanna of Banizoumbou in Niger and wet savanna of Djougou in Benin. Int. Res. J. Environmental Sci. 2018b;7(9):1-15.
29. Metzger SF, Dentener S, Pandis, and J. Lelieveld. Gas/aerosol partitioning: A computationally efficient model, Journal of Geophysical Research-Atmospheres. 2002;107(D16):4312. DOI: 10.1029/2001JD001102.
30. Galy-Lacaux C, Modi AI. Precipitation Chemistry in the Sahelian Savanna of Niger, Africa. J. Atmos. Chem. 1998;30: 319-343.
31. Singh AK, Mondal GC. Chemical caracterization of wet precipitation events and deposition of pollutants in coal miningregion, India. # J. Atmos. Chem. 2008;59:1-23.
32. Gradel TE, Crutzen PJ. Atmospheric change: An Earth System Perspective, W. H. Freeman and Company, New York, USA. 1993;446.
33. Galy-Lacaux C, Carmichae el GR, Song CH, Lacaux JP, Modi I. Heterogenous processes involving nitrogenous compounds and Saharan dust inferred from measurements and model calculations Region. J. Geophys. Res. 2001;106:12559-12578.
34. Kerminen VMR, Hillamo K, Teinila T, Pakkanen I, Allegrini R. Sparapani Ion balances of size-resolved tropospheric aerosol samples: implications for the acidity and atmospheric processing of aerosols, Atmospheric Environment. 2001;35(31):5255-5265.
35. Maruthi B, Sibsankar D, Soumen B, Bandari N, Subhashis K, Tanmoy G. Impact of Humic Acid-Based Bio-Stimulant 'Humetsu' on Growth and Yield Attributes of Potato (*Solanum Tuberosum* L.). International Journal of Environment and Climate Change. 2024;14(6):340-48. Available :https://doi.org/10.9734/ijecc/2024/v14i64233.

Peer-review history:
The peer review history for this paper can be accessed here:
https://www.sdiarticle5.com/review-history/124588