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Rainwater Chemistry and Wet Deposition over the Equatorial Forested Ecosystem of Zoétélé (Cameroon)

L. SIGHA-NKAMDJOU¹, C. GALY-LACAUX², V. PONT², S. RICHARD³,
D. SIGHOMNOU¹ and J. P. LACAUX²

¹*Centre de Recherches Hydrologiques, BP 4110 Yaoundé, Cameroon,
e-mail: lucsigna@hotmail.com; sighomno@camnet.cm*

²*Laboratoire d'Aérodologie 14, Av. Edouard Belin 31, F-400 Toulouse, France,
e-mail: {lacc; ponv}@aero.obs-mip.fr*

³*HYDRECO Laboratoire Environnement de Petit Saut, BP823 97388 Kourou Cedex,
French Guiana, France, e-mail: hydreco-labops@wanadoo.fr*

Abstract. Within the framework of IDAF (IGAC DEBITS AFRICA: International Global Atmospheric Chemistry/DEposition of Biogeochemically Important Trace Species/Africa) network, data analysis is realised on precipitation chemical composition collected in Zoétélé, in Southern Cameroon. This station, located at about 200 km from the Atlantic Ocean, is representative of a so-called 'Evergreen Equatorial Forest' ecosystem. An automatic wet-only precipitation collector was operated at the station from 1996 to 2000. The rainfall regime, associated with eastward advection of moist and cool monsoon air masses, amounts to an average of 1700 mm/year. Inorganic and organic content of the precipitation were determined by IC in 234 rainfall events, representing a total 4,583 mm of rainfall from an overall of 7,100 mm. The mean annual precipitation chemistry and wet deposition fluxes characteristic of an African equatorial forest are quantified. Typical atmospheric gases and particles sources influence the precipitation chemical content and the associated deposition of chemical species. Indeed, hydrogen concentration is the highest ($12.0 \mu\text{eq.L}^{-1}$) of the IDAF measurements, leading to acid rains with a low mean pH 4.92. The mineral species are dominated by nitrogenous compounds (NH_4^+ : 10.5 and NO_3^- : $6.9 \mu\text{eq.L}^{-1}$), Ca^{2+} ($8.9 \mu\text{eq.L}^{-1}$) and SO_4^{2-} $5.1 \mu\text{eq.L}^{-1}$. Relationship between Ca^{2+} and SO_4^{2-} indicated a terrigenous particulate source and an additional SO_4^{2-} contribution probably due to swamps and volcano emissions. Na^+ and Cl^- concentrations, around $4.0 \mu\text{eq.L}^{-1}$, seem very low for this site, accounting for the marine source. Besides, strong correlations between $\text{NH}_4^+/\text{K}^+/\text{Cl}^-$ indicate the biomass burning origin of these species. Accordingly, precipitation chemistry in Zoétélé is influenced by three major sources: biogenic emissions from soil and forest ecosystems, biomass burning from savannah, and terrigenous signature from particles emissions of arid zones; and three minor sources: marine, volcano and anthropogenic. In spite of the relatively low concentration of all these elements, the wet deposition is quite significant due to the high precipitation levels, with for example a nitrogenous compounds deposition of $34 \text{ mmol.m}^{-2}.\text{yr}^{-1}$.

Key words: rainwater chemistry, wet deposition, equatorial forest, acid rain, tropical atmosphere, Cameroon.

1. Introduction

Recently, atmospheric chemists have focusing on studying the chemistry of the tropical atmosphere, particularly rainfall composition and pollution. The latter is indeed an indicator for the associated gaseous and particles air content. Most of these studies have been developed particularly in South America and in Australia (Galloway *et al.*, 1982; Keene *et al.*, 1983; Ayers *et al.*, 1988; Likens *et al.*, 1987; Andreae *et al.*, 1988, 1990; Sanhueza *et al.*, 1992; Williams *et al.*, 1997). There has been little research activity over the African continent. Nonetheless, contrary to widespread ideas, tropical Africa is not devoid of atmospheric pollution. Indeed few studies on rainwater chemistry and wet deposition in Western and Central Africa especially in the framework of the DECAFE (Dynamique Et Chimie Atmosphérique en Forêt Equatoriale) Programme (Delmas *et al.*, 1995; Cachier and Ducret, 1991; Kouadio, 1991; Lacaux *et al.*, 1987, 1988, 1991, 1992, 1993; Lefeuvre, 1993; Modi *et al.*, 1995; Yoboue, 1991) showed that forest, savannah and anthropogenic activities emitted substances such as nitrogenous compounds (NO_x , NH_3 , particles) and organic acids (HCOOH , CH_3COOH , $\text{H}_2\text{C}_2\text{O}_4$ and $\text{C}_2\text{H}_5\text{COOH}$) which contributed to changes in the tropospheric chemistry.

Following the recommendations of the IDAF (International Global Atmospheric Chemistry/Deposition of Biogeochemically Important Trace Species/Africa) workshop held in Yamoussoukro (Ivory Coast, December 1994), it was decided to create a new network for estimating wet (rainfall) and dry (aerosols and gas) deposition in Africa. Among the 10 sites selected for this project and representing various ecosystems, the two sites of Zoétélé/Nsimi in South Cameroon and of Bomassa in North Congo, chosen as representative of the dense tropical rainforest ecosystem (Figure 1). First results were published by Freydier (1997) for the Zoétélé site.

In this paper, we analysed the chemistry of rainwater samples from the site representative of the 'evergreen equatorial forest': Zoétélé. The measuring campaign lasted from September 1996 until April 2000. The objectives were to:

- present the mean annual precipitation chemistry and mean wet deposition fluxes, characteristic of an African evergreen equatorial forest;
- analyse the seasonal chemical composition of rainwater;
- determine the relationships between emissions and deposition of chemical species (over ocean, land, forest) and role of anthropogenic activities;
- compare the results from this study to those obtained from other forested ecosystems.

2. Description of the Sampling Site and Climatic Environment

The Zoétélé station is located in the rainforest of Southern Cameroon, which extends between $1^{\circ}30'$ N and 5° N of latitude and from the Atlantic Ocean to 16° E. Outside the Mount Cameroon (4,075 m of altitude), it is essentially a plateau from 200 m high near the coastline to 1,500 m high inland. Mount Cameroon is an

Figure 1. Vegetation and location map of the 10 measuring stations from the IDAF 2002 network (IGAC DEBITS AFRICA).

active volcano with its last eruptions recorded at the beginnings of 1999 and 2000. A dense evergreen forest called the ‘Congo Forest’ covers the whole region. Nsimi ($3^{\circ}10' N$ of latitude and $11^{\circ}58' E$ of longitude, and 690 m of altitude), a village near Zoétélé, is located around 200 km from the Atlantic ocean and 120 km south of Yaoundé, the capital of the Republic of Cameroon (Figure 4(a)). The Nsimi basin of 0.6 km^2 , comprises two low altitude hills (700 m) separated by a wide swampy area.

The rainfall regime in the region is mainly dominated by the moist and cool monsoon air masses that generally follow the seasonal northward migration of the Inter-Tropical Convergence Zone (ITCZ). The ITCZ separates the moist and cool air masses (monsoon flow) coming from the equatorial Atlantic ocean to the warm and dry air masses (harmattan flow), coming from the Sahara desert. Nevertheless in this region even if rainfall occurs all year long, there is the so-called great dry season (November–March) when the ITCZ is found at its southernmost position around $5^{\circ} N$, the small rainy season (April–June with a rainfall maxima in May) after the ITCZ began its northward migration, the small dry season (July–August) when precipitation decrease, and the rainy season per-say with heavy rainfall

Figure 2. Mean monthly evolution of the rainfall amount (mm) – left ordinate – and associated monthly mean number of rain days – right ordinate – at Zoétélé from 1995 to 2000.

from September to October (with maxima in October) when the ITCZ reaches its northernmost position around 30° N. The seasonal variation of the mean monthly precipitation and the distribution of the rainy days in Zoétélé from 1995 to 2000 are presented in Figure 2. The total yearly amount of rainfall is of 1,830 mm, with 122 rainy days. At Sangmelima ($2^{\circ}56'$ N of latitude and $11^{\circ}59'$ E of longitude, and 713 m of altitude) located at 40 km south Zoétélé (Nsimi), the mean annual rainfall is of 1700 mm. Interannual variation of precipitation in Sangmelima (Figure 3) indicates that our measuring campaigns took place during a wetter period.

The spatial variability of the annual rainfall (Figure 4(a)) indicates that precipitation decrease rapidly from 10,000 mm at Debunscha on the Mount-Cameroon to 1,384 mm at Moloundou in the South-East (borders of Cameroon/Congo/Central African Republic) with 4,000 mm at Douala, 3,000 mm at Kribi and 1,700 mm at Sangmelima.

Along a Southwest–Northeast transect from the Atlantic coastline to Zoétélé and following roughly an axis from Kribi to Zoétélé (Figure 4(b)), precipitation decreases rapidly over a 200 km distance, from 3,000 mm at Kribi to 1,700 mm at Sangmelima, and with 2,000 mm at Ebolowa. This can be explained by the presence of the Ngoazip and Nkongnam mountains ranges (1,000–1,200 m) located at 100 km between the Atlantic ocean and Zoétélé. The subsequent orographic uplifting of the oceanic air masses and associated rainfall keep them off from reaching unchanged the Zoétélé zone. Thus, orography plays an important role on precipitation in our zone of interest.

In our zone of interest, the mean air temperature is around 25°C and the evapo-transpiration represents about 80% of the mean annual rainfall (Sighe-Nkamdjou,

Figure 3. Interannual variability of precipitation in Sangmelima calculated from the deviation of annual precipitation to the mean annual rainfall at this site (1,700 mm) and for the 1950–1991 period.

1994). The presence of a dense evergreen forest, which covers the whole region and modifies the water cycle, must not be neglected. According to Monteny and Casenave (1989), about 60–75% of precipitation falling over the moist forest region of African continent are attributed to continental recycled moisture. Thus, in addition to the influence of sea surface temperature, cloud formation over the Zoétélé area is associated with tropospheric water vapour through the forest evapotranspiration mechanisms. The local signature of precipitation contains gaseous compounds and particulate biogenic emission released by the equatorial forest.

3. Sampling and Chemical Analysis

3.1. SAMPLING

An automatic rain sampler for a surface of 225 cm² built for the IDAF network, is used as follows:

- In order to keep off dry deposition, leaves and insects, a single-use polyethylene bag is fixed on the sampler, which remains closed. At the beginning of the rainfall, a precipitation detector commands the opening of the cover. Immediately after the end of each rainy event, an operator collects the rainwater in a Greiner 50 ml tube.
- The sample is stored in a deep freeze environment, thus avoiding the microbial activities, which could modify the precipitation chemistry.
- All the frozen samples are brought for analysis to the IDAF Laboratory in Toulouse.

Figure 4a. Spatial variability map of the annual precipitation in the studied area (South Cameroon). The AB line goes approximately from Kribi to Zoétélé.

Figure 4b. Cross-section along the AB line (Southwest–Northeast) from the Atlantic Ocean (Kribi) to the IDAF site of Zoétélé.

Figure 5. Results of World Meteorological Organization (WMO) intercalibration for the analysis of the mineral ions (Na^+ , NH_4^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- , NO_3^- , SO_4^{2-}) using Ion Chromatography and for the pH and conductivity measurements at the Aerologie Laboratory (LA) in Toulouse for the 1998 to 2000 period.

At the Zoétéle site, and during our measuring campaigns (September 1996 to April 2000), 244 rainy events were sampled. The efficiency of the sampling procedure is presented in Figure 6. It shows that about 60% of the rainfall was effectively collected.

More information can be obtained from the IDAF Web Site: <http://medias.obs-mip/idadf/>

3.2. CHEMICAL ANALYSIS

The composition of the rainwater samples was determined at the IDAF Laboratory in Toulouse. Inorganic (Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , NO_3^- , SO_4^{2-}) and organic ions (HCOO^- , CH_3COO^- , $\text{C}_2\text{H}_5\text{COO}^-$, $\text{C}_2\text{O}_4^{2-}$) are measured by Ion Chromatography (IC) (see Galy-Lacaux and Modi, 1998 for details). According to the results of our laboratory since 1996 to the international intercalibration tests organized by WMO (World Meteorological Organization), analytical precision is estimated to be 5% or better for all the ions and represents the uncertainties on all the measurements presented in this paper. The histogram of the 1998, 1999 and 2000 results is presented in Figure 5.

Figure 6. Annual rainfall amount (mm) and sampled rainfall at Zoétélé – right ordinate – and associated evolution of the annual sampling efficiency (%) (SE) – left ordinate –.

To improve the IDAF data quality, we applied the WMO quality criteria to all the IDAF precipitation samples. This criteria is based on the calculation of the ID criteria for each sample, i.e., the ion difference in % to consider the ionic balance (Equation (1)).

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

AE is the anion sum in $\mu\text{eq.L}^{-1}$ and CE is the cation sum in $\mu\text{eq.L}^{-1}$. WMO acceptance criteria are presented in WMO report (1997).

In this study, the ID criteria has been applied to the 244 rainy collected in Zoétélé. 96% of the samples are in the WMO acceptance range and were only considered for calculation in this work. Finally, we considered 234 rainy samples; which totalled an amount of 4,583 mm of rainfall from an overall of 7,100 mm.

The 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. From the pH values, ion H^+ concentrations are calculated. The precision is of 0.01 pH unit.

Figure 7. pH relative frequency distribution measured from Zoétélé precipitation (September 1996–April 2000).

4. Chemical Composition of Rainwater and Wet Deposition at Zoétélé

In the next section, we determine the mean chemical composition of precipitation and the associated sources of gaseous and particulate species that determine the chemical precipitation content.

4.1. ANNUAL CHEMICAL COMPOSITION OF RAINWATER AND WET DEPOSITION

The range of pH values, calculated from the H^+ ions concentration, was from 4.1 to 6.5. The pH frequency distribution is presented in Figure 7. The latter shows that more than 90% of pH values are less than 5.6. This is the value of pH water in equilibrium with the atmospheric CO_2 and under which rainwater is considered as acidic one. Half of the values ranging from 4.6 to 5.0, confirm the acidic characteristic of the precipitation collected in equatorial regions.

The mean monthly concentrations for each species brought together and compared in cations (excepted for H^+ plotted alone because of the several gaps in the series), anions and organic acids (limited at formic and acetic acids) are presented in Figure 8. They have been calculated by taking into account the event rainfall. It is the Volume-Weighted Mean (VWM) for each chemical species, which is obtained from the equation below:

$$VWM (\mu eq.L^{-1}) = \frac{\sum_{i=1}^{n=234} C_i P_i}{\sum_{i=1}^{n=234} P_i} \quad (2)$$

Figure 8. Monthly variation of the Volume Weighted Mean (VWM) chemical composition of precipitation (anions, cations, hydrogen and organic acids) associated with the evolution of the monthly depth rainfall over the studied period (September 1996–April 2000).

with: C_i : Ion concentration for each sample in $\mu\text{eq.L}^{-1}$; P_i : Precipitation amount for each rainy event in mm.

High concentrations of the different ions have been measured from November to March every year. The low concentrations are observed from April to October. Globally, this repartition corresponds to the dry and extended rainy season. The high concentrations during the dry season can be explained by the input of other sources, such as wind erosion and savannah fires and also by low liquid content of precipitation. During wet season, concentrations are diluted by the high amount of precipitation. We note that monthly concentration of H^+ ion goes from $37 \mu\text{eq.L}^{-1}$ in November–December 1996 to $6 \mu\text{eq.L}^{-1}$ in September 1998, corresponding to 4.4 to 5.2 pH values.

In Table I the mean annual values for VWM and Wet Deposition (WD) are displayed. Hydrogen is the major ion present in the Zoétélé rainwater. The mean concentration of H^+ ($12.0 \mu\text{eq.L}^{-1}$) corresponds to a pH of 4.92. Globally, higher concentration are measured in precipitation above African equatorial forest, due mainly to organic compounds, particularly formate ($8.7 \mu\text{eq.L}^{-1}$) and acetate ($5.4 \mu\text{eq.L}^{-1}$). Overall, propionate and oxalate are very low (0.2 to $1.2 \mu\text{eq.L}^{-1}$). We calculated dissociated fractions of organic acids according the following dissociation constants: 3.75, 4.75, 4.67 and 4.19 respectively for formic, acetic, propionic and oxalic acids. The dissociated fraction of the former contribute respectively to 94 and 59% for the total of the organic compounds. The acidity will be discussed later in comparison with the others results of African sites (see paragraph 4).

Mineral species are dominated by nitrogen compounds ($\text{NH}_4^+ = 10.5 \mu\text{eq.L}^{-1}$; $\text{NO}_3^- = 6.9 \mu\text{eq.L}^{-1}$), calcium ($8.9 \mu\text{eq.L}^{-1}$) and sulphate ($5.1 \mu\text{eq.L}^{-1}$). Na^+ and Cl^- concentrations (4.0 and $4.3 \mu\text{eq.L}^{-1}$ in order) seem very low since the site is located not far from the ocean.

The WD has been calculated by taking into account a mean rainfall amount of 2,029 mm measured during the experimental period. The main contributors are nitrogen compounds ($\text{NH}_4^+ + \text{NO}_3^- = 35.2 \text{ mmol.m}^{-2}.\text{yr}^{-1}$) and organic compounds ($\text{HCOOH} + \text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{COOH} + \text{H}_2\text{C}_2\text{O}_4 = 30 \text{ mmol.m}^{-2}.\text{yr}^{-1}$). In a recent study, Lacaux *et al.* (2003) shows that for tropical Africa, due to the high contribution of wet deposition in mineral acidity by the biomass burning sources, the critical load is nearly reached in many parts of Western Africa. All the equatorial rainforests of South-America, Africa and Asia are classified in the most sensitive classes. For Central Africa soils, for example with a level of mineral acidity deposition of about $10\text{--}20 \mu\text{eq.m}^{-2}.\text{yr}^{-1}$ measured in Cameroon, future acidification problems may become severe if the development of land use change and industrial activities occur in these regions.

4.2. RELATIONSHIPS EMISSIONS/DEPOSITION OF THE CHEMICAL SPECIES

In order to study the relationships between emissions and deposition of the chemical species, seasonal VWM were computed. The wet season extended from April

Table 1. Volume-Weighted Mean (VWM) chemical composition and Yearly Wet Deposition (WD) at Zoétélé during the rainy season from September 1996 to April 2000

Events	Rainfall events (mm)	Total rainfall (mm)	Average rainfall (mm)	pH	H ⁺	Na ⁺	NH ₄ ⁺	K ⁺	Ca ²⁺	Mg ²⁺	NO ₃ ⁻	Cl ⁻	SO ₄ ²⁻	HCOOH	CH ₃ COOH	C ₂ H ₅ COOH	H ₂ C ₂ O ₄	
234	4,583	7,100	2,029	4.92	VWM	12.0	4.0	10.5	5.0	8.9	2.4	6.9	4.3	5.1	8.7	5.4	0.2	1.2
					$\mu\text{eq.l}^{-1}$)									(8.2) ^a	(3.2) ^a	(0.1) ^a	(1.0) ^a	
					WD	24.3	8.1	21.4	10.3	9.0	2.4	13.8	8.7	4.9	17.4	11.1	0.5	1.1
					(mmol.m ⁻² .yr ⁻¹)													

^a Dissociated organic acids.

Figure 9. Seasonal Volume Weighted Mean (VWM) chemical composition of precipitation collected at Zoétélé (September 1996–April 2000).

to October and the dry season from November to March. Stratified results from the dry season and wet season chemical species concentrations are displayed in Figure 9. The different ratio dry/wet increase from 1.5 for hydrogen to 5 for magnesium. Moreover and independently of the season, the levels of Cl^- , Na^+ and Mg^{2+} are relatively low.

4.2.1. The Marine Emissions and Conceptual Model of Precipitations

The annual VWM of sodium ($4.0 \mu\text{eq.L}^{-1}$) and chloride ($4.3 \mu\text{eq.L}^{-1}$), compared with those found Lacaux *et al.* (1993, 1992) at the other African sites (Lamto: $\text{Na}^+ = 6.4 \mu\text{eq.L}^{-1}$ and $\text{Cl}^- = 7.5 \mu\text{eq.L}^{-1}$; Boyélé: $\text{Na}^+ = 7.5 \mu\text{eq.L}^{-1}$ and $\text{Cl}^- = 8.5 \mu\text{eq.L}^{-1}$; Dimonika: $\text{Na}^+ = 11.1 \mu\text{eq.L}^{-1}$ and $\text{Cl}^- = 13.3 \mu\text{eq.L}^{-1}$) are very low for this site located only at 200 km from the Atlantic Ocean. These concentrations are lowest in wet season ($\text{Na}^+ = 3.2 \mu\text{eq.L}^{-1}$ and $\text{Cl}^- = 3.4 \mu\text{eq.L}^{-1}$).

In order to differentiate the marine contribution for each element, we calculated part of sea salt particles in the dissolved phase using Cl^-/Na^+ ratio obtained from the following equation:

$$[\text{X}]_{\text{marine}} = [\text{Na}]_{\text{rain}} \times [\text{X}/\text{Na}]_{\text{sea}} \quad (3)$$

with: $[\text{X}]_{\text{marine}}$ = marine contribution for the element X in $\mu\text{eq.L}^{-1}$; $[\text{Na}]_{\text{rain}}$ = sodium ion concentration in rainwater ($\mu\text{eq.L}^{-1}$); $[\text{X}/\text{Na}]_{\text{sea}}$ = concentration ratio in seawater after Keene *et al.* (1986).

In Table II, we compare the ratios of seawater compounds given by Keene *et al.* (1986) to similar ratios in rainwater samples. The ratio Cl^-/Na^+ is close with the seawater one (1.16) in wet (1.06) and dry season (1.09), with the annual mean calculated to 1.08. This is confirmed by the strong correlation obtained between sodium and chloride ($r = 0.937$) in Figure 10(a). This figure has been established as follows: let σ be the standard deviation and z_m the mean of each distribution.

Table II. Seasonal and annual Volume-Weighted Mean (VWM) chemical composition ($\mu\text{eq.l}^{-1}$) for the marine species from precipitation at Zoétélé from September 1996 to April 2000

	Na^+	Cl^+/Na^+	K^+/Na^+	K^+	$\text{Ca}^{2+}/\text{Na}^+$	Ca^{2+}	$\text{Mg}^{2+}/\text{Na}^+$	Mg^{2+}	$\text{SO}_4^{2-}/\text{Na}^+$	SO_4^{2-}
Xi/Na (seawater) (Keene <i>et al.</i> , 1986)		1.16	0.02		0.04		0.23		0.12	
Wet season	3.2	1.06	1.25	4.0 (0.1) ^a	1.93	6.1 (0.1) ^a	0.43	1.4 (0.7) ^a	1.19	3.8 (0.4) ^a
Dry season	7.5	1.09	1.22	9.1 (0.2) ^a	2.58	19.2 (0.3) ^a	0.83	6.2 (1.7) ^a	1.37	10.2 (1.0) ^a
Annual	4.0	1.08	1.25	5.0 (0.1) ^a	2.23	8.9 (0.2) ^a	0.60	2.4 (1.0) ^a	1.28	5.1 (0.5) ^a

^a Calculation of sea salt contribution of each marine species according to ratios from Keene *et al.* (1986).

Figure 10a. Standardised distribution (SD) of chlorine versus standardised distribution (SD) of sodium calculated for the complete rainy events database at Zoétélé (1996–2000).

Figure 10b. Standardised distribution (SD) of sulfate versus standardised distribution (SD) of calcium for the complete rainy database at Zoétélé. Rainy events with high sulfate concentrations and average calcium concentrations are highlighted.

For each rainy event (i), and for each distribution of element concentrations $z(i)$ during the considered period, we calculate $z_s(i)$:

$$z_s(i) = \frac{(z(i) - z_m)}{\sigma_z} . \quad (4)$$

Thus each distribution of chemical element is standardised, which gives an equal influence to each chemical element in graphic representation such as above. Then, the standardised values vary on a scale that finally stands for the variation of the

variable to the mean in standard deviation units (for example, if $z_s(i) = 1$, it means that the considered variable deviates from the mean value of 1 standard deviation). In Figure 10(a), the data distribution is found in the unit rectangle, which signifies that Na^+ and Cl^- follow a Gaussian distribution. We note that Na^+ and Cl^- are highly correlated ($r = 0.88$), which indicates a marine character to the overall precipitation regimes formed in the different air masses, independent of concentration levels.

These results indicate that in spite of their low values, Na^+ and Cl^- concentration come from marine contribution in Zoétélé precipitation. Nevertheless, due to the mountains located between the Atlantic Ocean and Zoétélé, which constitutes an orographic barrier to the monsoon air as explained in paragraph 1, the rainfall is devoid of most of these marine elements before reaching our site. This result is similar to the one found by Sigha-Nkamdjou *et al.* (1998) and also by Sigha-Nkamdjou (1994) and Njitchoua *et al.* (1999). Table III shows correlation coefficient between different chemical elements. High correlation could indicate that chemical compounds have the same origin and/or are being advected by the same air masses. There is no correlation between sodium (or chloride) and ions HCOO^- and CH_3COO^- signature of biogenic emissions released by the equatorial forest (Table III). This corroborates the concept of precipitation with marine tracers, over mountains range, upstream of the Zoétélé site, and water vapor loading including volatile organic compounds on the lee side of the mountain range.

When compared to the other ratios, only the $\text{Mg}^{2+}/\text{Na}^+$ during wet season (0.43) has the same order of magnitude as in the seawater (0.227–0.243). Our results are comparable to those found by Mphepya *et al.* (in press, 2002) at Louis Trichardt (South Africa) for chloride (1.08), magnesium (0.44) and sulphate (1.56).

The seasonal and annual results presented in Table II shows that sea salts concentrations are very low, excepted for chloride. In average, the marine contribution is equal to 37.8% (Mg^{2+}), 9.49% (SO_4^{2-}), 1.98% (Ca^{2+}) and 1.76% (K^+). High contributions are observed in wet season (excepted for potassium), due to the predominance of the monsoon flux. The mean marine contribution of sulphate and potassium ions is comparable to the one obtained by GalyLacaux and Modi (1998), at Banizoumbou (Niger), with 10.5 and 1.8% respectively.

4.2.2. The Terrigenous Sources

The annual non sea salt (nss) contribution in precipitation can be evaluated at $4.9 \mu\text{eq.L}^{-1}$ (K^+), $8.7 \mu\text{eq.L}^{-1}$ (Ca^{2+}), $1.5 \mu\text{eq.L}^{-1}$ (Mg^{2+}) and $4.6 \mu\text{eq.L}^{-1}$ (SO_4^{2-}). For each species, the ratio of the dry to the wet season is respectively 2.3; 3.1; 7.1 and 2.7. These ratios, especially high for magnesium and calcium, indicate an important input of these species coming probably from particles released by eolian erosion of the Sahelian and Saharan desert soils, which are lots of gypsum (CaSO_4), calcite (CaCO_3) and dolomite ($\text{CaMg}(\text{CO}_3)_2$) according to Bohn *et al.* (1985) and Loye-Pilot *et al.* (1986).

Table III. Correlation coefficients between the major chemical species measured in the precipitation at Zoétélé (Cameroon)

	H ⁺	Na ⁺	NH ₄ ⁺	K ⁺	Ca ²⁺	Mg ²⁺	NO ₃ ⁻	Cl ⁻	SO ₄ ²⁻	HCOO	CH ₃ COO
H ⁺	1	-0.1889	0.0965	-0.1113	-0.1531	-0.0921	0.5267	-0.1763	0.5310	0.5971	0.5730
Na ⁺	-0.1889	1	0.2779	0.6970	0.2328	0.2311	0.0498	0.9373	0.2237	-0.0270	-0.0514
NH ₄ ⁺	0.0965	0.2779	1	0.6203	0.4242	0.3628	0.4799	0.4533	0.5148	0.3691	0.2984
K ⁺	-0.1113	0.6970	0.6203	1	0.5906	0.6858	0.2852	0.8212	0.4330	0.0179	-0.0073
Ca ²⁺	-0.1531	0.2328	0.4242	0.5908	1	0.6915	0.4857	0.3162	0.5508	0.2669	0.2065
Mg ²⁺	-0.0921	0.2311	0.3628	0.6658	0.6915	1	0.4797	0.3370	0.5250	0.1223	0.0768
NO ₃ ⁻	0.5267	0.0498	0.4799	0.2852	0.4857	0.4797	1	0.1236	0.8459	0.5369	0.3817
Cl ⁻	-0.1763	0.9373	0.4533	0.8212	0.3162	0.3370	0.1236	1	0.2888	-0.0482	-0.0884
SO ₄ ²⁻	0.5310	0.2237	0.5148	0.4330	0.5508	0.5250	0.8459	0.2888	1	0.5454	0.4366
HCOO	0.5971	-0.0270	0.3691	0.0179	0.2669	0.1223	0.5369	-0.0482	0.5454	1	0.9270
CH ₃ COO	0.5730	-0.0514	0.2984	-0.0073	0.2065	0.0768	0.3817	-0.0884	0.4366	0.9270	1

Calculations significant at the 95% confidence interval.

The strong correlation between calcium and magnesium obtained in Table III ($r = 0.8915$), corroborates the common origin of these two species as indicated above. Contrary to this result, the correlation between calcium and sulphate ($r = 0.5508$) is relatively low, indicating that the whole sulphate is not originating from the terrigenous sources (Figure 10(b)). Since there is an increase of sulphate with constant values of calcium, we can assume an emission of sulphate in excess of the terrigenous source probably associated with H_2SO_4 production.

According to Seinfeld and Pandis (1998), H_2S is emitted by swamps and volcanoes. Consequently, a part of sulphate content in rainwater can be attributed to the oxidation of H_2S into SO_2 and H_2SO_4 . The H_2S sources around Zoétélé site are mainly associated with the proximity of swamps and probably with the volcanic eruption from the Mount Cameroon volcano which occurred twice, at the beginnings of 1999 and 2000.

The total concentration of the terrigenous species is $19.7 \mu\text{eq.L}^{-1}$, which is equivalent to 27% of the total species. This value is very low compared with 56% found by Galy-Lacaux and Modi (1998) at Banizoumbou in the Sahelian region, but is higher than the one found in the Amazonian forest (Williams *et al.*, 1997). We can conclude that precipitation chemistry in African forest is more influenced by the terrigenous compounds coming from Sahelian and Saharan desert soils. Meanwhile at the Zoétélé site, a part of sulphate is not terrigenous but due to the products of oxidation of H_2S emitted by swamps and volcano.

4.2.3. *Biogenic Emissions and Biomass Burning*

In the next section, nitrogenous and acidic contributions to the rainwater composition are described by mainly looking at the important biogenic and biomass burning emissions surrounding the Zoétélé site.

4.2.3.1. *Nitrogenous compounds.* The annual VWM of ammonium and nitrate have been calculated to 10.5 and $6.9 \mu\text{eq.L}^{-1}$ respectively. The concentration of ammonium is comparable to those found by Galy-Lacaux and Modi (1998) in the dry savannah site of Banizoumbou ($12.9 \mu\text{eq.L}^{-1}$) and by Lacaux *et al.* (1993) in the Congo equatorial forest site of Boyélé ($15.7 \mu\text{eq.L}^{-1}$). As for nitrate, its concentration is twice lower than that the one found at the former site ($12.3 \mu\text{eq.L}^{-1}$), and remains comparable to that found at the Dimonika site ($8.6 \mu\text{eq.L}^{-1}$). It is also comparable to values given by Yoboué (1991) in the wet savannah site of Lamto ($8.9 \mu\text{eq.L}^{-1}$).

The seasonal analysis of the ammonium and nitrate concentrations shows that they remain still high whatever the season (dry season: $\text{NH}_4^+ = 19.4 \mu\text{eq.L}^{-1}$ and $\text{NO}_3^- = 13.2 \mu\text{eq.L}^{-1}$; wet season: $\text{NH}_4^+ = 8.3 \mu\text{eq.L}^{-1}$ and $\text{NO}_3^- = 5.2 \mu\text{eq.L}^{-1}$). Considering the ammonium concentrations, we note they vary twice as much from the rainy to the dry season. Its presence in rainwater results from the inclusion of gaseous ammonia and particles containing (NH_4^+ in clouds and rainwater. Its animal origin in the tropical African precipitation due to breeding and

pasture lands has already been underlined in Niger by Modi (1995). In Cameroon, in addition to the breeding area to the North, pasture lands to the south with pigs, poultry farm and others domestic animals around Zoétélé site, could explain the high level of NH_4^+ . According to Schlesinger and Hartley (1992), bacterial decomposition of urea in animal excreta and emissions by natural or fertilized soils constitute the main sources of ammonia. Nevertheless, in the tropical regions, studies showed that savannah fires and domestic fuelwood burning are another significant sources of NH_3 (Lobert *et al.*, 1990; Delmas *et al.*, 1995; Brocard *et al.*, 1996). Its high levels in both seasons could also be explained by the savannah fires, which are produced from November to April in the North Hemisphere, and from may to September in the South Hemisphere, combined with natural emissions soils and domestic fuelwood burning. The high correlation between NH_4^+ and K^+ ($r = 0.6203$), NH_4^+ and Cl^- ($r = 0.4533$) confirm the hypothesis of the biomass burning origin of ammonium (Gaudichet *et al.*, 1995).

Concerning the nitrate component, the ratio of the concentrations of the dry to the rainy season (2.5) is the same as the ammonium one. Nitrate in rainfall is the final result of the multiphase reactions processes of nitrogenous gases and particles atmospheric air and cloud water. Natural soils and biomass burning are the main sources of the major oxide of nitrogen in the form of Nitric oxide (NO). High amounts are produced in dry season in the same way as ammonia. It is oxidised in the atmosphere by photochemical reactions into HNO_3 , which is very soluble in water and thus scavenged by clouds. Terrigenous and acidic compounds interactions are discussed in the next paragraph.

4.2.3.2. Acidic compounds. Acidity is a key aspect of the atmospheric chemistry in the African equatorial forest. In Zoétélé precipitation, H^+ , with an average concentration equal to $12 \mu\text{eq.L}^{-1}$, is the predominant ion. Its concentrations ranging from $11.2 \mu\text{eq.L}^{-1}$ in rainy season to $17.7 \mu\text{eq.L}^{-1}$ in dry season (ratio = 1.6), correspond to pH 4.95 and 4.75 respectively.

We defined a concept of potential acidity for our chemical precipitation composition as the sum of mineral and organic ions likely to contribute to the rainwater acidity. Taking into account NO_3^- , SO_4^{2-} , HCOO^- , CH_3COO^- , $\text{C}_2\text{O}_4^{2-}$ and $\text{CH}_3\text{CH}_2\text{COO}^-$, the annual potential acidity is equal to $24.5 \mu\text{eq.L}^{-1}$. By comparing with measured H^+ ion concentration: this value reveals an excess of potential acidity calculated to $12.5 \mu\text{eq.L}^{-1}$.

As we saw in Section 4.2.3: nitrate resulted from the oxidation of nitric oxide produced by soils and savannah burning. According to Clarke and Karani (1992), Dentener *et al.* (1996) and Galy-Lacaux and Modi (1998) and Galy-Lacaux *et al.* (2001), a large amount of terrigenous particles in tropical Africa is dominated by CaCO_3 . This alkaline compounds can neutralise gaseous HNO_3 through the reaction:

Figure 11. Standardised distribution (SD) of CH_3COO^- versus standardised distribution (SD) of HCOO^- for the complete rainy events database at Zoétélé.

The correlation between H^+ and NO_3^- ($r = 0.5267$) is found to be among the strongest correlation values for acidity; it indicates that in Zoétélé precipitation, only a part of nitrate content has been neutralized by terrigenous species. According to Galy-Lacaux *et al.* (2001), half of nitrate is neutralized in African forest. Considering these results, in Zoétélé precipitation, after neutralization: it would remain $3.5 \mu\text{eq.L}^{-1}$ of NO_3^- which, added to $11.4 \mu\text{eq.L}^{-1}$ of organic acids and a weak part of SO_4^{2-} (correlation coefficient with H^+ is of the same order ($r = 0.5310$)) will explain the acidity.

Organic acids, especially formic and acetic acids, result from the oxidation of the volatile organic carbon (VOC) into aldehyde (HCHO) (Graedel and Crutzen, 1993) and the dissolution of CO_2 , two compounds emitted by the tropical forested ecosystem. Apart from the important productivity of the African equatorial forest, the latter is submitted to the influence of savannah burning, with acids incorporated in the particulate phase. Without overlooking the others acids, we note that the two mentioned above also increase by twice as much from the wet to the dry season (2.8 for HCOOH and 1.9 for CH_3COOH), suggesting the importance of the input from fires. The highest correlations have been found between H^+ , HCOO^- , and CH_3COO^- (Table III and Figure 11); for that reason, it is deduced that these species contribute in the major part to the acidity of Zoétélé rainwater, with about 70% of organic acids and 30% of inorganic acids NO_3^- and SO_4^{2-}). As suggested by Lara *et al.* (2001) for tropical and subtropical South America, there are unidentified organic compounds which could be interacting and may be responsible of the potential acidity.

5. Zoétélé Rainwater Composition in the Tropical Context

Rainwater composition at the Zoétélé site compared with compositions not only in other tropical sites (Central African forest and the Guyana IDAF sites) but also in Amazonia and east Asian sites are presented in Table IV.

The ratio of chloride to sodium is close to the seawater ratio, but their concentrations are lower by twice as much than those found by Lacaux *et al.* (1992 and 1993) in two African equatorial forest in Congo (Dimonika: $11.1 \mu\text{eq.L}^{-1}$ of Na^+ and $13.3 \mu\text{eq.L}^{-1}$ of Cl^- ; Boyélé: $7.5 \mu\text{eq.L}^{-1}$ of Na^+ and $8.5 \mu\text{eq.L}^{-1}$ of Cl^-). In comparison with the results found by Richard *et al.* (pers. com.) at the IDAF site of 'Petit Saut' in French Guiana (Amazonian equatorial forest), the concentrations are lowest from 5.8 times for Na^+ ($23.8 \mu\text{eq.L}^{-1}$) and for Cl^- ($25.9 \mu\text{eq.L}^{-1}$). Moreover, by comparing with East Asian coastal sites highly influenced by the subtropical warm and humid air from the Asian Monsoon flow, we can note that the Zoétélé Na^+ and Cl^- concentrations are really low. As presented in Sections 2 and 4.2.1, the weak values of Na^+ and Cl^- in Zoétélé precipitation can be explained by dynamical processes due to orography, and with high precipitations and concentration around the mountains range. In fact, due to the spatial variability of the precipitation in our zone of interest (Figure 4(a)), the large amount of rainfall over the Cameroon ranges and the coastal areas suggest that while the monsoon air masses penetrate inland, they are depleted of their elements of marine and coastal origins.

Among terrigenous compounds, calcium concentration ($9 \mu\text{eq.L}^{-1}$) is equal to the one found at Dimonika and Boyele. This value is higher than the one obtained at 'Petit Saut' ($4.6 \mu\text{eq.L}^{-1}$) but largely lower than those measured in East Asia. Those latter sites are highly affected by continental cold and dry air masses (Fujita *et al.*, 2001). In the same order of idea, high concentrations of sulphate have been measured for African forest sites. As presented in Section 4.2.2, these results confirm that precipitation chemistry in African forest is influenced by particles originating from eolian erosion of Sahara desert. On the other hand, high values of nitrogenous compounds are measured in African forest precipitation as at Boyélé site ($15.7 \mu\text{eq.L}^{-1}$ of NH_4^+ and $19.4 \mu\text{eq.L}^{-1}$ of NO_3^-), in comparison with the one of 'Petit Saut' (NH_4^+ : $4.4 \mu\text{eq.L}^{-1}$ and NO_3^- : $5.6 \mu\text{eq.L}^{-1}$). All of these results suggest that contrary to the Amazon atmosphere, the tropical African area is influenced as well by eolian erosion as by the anthropogenic activities (biomass burning) and others sources. Nevertheless, these anthropogenic activities remain lower than those (fossil fuel combustion, continental anthropogenic activities ...) that highly influence East Asian rain concentrations (Table IV).

The hydrogen ion concentration in the Zoétélé precipitation, is found lower than in Dimonika ($18.1 \mu\text{eq.L}^{-1}$) and Boyélé ($41.0 \mu\text{eq.L}^{-1}$), but one and a half time higher than the value found at 'Petit Saut'. If we consider the concentrations of organic acids, and especially formic and acetic acids at 'Petit Saut' ($9.1 \mu\text{eq.L}^{-1}$), the excess of organic acids ($5 \mu\text{eq.L}^{-1}$) in Zoétélé is probably due to biomass burn-

Table IV. Volume weighted mean concentrations in $\mu\text{eq.l}^{-1}$ and wet deposition in $\text{mmol.m}^{-2}.\text{yr}^{-1}$ (in parenthesis) for precipitation collected in selected sites: comparison of African and Amazonian tropical forested sites, African semiarid savannas and East Asian sites

Zone	Location	Annual rainfall (mm)	Reference	pH	H ⁺	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	NH ₄ ⁺	NO ₃ ⁻	Cl ⁻	SO ₄ ²⁻	HCOO ⁻	CH ₃ COO ⁻	C ₂ O ₄ ²⁻	
Central Africa	Zoétélé (Cameroon)	2029 (1996/2000)	This study	4.92	12.0 (24.3)	4.0 (8.1)	5.0 (10.3)	8.9 (9.0)	2.4 (2.4)	10.5 (21.4)	6.9 (13.8)		4.3 (8.7)	5.1 (4.9)	8.7 (17.4)	5.4 (11.1)	1.2 (1.1)
	Dimonika (Congo)	1508 (1987)	Lacaux <i>et al.</i> (1992)	4.74	18.1 (27.3)	11.1 (16.7)	2.0 (3.0)	9.3 (7.0)	–	6.4 (9.7)	8.6 (13.0)		13.3 (5.2)	19.5 (10.0)	6.6 (4.5)	3.0	
	Boyélé (Congo)	1960 (1987)	Lacaux <i>et al.</i> (1993)	4.39	41 (80.4)	7.5 (14.7)	3.3 (6.5)	9.5 (9.3)	–	15.7 (30.8)	19.4 (38.0)		8.5 (16.7)	10.1 (9.9)	23.0 (45.1)	9.6 (18.8)	
	Banizoumbou (Niger)	489.5 (1996)	Galy-Lacaux and Modi (1998)	5.67	2.1 (1.0)	7.7 (3.7)	4.7 (2.3)	31.2 (7.6)	5.6 (1.4)	12.9 (6.3)	12.3 (6.0)		7.4 (3.6)	8.6 (2.1)	4.7 (2.1)	3.1 (2.3)	1.5 (1.5)
South Africa	Louis Trichardt (South Africa)	4678.1 (1986/1989)	Mphepya <i>et al.</i> (submitted)	4.91	12.2 (56.9)	9.3 (43.6)	3.8 (17.8)	12.0 (28.0)	4.1 (9.5)	9.7 (45.2)	8.0 (37.5)		10.0 (46.8)	14.5 (33.9)	12.9 (60.3)	8.2 (38.4)	
Central America	Brazil	2400 (1987)	Andreae <i>et al.</i> (1988, 1990)	4.91	12.2 (29.4)	4.0 (9.5)	1.8 (4.2)	4.2 (5.0)	–	4.0 (9.6)	2.1 (5.0)		4.7 (11.3)	3.5 (4.1)	6.3 (15.1)	4.3 (10.3)	
Central Amazon		2754 (1989/1990)	Williams <i>et al.</i> (1997)	4.70	17.0 (46.8)	2.4 (6.7)	0.8 (2.3)	2.4 (13.2)	0.9 (5.0)	3.0 (8.2)	4.2 (11.5)		4.6 (12.6)	2.0 (2.8)	2.9 (8.0)	9.3 (25.6)	
	French Guiana	3113 (1999)	Richard <i>et al.</i> (pers. com., 2002)	5.1	8.2 (25.5)	23.8 (74.1)	2.5 (7.8)	4.6 (7.2)	7.1 (11.1)	4.4 (13.7)	5.6 (17.4)		25.9 (80.6)	6.7 (10.4)	5.8 (18.1)	3.3 (10.3)	0.4 (0.6)
			Artaxo <i>et al.</i> (2003)														
East Asia		1579 (1992–1993)	Fujita <i>et al.</i> (2000)	4.89		96	7	43	26	34	20		111	73			
East Asia	Seoul (Korea)	1137 1996/1998	Lee <i>et al.</i> (2000)	4.7	21.3	10.5	3.5	34.9	6.9	66.4	29.9		18.2	70.9			
	Chinyang (Korea)	1127 1996–1998		4.6	23.9	10.8	2.5	22.6	5.2	29.8	19.8		18.7	46.2			

ing (savannah, forest and domestic fires). From the above results, we can deduce that high concentrations of organic acids at Zoétélé, all year long, are due to the combination of biogenic emissions, and savannah burnings. Indeed, in the Northern Hemisphere during the dry season savannah fires dominate while in the Southern Hemisphere rainy season is active, and vice versa. In contrary, in French Guiana, organic acid concentrations is mainly due to biogenic emissions.

Globally, the comparison with the Guiana results shows that, apart from the species influenced entirely by the ocean proximity (sodium and chloride) or partially (magnesium and sulphate), all the terrigenous, nitrogenous and acidic compounds are lower than those measured in Zoétélé. This confirms besides biogenic emissions in our study area, there is an important input of compounds coming from Saharan soils erosion and savannah fires. This is combined with a minor input of H_2S coming from the swamps, the Mount Cameroon volcano input, and the other mountain ranges as already mentioned. The East Asian sites are also affected by volcanoes activities, and both continental and monsoon air masses; their wet deposition measurements remain relatively high. Comparing these various sites measurements enable to estimate the added influence of large anthropogenic industrial activities on the precipitation chemical compositions.

6. Conclusion

In this paper, we show the specificity of the IDAF Zoétélé site. In spite of its geographical location near the Atlantic Ocean, the precipitation chemistry is poor in marine species, particularly Na^+ and Cl^- (compared to the results of the African forests sites) due to the orographic processes upstream. While the mountains ranges between the coastline and the Zoétélé site enhance precipitation, they deplete the air masses of their chemical compounds. Terrigenous compounds have been identified mainly during the dry season with the harmattan input of dust from Saharian and Sahelian eroded soils. The rainwater chemistry is influenced by biogenic emissions and biomass burning all year long with savannah fires in Northern Hemisphere during the dry season and in the Southern Hemisphere during the rainy season. Hence, the high acidity (pH 4.9) is enhanced by H_2SO_4 resulting from the oxidation of H_2S emitted by swamps and probably the volcanic eruptions of Mount Cameroon. The comparison of our results with those found in 'Petit Saut' in French Guiana (Amazon) showed that, apart from the marine elements, all the terrigenous, nitrogenous and acidic compound measured in 'Petit Saut' are lower than those measured in African equatorial forested ecosystem represented by the Zoétélé site. Thus, at the IDAF Zoétélé site typical atmospheric processes for an African equatorial forested ecosystem are at play. These processes include three important gaseous and particulate sources: biogenic emissions, biomass burning and terrigenous as well as three minor sources: marine, volcanic and anthropogenic.

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