Rainwater Chemistry and Wet Deposition over the Wet Savanna Ecosystem of Lamto (Côte d'Ivoire)

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Abstract. From the IGAC-DEBITS Africa network (IDAF), data sets on precipitation chemistry collected from the 'wet savanna ecosystem' site of Lamto (Côte d'Ivoire), are analyzed (1995–2002). Inorganic (Ca^{2+}, Mg^{2+}, Na^+, K^+, NH_4^+, Cl^-, SO_4^{2-}, NO_3^-) and organic ($HCOO^-$, CH_3COO^-) ions content were determined using Ion Chromatography. The analyzed 631 rainfall events represent 8420.9 mm of rainfall from a 9631.1 mm total. The precipitation chemistry at Lamto is influenced by four main sources: natural biogenic emissions from savanna soils (NO_x and NH_3), biomass burning (savanna and domestic fires), terrigeneous particles emissions from dry savanna soils, and marine compounds embedded in the summer monsoon. The inter-annual variability of the weighted volume mean concentration of chemical species linked with wet deposition fluctuates by ~20% over the period. Ammonium concentration is found to be the highest (17.6 μeq.l^{-1}) from all IDAF sites belonging to the West Africa ecosystems. Ammonia sources are from domestic animals, fertilizers and biomass burning. In spite of the high potential acidity of 30.5 μeq.l^{-1} from NO_3^-, SO_4^{2-}, $HCOO^-$ and CH_3COO^-, a relatively weak acidity is measured: 6.9 μeq.l^{-1}. The 40% acid neutralization is explained by the acid gas – alkaline soil particles interaction. The remaining neutralization is from inclusion of gaseous ammonia. When results from Lamto, are compared with those from Banizoumbou (dry savanna) and Zoetele (equatorial forest), a regional view for wet tropospheric chemistry processes is obtained. The high concentration of the particulate phase in precipitation emphasizes the importance of multiphases processes between gases and particles in the atmospheric chemistry of the West Africa ecosystems. For example, the nss Ca^{2+} precipitation content, main indicator of terrigeneous particles, goes from 30.8 μeq.l^{-1} in dry savanna to 9.2 μeq.l^{-1} at Lamto and 8.9 μeq.l^{-1} in the Cameroon forest. A similar gradient is obtained for rainfall mineral particles precipitation content with contribution of 80% in dry savanna, 40% in wet savanna, and 20% in the equatorial forest.

Key words: precipitation chemistry, African wet savanna, wet deposition, acid rain, heterogeneous chemistry

1. Introduction

During the last decade, within the framework of the International Global Atmospheric Chemistry (IGAC) programme, the tropics have been considered as a key region regarding global atmospheric chemistry (IGAC, 2003). Due to intense ultra-violet radiation and high water-vapor pressure, high [OH] radicals concentration

oxidizes inorganic and organic gases, and triggers removal of oxidized products from the atmosphere. Deep convection in the tropics results in processing and transporting large volumes of air masses loaded with gases and particles emitted by ecosystems. Knowledge of rainfall chemical composition, signature of the capture of gases and particles by cloud droplets and raindrops, allows to track emissions within rainfall events, their seasonal and interannual variability as well as trends and atmospheric chemistry processes. Wet-deposition studies are essential for understanding the key mechanisms controlling the overall atmospheric chemical content and to determining the nutrient imput or toxic impact for the biological functioning of the ecosystems.

From IGAC, the Deposition of Biogeochemically Important Traces (DEBITS) international project started in 1990. Syntheses of main results are available in IGAC Newsletters 27 and 28 (2003).The DEBITS scientific objectives have been:

– to determine, at the regional scale, the atmospheric removal rates of biogeochemically important trace species, by dry and wet depositions;
– to evaluate atmospheric budgets of key elements (S, N, Ca, C1 . . .) at the regional scale;
– to establish the chemical and physical factors that modulate these deposition fluxes;
– to develop parameterization for integration into regional and global atmospheric chemistry models.

To fulfil these objectives, the DEBITS scientific committee defined a set of experimental and analytical protocols to insure data quality, and permit inter-comparison of measurements from wet and dry deposits for all DEBITS stations. During the first half of 2004, fifty DEBITS measuring sites were activated in the tropical belt.

Concerning tropical Africa, the IGAC/DEBITS/Africa project or IDAF, started in 1994. The major objectives of IDAF were to measure wet and dry deposition fluxes, to identify the relative contribution of natural and anthropogenic sources and factors regulating these fluxes. The above objectives were attained at 10 specific sites (Figure 1). Six "paired sites" monitor three types of ecosystems over west and central Africa: dry savanna (Niger and Mali), wet savanna (Côte d'Ivoire and Central Republic of Africa), and equatorial forest (Congo and Cameroon).

As a part of IDA program, studies have been conducted for two of these regional ecosystems: dry savanna (Banizoumbou, Niger, see Galy-Lacaux and Modi, 1998) and rain forest (Zoetele, Cameroon, see Sigha *et al.*, 2003). These studies pointed out that the chemical composition of rainwater in each ecosystem present specific characteristics. They are linked to numerous factors such as the atmospheric emissions, meteorological parameters like rain amount, rain intensity, wind direction and velocity linked to seasonal variability. Table I indicates the major gases and particles emissions for the meridian transect: dry savanna-wet savanna-equatorial forest, during dry- and wet-seasons, associated with precipitation and their chemical signatures measured in the IDAF network. The incoming sources from dry
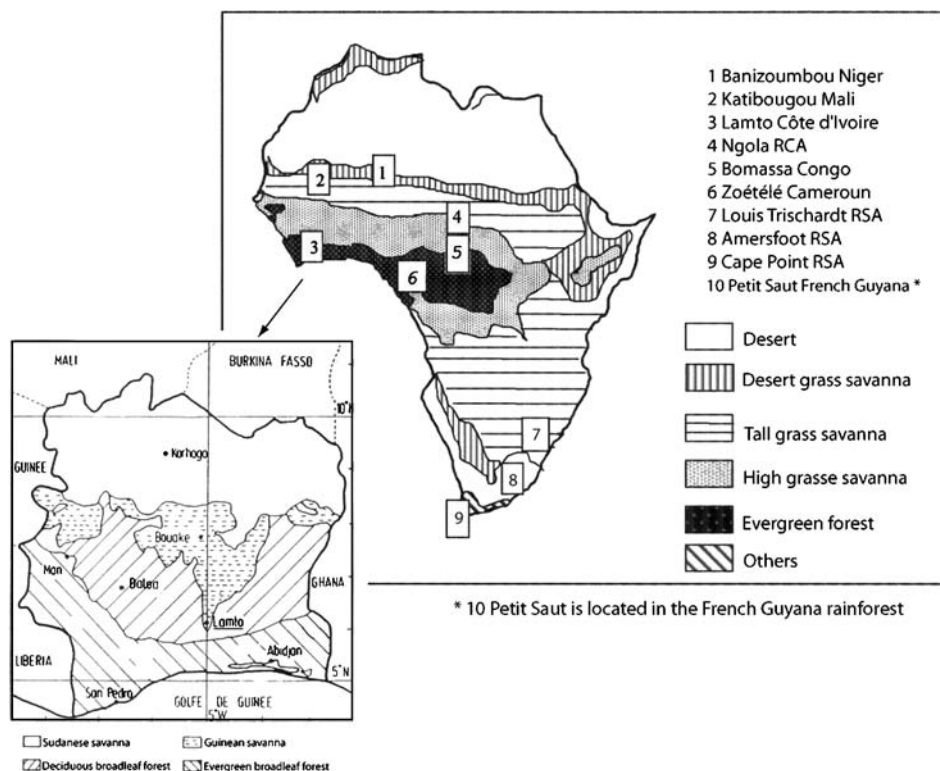
Figure 1. Vegetation and localization map of the IDAF sites with vegetation and localization of the Lamto site in Côte d'Ivoire.

savanna are mainly terrigeneous and nitrogen oxides respectively, linked to soils emissions and to ammoniacal emissions from domestic animals. In wet savanna, major emissions are from biomass burning, soils, vegetation and domestic animals. For forested ecosystems major sources are from vegetation and soils.

Using the precipitation chemistry database, collected at Lamto representative of wet savanna ecosystems (January 1995 to December 2002), the objectives were to:

determine the interannual variability and trend of the rainwater chemical composition and wet deposition;

determine the main annual chemical composition of precipitation and associated wet deposition, in relation with sources of gases and particles. Compare this chemical composition with that of three IDAF sites, representative of dry savanna and forest;

analyze the mean seasonal chemical composition of precipitation and to identify the atmospheric sources functioning during dry and wet seasons;

to analyze the relative contribution of mineral particulate and gas phases in precipitation to highlight the role of heterogeneous processes; and

to study the precipitation acidity over of the western-african ecosystems.

Table I. Major emissions (gases and particles) for the transect dry savanna-humid savanna-forest, in dry and wet seasons, associated with rain chemical indicator measured in the IDAF projet

Ecosystems		Sources	Gases (bold) and Particles emissions	Rain chemical indicators in IDAF
Dry Savanna	Dry season	Soils	NOx, mineral particles	NO_3^-, $nssCa^{2+}$, $nssK^+$, $nssMg^{2+}$, $nssSO_4^{2-}$
		Biomass burning	NOx, VOC carbonaceous particles	NO_3^-, $HCOO^-$, CH_3COO^-, $C_2H_5COO^-$, $C_2O_4^{2-}$
	Wet season	Soils	NOx, mineral particles	NO_3^-, $nssCa^{2+}$, $nssK^+$, $nssMg^{2+}$, $nssSO_4^{2-}$
		Vegetation	VOC	$HCOO^-$, CH_3COO^-, $C_2H_5COO^-$, $C_2O_4^{2-}$
		Animals	NH_3	NH_4^+
Wet Savanna	Dry season	Biomass burning	NOx, VOC carbonaceous particles	NO_3^- $HCOO^-$, CH_3COO^-, $C_2H_5COO^-$, $C_2O_4^{2-}$
	Wet season	Soils	NOx	NO_3^-
		Vegetation	VOC	$HCOO^-$, CH_3COO^-, $C_2H_5COO^-$, $C_2O_4^{2-}$
		Animals	NH_3	NH_4^+
Forest	Dry season	Soils	NOx	NO_3^-
	and Wet season	Vegetation	VOC	$HCOO^-$, CH_3COO^-, $C_2H_5COO^-$, $C_2O_4^{2-}$

Results presented here are to complete the assessment on wet deposition along the transect dry savanna-wet savanna-rain forest and to evaluate large scale tropospheric chemistry mechanisms, as already proposed by Galy-Lacaux and Modi (1998) and Sigha *et al.* (2003).

2. Experimental Design

The Lamto geophysical and ecological monitoring station has been activated in 1960 by Professors Lamotte and Tournier (hence the name of Lamto). For the last four decades, seismological, ecological and climatological data from this natural reserve have been compiled. They have been analyzed by international and African scientific communities, with results used as a reference for a 'wet savanna' environment. During 1994, the international program DEBITS/IDAF, included this site in its network, and build up results from already existing studies on atmospheric chemistry (Servant *et al.*, 1984; Baudet *et al.*, 1990; Yoboué, 1991; Delmas *et al.*, 1987; DECAFE Special Issue, 1991).

2.1. THE LAMTO SITE AND ITS METEOROLOGICAL CONDITIONS

Lamto is located, in the "V-shaped Baoulé" region (120 km north of Abidjan) at 6°N and 5°W. The average altitude is of 105 m, and it belongs to the wet savanna region of Côte d'Ivoire (Figure 1). The Lamto Reserve covers approximately 2600 ha and is constituted essentially of wet savanna with the, so-called, Gallery Forest along the Bandama river (Gautier, 1990).

The atmospheric chemical composition is influenced by emissions from the wet savanna modulated by local, regional and global processes. Local perturbations are mainly anthropogenic from coffee-cacao fields, from agro-industrial activities linked to pine-apple farming and domestic fires from small villages. At the regional and global scales, emissions are modified and transported by the summer monsoon and harmattan flows.

In general, the West African climate (and its variability) is a function of the position of the Intertropical Convergence Zone (ITCZ), the frontier between cool and humid marine air mass (monsoon) and warm and dry saharan air mass (Harmattan). Extreme latitudinal positions of the ITCZ are in January (~5°N) and August (~22°N). Kouadio (2002) has characterized the climatology of the Côte d'Ivoire in three climatic zones (from north to south): the sahelian dry zone, the forested savanna, and the degraded forested zone. Lamto, is located in the central zone with forested wet savanna. Over Côte d'Ivoire, annual precipitation amount vary from 700 mm (extreme North-East), to 1700 mm (South-Southeast).

The central region of Lamto, display a rainfall seasonal cycle with a bimodal structure characterized by four periods: two rainy seasons separated by a long dry season during December–February and a short dry season in August. The duration of the dry seasons is highly variable. During the dry season, Lamto is located
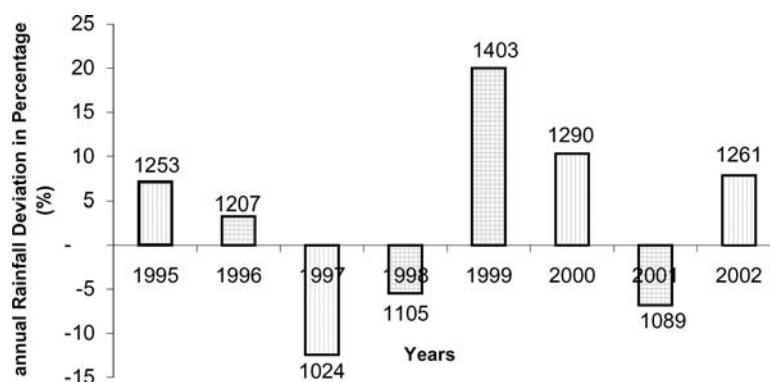
Figure 2. Interannual variability of precipitation at Lamto in %, calculated from the deviation of annual precipitation to the mean annual rainfall for the 1965–2000 period (1169 mm). Annual rainfall in mm is indicated on the bar.

to the North of ITCZ and is directly influenced by the continental air masses (or Harmattan) which contain terrigeneous particles and chemical species from savanna fires. During the wet season, from March/April to October, Lamto is now located to the south of ITCZ, under the influence of cool and humid maritime air masses, loaded with marine aerosols. During this period, the biogenic sources of the wet savanna ecosystem are extremely active. Moreover, the summer monsoon layer thickness and water-vapor availability allow for deep atmospheric convection.

The mean annual rainfall amount is of 1169 mm (1965–2000). During the period under study (1995–2002), a minimum of 1027 mm is observed in 1997 with a mean deviation of 12%, and a maximum of 1402 mm in 1999 with a mean deviation of 20% (see Figure 2).

In Table II, the yearly main characteristics for the dry and wet seasons distributions are displayed. Dry seasons last for 2 to 5 months with rainfall amount from 16.1 mm (1995/1996) to 222.4 mm (1999/2000). The mean dry season rainfall is of 96 mm which represent 8% of rainfall events (70% of rainfall events produce less than 10 mm of rain). Wet seasons last for 7 to 9 months, with an average rainfall amount of 1108 mm (54% of rainfall events produce less than 10 mm of rain). The two seasons, as defined, will be used to study the mean seasonal characteristics of the rain chemical composition and wet deposition.

2.2. MEASURING PROCEDURES, CHEMICAL ANALYSES AND DATA QUALITY

A brief description of experimental techniques is presented here (for further details see Galy-Lacaux and Modi, 1998; Sigha *et al.*, 2003; Mphepya *et al.*, 2003). Additional information can also be obtained from the IDAF Web Site: http://medias.obs-mip/idaf/

Table II. Yearly main characteristics for the dry and wet season distribution for the experimental period

	1995	1996	1997	1998	1999	2000	2001	2002
January	13.2 mm	11.0	51.2	68.4	190.0	171.8	17.7	52.8
February								
March								
April								
May	1234.4 mm	1167.1	972.4	1036.9	1162.3	1067.0	1021.9	1199.6
June								
July								
August								
September								
October								
November								
December	5.1 mm	28.8	0.0		50.6	51.0	49.8	8.1

Dry Season ☐   Wet Season ▨

2.2.1. *Measuring Procedures*

Rainwater samples were collected on rainfall event basis, with an automated 'wet-only' sampler of 225 cm^2, built for the DEBITS/IDAF network. At the end of each event, rainwater is collected in a Greiner 50 ml sampling tube. The samples are stored in a deep freeze environment, thus avoiding microbial activities and possible alteration of chemical composition. A total of 631 events, representing a total rainfall amount of 8420.9 mm, have been sampled during the period under study (see Table III). The total rainfall amount during the eight-year monitoring is equal to 9631.1 mm. In Table III, the efficiency collection is given year-by-year with a range from 68% to 94% and a mean of 87%. The

Table III. Rainwater collection in Lamto (1995–2002): Annual rainfall (H in mm), number of collected events (N), collected rainfall depth (Hc in mm)) and Efficiency Collection (EC in %)

Year	H	N	Hc	EC
1995	1252.7	61	852.8	68
1996	1206.9	78	971.1	80
1997	1023.6	75	945.5	92
1998	1105.1	76	1001.4	91
1999	1402.9	88	1260.4	90
2000	1289.8	84	1211.5	94
2001	1089.4	74	989.0	91
2002	1260.5	95	1189.2	94
Total	9631.1	631	8420.9	
Mean	1203.9	79	1052.9	87

sampling efficiency is then well representative of precipitation regime at the Lamto site.

2.2.2. *Chemical Analyses*

The presence of dissolved ions was determined by using ion chromatography at the IDAF laboratory in Toulouse. The ion chromatography system used, as well as the main characteristics of the analytical parameters for the determination of mineral ions (Ca^{2+}, Mg^{2+}, Na^+, K^+, NH_4^+, Cl^-, SO_4^{2-}, NO_3^-), and organic ions ($HCOO^-$, CH_3COO^-), are detailed in Galy and Modi (1998). The analytical precision for all the ions is 5% or better. H^+ was calculated from the pH measurements using an ATI Orion 350 instrument with a combined electrode (ATI Orion model 9252) filled with KCl (4M) and satured with AgCl. Two standard solutions (WTW) at pH 4.01 and 7.00 are used for its calibration. From the pH values, H^+ ions concentrations are calculated. The precision is of 0.01 pH unit.

2.2.3. *Data Quality*

At first, all the chemical analyses are doubled-checked through inter-laboratory comparison tests, organized annually by the World Meteorological Organisation (WMO) (http://marble.asrc.cestm.albany.edu/qasac/lab_ic.html). Secondly, the quality control for the entire database is checked for each rain sample by calculating the ionic balance test following Sigha *et al.* (2003). Computations are based on the 'percent ion balance criteria', as described by WMO (EPA, 1994). We applied these criteria to the 8-year samples in Lamto, and only data that passed the WMO specifications were used in the study. From 1995 to 2002 the range of WMO certified samples is between 88 to 100%. Over the eight years, 97% of the total samples passed the WMO criteria and were used here. Finally, after applying all the quality control procedures, we use a total rainfall amount of 8268.1 mm from an overall amount of 9631.1 mm (i.e., 86% corresponding to the 615 samples).

3. Chemical Composition of Rainwater and Wet Deposition

In this section, we study the interannual trends of the chemical composition of precipitation and wet deposition on 8 years of measurements. Then, we determine the mean annual chemical composition of precipitation and the associated wet deposition using the 8 years of measurements. This is to provide the precipitation chemistry characteristics of an african wet savanna ecosystem. The mean composition is compared to three IDAF sites, representatives of the semi arid savanna and forested ecosystems, in relation with the associated sources of gaseous and particulate species that determine the chemical precipitation content. Finally, we present the mean seasonal chemical composition of precipitation to estimate the
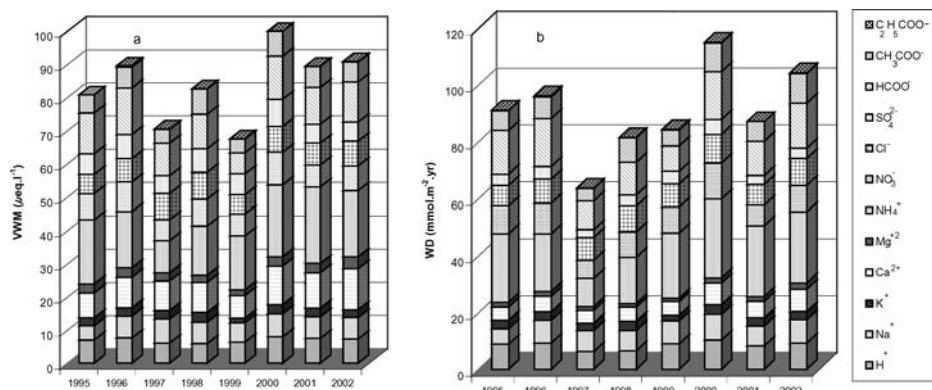
Figure 3. (a) Annual average volume weighted mean concentration (μeq.l^{-1}) in rainwater for the eight years (1995–2002) at the wet savanna site of Lamto and (b) Annual wet deposition (mmol.m^{-2}yr^{-1}).

relative contribution to the annual VWM concentrations and to the wet deposition fluxes.

3.1. INTERANNUAL VARIABILITY

The volume-weighted mean (VWM) concentrations of ionic constituents in rainwater from Lamto station have been calculated by using the following equation:

$$\text{VWM}(\mu\text{eq.l}^{-1}) = \sum_{i=1}^{n=615} C_i P_i \left/ \sum_{i=1}^{n=615} P_i \right. \tag{1}$$

C_i the ion concentration for each species in μeq.l^{-1}, P_i the precipitation amount for each rainy event in mm. The Wet Deposition (WD) has been calculated by using:

WD = VWM × P with VWM being the Volume Weighted Mean concentration for each species and P the mean rainfall amount measured during the studied period.

In Figures 3(a and b), annual weighed volume mean concentration and wet deposition fluxes year by year for precipitation, are displayed. This data set is analyzed to investigate the interannual variability of the major compounds in the wet savanna precipitation. This variability can be evaluated as a function of the amplitude of the main sources and the pluviometric regimes at the studied site.

It has been noticed that from one year to the next the dominant ions are the same over the eight-year period of rain collected at Lamto, i.e., ammonium followed by formate, calcium, nitrate, chloride and sulfate (Figure 3a), with variation of 9.7 and 22.9, 6.4 and 14, 6.8 and 12.4, 6.2 and 9.8, 5.8 and 8.1 and 5.3 and 8.2, respectively. We present in Figure 4(a–d) the variability, around the mean (1995–2002) as calculated in Section 3.2, by groups of elements, each representative of major source identified in the mean characteristics study of rainfall composition (Table I). We grouped for the marine contribution ssNa$^+$, ssCl$^-$, ssMg^{2+}, identified
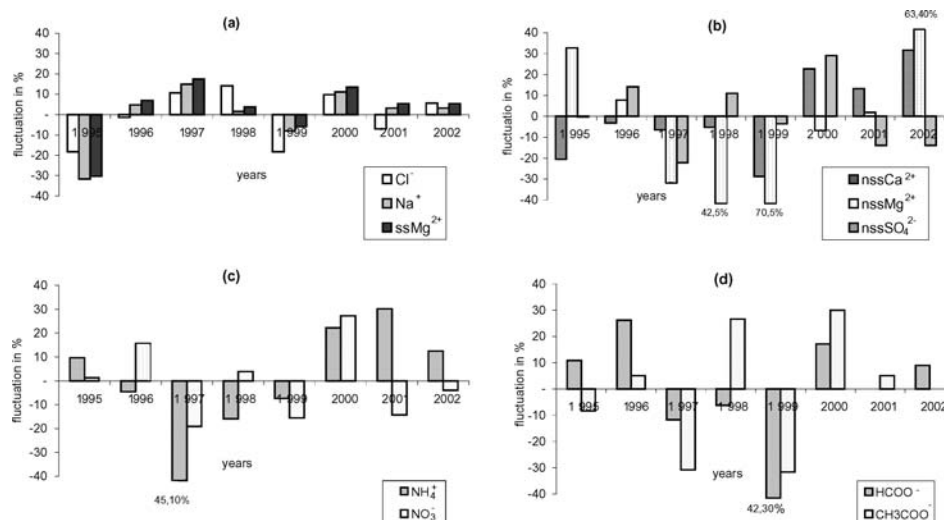
Figure 4. Interannual variability around the mean (1995–2002) of the Volume Weighted Mean (VWM) concentration in precipitation, by groups of elements, each representative of major source identified in the mean characteristics study of rainfall composition: 4(a) sea salt, 4(b) terrigeneous, 4(c) nitrogenous, 4(d) vegetation groups.

in Section 3.2, as major marine compounds (Figure 4a). $nssCa^{2+}$, $nssMg^{2+}$ and $nssSO_4^{2-}$ will represent the terrigeneous contribution (Figure 4b), NO_3^- and NH_4^+ for the nitrogenous contribution (Figure 4c), and the vegetation source by formate and acetate (Figure 4d). Calculation of contribution of sea salt (ss) particle in the dissolved phase is presented in Section 3.2.1.

The 8 years interannual variability (1995 to 2002) is displayed in Figure 4. The Na^+ and Cl^- VWM vary from 4.3 to 7.2 $\mu eq.l^{-1}$ and from 5.8 to 8.1, respectively. These fluctuations are in the same direction with a deviation of $\pm 18\%$. During 1995, we observe that VWM for marine species are very low implying a strong deficit around the mean (30% and 18% for Na^+ and Cl^- respectively). Except during 1995, all other years are within 10% of mean VWM (Figure 4a). The terrigeneous species vary from $\pm 30\%$ around the mean VWM with a range of 6.8–12.4 $\mu eq.l^{-1}$ and 1.7–3.6 $\mu eq.l^{-1}$ for $nssCa^{2+}$ and $nssMg^{2+}$, respectively (Figure 4b). For the vegetation group, besides 1999, the VWM values are quite homogenous. The main organic ions, formate and acetate vary from 6.4 to 14 $\mu eq.l^{-1}$ and from 4.1 to 7.8 $\mu eq.l^{-1}$ respectively. NH_4^+ and NO_3^- range is comprised between 9.7 and 22.9 $\mu eq.l^{-1}$ and 6.2 to 8.1 $\mu eq.l^{-1}$ respectively. Ammonium which correspond mainly to a local source, presents higher fluctuations than NO_3^-, with $\pm 35\%$ for ammonia and $\pm 20\%$ for nitrate. During 1997, all concentrations are very low for unknown reasons.

The year 1999 presents deficits for all elements, with a total annual load at 20% less that the mean. Rainfall presented positive anomalies during that year (17%

increases with 1402.9 mm) which diluted all chemical compounds. The largest deficits (30% to 50% less in concentration), are for Ca^{2+}, Mg^{2+}, K^+, NH_4^+, $C_2O_4^{2-}$. The dry season was indeed shorter by two months. The rainy season ended late during November of 1998, while it started earlier in 1999. The level of aerosol emission from savanna fires and soils were then subsequently reduced.

3.2. ANNUAL CHEMICAL COMPOSITION OF RAINWATER

The yearly mean chemical characteristics of wet savanna rainfall at Lamto are analyzed and compared through correlation, to that from other sites, ecosystem and sources. In Table IV the mean annual VWM concentrations and the wet deposition for four IDAF sites are displayed: Lamto for the wet savanna, Banizoumbou for dry savanna, Zoetele and Petit Saut for the rainforest. Petit Saut located in the French Guyana rainforest is a reference site for forested ecosystem, with Amazonian atmospheric influences. Banizoumbou, Lamto, and Zoetele along the african transect: dry savanna- wet savanna-forest.

Correlation coefficients between the various chemical parameters will be examined in order to determine the potential sources that influence the rainwater composition, and/or potential origin of some of the components that are subsequently transported in the same air masses. Correlation coefficients using the "Spearman method", with a 1% confidence level, are displayed in Table V.

3.2.1. *The Marine Contribution*

Sodium chloride and potassium, magnesium and calcium salts are major chemical components or marine aerosols. Studies by Crozat in Côte d'Ivoire (Crozat, 1978). Have shown that Na and Cl have a main contribution to marine aerosols chemical composition. Sodium concentration in dissolved terrigeneous aerosol as quantified by Crozat (i.e., Na/Al ratio of 0.09) is significant when compared to that of chlorine ($\sim$100 ppm in savanna soils). This is one of the reason we use Cl as a tracer for presence of marine environment in this study. The most common method of evaluating the contribution of sea salts to ion concentrations in precipitation, is then to compare the Cl^-/Na^+ ratio in measured precipitation to that in seawater.

The annual VWM concentrations of sodium and chloride are equal to 6.3 and 7.1 μeq.l^{-1}, respectively (Table IV). These two components are highly correlated ($r = 0.85$) Table V and present a mean annual ratio of 1.1 closed to the sea water ratio (1.16) (Keene *et al.*, 1986). These concentrations are representative of the marine influence that affects the Lamto site, located at about one hundred kilometers far from the coast. For comparison, the coastal site of Petit Saut in Amazonia has concentrations of Na^+ and Cl^- four times higher than that in Lamto (Artaxo *et al.*, 2003). In Zoétélé, located at 200 km from the Atlantic Ocean, concentrations falls to 4.0 μeq.l^{-1} for Na^+ and 4.3 μeq.l^{-1} for Cl^- (Sigha *et al.*, 2003). In order to differentiate the marine contribution for each element, we calculated the part of

Table IV. Volume weighted mean annual concentrations in $\mu eq.l^{-1}$ and wet deposition in $mmol.m^{-2}.yr^{-1}$ (in parenthesis) for precipitation collected in selected IDAF sites

Ecosystem	Location	Yearly rainfall*	Reference	pH	H^+	Na^+	K^+	NH_4^+	Ca^{2+}	Mg^{2+}	NO_3^-	Cl^-	SO_4^{2-}	$HCOO^-$	CH_3COO^-	$C_2O_4^{2-}$
SAVANA																
Dry	Banizoumbou Niger Africa	489.5 (1996)	Galy-Lacaux et Modi (1998)	5.67	2.1 (1.0)	7.7 (3.7)	4.7 (2.3)	12.9 (6.3)	31.2 (7.6)	5.6 (1.4)	12.3 (6.0)	7.4 (3.6)	8.6 (2.1)	4.5[a] (2.3)	2.7[a] (1.5)	
Wet	Lamto Côte d'Ivoire Africa	1204 (1995–2002)	This work	5.16	6.9 (8.4)	6.3 (7.6)	2.4 (2.9)	17.6 (21.2)	9.5 (5.7)	2.7 (1.6)	7.7 (9.2)	7.1 (8.5)	6.5 (3.9)	11.1[a] (13.4)	6.0[a] (7.2)	1.4 (0.8)
FOREST	Zoétélé Cameroon Africa	2029 (1996–2000)	Sigha et al. 2003	4.92	12.0 (24.3)	4.0 (8.1)	5.0 (10.3)	10.5 (21.4)	8.9 (9.0)	2.4 (2.4)	6.9 (13.8)	4.3 (8.7)	5.1 (4.9)	8.2[a] (17.4)	3.2[a] 11.1	1.2 (1.1)
	Petit Saut French Guyana Amazonia	3113 (1999)	Richard et al. (pers. com., 2002) Artaxo et al. (2003)	5.1	8.2 (25.5)	23.8 (74.1)	2.5 (7.8)	4.4 (13.7)	4.6 (7.2)	7.1 (11.1)	5.6 (17.4)	25.9 (80.6)	6.7 (10.4)	5.5[a] (18.1)	2.3[a] (10.3)	0.4 (0.6)

* Yearly rainfall in mm.

[a] For organic acids, we consider the dissolved par.

Table V Correlation coefficients between ions in rainwater over the eight years (1995–2002). The 'Spearman' method was used with a 1% confidence level

	H^+	Na^+	K^+	NH_4^+	Ca^{2+}	Mg^{2+}	$NO3^-$	Cl^-	SO_4^{2-}	$HCOO^-$	$CH_3 COO^-$	$C_2O_4^{2-}$
H^+	1.000											
Na^+	0.136	1.000										
K^+	0.011	0.635	1.000									
NH_4^+	0.051	0.330	0.462	1.000								
Ca^{2+}	−0.171	0.412	0.643	0.558	1.000							
Mg^{2+}	0.005	0.721	0.737	0.563	0.819	1.000						
$NO3^-$	0.313	0.392	0.561	0.593	0.624	0.621	1.000					
Cl^-	0.187	0.854	0.550	0.400	0.362	0.590	0.505	1.000				
SO_4^{2-}	0.353	0.501	0.508	0.553	0.550	0.591	0.742	0.681	1.000			
$HCOO^-$	0.178	0.273	0.455	0.638	0.678	0.594	0.668	0.341	0.580	1.000		
CH_3COO^-	0.090	0.294	0.454	0.537	0.676	0.583	0.549	0.336	0.521	0.868	1.000	
$C_2O_4^{2-}$	0.062	0.384	0.536	0.716	0.681	0.638	0.644	0.470	0.635	0.834	0.749	1.000

sea salt (ss) particles in the dissolved phase using Cl^-/Na^+ ratio obtained from the following equation:

$$[X]_{\text{marine}} = [Na]_{\text{rain}} \times [X/Na]_{\text{sea}} \qquad (2)$$

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

Results from Lamto indicate that the marine contribution is high for chloride (99%) and magnesium (54%). The calculated correlation between Mg^{2+} and Na^+ and between Mg^{2+} and Ca^{2+} are: $r = 0.72$ and $r = 0.82$, respectively. It shows that magnesium concentration has a double origin, i.e., marine and terrigeneous estimated at 54% and 46%, respectively. The marine contribution for sulphate, potassium and calcium concentrations are 2.6 and 3%, respectively.

3.2.2. *The Terrigeneous Contribution*

The annual non sea salt (nss) contributions in precipitation are evaluated at 9.2 μeq.l^{-1} (nssCa^{2+}), 5.7 μeq.l^{-1} (nssSO$_4^{2-}$), 2.3 μeq.l^{-1} (nssK$^+$) and 1.3 μeq.l^{-1} (nssMg^{2+}). The multiple regression analysis gives correlation coefficient equal to $r = 0.82$ for Ca^{2+} and Mg^{2+}, $r = 0.55$ for Ca^{2+} and SO_4^{2-} and $r = 0.64$ for Ca^{2+} and K^+ (Table V). These correlations indicate that the main terrigeneous ions were associated with the formation of eolian particles which include gypsum ($CaSO_4$), calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$) (Bohn *et al.*, 1985; Loÿe-Pilot *et al.*, 1986; Galy-Lacaux and Modi, 1998). The origin of potassium ion in rainwater is from washout of desert aerosols (from soil wind erosion), aerosols from combustion (Yoboué, 1991; Andreae *et al.*, 1988a), and biogenic aerosols (Crozat *et al.*, 1978). Emission from sea surface, associated with that of Cl ion are much less.

The study of the terrigeneous species VWM concentrations along the transect dry savanna- wet savanna-forest shows us a negative gradient from north to south of western Africa (see Table IV). Non sea salt calcium concentrations, associated with dust emission, vary from 30.8 μeq.l^{-1} in dry savanna, to 9.2 in wet savanna and 8.7 μeq.l^{-1} and 3.6 μeq.l^{-1} in forests. Non sea salt sulfate and magnesium concentrations display a similar gradient with 7.7 and 3.8 μeq.l^{-1} in dry savanna, 5.7 and 1.3 in wet savanna and 4.6 and 1.5 in equatorial forests respectively. In Africa, the convective rainfall includes marine elements from the boundary layer and terrigeneous elements from layers above which include continental air masses. This is why these two chemical signatures are being found in rainfall, which include seasonal to interannual variability.

3.2.3. *The Nitrogenous Contribution*

Ammonium is the most abundant ion found in the rain samples. The NH$_4^+$ VWM (17.6 μeq.l^{-1}) is the highest when compared to Banizoumbou samples from dry

savanna (10.9 μeq.l^{-1}), Zoetele (10.5 μeq.l^{-1}) and Petit Saut (4.4 μeq.l^{-1}) from equatorial forests. The ammonium content in precipitation results from incorporation in cloud and rain water of gaseous ammonia and particles containing NH_4^+. Major sources of NH_3 include bacterial decomposition of urea in animal excreta and emission by natural or fertilized soils (Schlesinger and Hartley, 1992). In tropical regions, another significant source of ammonia is produced by savanna fires and domestic fuelwood burning (Lobert *et al.*, 1990; Delmas *et al.*, 1995; Brocard *et al.*, 1996). The ammonium content in precipitation originating from the particulate phase. Seinfeld (1986) reported that generally in the atmosphere ammonia occurs as $(NH_4)_2SO_4$ but it is also possible to found it in the form of NH_4NO_3 (Parmar *et al.*, 2000). In the way, gaseous sulfuric and nitric acids can be partially neutralized by gaseous NH_3 to form $(NH_4)_2SO_4$ and NH_4NO_3 particles. Significant correlation found between NH_4^+ and NO_3^- ($r = 0.59$) and between NH_4^+ and SO_4^{2-} ($r = 0.55$) confirms the fact that the above particles originate from similar processes. On the other hand, gaseous NH_3 can be a significant contributor to the NH_4^+ content in the precipitation of Lamto. Ourabi's measurements show a mean annual concentration of NH_3 equal to 5 ppb (Al-Ourabi, 2002). In Section 4.1, we will analyze specifically the relative contribution of particles and gases to the integrated chemical content of the studied precipitation. At the scale of the wet savanna of Lamto, that presents the highest ammonium concentration of all the western African ecosystems, we assume that it is representative of the signature of a combination of sources: domestic animals, agro-systems, domestic combustion and biomass burning.

Nitrate VWM in the rain samples of Lamto with 7.7 μeq.l^{-1} is comparable to the african forest (6.9 μeq.l^{-1}). However, it is lower than in dry savanna (12.3 μeq.l^{-1}). Nitrate concentration in precipitation is the final result, in atmospheric air and cloud water, of homogeneous and heterogeneous processes, and the collection of nitrogenous gases and particles. Nitric oxide (NO), in the non-burning season, is the major nitrogen compound released from savanna soils. Sodium chloride and potassium, magnesium and calcium salts are major chemical components or marine aerosols. Studies by Crozat in Côte d'Ivoire (Crozat, 1978) have shown that Na and Cl have a meanly contribution to marine aerosols chemical composition. Sodium concentration in dissolved terrigeneous aerosol as quantified by Crozat (i.e., Na/Al ratio of 0.09) is significant when compared to that of chlorine ($\sim$100 ppm in savanna soils). This is one of the reason we use Cl as a tracer for presence of marine environment in this study. The most common method of evaluating the contribution of sea salts to ion concentrations in precipitation, is then to compare the Cl$^-$/Na$^+$ ratio in measured precipitation to that in seawater.

A large fraction of the NO produced is oxidized in the atmosphere by photochemical reactions into HNO_3 or organic nitrates. HNO_3 is very soluble in water and is thus easily scavenged by clouds and rain. High precipitation nitrate levels measured in the dry savanna has been mainly attributed to local sources represented

by animals and savanna soils strong emitters of Nitric Oxide (Jaegle *et al.*, 2004; Serça *et al.*, 1998). Lower nitrate levels in Lamto can be explained by low NO_x emissions fluxes as measured by Serça *et al.* (1998). Moreover, IDAF gaseous measurements integrated from 1998 to 2001 confirm this result. Mean annual NO_2 concentrations are about 1.3 ppbv in Lamto and 2.4 ppbv in Banizoumbou (Niger) (Al-Ourabi, 2002; Jaegle *et al.*, 2004).

The nitrate concentration, for the different ecosystems, show a similar gradient to that observed for the terrigeneous compounds. The significant correlations between Mg^{2+} and NO_3^- and between Ca^{2+} and NO_3^-, both equal to 0.62, indicate potential heterogeneous and multiphase chemical processes occurring between alkaline dust and gaseous nitric acid (Dentener *et al.*, 1996; Galy-Lacaux *et al.*, 2001). In Section 4, we will investigate the importance and the role of these heterogeneous processes on rain acidity.

3.2.4. *The Acidic Compounds*

The mean pH, calculated from the VWM of H^+ ion, in the wet savanna of Lamto is of 5.16 corresponding to a VWM (H^+) of 6.9 μeq.l^{-1}. It is recognized that in tropical zone, the rainfall acidity vary with season (Sigha *et al.*, 2003; Mphepya *et al.*, 2004). In the wet savanna of Lamto, pH in the dry season is equal to 5.0 and to 5.2 during the wet season. The mean pH value in the savanna is comprised between the acidic pH measured in the forest of Zoétélé (4.92) and the high pH measured in the dry savanna (5.67). A positive gradient for acidity is noticed along the transect dry savanna-wet savanna- equatorial forest.

Formate and acetate concentrations present a high correlation ($r = 0.87$). These two organic compounds are originating from the oxidation of volatile organic carbon (VOC) into aldehyde and acid (Graedel and Crutzen, 1993) .Volatile organic carbon are emitted by the vegetation source, and by savanna burning during the dry season. This is corroborated by significant correlation between formate and acetate with NO_3^- ($r = 0.67$ and $r = 0.55$) and NH_4^+ ($r = 0.64$ and $r = 0.54$) (see Table V).

The calculated contribution of the organic acidity (HCOOH, CH_3COOH, CH_3CH_2COOH) is equal to 56%. The contribution of mineral acidity, mainly related to the incorporation of H_2SO_4 and HNO_3 is equal to 44% (Table VI). This equivalence is characteristic of the african rainwater collected in equatorial Africa (Sigha *et al.*, 2003; Andreae *et al.*, 1994; Lacaux *et al.*, 1992; Ayers *et al.*, 1988; Galloway *et al.*, 1982). This contribution characteristic of dry savanna can be compared to that of african forests where the acidity contributed by organic acids (40–60%) is equivalent to that of mineral acids (60–40%). The Amazonian composition is very much different, with the dominance of organic acids that account for 80–90% of the total acidity. In Amersfoort, an industrial site in dry savanna (South Africa), organic acids contribute to only 16% of the total acidity (Mphepya *et al.*, 2004). A

Table VI. Relative contribution of organic and mineral acidity to the total acidity measured at Lamto

Acidity	Concentration in μeq.l^{-1}	Acidity (%)
Organic acidity		
– HCOO$^-$	11.1	36
– CH$_3$COO$^-$	6.0	20
Total	17.1	56
Mineral acidity		
– NO$_3^-$	7.7	25
– SO$_4^{2-}$	5.7	19
Total	13.4	44
Total H$^+$ potential	30.5	
H$^+$ measured	6.9	

detailed study on acidity and its linkages with chemical, gaseous, and particulate composition in rainfall is presented in Section 4.

Acidic deposition, calculated from nitrate, sulfate, formate, and acetate concentrations, reaches 33.4 meq.m^{-2}.yr^{-1} in wet savanna. The Stockholm Environment Institute (SEI) has recently proposed a global assessment of terrestrial ecosystem sensitivity to acidic deposition (Cinderby *et al.*, 1998). This assessment depends on the buffering capacity of the base saturation to identify soils that have high weathering rate and the cation exchange capacity to quantify the capacity of a soil to buffer acidity. A global map prepared by SEI, with five classes of sensitivity to acidic deposition, from a critical load of 200 meq.m^{-2}.yr^{-1} for the insensitive class to a critical load of 25 meq.m^{-2}.yr^{-1} for the most sensitive class. At Lamto, which belong to the most sensitive class, the measured acidic deposition of 33.4 meq.m^{-2}.yr^{-1} shows that a potential risk of acidification is important.

3.3. MEAN SEASONAL CHEMICAL COMPOSITION

In this section, the mean seasonal chemical composition of rainfall is studied. Wet seasonal deposition over wet savanna is also examined. This is to evaluate the seasonal relative contribution to total amounts and discriminate the various sources.

Referring to the seasonal rainfall distribution displayed in Table II, the mean seasonal VWM concentrations have been determined for dry and wet seasons (see Figure 5). During the 8 dry seasons, 74 samples out of 615 are used. During the dry season, the level of VWM concentration is about 2.5 times higher than that of wet season. The highest levels of VWM concentration were found in samples with strong signature of the terrigeneous and biomass burning sources. The ratio dry season/wet season varies from 2 to 3. The ammonium concentration during
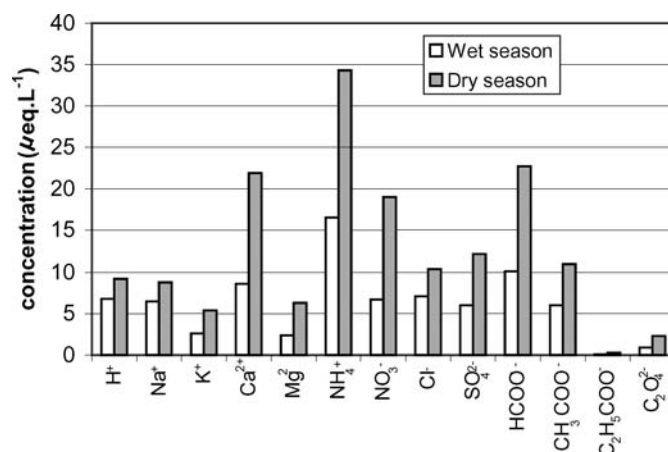
Figure 5. Seasonal Volume Weighted Mean (VWM) chemical composition of precipitation collected at Lamto (January 1995–December 2002).

the dry season remains the highest (34.3 μeq.l^{-1}), followed by that of formate (22.7 μeq.l^{-1}), calcium (21.9 μeq.l^{-1}), nitrate (19 μeq.l^{-1}), sulfate (12.2 μeq.l^{-1}), and acetate (11 μeq.l^{-1}). Also 70% of rain samples have less than 10 mm of rainfall. The weak enrichment factor of 1.35 for Na (from marine source) might be due to the dilution by the rainwater liquid content during the dry season. Since the enrichment factor from fires and terrigeneous sources is 2.4 for NO_3^-, K^+, Ca^{2+}, Mg^{2+}, NH_4^+, we speculate that the latter emissions almost double during the dry season. This is corroborated at Lamto, where high gaseous concentrations are measured during the dry season: 4.2 ppbv for nitrogen dioxide, 11.3 ppbv for ammonia (Al-Ourabi, 2002). In spite of high VWM during dry seasons, the wet deposition is only 4% to 10% that of wet deposition, annually (Figure 5).

3.4. ANNUAL WET DEPOSITION FLUXES

The annual wet deposition depends both of the annual rainfall amount and the chemical content measured in the precipitation. Figure 3b presents the wet deposition fluxes in mmol per year per squared meter by year. We notice that the global tendency of the total deposition of all the chemical species follows the same trends observed for the chemical concentration year by year. The total deposition varies in the range of 64 to 104 mmol.m^{-2}.yr^{-1} with maximum deviation of ± 20% around the mean 90 mmol.m^{-2}.yr^{-1} (Figure 3b).

To investigate the wet deposition fluxes, it is important to note that fluxes were directly linked to the rainfall gradient in the semi-arid savanna of Niger, equatorial forests in Cameroon and in Amazonia with a range from 500 to 2000–3000 mm.yr^{-1}. Lamto with a pluviometry of 1200 mm.yr^{-1} presents wet deposition of marine and terrigeneous elements such as Ca^{2+}, Mg^{2+}, Cl^- and SO_4^{2-}

(Table IV), within the same range than a forested ecosystem. Ammonium with 21.2 $mmol.m^{-2}.yr^{-1}$ is the highest wet deposition flux and is similar to that from the equatorial forest and 3.5 times higher than that in Niger. Recently, results about the wet atmospheric nitrogen deposition in Africa have revealed that it was dominated by NH_4, which accounts for about 60% of the total N flux (IGAC, 2003). In the wet savanna of Lamto, a total mean wet deposition of about 4.2 kg N/ha.yr have been recorded with 70% coming from $N(NH_4)$ and 30% of $N(NO_3)$. For nitrate deposition, the wet savanna with 9.2 $mmol.m^{-2}.yr^{-1}$ is in the average range measured from the dry savanna in the forest (6.0–3.8 $mmol.m^{-2}.yr^{-1}$). A gradient of H^+ deposition is measured with 1 $mmol.m^{-2}.yr^{-1}$ in the dry savanna, 8.4 in the wet savanna, 24.3 in the African forest and 25.5 in the Amazonian forest. This gradient of acidity is correlated to the nitrate and the organic ions deposition gradients.

The above results underline the importance of terrigeneous source in a dry ecosystem when compared to African wet savanna and forest ecosystems. Conspicuous gradient of calcium, magnesium and sulfate VWM concentrations from Niger to Cameroon are noticed. The wet savanna is also characterized by a strong nitrogenous contribution especially in ammonium, the higher VWR concentrations of all the ecosystems. Also high VWR concentrations in organic ions are measured. These latter two contributions are explained by the simultaneous contribution of local sources (animals, agriculture) and regional and global sources such as biomass burning and terrigeneous sources. To finalize, the global analysis of the data base, seasonally and interanually, allows to characterize for the first time, the average chemical content and wet deposits in wet savanna, with $\pm 20\%$ variations.

4. Relative Contribution of Particles and Gases and Acidity in Precipitation

4.1. RELATIVE CONTRIBUTION OF PARTICLES AND GASES

Heterogeneous chemistry processes, represented by the potential interactions between gases, water and particles, have a significant impact on the chemistry of the troposphere. In this context, mineral dust aerosols are important reactive surface for gaseous uptake (SO_2, NOy, and O_3). Smith and Chughtai (1995) have also demonstrated the importance of heterogeneous reactivity of black carbon with H_2O, SO_2, O_2, HNO_3 and mineral particles interactions have been previously studied according field measurements in the Atlantic and Pacific Oceans (Savoie *et al.*, 1989; Prospero *et al.*, 1995), in wet savannas of Africa (Servant *et al.*, 1984; Yoboué, 1991) and in Asian aerosol (Gao *et al.*, 1991; Carmichaël *et al.*, 1996, 1997). Moreover, recent modeling studies have included these HNO_3 and mineral particles interactions (Dentener *et al.*, 1996; Tbazaedeh *et al.*, 1998). In Africa, an original study in the Sahelian region has been conducted through IDAF field measurements and SCAPE modeling simulations (Galy and Modi, 1998; Galy *et al.*, 2001). The results of this study point out the major role of heterogeneous processes in the Sahelian region in regulating the acidity deposition. It allowed proposing a conceptual model of

atmospheric chemistry representative of the chemical reactions of soil dust parti-
cles with water vapor, nitric acid and organic acid. Considering the importance of
heterogeneous process in the tropical chemistry, in this section and from the mea-
surements made at Lamto, Banizoumbou and Zoetele (IDAF sites), an estimation
of the gaseous and the particulate phases contribution to the chemical content of the
precipitation is given. Then, potential and measured acidity are compared and their
relationship with the particulate phase and the associated heterogeneous processes.

To investigate the relative contribution of particles and gases in rainwater, we
propose a new concept. PCrain is for relative particulate contribution, while GCrain
stands for gaseous contribution gazeuse. The non volatile cations Ca^{2+}, Na^+, Mg^{2+}
and K^+ are considered as representative of the mineral particulate phase. In order to
apply the neutrality principle, the sum of the cations is equilibrated into an equivalent
sum of anions. Thus particulate contribution is estimated by multiplying the cations
sum by 2. The PCrain contribution is then obtained from: PCrain $= 2 \times (Ca^{2+} +$
$Mg^{2+} + K^+ + Na^+)/(\Sigma AE + \Sigma CE)$. AE is the anions sum in $\mu eq.l^{-1}$ ($Cl^- + NO_3^-$
$+ SO_4^{2-} + HCOO^- + CH_3COO^- + C_2H_5COO^- + HCO3^-$) and CE is the cations
sum in $\mu eq.l^{-1}$ ($H^+ + Ca^{2+} + Na^+ + Mg^{2+} + NH_4^+ + K^+$). The VWM carbonates
implied in the computation are: 26.3 $\mu eq.l^{-1}$ for Banizoumbou, 20 $\mu eq.l^{-1}$ for
Lamto, and 30.8 $\mu eq.l^{-1}$ for Zoetele. In our computation, PCrain does not take into
account particulate originating from gaseous reaction (i.e., NH_4NO_3, $(NH4)_2SO_4$).
As such the PCrain is underestimated. The gas contribution (GCrain) is defined
by the difference 1-PCrain. Results of yearly PCrain and GCrain are presented in
Figure 6. The relative contribution of gases and particles to the chemical content of
the precipitation is 40% for particles and 60% for gases. The interannual variability
is somewhat weak. Years 1995 and 1997 are extremes with 33% and 47% of particles
contribution, respectively. Using the same concept in the two other IDAF sites, the
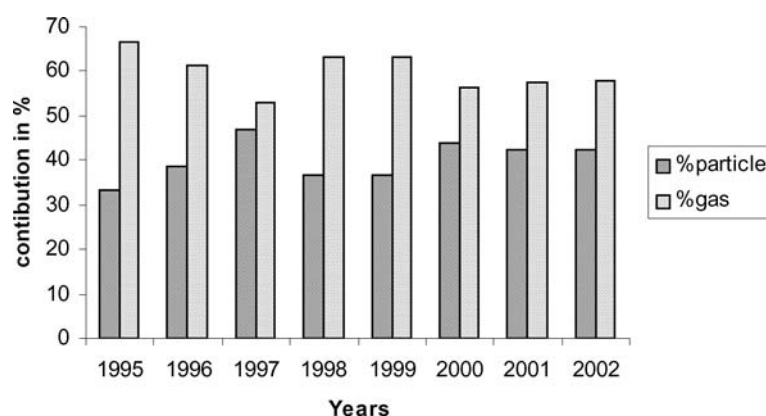gaseous and the particulate contributions have been calculated. In the dry savana

Figure 6. Yearly relative contribution of gases and particles to the total chemical content of
the precipitation.

of Banizoumbou, 80% is in the particulate phase and 20% is in the gas phase. To the opposite; in the forest of Zoetele 20% is in the particulate phase and 80% in the gas phase. The particle contribution decreases by 80% in dry savanna to 20% in forest. A 40% particle contribution is found in wet savanna. This is consistent with the high dust emissions from the Sahel, and the progressive washout of particles along the transect.

4.2. RAIN ACIDITY AT LAMTO

Sigha *et al.* (2003) have defined potential acidity (pA) for Zoetele rainfall as the sum in nitrate, sulfate, formate and acetate concentration, considering that all ions are associated with H^+. If computed from the same manner the Lamto pA is of 30.5 μeq.l^{-1}. The measured acidity (mA) for Lamto is 6.9 μeq.l^{-1} (Table VI). So, 23.6 μeq.l^{-1} of H^+ have been neutralized. According to recent rain chemistry studies in West Africa, one of the major neutralization mechanisms is the uptake of strong acid gases by soil dust particles (Galy-Lacaux *et al.*, 2001; Sigha *et al.*, 2002). In particular, dust alkaline particles favors the uptake of HNO_3. Alkalinity in soil particles is to a large part determined by the $CaCO_3$ content. Our results point out that this is a key process in the wet savanna of Lamto. On one hand, we determine a significant correlation ($r = 0.62$) between calcium and nitrate in Lamto precipitation. Moreover, Lamto measurements of aerosol chemical composition as a function of granulometric spectra clearly indicate that NO_3^- is captured by terrigeneous coarse particles mainly formed by calcium and magnesium (Yoboué, 1991).

To illustrate the heterogenous chemical interactions all over the west central african transect (dry savana, humid savana, equatorial forest), the calcium concentration versus the difference between the potential acidity (pA) and the measured acidity (mA) for the precipitation of three IDAF sites is presented in Figure 7. For
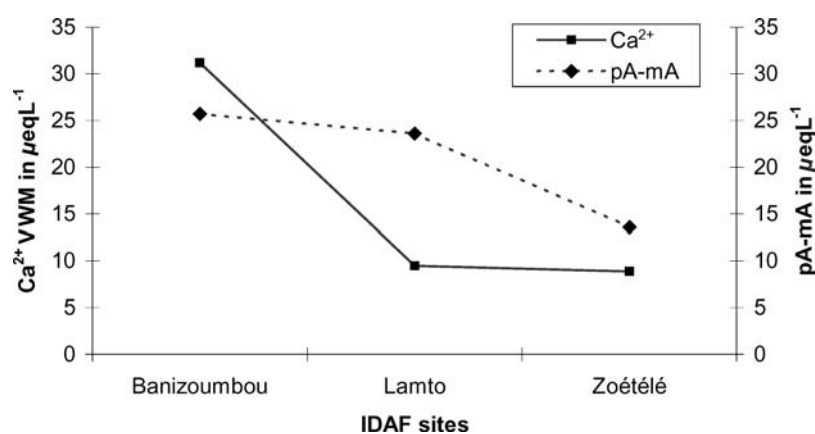

Figure 7. Calcium concentration versus the difference (pA-mA) between the potential acidity (mA) for the precipitation of 3 IDAF sites.

Banizoumbou in Niger, Figure 7 shows that the neutralization of HNO_3 is completed by the dust calcium content as Galy *et al.* (2001) have already demonstrated. In Lamto, the calcium content can only explain 40% of the neutralized acidity. This result is consistent with EXPRESSO measurements over the wet savanna of Central Africa Republic (Galy *et al.*, 2001; Ruellan *et al.*, 1999). In both sites, our results confirm the existence of heterogeneous processes between mineral aerosols and nitrogenous compounds. In Zoetele (Cameroon), the calcium content can only explain 65% of the neutralized acidity. To explain the remaining acidity in Lamto, we hypothetize that the direct absorption of gaseous NH_3 by the cloud droplets and raindrops has to be taken into account. This hypothesis is confirmed by the highest ammonium concentrations in Lamto rain water (17.6 μeq.l^{-1}). NH_3 IDAF gas measurements in Lamto presents an annual mean of 5 ppbv. Other heterogeneous mechanisms must imply alkaline particles with Mg^{2+}, K^+ among others and can contribute to neutralization of acid rain in wet savanna and forest.

5. Conclusion

In this paper, new results from a study on rainfall chemistry at the Lamto site (Côte d'Ivoire), representative of a wet savanna are presented. Results are to be associated with those from the IDAF programme over West Africa, at Banizoumbou (dry savanna, Niger) and at Zoetele (equatorial forest, Cameroon).

The rainfall mean chemical content at Lamto is computed on seasonal, interannual time scales and for the full 1995–2002 period. Interannual variability of the wet deposit is ~20%, associated to variability of atmospheric sources and rainfall amounts. Chemical signatures from gas and particles over West Africa are present at Lamto. Concentration of marine ions (Na^+, Cl^-, Mg^{2+}) is comparable to that obtained from other sites away from the Ocean. Ammonium with a VWM of 17.6 μeq.l^{-1} is the most abundant, representing the NH_3 source, and attributed to domestic animal wastes. 70% of the total nitrate settling (4.2 kg.ha^{-1}.yr^{-1}) is from NH_4. Rainfall concentration of nssCa^{2+}, nssSO_4^{2-}, nssK^+, and nssMg^{2+} are linked to terrigeneous sources from wind erosion of Sahara-Sahelo soils. Particles embedded in air masses are then carried away by the Harmattan, and slowly washed down, from the dry savanna to the wet savanna and equatorial forest. The negative concentration gradient for nssCa^{2+} goes from 30.8 μeq.l^{-1} in dry savanna to 9.2 μeq.l^{-1} in wet savanna at Lamto and 8.9 μeq.l^{-1} in the Cameroon forest. A similar gradient is also obtained from mineral particles raifall content with concentration of 80% in dry savanna, 40% in wet savanna, and 20% in equatorial forest. The latter emphasize the importance of multiphases processes between gases and particles in West African ecosystems. In particular, the classic acid gas-particles chemistry explains the acid rain and its gradient along the transect dry savanna, wet savanna and equatorial forest. The weak acidity of 2.1 μeq.l^{-1} in dry savanna, is due to neutralization of gaseous nitric acid by alkaline particles (Galy and Modi, 1998). The measured acidity at Lamto (6.9 μeq.l^{-1}) requires, when compared to a

potential acidity of 30.5 μeq.l^{-1}, the neutralization of 23.6 μeq.l^{-1} of acidity. This is accomplished at the 40% level by gas-particles interactions and by absorption of NH_3 in the clouds liquid phase (60%), as shown by the analyses of rainfall content.

The rainfall chemistry, quality-controlled from the IDAF network over West Africa has allowed to characterize multiphases chemistry, as a function of seasonal and interannual variability, and to estimate the critical wet deposition processes for proper functioning of African ecosystems. In the near future, maintenance of the IDAF measuring network, will allow to complete quantification of gaseous and particles dry deposition. In the longer term, study of total deposits (dry and wet) from long time series, will permit to analyze the slow temporal evolution of tropospheric chemistry, linked to climate variability and anthropogenic actions on tropical ecosystems.

Acknowledgements

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