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Heterogeneous processes involving nitrogenous compounds and Saharan dust inferred from measurements and model calculations

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Abstract. Experimental data on aerosol chemical composition and gaseous concentrations in various African ecosystems have been obtained under the IGAC DEBITS AFRICA (IDAF) program. In this paper, data covering a complete wet and dry season (1996 and 1998) in the semiarid savanna of the Sahelian region of Niger are presented. The analysis of the aerosol chemical composition and the gas phase concentrations at the Banizoumbou station indicates two strong signatures: a nitrogenous component composed of nitric acid, ammonia, particulate ammonium, and nitrates; and a terrigenous component originating from semiarid and desert soils (calcium, carbonates, magnesium, potassium, sulfate). To further investigate the interactions between gas and particles and to help interpret the IDAF experimental data, these data are analyzed using a gas aerosol equilibrium model (Simulating Composition of Atmospheric Particles at Equilibrium (SCAPE)). The model is found to accurately represent the mean aerosol composition for the dry and the wet season of the studied region. It is found that heterogeneous processes involving terrigenous compounds are important and play a major role in partitioning semivolatile species, such as nitric acid, between the gas and aerosol phases. The important role of these heterogeneous processes in the atmospheric chemistry in the Sahelian region is discussed. To compare results obtained in the semiarid savanna of Niger and other African ecosystems, SCAPE model is also applied to humid savanna and forest using IDAF and Experiment for Regional Sources and Sinks of Oxidants (EXPRESSO) measurements.

1. Introduction

Deposition of Biogeochemically Important Trace Species (DEBITS) was created, in the framework of the core project International Global Atmospheric Chemistry (IGAC) of the International Geosphere-Biosphere Programme (IGBP), to promote new activities in the final step of the biogeochemical cycles, i.e., the deposition of the chemical species to the Earth's surface. DEBITS was recently refocused with the following scientific objectives: (1) to determine, primarily through measurements, the atmospheric removal rates by dry and wet deposition of biogeochemically important trace species at regional scales; and (2) to establish the chemical and physical factors that regulate deposition fluxes and

develop parameterizations for inclusion in regional and global atmospheric chemistry models.

The DEBITS programs are based on controlled quality measurements of (1) precipitation chemistry to quantify wet deposition; (2) aerosols chemical composition; and (3) gases concentrations to estimate dry deposition. DEBITS's sites are located throughout the world in the tropics (48 stations). These stations have adopted the same experimental protocols to collect, preserve, and analyze the atmospheric samples. The DEBITS activity started in August 1990, with an experiment in Southeast Asia, and focused on field measurement programs encompassing precipitation, gas, and aerosol sampling aimed to help quantify the tropospheric S and N cycles in the Asia/Oceania region. The scope of DEBITS was expanded in 1994 to Africa, with the launch of the IGAC DEBITS AFRICA (IDAF) program with the establishment of 10 IDAF sites representative of the major African ecosystems (Figure 1).

In this paper, we use experimental data covering a complete wet (1996) and dry season (1998) from the IDAF station at Banizoumbou (Niger) in the Sahelian region (Figure 1). In our previous work [Galy-Lacaux and Modi, 1998], the

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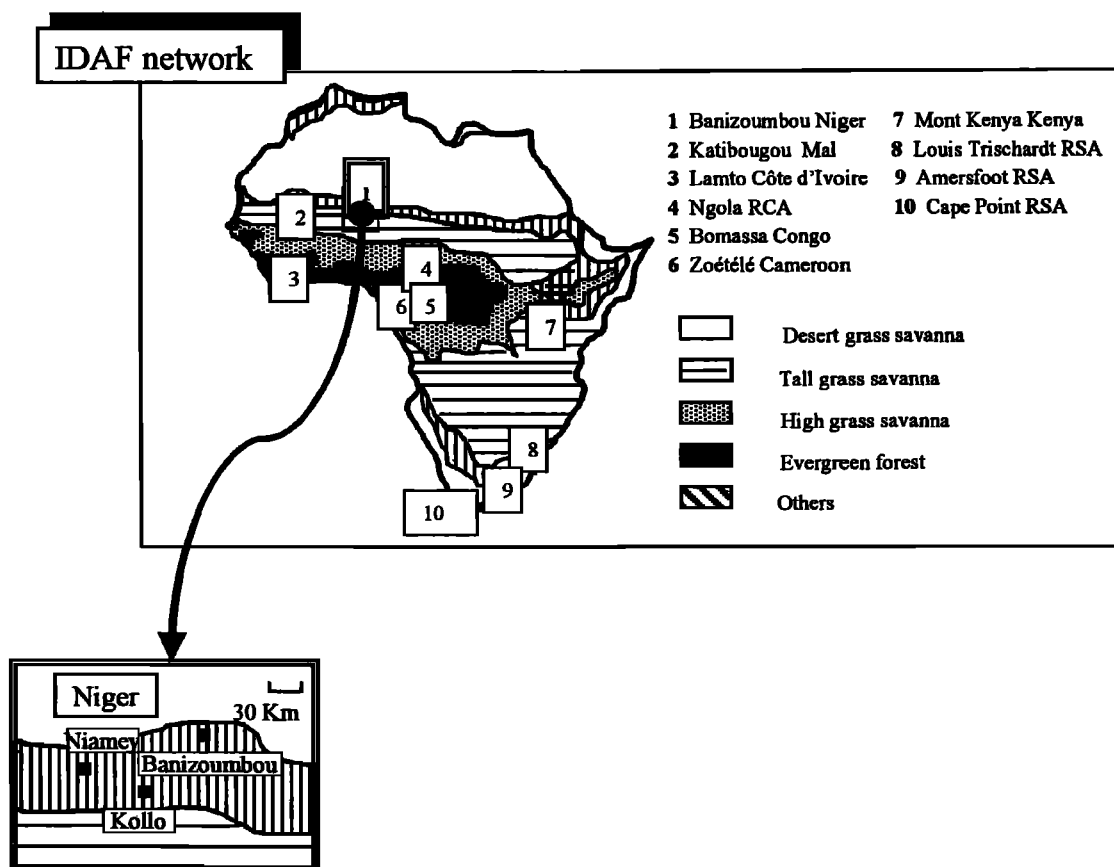


Figure 1. Location of the 10 measurements stations of the IDAF 1999 network (IGAC DEBITS AFRICA) and vegetation map. Identification of the Banizoumbou sampling site of aerosol and gas in the Sahelian region (Niger).

main characteristics of precipitation and aerosol chemical composition at this station were analyzed for the wet season of 1996. This study identified in the measurements an important terrigenous contribution related to mineral aerosol and a significant signature of nitrogenous compounds. Moreover, we emphasized the major role of heterogeneous chemistry in determining the chemical characteristics of wet deposition. Results of this work led us to propose a conceptual model to describe the cycling of atmospheric compounds in the Sahelian region, which highlighted the important role of heterogeneous interactions between gas and mineral particles.

In this paper we extend this previous study and focus on the interactions between nitric acid (HNO_3) and mineral particles. In the Sahelian region during the wet season, we have experimentally demonstrated that the alkalinity of the dust particles favors the uptake of nitrogenous compounds, especially HNO_3 [Galy-Lacaux and Modi, 1998]. A similar strong correlation of high particulate nitrate with high dust concentrations has been previously noted in measurements at sites in the Atlantic and Pacific Oceans [Savoie *et al.*, 1989; Prospero and Savoie, 1989; Prospero *et al.*, 1995], in humid savannas of Africa [Servant *et al.*, 1984; Yoboué, 1991] and in Asian aerosol [Gao *et al.*, 1991; Carmichael *et al.*, 1996, 1997; L. L. Chen *et al.*, unpublished manuscript, 1997]. Moreover, recent studies have emphasized the importance of including the HNO_3 /mineral particles interactions in tropospheric chemistry models [Dentener *et al.*, 1996;

Tbazaedeh *et al.*, 1998; Song and Carmichael, 2001]. For example, Tbazaedeh *et al.* [1998] showed that biomass burning and mineral aerosols can affect HNO_3 gas phase abundances in the upper troposphere by providing a chemical sink for HNO_3 .

In this paper we present experimental data covering a complete wet and dry season. Measurements were carried out at the station of Banizoumbou from June to October 1996 for the wet season (29 samples) and from November 1997 to May 1998 for the dry season (28 samples). Moreover, measurements of gas concentrations were initiated at several IDAF stations beginning in January 1998. Here we present monthly surface measurements of gaseous ammonia (NH_3) and nitric acid (HNO_3) from 1998 through 1999 at Banizoumbou. These gas concentrations measured from June to December and from January to May allow us for the first time to characterize ambient NH_3 and HNO_3 concentrations representative of the wet and dry seasons in the Sahel.

We also present results of a gas-aerosol equilibrium model analysis used to: (1) simulate the interactions between the gas and aerosol phases in the Sahelian region, in order to help interpret the experimental data of the IDAF network; (2) provide a better understanding of chemical reactions involved in heterogeneous processes occurring between HNO_3 and mineral particles in the dry and in the wet season; and to examine the influence of various factors which control the partition of particulate nitrate in the Sahelian region; and (3)

explore the interactions between the gas and aerosol phases in the humid savanna and the forest of central Africa, using IDAF and Experiment for Regional Sources and Sinks of Oxidants (EXPRESSO) measurements, and compare these results to those obtained for the semiarid savanna of Niger.

2. The Experimental Site: Meteorological Conditions

Banizoumbou (13.33°N, 2.41°E) is located in a rural unperturbed area of the Sahelian region of Niger, approximately 60 km north of Niamey. This station is representative of the semiarid savanna ecosystem, that is, the Sahelian savanna (Figure 1). This region has a seasonal semiarid climate with a dry season from October to May, and a wet season from June to September. These seasons are schematically determined by the shift in latitude of a surface separating hot and dry continental air masses coming from the Sahara desert and the more humid maritime air masses coming from the Atlantic Ocean, called the harmattan and the monsoon, respectively. This surface formed by the convergence of Saharian and oceanic air masses is the Intertropical Convergence Zone (ITCZ). The seasonal shift in the latitude of the ITCZ determines the wet and the dry season. During the wet season the monsoon layer is thin and varies from 1 to 2 km depth. When the intensity of the monsoon is reduced, the dry season occurs. The harmattan wind blows from northeastern desertic regions and has a major ground influence in the dry season. The harmattan winds are located over the monsoon layer (above 2 km in the wet season). In this paper we used meteorological data registered in Niamey from 1996 to 1998 in order to characterize the wet and the dry seasons. Mean ground relative humidity recorded for the wet season 1996 and the dry season 1997-1998 were ~76% and 30%, respectively. For both seasons the mean temperature was ~30°C.

3. Collection Procedure and Chemical Analysis

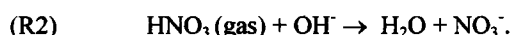
3.1. Collection Procedure

3.1.1. **Aerosols.** During the 1996 wet season and the 1997-1998 dry season, bulk particles were collected once per

week on Teflon Millipore filters of 1 µm pore size and 37 mm of diameter. Sampling was performed at 10 m above ground level with a power autonomous mobile pumping unit consisting of a 12 V pump, battery, and gasmeter using an average sampling duration of 24 hours. The bulk aerosol sampler operated at a flow rate of ~500 L h⁻¹. Each filter was preserved by refrigeration before and after exposure in sealed individual Millipore containers.

3.1.2. **Gaseous passive samplers.** Gaseous NH₃ and HNO₃ were collected as monthly integrated samples using passive sampling techniques. These measurements are based on the property of molecular diffusion of gases and species-specific collection on an impregnated filter specific to each pollutant measured. In the IDAF project we have developed at the laboratory of Aerologie in Toulouse a set of passive samplers. These samplers have been developed according to the DEBITS procedures based on the work of Ferm [1991, 1994]. Passive samplers have been tested and validated since the beginning of 1998 in the IDAF network at six African stations [*Al Ourabi and Lacaux, 1999; Lacaux, 1999*]. This technique has also been tested in different tropical and subtropical regions [*Ferm and Rodhe, 1997; World Meteorological Organization (WMO), 1997; Carmichael et al., 1996*].

The IDAF passive sampler is described in Figure 2. Two separate samplers are required for NH₃ and HNO₃ since different impregnated filters are needed. For NH₃ we used 1 g of citric acid diluted in 50 mL of methanol and for HNO₃ we used 0.5 g of NaOH diluted in 50 mL of methanol. The sorption processes for these two gases occur by way of the following reactions:



The collecting filter is placed inside the sampler and protected against mechanical impact (insect) and wind turbulence by a metallic thin stainless-steel mesh. In addition, a 1 µm teflon filter is used to exclude aerosol particles contamination by impaction onto the impregnated filter. Samplers were sent to and from the field in sealed plastic containers as recommended by Ferm [1991]. To prevent

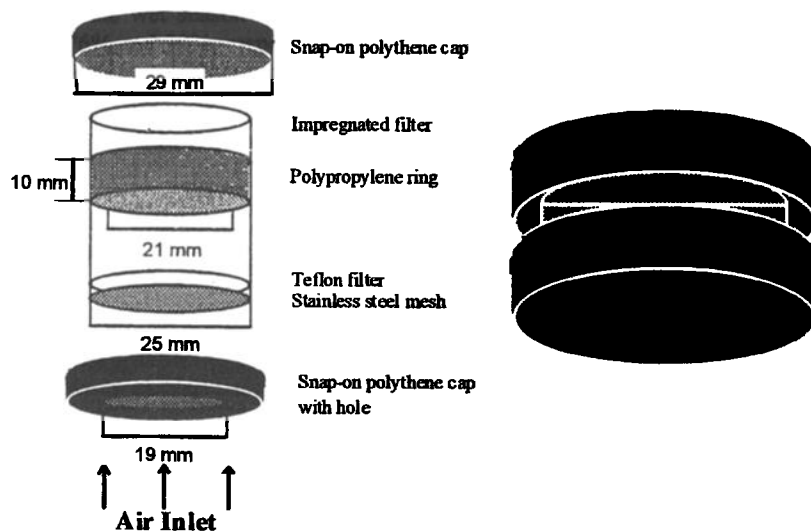


Figure 2. Diagram of the IDAF passive diffusion sampler (adapted from Ferm [1991]).

contamination of NH₃ samplers by particles, we replaced the inlet part of the sampler by a solid cap immediately after sampling [Ferm and Rohde, 1997].

In the field the passive gas samplers were exposed for 1 month periods. They were mounted under a plastic disc to avoid direct effect of wind transport and splashing from precipitation. The plastic disc was attached to a pole at 1.5 m high or more. Samplers were exposed in pairs to check reproducibility.

The ambient concentration of the gas, C_x , collected by the passive sampler was calculated from the amount trapped on the sorbent filter (X in mol), the time of exposure (t in s), the diffusion coefficient of the gas (D_x), and a number of geometric characteristics of the sampler where L_R is the length of the ring (10^{-2} m), A_R is the area of the ring

$$(R3) \quad C_x = \frac{X}{tD_x} \left(\frac{L_R}{A_R} + \frac{L_F}{A_F} + \frac{L_N}{A_N} + \frac{L_{LBL}}{A_T} \right),$$

(3.46×10^{-4} m²), L_F is the thickness of teflon filter (175×10^{-6} m), A_F is the total area of the filter pores (2.67×10^{-4} m²), L_N is the thickness of the stainless screen (90×10^{-6} m) and A_N its open area (2.98×10^{-5} m²), L_{LBL} is the thickness of the laminar boundary layer (4.25×10^{-3} m), and A_T is the total area of the inlet pores (2.84×10^{-4} m²) [Al Ourabi and Lacaux, 1999; Ferm, 1991]. Using these values, equation (R3) becomes

$$(R4) \quad C_x = \frac{X}{tD_x} (47.5). \quad (\text{mol m}^{-3})$$

3.2. Chemical Analysis

To determine the water-soluble content of the aerosol, inorganic anions and cations of the aerosols samples were extracted in 15 mL of 18 MΩ water by ultrasonic stirring (15 min). In the same way, ammonium and nitrate captured on the impregnated membranes of the gas passive samplers were extracted in 10 mL of deionized water by ultrasonic stirring (15 min). Subsequent solution analysis was performed by ion chromatography (IC) at the IDAF Laboratory of Toulouse. The ion chromatography system used in this study and the main characteristics of the analytical parameters for the determination of mineral ions (sodium, ammonium, potassium, magnesium, calcium, chlorine, nitrate, and sulfate) have been presented by Galy-Lacaux and Modi [1998].

Because of the high content of terrigenous matter in the aerosols collected at Banizoumbou, additional determination of total carbonate was undertaken on the dry season samples. Total carbonate (HCO₃⁻ and CO₃²⁻) was measured by exclusion ion chromatography with a ICE AS1 Dionex column. The eluant was deionized water at a rate flow of 1 mL.min⁻¹ and the injection volume was around 100 μL. The

data were corrected considering atmospheric CO₂ equilibrium with samples based on Henry's law.

Using the software Peaknet of Dionex to analyze the chromatograms, and according to the 1998 and 1999 international intercalibration tests organized by World Meteorological Organization (WMO), analytical precision is estimated to be 5% or better for mineral ions and represents the uncertainties on the aerosols measurements presented in this paper. Results of the 1996 World Meteorological Organization intercalibration for the Aérologie Laboratory are presented by Galy-Lacaux and Modi [1998].

We have estimated the detection limit of our passive samplers with the variations in the blank amounts of the impregnated filters (50 blank samples for 1998 and 1999 were deployed). The blanks and the standard deviations in the blanks were 0.38 ± 0.03 μg m⁻³ for NH₃ and 0.18 ± 0.10 μg m⁻³ for HNO₃. Duplicate samples were taken for both gases. The reproducibility defined as the relative standard deviation between duplicate samples was ~10% for NH₃, for the concentration range representative of the station of Banizoumbou. The reproducibility between duplicates was 20-25% for HNO₃, mainly due to the low concentrations measured at this station.

4. Analysis of the Aerosol Composition and Gas Measurements

4.1. Aerosol Composition

The volume weighted mean (VWM) chemical composition of the aerosol collected was computed from the ionic concentration C_n (mineral ions) and the sampling air volume V_n via the equation:

$$(R5) \quad \text{VWM} = \frac{\sum C_n V_n}{\sum V_n}.$$

The volume weighted mean (VWM) chemical composition of aerosols (μg m⁻³) at Banizoumbou during the 1996 rainy season and the dry season 1997/1998 are given in Table 1. Banizoumbou is mainly influenced by mineral terrigenous aerosols produced by wind erosion of arid and semiarid soils rich in calcium compounds [Jaenicke, 1993; Andreae, 1994; Bohn et al., 1985; Loÿe-Pilot et al., 1986; D'Almeida and Schütz, 1983]. Calcium in Saharan and Sahelian soils is associated with other mineral elements in the form of gypsum (CaSO₄), calcite (CaCO₃), and dolomite (CaMg(CO₃)₂) [Gomes and Gillette, 1993; Bohn et al., 1985; Loÿe-Pilot et al., 1986]. This is clearly seen in the aerosol measurements where the Ca²⁺ ion was the most abundant component after carbonates (1.8 and 2 μg m⁻³ during the wet and dry seasons). Furthermore, Ca²⁺ is significantly correlated, at a level of confidence better than 1%, with Mg²⁺ and SO₄²⁻ in both

Table 1. Volume Weighted Mean (VWM) Chemical Composition of Aerosols at Banizoumbou During the 1996 Rainy Season and the 1997-1998 Dry Season^a.

	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	SO ₄ ²⁻	Cl ⁻	NO ₃ ⁻	NH ₄ ⁺	<i>t</i> _{carbonate}
Wet season 1996	0.8 ± 0.3	0.3 ± 0.1	1.8 ± 0.7	0.2 ± 0.05	1 ± 0.4	0.2 ± 0.05	0.3 ± 0.1	0.2 ± 0.1	-
Dry season 1997-1998	0.5 ± 0.3	0.3 ± 0.1	2 ± 0.8	0.2 ± 0.06	1 ± 0.3	0.1 ± 0.02	0.6 ± 0.2	0.2 ± 0.05	5.9 ± 2

^aUnits are in μg m⁻³.

seasons. To determine the marine contribution in the measured aerosol, we calculated enrichment factors using composition relations found in seawater [Keene *et al.*, 1986]. Results indicated that the marine contribution was very high for chloride ions in the dry and wet seasons (80 to 90%). In contrast, 2/3 of the sodium present in the aerosol of the Sahelian region was found to originate from mineral salts contained in soils. The marine contributions for magnesium, potassium, and calcium were also low for both seasons (5-7%, 1-2%, 1%, respectively).

The NO_3^- concentration in the aerosol varied from 0.3 ± 0.1 and $0.6 \pm 0.2 \mu\text{g m}^{-3}$ for the wet and dry seasons, respectively, while the NH_4^+ concentration was independent of season ($0.2 \pm 0.1 \mu\text{g m}^{-3}$). These concentrations are similar to those measured at the Kollo station in the Sahelian region by Modi *et al.* [1995]. A statistical analysis of the aerosol chemical composition highlights a significant correlation already observed in the analysis of precipitation composition [Galy-Lacaux and Modi, 1998]. At Banizoumbou for both seasons, a strong correlation ($0.95 < r < 1$) between Ca^{2+} , Mg^{2+} and NO_3^- was observed. This is also the case at the neighboring station of Kollo in Niger [Modi *et al.*, 1995]. This strong correlation indicates that high concentrations of nitrate are associated with soil dust particles rich in calcite and dolomite. The same correlation between high total nitrate and high dust concentrations has also been observed in other data sets, including measurements at sites in the Atlantic or Pacific Oceans [Savoie *et al.*, 1989; Prospero and Savoie, 1989; Prospero *et al.*, 1995] and in Asian aerosol [Gao *et al.*, 1991; Carmichael *et al.*, 1996, 1997; L.L. Chen *et al.*, unpublished manuscript, 1997]. All these studies indicate that nitrate content is mainly related to the uptake of nitrogenous compounds gases (nitric oxides transformed into nitric acid). Our data suggest that it is the case in the Sahelian region where soil dust greatly affects the chemical characteristics of the aerosol. One of the biggest effects is that the particle alkalinity, both in the dry and the wet seasons, favors the uptake of nitrogenous compounds by chemical heterogeneous processes.

In the Sahelian savanna, nitric oxide (NO) in the nonburning season is the major nitrogen compound released from savanna soils and fuel wood consumption [Brocard *et al.*, 1998]. NO emissions from savanna soils present high spatial and temporal variability linked to a large number of parameters (soil texture, soil water content, soil nitrogen status, burning, etc.) [Matson *et al.*, 1990; Ambus and Christensen, 1994; Levine *et al.*, 1996; Parsons *et al.*, 1996; Serça *et al.*, 1998; Cardenas *et al.*, 1993]. Once released to the atmosphere a large fraction of the NO produced is rapidly oxidized in the atmosphere by photochemical reactions into HNO_3 and organic nitrates. HNO_3 is very soluble in water and is thus easily scavenged by wetted particles or cloud droplets. During the 1996 wet season, we previously demonstrated the importance of multiphase reactions and heterogeneous processes occurring between Sahelian mineral dust particle and nitrogenous compounds [Galy-Lacaux and Modi, 1998]. Our understanding of these chemical processes led us to explain the acidity of the precipitation and associated wet deposition characteristics in the semiarid Sahelian savanna.

During the dry season, in addition to NO emissions from savanna soils, we have to consider the strong influence of nitrogen oxides emissions due to biomass burning [Delmas *et al.*, 1991; Sanhueza *et al.*, 1990; Levine *et al.*, 1996]. The

photochemical oxidation of nitrogen oxides leads to nitric acid formation. Thus the higher mean aerosol concentration of NO_3^- in the dry season is likely the result of the high emissions of nitrogen oxides due to savanna burning [Lacaux *et al.*, 1992a, 1993; Delmas *et al.*, 1995]. Mineral aerosol levels are also expected to be high in the dry season, due to long-range transport of Saharan soils, and due to soil particles lifted into the atmosphere as the result of the convective activity within the fires. The high particulate nitrate and calcium suggest that heterogeneous processes between nitrogenous compounds and dust particle may also be important during the dry season.

The consequence of HNO_3 being partitioned onto mineral dust, instead of the gas phase may be significant in Sahelian dry deposition processes. For example, HNO_3 reacting with mineral aerosol in or close to the dust regions may be removed faster than gas phase HNO_3 due to sedimentation of coarse particles. On the other hand, HNO_3 , associated with the fine fraction of mineral aerosol could be transported long distances, and thus provide a mechanism for nitrate to be transported to more remote regions. In contrast HNO_3 in the gas phase cannot survive long transport distances, due to the high dry deposition velocity of this gas [Seinfeld and Pandis, 1998].

4.2. Gaseous NH_3 and HNO_3 Concentrations

Table 2 presents results of monthly mean concentrations of NH_3 and HNO_3 for the dry season (November to May) and for the wet season (June to October) in the Sahelian station of Banizoumbou. The mean NH_3 concentration in the dry season was $1.2 \pm 0.5 \mu\text{g m}^{-3}$ and was $1.8 \pm 0.4 \mu\text{g m}^{-3}$ in the wet season. NH_3 measurements performed within the IDAF network indicate that there are no major differences in NH_3 concentrations for the two representative stations of the semiarid savanna, that is, Banizoumbou in Niger and Katibougou in Mali. For Katibougou the mean regional NH_3 concentration in the dry season was $2.0 \pm 0.5 \mu\text{g m}^{-3}$ and was $3.2 \pm 0.2 \mu\text{g m}^{-3}$ in the wet season (H. Al Ourabi, personal communication, 2000). In other African sites, Ferm and Rodhe [1997] measured NH_3 in the humid savanna of Lamto (Ivory Coast) and found a mean of $\sim 3 \mu\text{g m}^{-3}$. This value is comparable to our measurements at the same station (Lamto) and also to Ngola measurements (central Africa), which is representative of the same ecosystem (Table 3). These gaseous measurements in the humid savannas of central Africa and Ivory Coast will be further discussed in section 7.

The 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]. In the Sahelian region during the wet season, the burning of the savanna is improbable and the main source of ammonia is certainly the hydrolysis of urea from animal urine deposited in pasture grazing areas. High densities of domestic animals are concentrated on the fresh natural pastures greening during the rainy season in Niger. Ammonium wet deposition of $6.3 \text{ mmol m}^{-2} \text{ yr}^{-1}$ in 1996 at Banizoumbou confirms the intense source of ammonia in this semiarid savanna related to a local density gradient of animals [Galy-Lacaux and Modi, 1998]. In the dry season ammonia is also produced by animals; but the senescence of the vegetation and biomass burning are possible

Table 2. Monthly Mean Concentrations of Ammonia (NH₃) (1998) and Nitric Acid (HNO₃) (1999) at Banizoumbou^a.

	NH ₃ (1998 Measurements)	HNO ₃ (1998-1999 Measurements)
November	1.4	0.4
December	1.5	0.3
January	0.9	0.8
February	0.5	0.06
March	0.8	0.1
April	1.6	0.6
May	1.9	1.3
Mean dry season	1.20± 0.5	0.5± 0.1
June	1.6	0.18
July	2.3	0.07
August	1.7	0.1
September	1.2	0.15
October	2.1	0.15
Mean wet season	1.80± 0.4	0.13± 0.05

^aUnits are in $\mu\text{g m}^{-3}$. Mean values representative of the dry and the wet season.

additional sources. During the dry season mean NH₃ concentrations in the semiarid savanna remain in the range of 0.5 to 2 $\mu\text{g m}^{-3}$. These high levels of NH₃ in both seasons seem to hold true all over African ecosystems.

There are few gaseous measurements of HNO₃ in Africa. The existing measurements mainly deal with the estimation of emissions factors of nitrogen compounds from biomass burning in West Africa [Brocard *et al.*, 1996, 1998; Lacaux *et al.*, 1992a, 1992b, 1995; Delmas *et al.*, 1991, 1995; Lobert *et al.*, 1990] (See also the special issue on FOS/DECAFE 91 in *Journal of Atmospheric Chemistry*, 22, 1-239, 1995). The mean measured HNO₃ concentration in Banizoumbou by passive samplers in the dry and in the wet season were 0.5±0.1 $\mu\text{g m}^{-3}$ and 0.13 ±0.05 $\mu\text{g m}^{-3}$, respectively (Table 2). According to the detection limit for HNO₃ measurements (0.18±0.10 $\mu\text{g m}^{-3}$ of HNO₃) and the measurement reproducibility (20-25%), we conclude that the mean ambient HNO₃ concentration in the wet season is near zero in the Sahelian region. HNO₃ concentrations measured at other semiarid sites are also very low (H. Al Ourabi, unpublished data, 2000, for the station located in Mali). These results are consistent with the absence of biomass burning emissions in the wet season. At the station of Ngola (central Africa) we measured HNO₃ in the 1998 and 1999 wet seasons to be 0.22±0.03 $\mu\text{g m}^{-3}$ and 0.50±0.08 $\mu\text{g m}^{-3}$, respectively (Table

3). These higher values probably relate to a more intense biogenic source of nitrogen oxide by the soils in the humid savanna.

In the dry season, gaseous nitric acid levels were found to be higher, showing the overwhelming influence of the savanna fires in this part of Africa [Delmas *et al.*, 1999] (See also the special issue on FOS/DECAFE 91, 1995). The Sahelian region is mainly influenced by Western Africa savannas fires. The harmattan layer allows the redistribution of nitrogen oxides emitted by savannas fires over large areas. This influence mainly contributes to the higher measured HNO₃ concentration in Banizoumbou in the dry season (0.5±0.1 $\mu\text{g m}^{-3}$) compared to the wet period. For comparison, the HNO₃ measurements at Ngola, that are under the direct influence of savannas fires emissions, were 1.32±0.5 $\mu\text{g m}^{-3}$ and 1.02±0.3 $\mu\text{g m}^{-3}$ in 1998 and 1999 dry seasons, respectively (Table 3). These measurements are also consistent with EXPRESSO data in central Africa savannas. Marion *et al.* [2000] estimated mean gaseous HNO₃ concentrations in the boundary layer (0-1000 m high) in the range of 1.30 to 2.10 $\mu\text{g m}^{-3}$. In the harmattan layer (>1000 m), the mean concentration of HNO₃ were higher ~4.1 $\mu\text{g m}^{-3}$ for the savanna and 5.4 $\mu\text{g m}^{-3}$ for the forest. However, analysis of the air mass transport associated with the dynamic vertical structure of the atmosphere indicated substantial

Table 3. Mean Concentrations of Ammonia (NH₃) and Nitric Acid (HNO₃) at Ngola (Central Africa) for Wet and Dry Seasons of 1998 and 1999^a.

	NH ₃	HNO ₃
Ngola (central Africa) wet season	2.8 ± 0.9 (1998) 2.0 ± 0.6 (1999)	0.22 ± 0.3 (1998) 0.50 ± 0.3 (1999)
Ngola (central Africa) dry season	3.3 ± 0.1 (1998) 3.5 ± 0.4 (1999)	1.32 ± 0.1 (1998) 1.02 ± 0.3 (1999)
Lamto (Ivory Coast) [Ferm and Rodhe, 1997]	3.0 ± 0.1	
EXPRESSO airborne measurements [Marion <i>et al.</i> , 2001]		1.30 - 2.10

^aUnits are in $\mu\text{g m}^{-3}$. Comparison with data representative of the same African ecosystem (humid savanna and forest).

variability in gaseous concentrations corresponding to local intense burning activity [Delmas *et al.*, 1999; Marion *et al.*, 2001; Delon *et al.*, 2000].

5. Modeling Analysis

The analysis of the aerosol chemical composition and the gas phase concentrations indicate that throughout the year the Sahel is characterized by significant quantities of mineral dust and nitrogenous compounds. The data further suggest that the presence of the mineral aerosol affects the partitioning of the nitrogenous compounds between the gas and aerosol phases. To further investigate the nature of these interactions, a modeling analysis was performed. In section 6 we present the complete modeling analysis performed on the Sahelian data. Then, the model will be applied (section 7) to other type of African ecosystem, that is, the humid savanna and forest of central Africa

5.1. SCAPE Model

The data of the Sahelian region were studied using the Simulating Composition of Atmospheric Particles at Equilibrium (SCAPE model) [Kim *et al.*, 1993a, 1993b; Kim and Seinfeld, 1995]. The thermodynamic model SCAPE predicts the chemical state and composition of inorganic soluble species (sodium, potassium, calcium, magnesium, ammonium, sulfate, nitrate, and chloride) and the equilibrium distribution of volatile species (ammonium, nitrate, and chloride) between the gas and the aerosol phase. Modeling analysis was performed to further investigate the interactions between the gas and aerosol phases in the Sahelian region, and to provide a better understanding of the heterogeneous processes involved in the mechanisms of wet and dry deposition in Africa. This model has been widely and successfully used in urban environment (Los Angeles) [Meng *et al.*, 1998], and is beginning to be used in other regions, especially in Asia, to interpret experimental data [Carmichael *et al.*, 1996, 1997; Song and Carmichael, 2001]. In this work, it is applied for the first time to Africa data.

The initial versions of the SCAPE model simulates the equilibrium between a gas phase and an aerosol phase taking into account one unique mode for the aerosol size distribution, that is, the one-bin SCAPE model [Kim *et al.*, 1993a, 1993b; Kim and Seinfeld, 1995]. In this analysis, we used the extended version of SCAPE developed by Hayami and Carmichael in [1997 and 1998] that considers the simultaneous equilibrium between gas phase and two aerosol modes to take into account the fine and the coarse modes in the aerosol size distribution. The fine mode corresponds to submicron particles (0.01 to 1 μm) and the coarse mode to particles larger than 1 μm . The use of the two mode version allows us to explore what might be learned by extending the IDAF aerosol measurements to include some size resolution.

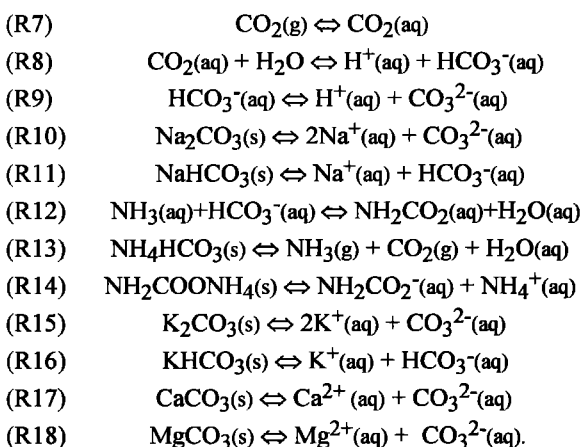
The distribution of the volatile inorganic species is a function of the mass (or mole) of the nonvolatile cations (Na^+ , Ca^{2+} , Mg^{2+} , and K^+). In the model the deposition of the volatile species (NH_3 , HCl , and HNO_3) are governed by thermodynamic relations, satisfying charge neutrality condition between the gas and the two aerosol modes. In the calculation, SCAPE is repeatedly called to estimate the gaseous and fine and coarse aerosol concentrations of the volatile species at equilibrium until both the fine and the coarse modes share the same gas phase concentrations [Song and Carmichael, 2001; Hayami and Carmichael, 1997, 1998].

The ZSR method [Stokes and Robinson, 1966] has been used to estimate the atmospheric aerosol water content in SCAPE [Kim and Seinfeld, 1995]. The ZSR method allows the estimation of the water activity in the model. A comparison of this method with four other semiempirical methods of the water activity estimation showed that there are no major differences in accuracy among them [Saxena and Peterson, 1981]. The method assumes that the Kelvin effect is neglected and then, the water activity a_w is equal to the relative humidity (RH). Thus the water content of aerosol is given by

$$(R6) \quad W = \sum \frac{Mi}{m_{i0}(a_w)},$$

where Mi is the molar concentration of the species i in the air, $m_{i0}(a_w)$ is the molality of the single solution component at the define a_w of the multicomponent solution, and W is the mass concentration of water in the aerosol.

The observations at Banizoumbou showed that the chemical composition of dust particles is dominated by terrigenous species, especially carbonates and calcium (section 4.1). It has been suggested that analysis of aerosols with a large terrigenous component should consider carbonates in order to balance excess cations [Clarke and Karani, 1992; Nishikawa and Kanamori, 1991; Hayami and Carmichael, 1997]. Our study of the chemical composition of precipitation in the Sahelian region led us to the same suggestion [Galy-Lacaux and Modi, 1998]. Since a considerable fraction of the crustal species (Ca^{2+} , Mg^{2+} , K^+) are in the form of carbonates in the Sahelian region, it is necessary to use the expanded SCAPE code [Hayami and Carmichael, 1997, 1998; Meng *et al.*, 1995]. This SCAPE code includes the interaction of crustal elements (calcium, potassium, and magnesium) and carbonates with the gas phase mainly represented by nitric acid and ammonia in our study case. The corresponding carbonate/bicarbonate concentrations are estimated by the following equilibrium reactions in the SCAPE module:



Carbonate and bicarbonate ion concentrations can be estimated by constraints in the SCAPE module to meet ion balance in each mode when nonvolatile cation composition is input.

5.2. Assumptions and Preparation of the Simulations Conditions

The initial data set representative of the Sahelian region for the wet and the dry season was prepared from the measurements at Banizoumbou. Two base case situations

Table 4. Initial Conditions Representative of the Sahelian Region for SCAPE Model Simulations^a.

Parameters	Values Wet Season	Values Dry Season
Temperature, K	303	303
Relative humidity, %	70	30
CO ₂ concentration, ^b ppm	360	360
Mineral particle composition, ^c μg m ⁻³		
ss-Na ⁺	0.122	0.055
nss-Na ⁺	0.677	0.450
nss-K ⁺	0.295	0.297
nss-Ca ²⁺	1.795	1.997
nss-Mg ²⁺	0.186	0.193
nss-SO ₄ ²⁻	0.960	0.986
Total composition of volatile components, μg m ⁻³		
t-ammonium	1.8	1.2
t-nitrate	0.3	1.1
t-chloride	0.2	0.1

^aDetermination of two base cases representative of the dry and the wet seasons.

^bBoth carbonate and bicarbonate ion concentrations are estimated by constraints in the SCAPE module to meet ion balance in each mode when nonvolatile cation composition is input.

^cSea-salt (ss) and non-sea-salt (nss) contribution of each species to mineral particles composition is calculated according to Keene *et al.* [1986] ratios in seawater

representative of the wet and the dry season, were determined based on the mean seasonally gaseous measurements and mean seasonally aerosols chemical composition (Tables 1 and 2). The values used are presented in Table 4.

The SCAPE model requires the total (gaseous plus particulate) concentration of each inorganic soluble species along with temperature and relative humidity. Considering the climatic parameters, we used the average conditions measured over the dry and the wet seasons at Niamey (close to Banizoumbou station). The mean temperature was taken to be 30°C in the both seasons with a mean relative humidity for the wet and the dry season equal to 70% and 30%, respectively. The average measured concentrations of non volatile cations (Na⁺, K⁺, Ca²⁺ and Mg²⁺) for the wet and dry season were used directly as model inputs. Sulfate was treated as a nonvolatile species. We assumed that the major part of the sulfate measured in the aerosol of the Sahelian region is provided by gypsum (Ca₂SO₄) contained in Saharan and Sahelian soils [Loÿe-Pilot *et al.*, 1986, Bohn *et al.*, 1985; Gomes and Gilette, 1993]. Effectively, this region seems to be not affected by local anthropogenic sources of sulfur (industries or diesel vehicles). However, recent sulfur modeling studies show that sulfur biogenic sources related to biomass burning could affect tropical regions [Chin and Jacob, 1996]. With these considerations, the average measured concentrations of sulfate in the aerosol were directly considered in the initial input data set.

For the volatile species, nitrate, chloride and ammonium, we made different assumptions. We first assumed that all measured nitrates in the aerosol phase represent the final result of interactions between nitrogenous gases and atmospheric particles (nitric oxide (NO) oxidized into nitric acid (HNO₃)) [Galy-Lacaux and Modi, 1998]. The total nitrate species concentration was assumed to be the sum of the mean gaseous nitric acid and particulate nitrate measurements. Ammonium concentrations measured in the aerosol result from the incorporation of ammonia and also from ammonium salts contained in the soil. Since the measurements of particulate concentrations were very low the initial total concentration of ammonium was assumed to be equal to the

mean gaseous measurements of ammonia. We assumed that all measured chloride came from seasalt particles. The average measured concentrations of chloride in the aerosols were used as inputs for the total chloride concentration.

Nonvolatile cations as Na⁺, K⁺, Ca²⁺ and Mg²⁺ and, SO₄²⁻ were partitioned into two size modes, using a basic partition factor of 0.1 [Nishikawa and Kanamori, 1991; D'Almeida, 1985; Pye, 1987] (i.e., 10% of the nonvolatile species were placed in the fine mode, and the remaining 90% were placed in the coarse mode). Original measurements of the mass-size distribution of the sahelian aerosol have been realized in Niger (Banizoumbou) in 1986 and 1992. The analysis of these data confirms that the choice of a partition factor equal to 0.1 is quite representative of the size distribution of aerosol collected in Banizoumbou (E. Serie and B. M. Abdelkrim, personal communication, 2000). The initial carbonates and bicarbonates ion concentrations were estimated in the SCAPE module considering the different equilibrium equations presented in section 5.1. We used an atmospheric gas concentration of 360 ppm of carbon dioxide.

The two initial data sets used are considered to represent the mean conditions for the wet and the dry season of the Sahelian region. The mean composition determined above were used as the base case for the various sensitivity calculations discussed in the following sections.

6. Modeling Results of the Sahelian Region and Discussion

In section 6.1, we presented modeled results for the Sahelian region in the wet and dry seasons, respectively. We described the SCAPE predictions of the mean aerosol and gas composition of each season according to the simulation conditions given in Table 4. Then, section 6.2 allows us to compare more thoroughly model predictions with experimental data (aerosol and gas phase). Finally, sensitivity tests were performed to further investigate and interpret the influence of various factors on the mean aerosol and gas composition simulated by the SCAPE model (section 6.3).

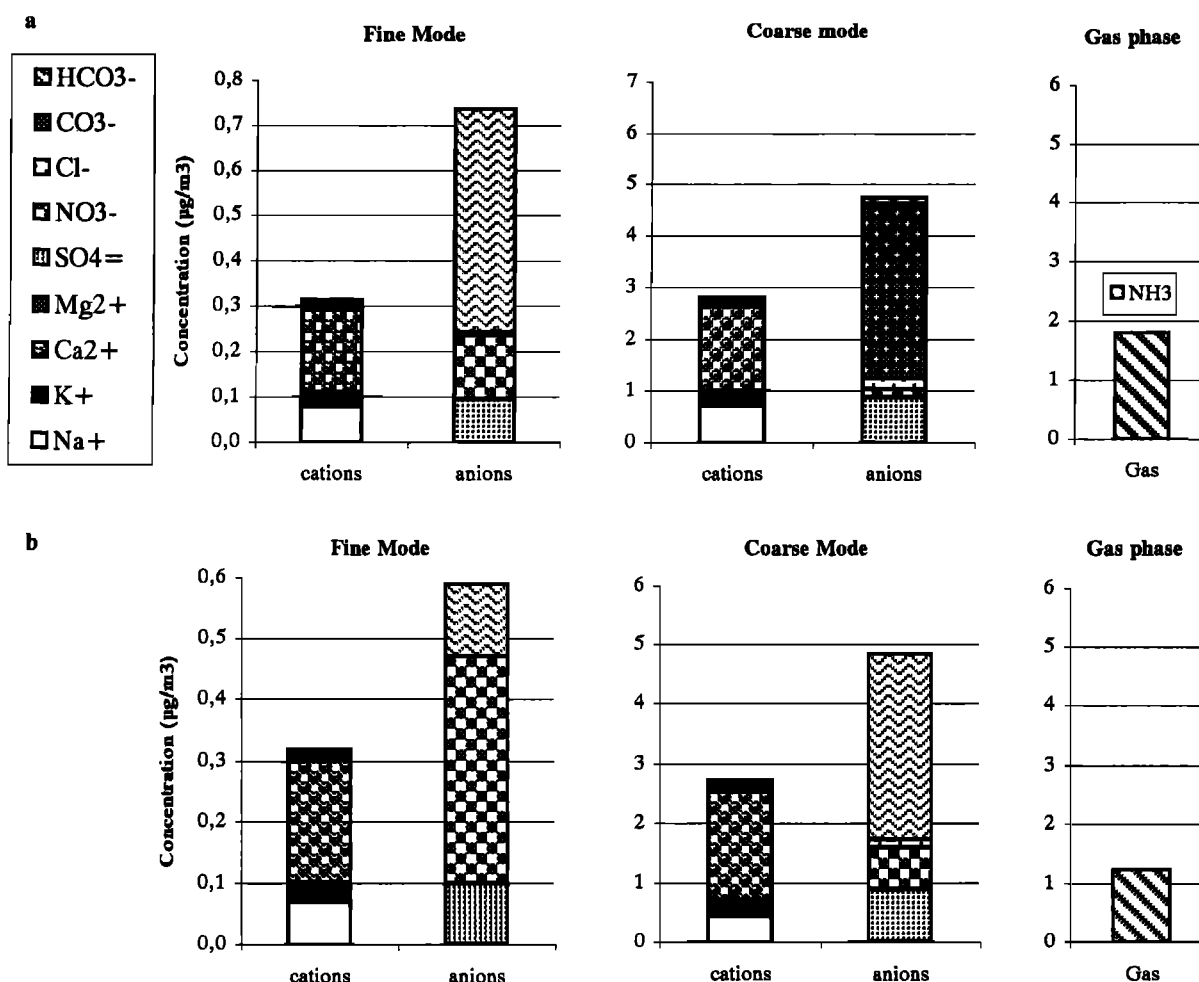


Figure 3. Calculated mean aerosol and gas composition for (a) the wet and (b) the dry season of the Sahelian region. Species are shown as ions in $\mu\text{g m}^{-3}$.

6.1. Mean Aerosol and Gas Composition in the Wet and Dry Seasons

6.1.1. Wet season. The calculated aerosol for the mean conditions during the wet season in the Sahelian region are presented in Figure 3a. SCAPE predictions indicate that the aerosol contained $\sim 3 \mu\text{g m}^{-3}$ of water. In the wet season, simulation conditions consider a total mass aerosol (gas and particles) of $\sim 6 \mu\text{g m}^{-3}$ and a mean relative humidity of 70%. This result is consistent with several field observations of dust in Sahara and the Sahelian region [Hanel, 1976], and also in Asian regions [Parungo et al., 1996]. When relative humidity is high (50–80%), as is the case in the monsoon layer in Sahel during the wet season, soil particles absorb water to form a water shell on their surfaces. Each species was predicted to exist in the aerosol in ionic form and no solid phase was predicted. According to this SCAPE result, all the species given in Figure 3a in the fine and coarse modes are represented in ionic form. The second important result well represented by the SCAPE model is the total transfer of HNO_3 (gas) to the particulate phase to form particulate nitrate ($0.3 \mu\text{g m}^{-3}$ p- NO_3^-). On the basis of the mass conservation principle, particulate nitrate was predicted to be mass distributed 46% in the fine mode and 54% in the coarse mode. The SCAPE model predicted that the initial total ammonium

concentrations were unchanged at the end of the simulation and all the ammonia was partitioned in the gas phase in the form of ammonia ($1.8 \mu\text{g m}^{-3}$). In the wet season, SCAPE calculated that the aerosol contains $4 \mu\text{g m}^{-3}$ of total carbonate. The coarse mode was predicted to contain $3.4 \mu\text{g m}^{-3}$ of carbonates and $0.1 \mu\text{g m}^{-3}$ of bicarbonates. The fine mode was predicted to contain $0.5 \mu\text{g m}^{-3}$ of total carbonates.

6.1.2. Dry season. The calculated mean conditions of the aerosol during the dry season in the Sahelian region are presented in Figure 3b. Solid and ionic phases were predicted in both modes of the aerosol. However, to facilitate comparison, we adopted the same representation as used in the previous case, where each component was presented as an ion. The SCAPE model predicted that even in the dry season the aerosol was wetted and contained $\sim 0.1 \mu\text{g m}^{-3}$ of water. In the dry season, simulation conditions consider a total mass aerosol (gas and particles) of $\sim 6 \mu\text{g m}^{-3}$ and a mean relative humidity of 30%. The calculated water content of the aerosol in the dry season is also consistent with Hanel's [1976] field observations in Sahara and Sahel. As was the case for the wet season, the model predicted that the volatile nitrates were entirely partitioned in the particulate phase ($1.1 \mu\text{g m}^{-3}$). A major difference in the predictions concerns the chemical state of the p- NO_3^- . For the dry season conditions HNO_3 (gas)

was transformed to $p\text{-NO}_3^-$ in the aerosol phase, with 94 % of the nitrate in solid form ($p\text{-NO}_3^-)_s$ and 6% in ionic form ($p\text{-NO}_3^-)_i$). Considering the solid state, 30% of the $p\text{-NO}_3^-$ was partitioned in the fine mode, and 70% was partitioned in the coarse mode. All the nitrate in ionic form was distributed in the fine mode. The SCAPE module predicts the different chemical states of the terrigenous elements in the two modes of the aerosols. Under the conditions studied, solid ($(\text{Ca}^{2+})_s$) and ionic forms ($(\text{Ca}^{2+})_i$) were of equal importance (41% of solid, 59% of ionic forms). In addition, equivalent concentrations of $(\text{Ca}^{2+})_s$ to $p\text{-NO}_3^-)_s$ were predicted in the fine mode. As was the case for the wet season, the SCAPE model did not predict the formation of $p\text{-NH}_4^+$ for the dry season. Total ammonium is partitioned in the gas phase in the form of ammonia ($1.2 \mu\text{g m}^{-3}$). The Sahelian aerosol of the dry season was predicted to contain about $3.2 \mu\text{g m}^{-3}$ of total carbonates, mainly in the form of HCO_3^- ions. Bicarbonates were predicted to be solely in ionic form with 96% distributed in the coarse mode.

6.2. Comparison of Modeled Results With Experimental Data

6.2.1. Nonvolatile species. The SCAPE model predicts the partition of nonvolatile species in the fine and coarse modes of the aerosol. Results are presented in Table 5. On the basis of the mass conservation principle, the concentrations predicted as model outputs are consistent with the measured chemical composition of the Sahelian aerosol given in Table 1. We found in the wet season a total of $0.8 \mu\text{g m}^{-3}$ of Na^+ , $0.3 \mu\text{g m}^{-3}$ of K^+ , $0.2 \mu\text{g m}^{-3}$ of Mg^{2+} and $1.0 \mu\text{g m}^{-3}$ of SO_4^{2-} partitioned according to the initial partition factor equal to 0.1. In the same way, in the dry season we found a total of $0.5 \mu\text{g m}^{-3}$ of Na^+ , $0.3 \mu\text{g m}^{-3}$ of K^+ , $0.2 \mu\text{g m}^{-3}$ of Mg^{2+} and $1.0 \mu\text{g m}^{-3}$ of SO_4^{2-} . In this case, K^+ , Mg^{2+} and SO_4^{2-} were also partitioned according to the initial partition factor. For Ca^{2+} , we found a total of 1.8 and $2 \mu\text{g m}^{-3}$ of Ca^{2+} in the wet and dry seasons, respectively. However, for both seasons, we found that the partition of calcium in the fine and coarse modes mainly depended on the partition of volatile species, especially total nitrate.

6.2.2. Volatile species. As far as NO_3^- , Cl^- , NH_4^+ and t-carbonates are concerned, SCAPE results indicate a partition dependent on the nonvolatile species distribution in the aerosol phase. In the wet season the model predicts the formation of $0.3 \mu\text{g m}^{-3}$ of particulate nitrate in ionic form (Table 5). This result does agree with the NO_3^- concentration measured in the Sahelian aerosol (Table 1). This indicates that under the conditions simulated, the soil mineral cations

partitioned in the fine and coarse modes were quantitatively sufficient to neutralise all the gaseous HNO_3 during the wet season. We have seen that the aerosol composition of the Sahelian region is dominated by large quantities of terrigenous species (Ca^{2+} , Mg^{2+} , K^+). For both seasons a strong correlation ($0.95 < r < 1$) was found in the measurements between Ca^{2+} , Mg^{2+} , and NO_3^- . This strong correlation indicates that high concentrations of nitrate are associated with soil dust particles rich in calcite and dolomite [Modi *et al.*, 1995; Galy-Lacaux and Modi, 1998]. The model predictions are consistent with these observations. We found the same correlation between Ca^{2+} , Mg^{2+} and NO_3^- in the model results illustrated by the formation of particulate nitrate distributed in the fine and coarse modes according to the non-volatile species partition. In the dry season the predicted particulate nitrate concentration was $\sim 1.1 \mu\text{g m}^{-3}$ (Table 5). This value is high compared to the averaged concentration of nitrate measured in the aerosol composition of the dry season ($0.6 \pm 0.2 \mu\text{g m}^{-3}$). The major difference is that predictions indicate a total partitioning of nitrate to the particle phase, while in the observations gaseous HNO_3 was measured, thus indicating that the partitioning was not one-sided. In the dry season, SCAPE results concerning the partition of solid and ionic particulate Ca^{2+} suggest that nitrate is associated with calcium in the solid form ($\text{Ca}(\text{NO}_3)_2$). This result is consistent with the mean relative humidity used to represent the dry season (30%) compared with the relative humidity corresponding to the deliquescence point of this solid (RHD), that is, $\sim 49\%$. The same type of correlation between NO_3^- and nonseasalt Ca^{2+} has also been observed in East Asia [Dentener *et al.*, 1996; Fujita and Takahashi, 1994; Hayami and Carmichael, 1997]. In the same way, $p\text{-NO}_3^-$ was predicted to be associated with Ca^{2+} in solid form in the coarse mode. However, in this mode, $(\text{Ca}^{2+})_s$ concentration was in excess compared with $p\text{-NO}_3^-$ concentrations. In order to try to understand better the distribution of $p\text{-NO}_3^-$ and the capacity of the Sahelian aerosol to neutralise nitric acidity in the aerosol, a sensitivity study to investigate the influence of the partition factor will be conducted in the following section (6.3).

SCAPE calculations indicate that total ammonium was predicted to be only in the gas phase with ammonia concentrations of $1.8 \mu\text{g m}^{-3}$ et $1.2 \mu\text{g m}^{-3}$ in the wet and dry seasons, respectively. However, $p\text{-NH}_4^+$ was measured in the aerosol phase, though at low levels ($0.2 \mu\text{g m}^{-3}$). According to the alkalinity of the aerosols, it seems that ammonia cannot interact with the particulate phase or with the water surface shell. A specific sensitivity study will be developed in section 6.3 in order to understand under which conditions $p\text{-NH}_4^+$ may

Table 5. SCAPE Predictions of the Partition and the Calculated Concentrations of the Mean Aerosol and Gas Composition for the Wet and Dry Season of the Sahelian Region^a.

	Na^+	K^+	Ca^{2+}	Mg^{2+}	SO_4^{2-}	Cl^-	NO_3^-	NH_4^+	t carbonate
<i>Wet Season (Sahel)</i>									
Fine mode	0.08	0.03	0.20	0.02	0.12	0.01	0.14	0	0.50
Coarse mode	0.72	0.27	1.60	0.18	0.88	0.21	0.16	0	3.50
Gas								1.8	
<i>Dry Season (Sahel)</i>									
Fine mode	0.07	0.03	0.2	0.02	0.1	0	0.37	0	0.12
Coarse mode	0.43	0.27	1.8	0.18	0.9	0.13	0.73	0	3.11
Gas								1.2	

^aUnits are in $\mu\text{g m}^{-3}$.

be formed. The result of this study will allow us to discuss the discrepancy observed between modeled and measured ammonium.

Total carbonates were predicted to be equal to $4 \mu\text{g m}^{-3}$ and $3.2 \mu\text{g m}^{-3}$ in the wet and dry seasons, respectively. In the wet season the fine mode was predicted to contain 38% of the predicted carbonates required to complete the neutralisation of terrigenous elements (Ca^{2+} , Na^+ , Mg^{2+} , K^+) in the fine mode. This result confirms the need to take carbonates into account in the interpretation of the ion balance of the aerosol [Galy-Lacaux and Modi, 1998; Nishikawa and Kanamori, 1991; Hayami and Carmichael, 1997]. Measurements of the aerosol carbonate content are not available for the wet season and this lack mainly explains the ion imbalance in the aerosol composition [Galy-Lacaux and Modi, 1998]. In this case, we cannot directly compare experimental data and model results. However, SCAPE calculations of total carbonates ($4 \mu\text{g m}^{-3}$) lead to a correct ionic balance (1.1 ± 0.1). In the dry season, $3.2 \mu\text{g m}^{-3}$ of total carbonates are predicted to be contained in the aerosol phase. Measurements have been conducted downward the Saharan desert from the station of Banizoumbou, which is representative of the dry savannah. These particles have been transported over long distances and have been chemically transformed. For this reason, we assumed that the reported dust composition in section 4.1 is already aged (Table 1). With this assumption, the total carbonate concentration measured in the aerosol composition of the dry season could be directly compared to SCAPE calculations. We observed that the total carbonate concentrations predicted by SCAPE are of the same order of magnitude as the experimental measurements represented by a mean concentration of $5.9 \pm 2 \mu\text{g m}^{-3}$. HCO_3^- in ionic form in the fine mode allows an explanation of the equilibrium of the ion balance with the presence of ionic Mg^{2+} and K^+ in the same mode. The most important part of the HCO_3^- ions was found in the coarse mode and was needed to equilibrate the large amount of Ca^{2+} ions. SCAPE calculations of the total carbonate concentration lead to an ion balance of 0.99 ± 0.1 .

Finally, the modeled results of the mean aerosol and gas composition in the wet and dry seasons of the Sahelian region tend to roughly agree with experimental data, especially for non-volatile species, total nitrate, chloride and carbonates. However, there are discrepancies concerning the observed and calculated total ammonium in both seasons, and the total nitrate in the dry season. Section 6.3 especially aims at discussing these two observations.

6.3. Sensitivity Tests

The above modeling results indicate that mineral components play a large role in controlling the partitioning of the nitrogenous compounds between the gas and aerosol phases in both the dry and wet seasons. However, under the conditions simulated, two major discrepancies between the observed and calculated values remain: (1) the gas phase nitric acid levels observed in the dry season; and (2) the particulate ammonium observed in both the dry and wet seasons. To understand better the processes involved in the neutralisation of volatile nitrogenous compounds by the mineral aerosol, we investigated the sensitivity of particulate nitrate to various initial conditions.

6.3.1. Temperature and relative humidity. The equilibrium coefficients of the different chemical reactions

used in the SCAPE model are dependent on temperature. Deliquescence points are also a function of this parameter. The wet and dry season calculations were repeated using temperatures of 25°C and 35°C in order to compare results to the base case temperature of 30°C . Results for both seasons, and especially the particulate nitrate fraction, was found to be insensitive to this range of temperature. Relative humidity is also an important parameter in considering the state of components, especially for solid/ionic partition with relative humidity of deliquescence (RHD), and the water activity in aerosols. Additional calculations were performed using 60 and 80% relative humidity in the wet season, and 20 and 40% in the dry season. In the wet season, for 60% relative humidity, several species changed state. First $p\text{-NO}_3^-$ was entirely distributed in the fine mode and associated with Ca^{2+} in solid form. In the coarse mode 1/3 of the predicted carbonates were in solid form, apparently associated with Mg^{2+} in solid form. SO_4^{2-} and Na^+ were also predicted to be in the solid and mainly distributed in the coarse mode. Results for 80% RH were comparable to the base case. In the dry season, the particulate nitrate distribution was insensitive to the variations of relative humidity from 20 to 40%.

6.3.2. Volatile ammonium and volatile nitrate. To study the influence of ammonium on the partition of volatile nitrate, calculations were performed for various total ammonium concentrations ranging between 0.5 to $10 \mu\text{g m}^{-3}$. Maximum experimental values in the station of Banizoumbou were found equal to $\sim 2.5 \mu\text{g m}^{-3}$. Results showed no variation compared with the base case calculation. For all the calculations, ammonia remained in the gas phase with no formation of particulate ammonium. Particulate nitrate distribution was found to be insensitive to decreasing or increasing ammonia values.

In the Sahelian region, SCAPE results indicate that high amounts of dust associated nonvolatile cations were sufficient to neutralize $p\text{-NO}_3^-$ and particulate sulfate. Thus, even through non-sea-salt sulfate concentrations were relatively high in the base case composition ($1 \mu\text{g m}^{-3}$), volatile ammonium did not lead to $p\text{-NH}_4^+$ formation, but instead was partitioned into the gas phase. A series of simulations were conducted to see under what conditions $p\text{-NH}_4^+$ could be formed. We found that if we included an additional sulfate source not associated with mineral soils or sea salt (e.g., a source driven by oxidation of gas phase SO_2) then $p\text{-NO}_3^-$ could be completely neutralized and $p\text{-NH}_4^+$ could be formed to neutralize sulfates (and form solid $\text{SO}_4(\text{NH}_4)_2$). In section 7 we use the SCAPE model to calculate the mean aerosol composition during the Experiment for Regional Sources and Sinks of Oxidants (EXPRESSO), where there is a clear additional source of sulfate associated with biomass burning. The application of SCAPE to this ecosystem (humid savanna and forest in central Africa) predicts the formation of $p\text{-NH}_4^+$. These results suggest that the partitioning of particulate sulfate is a key factor in determining whether $p\text{-NH}_4^+$ can form. In the Sahelian region, the sources of sulfate (particulate and gas phase) and the atmospheric processes leading to $p\text{-NH}_4^+$ formation require further investigation.

Nitric acid in the gaseous phase interacts mainly with terrigenous compounds. We have shown that HNO_3 is entirely captured by the aerosol and associated in ionic or solid form with calcium under the base conditions assumed for the wet or the dry seasons. To further investigate the heterogeneous

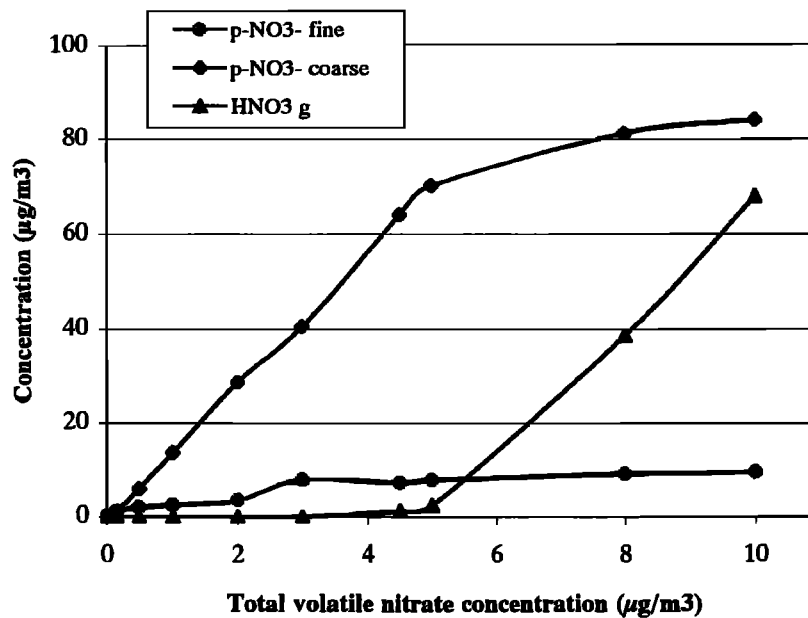


Figure 4. Calculated concentrations of particulate nitrate in fine and coarse mode ($p\text{-NO}_3^-$), and of gaseous nitric acid ($\text{HNO}_3(\text{g})$) for various concentrations of total volatile nitrate (particulate plus gas) for the wet season.

processes between $\text{HNO}_3(\text{g})$ and Ca^{2+} in both seasons, and to estimate the limit condition of $\text{HNO}_3(\text{g})$ uptake by the mineral aerosol, calculations were performed for total nitrate concentrations ranging from 0–10 $\mu\text{g m}^{-3}$. Results for the wet season are presented in Figure 4. As the total nitrate concentration was increased the concentration of both $p\text{-NO}_3^-$ in the coarse and fine modes increased. Mineral species distributed in the two modes were initially in excess compared to $p\text{-NO}_3^-$ concentration and thus had excess capacity to neutralize increasing amounts of volatile nitrate. When the HNO_3 concentration reached $\sim 4.5 \mu\text{g m}^{-3}$, the mineral species concentrations were no longer sufficient to completely neutralize $\text{HNO}_3(\text{g})$. Subsequently, a portion of HNO_3 remained in the gas phase (Figure 4). The results for the dry season are presented in Figure 5. The $p\text{-Ca}^{2+}$ and $p\text{-NO}_3^-$ in the fine mode did not show important variations. If we look at the results in the coarse mode, it was found that at first $p\text{-(NO}_3)_s$

increased and reached a steady state governed by the solid Ca^{2+} concentration. Then, $p\text{-(NO}_3)_i$ increased rapidly, and leveled off when $\text{HNO}_3(\text{g})$ appeared in the gas phase (Figure 5a). These results allow the determination of the limit condition for the complete neutralization of $\text{HNO}_3(\text{g})$ by the particles. We observed for both seasons that HNO_3 remains in the gas phase for a total nitrate concentration of $\sim 4.5 \mu\text{g m}^{-3}$ (Figures 4 and 5). Bicarbonate concentrations decreased rapidly and fell to zero when HNO_3 partitioned into the gas phase (Figure 5b).

These results provide key information regarding the chemical reactions involved in the neutralization of HNO_3 in the dry season. We can propose the following chemical reaction of neutralization:

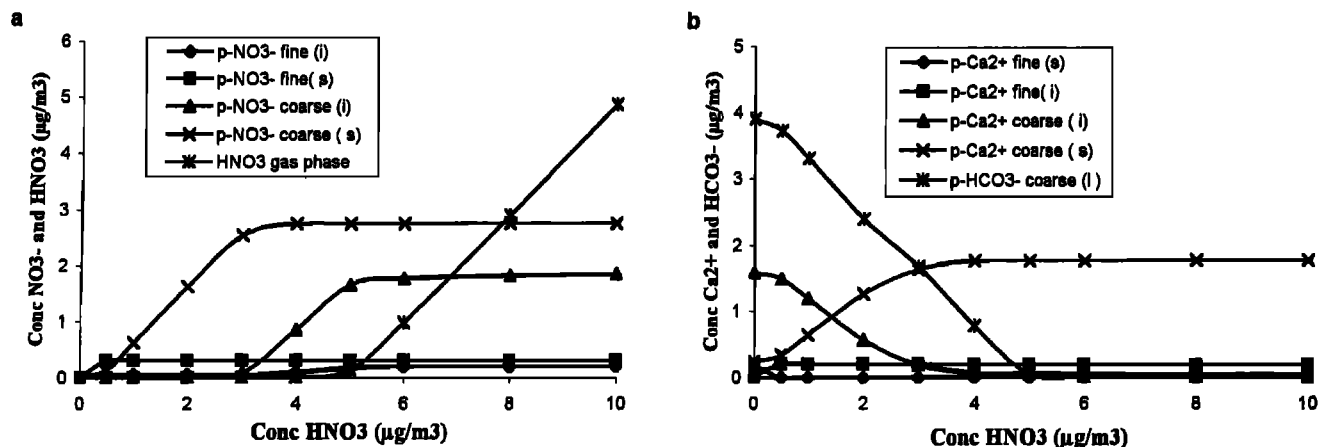
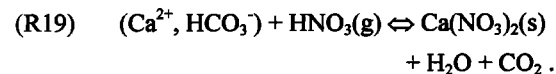


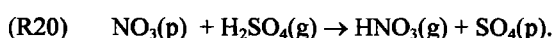
Figure 5. Calculated concentrations of (a) particulate nitrate ($p\text{-NO}_3^-$) and (b) particulate calcium ($p\text{-Ca}^{2+}$) in the fine and coarse modes, particulate bicarbonates ($p\text{-HCO}_3^-$) in the coarse mode, and gas phase nitric acid (HNO_3) for various concentrations of total volatile nitrate (particulate plus gas) for the dry season. Both solid (s) and ionic (i) forms are shown.

Initially, calcium and bicarbonates are associated in ionic form. When $\text{HNO}_3(\text{g})$ increases, bicarbonates are substituted by $p\text{-NO}_3^-$ to form the solid $\text{Ca}(\text{NO}_3)_2$, and $p\text{-Ca}^{2+}$ follows the same decrease as HCO_3^- ions.

The experimental data at Banizoumbou showed that HNO_3 concentrations never exceeded $1.5 \mu\text{g m}^{-3}$ HNO_3 . The SCAPE numerical analysis supports quantitatively the assumption that gaseous HNO_3 cannot contribute to wet deposition (since it is partitioned to the aerosol phase) and helps explain the weak acidity found in the Sahelian precipitation [Galy-Lacaux and Modi, 1998]. Moreover, this result is very important if we consider other African ecosystems, for example, the humid savanna and/or forests. In the IDAF network, three stations are representative of the humid savanna and forest in unperturbed areas: Lamto, Ngola, and Bomassa (Figure 1). Lacaux *et al.* [1987, 1988, 1992b] studied wet deposition in the African equatorial forest. They experimentally found that the acidity of wet deposition at these sites was high and contained both mineral and organic acids. In the next section, the application of SCAPE to the EXPRESSO measurements (central Africa near Ngola station) allows us to better understand this experimental result. SCAPE prediction will show that the neutralization of HNO_3 over the humid savanna and the forest is not complete and that an important part of HNO_3 remains in the gas phase (thus accounting for the mineral acid in precipitation).

In the dry season, SCAPE also predicts a complete capture of HNO_3 by the mineral aerosols. However, this is in contrast to the gaseous measurements, where we found that gaseous HNO_3 remains in the boundary layer with a mean of $0.5 \pm 0.1 \mu\text{g m}^{-3}$. There are several possible causes for this discrepancy. One possibility is related to the measurement sampling times. The gas samples represent monthly average values, and thus are unable to resolve finer temporal structure of the ambient levels (e.g., diurnal variations, biomass plumes, etc.), while the aerosol samples were 24 hour averages taken once per week. It is known that in the boundary layer, local heterogeneity with strong influence of biomass burning can be important [Delon *et al.*, 2000; Marion *et al.*, 2001] and these features are not captured by the measurement strategy. Furthermore, the time scales to reach equilibrium between the gas and aerosol phase can be long (e.g., 1 to 10 days) [Song and Carmichael, 2001]. For these reasons, it is possible (and probable) that the gas and aerosol measurements do not necessarily represent an equilibrium state, and this could account for the presence of nitric acid in the gas phase (on average) even though the equilibrium state would have nitrate partitioned solely to the aerosol phase.

A second possibility is related to positive "artifacts" in the measurements and modeling analysis, especially related to possible interactions with gaseous nitric acid according the equation:



In our interpretation of the observations and the setting of the initial conditions for the modeling analysis we assumed that in this region the observed sulfate was largely of crustal origin; that is, gypsum. However, the presence of additional sulfuric acid sources would result in reactions such as (R19) and are expected to influence the partitioning of nitrates both in the measurements and in the model. The sulfur modeling studies of Chin *et al.* [1996] and Chin and Jacob [1996], show that biogenic sources of sulfur associated with biomass burning can account for as much as 80% of SO_4^{2-} in the

troposphere throughout the tropics. A biomass burning source of sulfate (via the gas phase oxidation of the emitted SO_2) would provide this source of sulfate in the dry season only and thus could account for the observations of particulate ammonium in the dry season. To test this hypothesis and study the influence of an additional source of sulfate, calculations were performed for various total sulfate concentrations ranging between 1 to $1.7 \mu\text{g m}^{-3}$. Results showed a variation compared with the base case calculation with a proportional increase of particulate ammonium from 0 to $0.2 \mu\text{g m}^{-3}$. Moreover, for higher concentrations of sulfate (around $5 \mu\text{g m}^{-3}$), nitrate was replaced by sulfate and low concentrations of gaseous HNO_3 was predicted. To further test this hypothesis, we need to add the measurement of gaseous SO_2 to the IDAF stations. Passive sampling of SO_2 is now underway, and will help to quantify the additional sources of sulfur in the region.

6.3.3. Dust amount and partition factor. To better understand the partitioning of volatile species between the gas and the aerosol phases, especially nitrate, we investigated in this section the influence of the nonvolatile composition in the two aerosols mode. Two sensitivity tests are performed with (1) various dust amounts; and (2) various partition factors. The objectives of this study are to investigate: first, the influence of the quantities and then the influence of the partition of terrigenous species in order to finally better understand the neutralization of gaseous nitric acid by the mineral particles content.

Calculations were performed for various dust amounts corresponding to variations of terrigenous species concentrations. Concentrations of Ca^{2+} , Na^+ , Mg^{2+} , K^+ , and SO_4^{2-} were varied from 0.5, 2, 3, and 4 times of the base case concentration, with the other species (total chloride, ammonium and nitrate) held fixed with respect to those in the base case. Recall that the main difference between seasons is in the initial volatile nitrate concentration, that is, $0.3 \mu\text{g m}^{-3}$ in the wet season and $\sim 1 \mu\text{g m}^{-3}$ in the dry season. Calculations results are presented in Figure 6 for the dry and wet seasons.

Results of the different calculations indicate that the distribution of $p\text{-NO}_3^-$ in the two modes of the aerosol respond in similar ways for the wet and dry seasons. In the 0.5x case, $p\text{-NO}_3^-$ in the fine mode decreased compared with the base case by a factor 2. This is directly related to the amount of terrigenous species in the fine mode divided by 2 in the ionic form for the wet season and in solid form for the dry season. For the 2x, 3x, and 4x cases we observed for both seasons a quasi-linear increase of the $p\text{-NO}_3^-$ in the fine mode (Figure 6a).

In the wet season we decided to represent only Ca^{2+} to give the general evolution of all the others terrigenous species (Na^+ , Mg^{2+} , K^+). Results showed that Ca^{2+} increased linearly in the fine and the coarse modes with the different calculations (0.5x, 2x, 3x, 4x). For the dry season, Figure 6 only represents the distribution of solid Ca^{2+} . SCAPE predictions for the different calculations found that 94% of $p\text{-NO}_3^-$ was in solid form, as was the case for the mean conditions of the dry season. Moreover, we observed that $p\text{-NO}_3^-$ s exactly followed the same partition that solid Ca^{2+} did in the fine mode. In the 2x case, we observed the opposite result as that found in the base case (62% of $p\text{-NO}_3^-$ in the fine mode and 37 % in the coarse mode). For the 3x and 4x calculations, we reached a limit condition where $p\text{-NO}_3^-$ s was entirely distributed in the fine mode. Figure 6b shows that

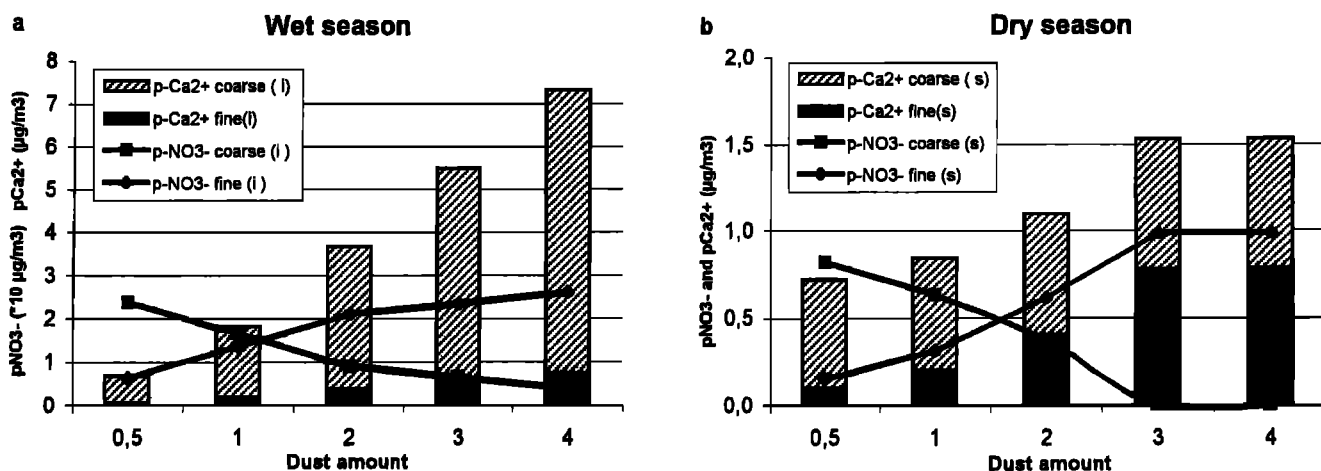


Figure 6. Calculated concentrations of particulate nitrate ($p\text{-NO}_3^-$) and particulate calcium ($p\text{-Ca}^{2+}$) in the fine and coarse mode for various amounts of dust for (a) the wet season and (b) the dry season.

solid $p\text{-NO}_3^-$ concentration in the fine mode is equivalent to the solid Ca^{2+} concentration in the 0.5x, 1x, and 2x. For the 3x and 4x cases, Ca^{2+} concentration is in excess compared with $p\text{-NO}_3^-$. Moreover, it was found that carbonates and bicarbonates concentrations vary according to the proportion of the amount of terrigenous species in the two modes.

We also conducted a sensitivity analysis according to variations of the partition factor. The partitioning of volatile species (especially nitrate) between the gas and aerosol phases is influenced by the nonvolatile composition of the fine and coarse modes. To study the interaction between nitric acid and particulate phase with respect to the partition factor, we varied the partition factor from 0.1 to 0.3. The partition factor is defined as the repartition in percentage of nonvolatile species of the particulate phase in the fine and the coarse modes (section 5.2). This analysis was carried out with the base case of aerosol composition representative of dry and wet season. We found comparable results with the previous analysis related to variations of dust amounts, with the nitrate distribution largely determined by the mineral species. When the partition factor increased from 0.1 to 0.3, more minerals and especially calcium were partitioned into the fine particles. For this reason, the $p\text{-NO}_3^-$ distributions are similar in the 2x and 3x cases in the previous study to those found for partition factors of 0.2 and 0.3, respectively.

The above studies further demonstrate that the partition characteristics of particulate nitrate are governed by the amount of terrigenous material in the two aerosol modes. For the dry season, SCAPE calculations indicate that Ca^{2+} is the key parameter. Furthermore, the neutralization of volatile nitrate occurs first in the fine mode. This result is important if we consider that the fine and coarse mode particles do not have the same atmospheric pathway in the biogeochemical cycles. Fine dust particles (diameter $<1\ \mu\text{m}$) can be transported over long distances [Savoie et al., 1989; Schutz et al., 1981; N'Tchayi Mbourou et al., 1997], while coarse particles are more rapidly removed from the atmosphere with higher dry deposition (gravitational settling) [Seinfeld and Pandis, 1998]. The neutralization of volatile nitrate by fine dust particles can directly affect the chemical nature of dry deposition and also may enable the transport of nitrogenous compound far from their initial sources. This process can take place only if fine particles do not meet clouds and form cloud

condensation nuclei scavenged in precipitation. These result need to be confirmed by experimental observations. Size-resolved aerosol composition measurements are needed.

We can summarize the main results obtained in the analysis of the aerosol composition of the Sahelian region using the SCAPE model. In the calculated aerosol for the wet season, the aerosol is wetted and all the species are predicted to be in an ionic form. This result suggests that heterogeneous processes between gas and mineral particles during the wet season are mainly governed by chemistry in the aqueous phase. The liquid water shell on the particles constitutes a concentrated environment for chemical reactions. We have previously postulated this idea in the interpretation of the main characteristics of precipitation and aerosol chemical composition contents at Banizoumbou [Galy-Lacaux and Modi, 1998]. Concerning the calculations of the mean conditions in the dry season, SCAPE results indicate that some species are in solid form. The most important result shows the association of nitrate and calcium in the solid phase ($\text{Ca}(\text{NO}_3)_2$).

7. Application to EXPRESSO Measurements

The results for the Sahel region can be compared to recent results obtained from humid savannas. The international Experiment for Regional Sources and Sinks of Oxidants (EXPRESSO), designed to investigate processes controlling chemical composition in the tropical troposphere above central Africa, was conducted in November and December 1996. This period corresponds to the beginning of the dry season of the studied region and also to an intense burning activity [Delmas et al., 1999]. The field experiment extended from humid savannas (southern Tchad) to the equatorial forests of the Republic of Congo. Several types of investigations were conducted in this multidisciplinary program. Among these investigations, airborne aerosol samples were obtained and further analyzed for mineral and carbonaceous chemical composition [Ruellan et al., 1999]. The chemical composition of the particles has been interpreted as a function of the different atmospheric layers (i.e., savanna and forest boundary layer, harmattan layer) where particles were collected. Moreover, nitrogen oxides and their oxidation products, and ozone were measured during the

Table 6. Mean Chemical Composition of the Mineral Aerosols Over the Savanna and the Forest for all the Flights in the Boundary Layer During the EXPRESSO Experiment^a.

Concentrations, $\mu\text{g m}^{-3}$	Mean EXPRESSO Flights ($n=15$)
Na ⁺	0.9 ± 0.3
K ⁺	0.8 ± 0.5
Ca ²⁺	0.35 ± 0.30
Mg ²⁺	0.08 ± 0.06
SO ₄ ²⁻	3.3 ± 1.8
Cl ⁻	0.3 ± 0.2
NO ₃ ⁻	0.6 ± 0.4
NH ₄ ⁺	0.4 ± 0.2

^aThe number n of samples are in parenthesis.

airborne EXPRESSO experiment, allowing the estimation of gaseous HNO₃ profiles in the troposphere (from the boundary layer to harmattan layer) [Marion et al., 2001].

In this section we performed an analysis using the one-bin SCAPE gas-aerosol equilibrium model [Kim et al., 1993a, 1993b; Kim and Seinfeld, 1995]. This modeling analysis was performed (1) to simulate the interactions between the gas and ionic particulate phases in order to help interpret the EXPRESSO experimental data; (2) to compare modeling results for different African ecosystem, that is, humid savanna and forest (central Africa) with semiarid savanna (Sahel).

The initial data set representative of the EXPRESSO experiment was prepared using the mean ionic inorganic aerosol composition for all the EXPRESSO flights (Table 6). We used averaged meteorological conditions measured in the boundary layer over the forest and the savanna [Delon et al., 2000]. We used gas measurements performed in the IDAF program at the station of Ngola. (Ngola was also an intensive ground station during the EXPRESSO program). The mean concentration of ammonia (NH₃) determined at Ngola in the

dry season was $\approx 3 \mu\text{g m}^{-3}$ (Table 3), and the mean concentration of nitric acid (HNO₃) was estimated from NO₂ (NO₂-NO_x) measurements during EXPRESSO was $4.6 \mu\text{g m}^{-3}$ [Marion et al., 2001; Ruellan et al., 1999]. The simulation conditions are summarized in Table 7. It is interesting to note that the mean chemical composition for all the EXPRESSO flights (forest and savanna) are similar to the mineral aerosol chemical composition of the harmattan layer [Ruellan et al., 1999].

As discussed by Ruellan et al. [1999], the EXPRESSO aerosol is a combination of a high content of carbonaceous (graphitic carbon + organic carbon + inorganic coating) and a relatively small amount of mineral aerosols. The inorganic soluble part of the aerosol contains two main contributions. First, a terrigenous contribution with mean concentrations of 0.35 ± 0.30 , 0.08 ± 0.06 , 0.8 ± 0.5 , 0.9 ± 0.3 , $3.3 \pm 1.8 \mu\text{g m}^{-3}$ for Ca²⁺, Mg²⁺, K⁺, Na⁺, SO₄²⁻, respectively. Low concentrations of Ca²⁺ and Mg²⁺ confirm the small amount of mineral particles measured in EXPRESSO, compared for example with concentrations registered in the Sahelian region [Galy-Lacaux and Modi, 1998]. A small portion of the SO₄²⁻ measured in the aerosols was provided by gypsum (Ca₂SO₄) contained in soils [Loÿe-Pilot et al., 1986; Bohm et al., 1985]. Sulfate originated mainly from the secondary conversion of SO₂ emitted by fires [Ruellan et al., 1999]. In addition to terrigenous K⁺, the high levels of K⁺ reflect the biomass burning source during the dry season in central Africa. The second major contribution in the aerosol is a nitrogenous component with $0.6 \pm 0.4 \mu\text{g m}^{-3}$ of NO₃⁻ and of $0.4 \pm 0.2 \mu\text{g m}^{-3}$ of NH₄⁺. We assumed that measured nitrates in the aerosol phase represent the final result of interactions between HNO₃, and atmospheric particles [Cachier et al., 1991; Dentener et al., 1996; Galy-Lacaux and Modi, 1998; Ruellan et al., 1999]. In the same way, ammonium in the aerosol results in the incorporation of NH₃ and also from ammonium salt contained in the soil. The relatively high concentrations of NH₄⁺ could be an indicator of the intense biomass burning source during the EXPRESSO experiment [Ruellan et al., 1999].

Table 7. Initial Conditions Representative of the Humid Savanna and Equatorial Forest in Central Africa (EXPRESSO Experiment) for SCAPE Model Simulations.

Parameters	Values
Temperature, K	304
Relative Humidity, %	64
CO ₂ concentration, ^a ppm	360
Mineral particle composition, ^b $\mu\text{g m}^{-3}$	
ss-Na ⁺	0.167
nss-Na ⁺	0.693
nss-K ⁺	0.834
nss-Ca ²⁺	0.344
nss-Mg ²⁺	0.061
nss-SO ₄ ²⁻	3.258
Total composition of volatile components, $\mu\text{g m}^{-3}$	
t-ammonium	3.5
t-nitrate	5.2
t-chloride	0.3

^aBoth carbonate and bicarbonate ion concentrations are estimated by constraints in the SCAPE module to meet ion balance in each mode when nonvolatile cation composition is input.

^bSea-salt (ss) and non-sea-salt (nss) contribution of each species to mineral particles composition is calculated according to Keene et al. [1986] ratios in seawater

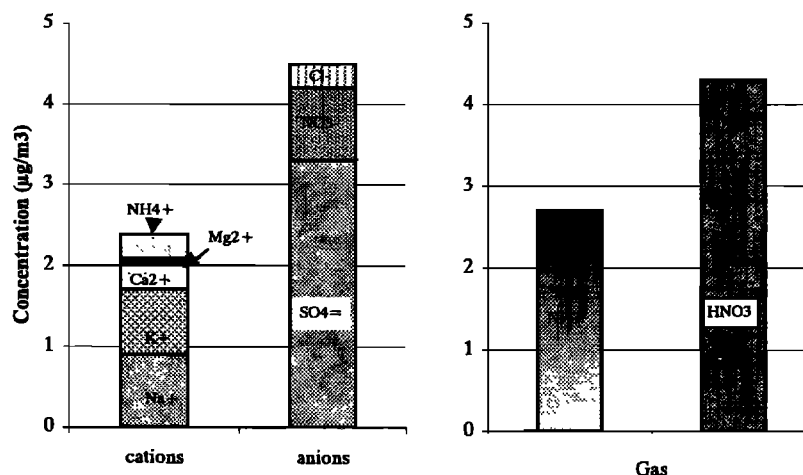


Figure 7. Calculated mean aerosol and gas composition for the EXPRESSO simulation representative of the wet savanna and forest. Species are shown as ions in $\mu\text{g m}^{-3}$.

The calculated aerosol composition for the mean conditions during the EXPRESSO experiment is presented in Figure 7. Both solid and ionic phases were predicted. However, to expose the results in a simple way, each species is presented as an ion. SCAPE predicted that the aerosol was wetted and contained $\sim 3 \mu\text{g m}^{-3}$ of water. The second important result is that for these EXPRESSO conditions particulate nitrate ($p\text{-NO}_3^-$) and particulate ammonium ($p\text{-NH}_4^+$) were both predicted; with $p\text{-NO}_3^-$ and $p\text{-NH}_4^+$ concentrations of 0.9 and $0.3 \mu\text{g m}^{-3}$, respectively. These values are in the same order of magnitude as the experimental measurements ($0.6 \pm 0.4 \mu\text{g} [\text{NO}_3^-] \text{m}^{-3}$ and $0.4 \pm 0.2 \mu\text{g} [\text{NH}_4^+] \text{m}^{-3}$). This result is in contrast to the Sahelian simulations. This result confirms the critical influence that sulfate plays in determining $p\text{-NH}_4^+$ formation (as discussed in section 6.3). Furthermore the simulation results indicate that the cations in the mineral aerosol (Na^+ , Ca^{2+} , Mg^{2+} , K^+) only partially neutralized the gaseous HNO_3 , with a fraction of HNO_3 partitioned to the gas phase ($\sim 4 \mu\text{g m}^{-3}$). This result is also in agreement with the analysis of EXPRESSO experimental data [Ruellan *et al.*, 1999; Marion *et al.*, 2001]. Volatile chloride was predicted to be partitioned between the particulate phase ($p\text{-Cl}^-$) with a concentration of about $0.3 \mu\text{g m}^{-3}$. The predicted concentration of $p\text{-Cl}^-$ compares well with the experimental data ($0.3 \pm 0.2 \mu\text{g m}^{-3}$). No measurements of $\text{HCl}(\text{g})$ were performed during the experiment. In addition, it was calculated that half of the particulate calcium ($p\text{-Ca}^{2+}$) and all the SO_4^{2-} were present in solid form. This implies that Ca^{2+} is mainly associated with SO_4^{2-} to form gypsum (Ca_2SO_4). Finally, it was predicted that the studied aerosol did not contain any carbonates/bicarbonates, indicating the ability of the volatile nitrates to displace all the carbonates initially associated with terrigenous species.

Compared to the SCAPE predictions in the Sahelian region, the EXPRESSO simulation shows that the neutralization of HNO_3 over the wet savanna and the forest cannot be complete and that an important part of HNO_3 remains in the gas phase. This result is consistent with the EXPRESSO measurements and confirms the hypothesis of Ruellan *et al.* [1999] concerning the presence of heterogeneous processes between mineral aerosols and gaseous nitric acid over savanna and forest ecosystems.

SCAPE results are also in agreement with Dentener *et al.* [1996] simulation of the ratio of nitrate present on mineral dust in the central Africa.

These results have important implications regarding dry deposition processes. As we explained for the semiarid savanna, dry deposition of HNO_3 may be significantly altered when HNO_3 reacts with mineral aerosol over the humid savanna and forests. Moreover, the EXPRESSO simulation corresponds to the end of the wet season and the beginning of the dry season in central Africa. In the wet season, over humid savanna and forest, the atmosphere is less influenced by dust because of the reduction of dust transport from semiarid region and scavenging by clouds. Measurements in the wet season of the humid savanna of Lamto [Cachier *et al.*, 1991] show low levels of mineral compounds in the aerosol phase compared to those observed in EXPRESSO. If we consider the nonnegligible mean gaseous HNO_3 concentrations measured at the station of Ngola (around $0.5 \mu\text{g m}^{-3}$) in the wet season, SCAPE predictions in central Africa suggest that the partitioning between the gaseous and the particulate phase is also in favor of the gas phase in the wet season; as is the case in the dry season. This assumption could help to explain the high levels of acidity measured in the precipitation over the equatorial forest according to the availability of HNO_3 to contribute to the acidity of the wet deposition and confirms Lacaux *et al.* [1987, 1988, 1992b] experimental results.

8. Conclusion

Aerosols representative of the wet season in 1996 have been analyzed in the Sahelian region in a previous work [Galy-Lacaux and Modi, 1998]. In this paper, we analyzed the aerosol composition of the dry season and gas concentrations in the same region. Moreover, we performed a modeling analysis using the entire data set with a two mode gas/aerosol equilibrium model named SCAPE [Kim *et al.*, 1993a, 1993b; Kim and Seinfeld, 1995]. The mean mineral aerosols composition in both seasons showed no significant differences, especially for terrigenous compounds concentrations (Ca^{2+} , Mg^{2+} , Na^+ , K^+ , and SO_4^{2-}). The station of Banizoumbou is shown to be mainly influenced by mineral particles produced by semiarid and Saharan soil erosion. This

terigenous contribution confers to the aerosol a strong alkalinity. The major difference in the aerosol composition during the wet and dry seasons is related to nitrate concentrations which are higher in the dry season. It is explained by higher concentration of gaseous HNO₃ produced by the biomass burning. Particulate ammonium and gaseous ammonia were found to be independent of season. Finally, we found that the aerosol of the Sahelian region has two major signatures, that is, terrigenous and nitrogenous. Moreover, the analysis of gas measurements coupled with mean aerosol composition, and the analysis of aerosol and precipitation chemical composition of *Galy-Lacaux and Modi* [1998], allow us to conclude that there are important interactions between mineral particles and nitrogenous gaseous compounds. The alkalinity of particles strongly favors the uptake of nitrogenous compounds, especially nitric acid.

We used the SCAPE model in this study to further investigate the interactions between mineral particles and nitric acid and to help interpret IDAF experimental data. We found that the model accurately represents the mean aerosol and gas chemical composition of the Sahelian region in the dry and the wet season. The model predictions accurately simulated the interactions between HNO₃ and terrigenous

compounds. Nonvolatile cation species (Ca²⁺, Mg²⁺, Na⁺, K⁺) were found to neutralize gaseous HNO₃ in the two modes and were identified as the key parameter to retain nitrate in the aerosol phase for the both seasons. Moreover, particulate nitrate was found to first neutralize in the fine mode. In the Sahelian region, nonvolatile cations species are sufficient to entirely neutralize gaseous HNO₃. Results indicated that the particulate nitrate fraction is insensitive to temperature, relative humidity, and gaseous ammonia concentration. Caution should be taken here according to the predictions of particulate ammonium, where the model analysis could not account for observed *p*-NH₄⁺ levels. The extended version of SCAPE [Hayami and Carmichael, 1997, 1998; Meng et al., 1995] predicted significant amounts of carbonates and bicarbonates concentrations for both seasons, needed to equilibrate the ion balance of the aerosol.

Moreover, the SCAPE model has been applied to other African ecosystems, that is, humid savanna and forest in central Africa. In addition to IDAF gaseous measurements, we used aerosol chemical composition and gaseous profiles measured during the airborne EXPRESSO experiment. In this case, the mineral amounts of species concentrations are no longer sufficient to neutralize completely HNO₃(g), as it was

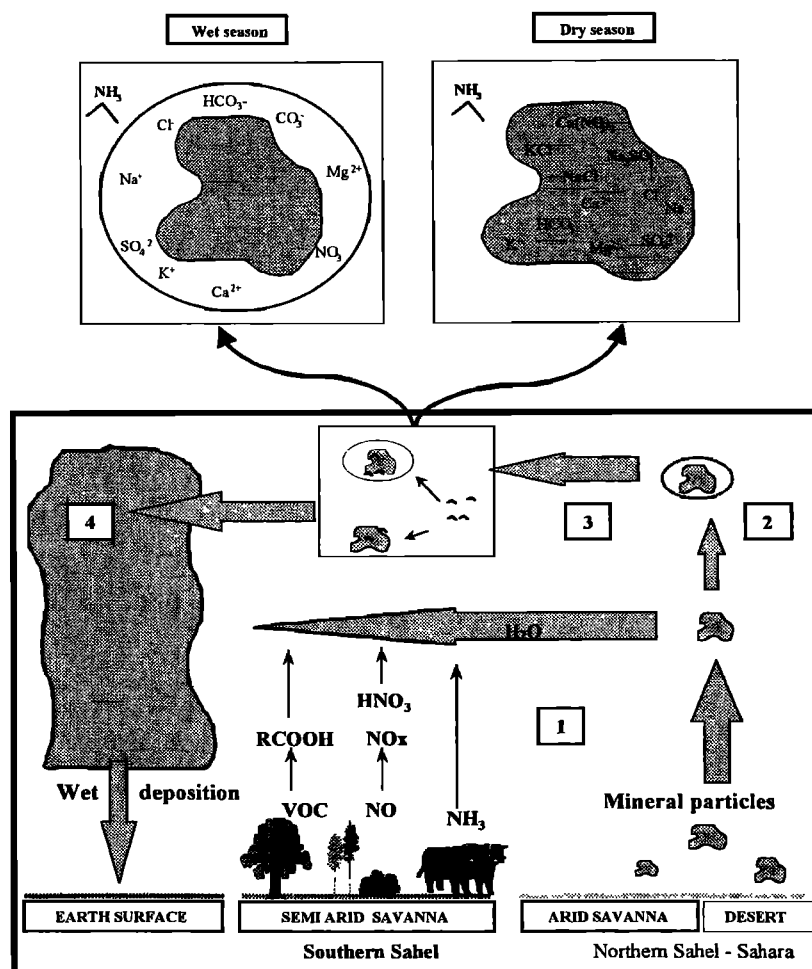


Figure 8. Conceptual model of atmospheric chemistry in the Sahelian region adapted from *Galy-Lacaux and Modi* [1998]. The zoom in upper panels shows the heterogeneous processes between gas and particles for the wet and dry season. Species in bold indicate species in the solid form, other species are in the ionic form, and the smallest characters indicate lower concentrations.

the case in the Sahel. The EXPRESSO simulation allows us to accurately represent (1) heterogeneous processes occurring between mineral aerosols and gaseous nitric acid over savanna and forest ecosystems in the dry season and (2) the mean gaseous and mineral aerosol composition measured over the wet savanna and the forest.

The entire modeling analysis indicates that the SCAPE model can provide a valuable analysis of the equilibrium gas-aerosol representative of the semiarid and wet savanna, and the forest ecosystems in Africa. These numerical calculations provide the first successful analysis of heterogeneous processes between gas and particles in the IDAF Africa measurements.

This analysis leads to a good prediction of the mean aerosol composition and gas concentrations in the Sahelian region. The model provides a better understanding of the chemical reactions involved in the neutralization process between HNO_3 and mineral particles during the dry and the wet seasons. To represent these main results, we propose to detail the step 3 of our previous conceptual model of the atmospheric chemistry in the Sahelian region (Figure 8). For the wet season we assume that the heterogeneous processes occurring between gas and mineral particles are mainly governed by chemistry in the aqueous phase. Concerning the dry season, gas/particle interactions occur both in ionic and solid form. The most important result shows that the neutralization of HNO_3 is mainly performed by calcium to form the solid $\text{Ca}(\text{NO}_3)_2$.

Finally, these results point out the major role of heterogeneous processes in the Sahelian region in regulating the atmospheric chemical composition (gas and particles) and affecting wet and dry deposition chemical characteristics. In the tropics and in Africa, understanding gas/particles interactions, that is, heterogeneous and multiphase reactions, is key in the assessment of the atmospheric chemistry. This assumption has been previously emphasized by authors such as Dentener *et al.* [1996], Ravishankara [1997], Andreae and Crutzen [1997] and Galy-Lacaux and Modi [1998]. The African atmosphere is an excellent opportunity for studying these interactions, and this study demonstrates that IDAF measurements are adapted to study both experimentally and numerically heterogeneous processes in Africa. In this way, there is a clear need to perform additional observations in the tropics with simultaneous measurements of gas, aerosol, and precipitation chemistry. This is the aim of the IDAF project for Africa to provide data on long-term evolution trends, essential to identify the main factors that regulate the tropical atmospheric chemistry.

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