



# Activities Newsletter

*of the International Global Atmospheric Chemistry Project*

**Issue No. 27  
January 2003**

**DEBITS Special Issue**

## In this Issue

**A Note from the Chair**

### **Science Features**

- 2 Debits: Past, Present, and Future
- 6 Dry and wet atmospheric nitrogen deposition in Africa
- 12 Dry and wet deposition in Amazonia
- 17 Acid wet deposition in the Tropics
- 20 Heterogeneous processes involving nitrogenous compounds
- 23 Measurement of sulfur dioxide, ozone and ammonia concentrations in Asia, Africa, and South America
- 25 Correction
- 26 Announcements

## **A Note From the IGAC Co-Chairs: *Mary Scholes and Tim Bates***

IGAC has made great progress over the year in reviewing the last decade of research as well as preparing for the future. After a number of meetings and extensive consultation the Science Plan and Implementation Strategy for the second phase of IGAC is nearing completion and is posted on the IGAC web site. We would like to thank all those who have commented so positively and provided written material and graphics.

In the review process, one of the long-standing activities (Deposition of Biogeochemically Important Trace Species - DEBITS) was highlighted as being an extremely successful entity of IGAC I. In the 1990s, due to the lack of information on wet deposition in the tropics, a co-operative program was undertaken, involving the Global Atmosphere Watch Project (GAW) of the World Meteorological Organisation and the DEBITS activity of IGAC, mostly in Asia. This was followed by the Composition and Acidity of the Asian Precipitation (CAAP) program, later expanded into Africa and South America. The results of these studies are the focus of this issue of the newsletter. DEBITS is a program that has fulfilled many much needed functions. At all conferences and meetings of IGAC/CACGP, processes associated with emissions were always given much more emphasis than those associated with deposition. It was only through the continual persuasion of Henning Rodhe and Jean-Pierre Lacaux that the DEBITS program grew into the success it is today.

The participants have worked long and hard to establish their networks, ensuring that the data emerging are of the highest quality. They have focused in the tropics where the data needs were greatest and slowly the gaps are being filled. Our understanding of wet and dry deposition has been much improved. Standardized measurement protocols have led to improved wet deposition calculations and dry deposition estimations. In addition to the excellent science that has emerged, the program has been extremely successful in training researchers and students from developing countries by having a range of activities including training workshops and exchanges and visits of researchers and students. This is highly commendable.

Another IGAC highlight this year was the 7th IGAC Scientific Conference/10th Symposium of the International Association of Meteorology of Atmospheric Sciences (IAMAS) Commission for Atmospheric Chemistry and Global Pollution (CACGP). We would like to thank Maria Kanakidou, the Science Program Committee, the Local Organizing Committee, and our many sponsors for this extremely successful and well attended meeting. Highlights from the conference will be the subject of the next IGAC newsletter.

As we begin the next phase of IGAC we would like to encourage atmospheric scientists to join us in international atmospheric chemistry research that will lead to a better understanding of the Earth System. Guidelines for proposing IGAC Research Tasks are now on the IGAC website. We look forward to another exciting decade of international research.

GLOBAL  
I G B P  
CHANGE

CACGP

# SCIENCE FEATURES

## DEBITS: Past, Present, and Future

Contributed by **Jean-Pierre Lacaux** (lacaux@medias.cnes.fr), *MEDIAS-France, 18 Avenue E. Belin, 31401 Toulouse Cedex 4, France*, **Paulo Artaxo** (artaxo@if.usp.br) *Instituto Fisica, Universidade de Sao Paulo, Rua do Matao, Traverssa R – 187, CEP 05508-900, Sao Paulo, S.P., Brazil*

### Why study atmospheric deposition?

The concentration of a chemical substance in the atmosphere depends on several interacting mechanisms, such as:

- amplitude of the source of the substance or of its precursors
- transport and dynamic transfer in the atmosphere
- chemical evolution of the substance including formation from other chemical compounds
- amplitude of the dry and wet deposition of the substance or of the associated compounds

For an atmospheric chemist, it is fundamental to understand and quantify fluxes of chemical compounds while they are being transported by atmospheric circulation. Deposition is a critical part of this system.

In general, the spatial and temporal scale of deposition depends on the lifetime of atmospheric gases and aerosols which is determined by their chemical reactivity in the atmosphere. As noted by Paul Crutzen, “the atmosphere is an oxidizing machine which produces hydroxyl radical from tropospheric ozone.” Hydroxyl radical reacts with a large number of molecules. The resulting oxidized products are generally more water soluble, and consequently, more rapidly scavenged from the atmosphere. It is remarkable to note that a very small hydroxyl radical concentration controls the composition of the atmosphere and therefore influences key ecological processes on Earth.

The atmospheric deposition of chemical species within the Earth’s biosphere, hydrosphere, lithosphere, and cryosphere not only provides a natural sink but acts also as a source of nutrients. Examples include:

- iron deposition to the ocean is a limiting factor in algae blooms
- nitrogen and/or phosphorus deposition is essential to the function of terrestrial ecosystems and therefore essential in regulating the global carbon cycle
- acid deposition has hindered the ability of some affected ecosystems to neutralize acidity, and while

it has declined in North America and Europe, it is a growing problem in Asia

- the biogeochemical cycling of many chemical species has been grossly perturbed by anthropogenic activities in many regions where atmospheric deposition has become an important source of toxic substances to the biosphere

### Why study atmospheric deposition in the Tropics?

The IGAC project was initiated in the 1990 in response to growing international concern about rapid atmospheric composition changes and the potential impact on mankind. A major success of IGAC has been the initiation of projects investigating atmospheric chemistry in the Tropics which have stressed the important influence of tropical atmospheric chemistry on global atmospheric composition. The primary reasons for focusing on the tropical regions include:

- urbanization, industrialization, agriculture and biomass burning are increasing rapidly, producing significant emissions of trace gases and aerosol particles
- high UV radiation flux, high temperature, and high atmospheric water vapour content promote intense photochemistry all year round
- deep convection provides rapid vertical transport that lifts substances emitted at the surface efficiently into the upper troposphere, lengthening their lifetime

These unique characteristics inspired Paul Crutzen to summarize the importance of the Tropics by stating that “the Tropics are the washing machine of the planet, the hydroxyl radical being the detergent.”

### DEBITS: past and present activities

In 1990, a cooperative research program was conceived to address the scarcity of atmospheric deposition data. The Global Atmosphere Watch (GAW) of the World Meteorological Organisation (WMO) and IGAC established the Deposition of Biogeochemically Important Trace Species (DEBITS) activity.

The DEBITS scientific objectives, as stated in the original IGAC operational plan, were:

- to determine, through quality-controlled measurements, the atmospheric removal rates of biogeochem-

ically important trace species by dry and wet depositional processes

- to investigate the chemical and physical factors that regulate deposition fluxes

To accomplish these objectives, the first actions of the DEBITS committee included the definition of experimental and analytical protocols to ensure data quality (Box 1) and the establishment of guidelines for inter-comparisons of wet and dry deposition measurements for all DEBITS stations.

In 1998, the scientific objectives of DEBITS were redefined and as follows:

- to determine, at the regional scale, and mainly through measurements, the atmospheric removal rates of biogeochemically important trace species by dry and wet deposition
- to resolve atmospheric budgets of key elements (S, N, Ca, Cl ...) at the regional scale
- to ascertain the chemical and physical factors that regulate deposition fluxes and to develop parameterizations to be integrated into regional and global atmospheric chemistry models

The organizational framework of DEBITS was established with the initiation of three scientific programs in important tropical regions: Composition and Acidity of Asian Precipitation (CAAP) in 1990, IGAC DEBITS Africa (IDAF) in 1994, and the Large Scale Biosphere Atmosphere Experiment in Amazonia (LBA) in 1998. A map of the DEBITS network is presented in Figure 1.

## The CAAP program

CAAP began in 1990 following the publication of Acidification in Tropical Countries by Rodhe and Herrera (1988). At that time, it was acknowledged that there was a major gap in our knowledge of deposition in Asia. This was particularly true for high quality monitoring data and regionally representative deposition data. Indeed, most of the existing wet deposition studies had been limited to urban areas. The main goals of CAAP were:

- to quantify the wet deposition component of the atmospheric cycles of nutrients such as S, N, C, P and sea salt
- to assess the current rate of rainwater acidity throughout the region and to identify the acid/basic species involved

CAAP has organized workshops within the region several times during the past decade including Singapore in 1990, Bombay in 1992, and Bangkok in 1998. The purpose of these meetings was to discuss the achievements of the program up to that time and to propose future goals. These included the measurement of the chemical composition of precipitation and the surface air concentration of reactive trace gases and aerosol particles from which dry deposition can be estimated. Additional agenda items included the discussion of procedures for quality control, the representativeness of measurement stations and the publication of results.

### Box 1 – DEBITS experimental and analytical protocols

DEBITS measurements require the adoption of standardized rainwater sampling, preservation and chemical analysis. To obtain comparable and high quality data sets for precipitation chemistry, a standard experimental strategy was established which includes:

- wet-only sampling for a specific event or a daily basis,
- efficient preservation of chemical content using a biocide or freezing
- use of U.S. Environmental Protection Agency criteria based on ionic and conductivity balances,
- annual analytical laboratory performance check with WMO protocols for chemical analysis

Dry deposition measurements require measurement of gaseous concentrations by passive gas sampling for SO<sub>2</sub>, NO<sub>2</sub>, NH<sub>3</sub>, HNO<sub>3</sub> and O<sub>3</sub>. Dry deposition of particles will be estimated from PM<sub>10</sub> sampling, or in two size classes (fine and coarse modes), on membrane filters followed by chemical analysis.

## The IDAF program

The scientific objectives of the IDAF program were defined at the Yamoussoukro Workshop in Ivory Coast in 1994. Fifty participants attended this meeting, representing nineteen African countries (Morocco, Algeria, Tunisia, Senegal, Mali, Niger, Burkina-Faso, Ivory Coast, Ghana, Benin, Togo, Nigeria, Central Africa, Cameroon, Congo, Kenya, Zambia, Zimbabwe and South Africa), international organizations (WMO, START/IGBP, IGAC/DEBITS, EC, and the French mission of Co-operation) and experts in tropical atmospheric chemistry. The text that outlines the IDAF objectives, which was unanimously adopted by the participants, is presented below.

IDAF rationale - DEBITS/AFRICA acknowledges the global importance of biomass burning, land use change and industrial activity resulting from rapid population growth. These activities lead to significant anthropogenic emissions and desertification, which may generate atmospheric reactive carbon, nitrogen, sulphur, and dust. These compounds are likely to produce:

- atmospheric acidity and acid deposition which adversely effect vegetation, soil, and water systems
- high levels of aerosol haze which produces a significant forcing on global climate
- related effects, e.g. high tropospheric ozone concentrations as a result of precursor emissions

IDAF objectives - considering the contributions of biomass burning and desertification (soil dust) to atmospheric chemistry, especially in Africa, the objectives of DEBITS/AFRICA are:

- to estimate the flux of important chemical species (especially N, C [organic acids], and S) from measurements of wet and dry deposition at regionally representative sites
- to identify the relative contributions of natural and anthropogenic sources to these deposition fluxes

These objectives have been addressed by an initial measurement program which included:

- rainwater sampling for chemical analysis
- measurement of SO<sub>2</sub>, NO<sub>2</sub> and organic acid concentrations (to estimate dry deposition flux)
- collection of bulk aerosol samples for chemical analysis (to estimate dry deposition flux)

Ten IDAF sites representative of the great African ecosystems are operating in 2002 and several meetings have been organized (Abidjan 1995, Toulouse 1998 and 2001). African scientists in charge of monitoring stations have also visited Toulouse (1 to 3 months). A database including

the description of the stations and chemical analyses with rainfall, gaseous, and particles data is available at <http://medias.obs-mip.fr>.

## The LBA program

Amazonia is an important tropical region that is pressured by land use and land cover changes. The LBA experiment is a large (more than 700 researchers) and long term (about 10 years) research effort intended to improve our understanding of the function of this key tropical ecosystem. Within the scope of the LBA program, 4 wet and dry deposition sampling stations have been constructed in Brazil. In 1998, a sampling station in Petit-Saut, French Guiana, implemented within the IDAF framework, was integrated into the LBA network.

One of the foci of the 5 wet and dry deposition stations is to determine the importance of the atmospheric contribution to nutrient cycling in natural and secondary forests and managed lands. The natural forest has developed an unusual and efficient phosphorus exchange mechanism. The aerosol component of this cycle is a critical part of the mechanism. Observations at the five DEBITS sites, located along gradients of land use intensity and climate, have been performed over several years. These data are complemented by periodic large scale airborne observations and intensive ground based experiments. An overview of scientific results is presented in this issue.

## The future of DEBITS

The DEBITS activity consists of two primary foci; the production of quality-controlled measurements of precipitation chemistry, aerosols, and gases and the use of these data to estimate wet and dry deposition of chemical species and the factors that regulate these fluxes. The three DEBITS projects – CAAP, IDAF and LBA – have produced 3 to 8 years of measurements. These data will be used to estimate deposition and associated processes with a goal of developing parameterizations that can be integrated into nutrient cycling and atmospheric chemistry models.

In Africa, each DEBITS site is under the scientific and technical responsibility of African scientists. From these measurements, 9 Ph.D. theses (3 in Ivory Coast, 2 in South Africa, 1 in Niger, Cameroon, Congo and RCA) have been defended and 4 are still in progress. In addition, synthesis papers have been published for dry savanna ecosystems (Sahel and South Africa), submitted for forests ecosystems (Congo, Cameroon and French Guyana), and in preparation for wet savannah ecosystems.

In Asia, the scientific collaboration and activities are similar to those in Africa. However, measurements have been organized geographically rather than on an ecosystem



basis. Results are in publication or to be submitted that describe measurements in countries with DEBITS sites including Australia, China, India, Indonesia, Malaysia, Singapore, Thailand and Vietnam.

In Amazonia, the situation is distinctive because of the intense collaboration and merging of DEBITS and LBA which allows high quality validation of measurements (see article in this issue). This type of scientific interaction between a regional program and DEBITS is an ideal model for the future implementation of DEBITS. The linkage between atmospheric deposition and regional development strategies is not only critical for Amazonia but also for tropical regions around the world.

In the near future, DEBITS must take into consideration the evolving goals of IGAC and IGBP as they enter their next phase. The new structure of IGBP includes six research activities focused on the three primary Earth System components (ocean, land, and atmosphere) and the interfaces between them. Atmospheric deposition studies position DEBITS at the interface of the land and atmosphere. The IGAC steering committee has proposed to integrate DEBITS within the new Land – Atmosphere project (iLEAPS).

DEBITS can also serve as a model for the new projects within the integrated Global Change programs (IGBP, IHDP, WCRP and DIVERSITAS) as they develop Integrated Regional Studies. These interdisciplinary regional studies will focus on specific regions which are thought to be of primary importance for the functioning of the Earth system. An integrated social, economic, and physico-chemical approach will maximize the benefit of

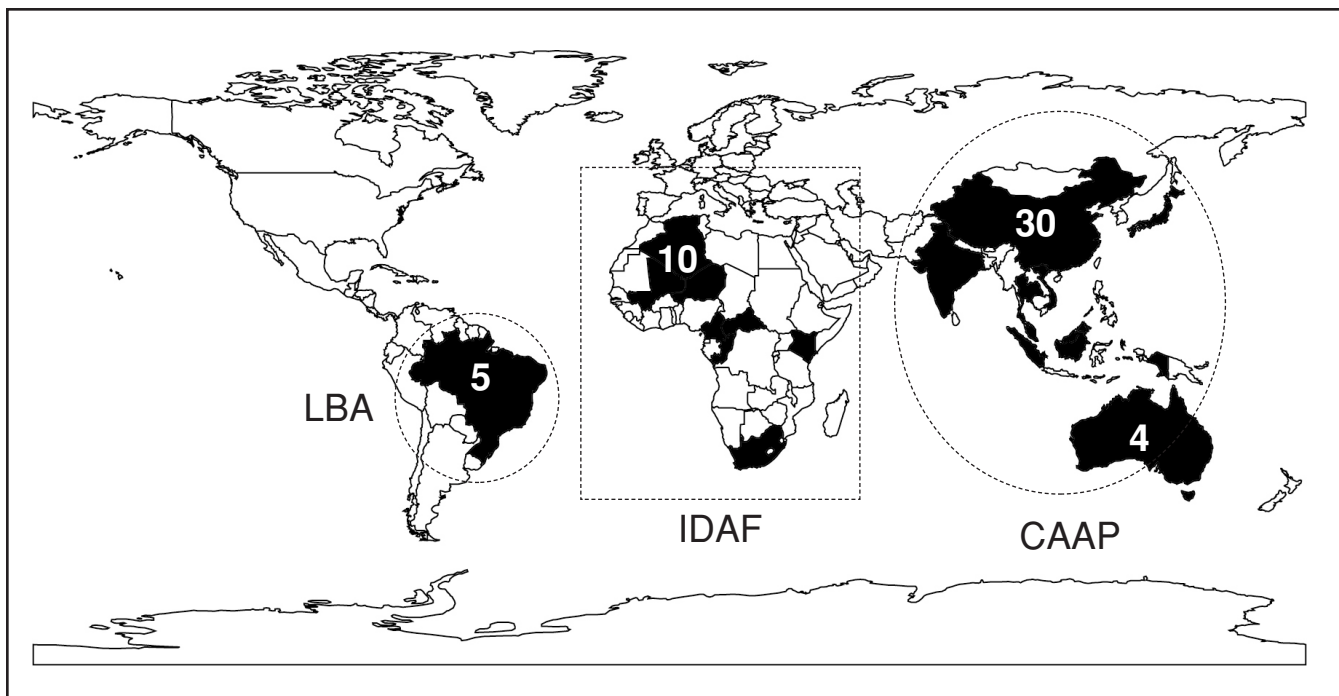
this large international and integrated research effort. DEBITS could adopt a dual approach in the future:

- 1) A network strategy that maintains the existing measurement structure, including already established collaborations, and continues dry deposition measurements and associated modelling activities with a goal of producing long term data sets. These data can be used to address the significant questions that remain in our understanding of key aspects of the chemical processes that regulate the multiple phases (gas, aerosol, clouds) of deposition,
- 2) An integrated regional strategy within the new global scientific context of IGBP II. The iLEAPS framework and the Integrated Regional studies appear to favour an approach similar to the regional tactic used by LBA in Amazonia.

To implement this dual approach, a team of 3-4 DEBITS scientists from the existing activity will compose a new DEBITS science plan. Following the advice of the present convenors, this team will include Paulo Artaxo (LBA), Kobus Pienaar (Africa), and one or two members from the Asian component. The enthusiastic support of all DEBITS scientists will be essential to ensure the continuing success of the DEBITS activity.

## REFERENCES

*Acidification in Tropical Countries*, H. Rodhe and R. Herrera (eds.), SCOPE 36, John Wiley & Sons, UK, 1988. <http://www.icsu-scope.org/>



**Figure 1** - DEBITS network in 2002. Numbers indicate the number of stations in each region.

# Dry and wet atmospheric nitrogen deposition in Africa

Contributed by **Corinne Galy-Lacaux** (lacc@aero.obs-mip.fr), **H. Al Ourabi**, **Jean-Pierre Lacaux**, **V. Pont**, *Laboratoire d'Aérodologie, UMR Université Paul Sabatier/CNRS 5560, Observatoire Midi-Pyrénées Toulouse, France*, **J. Galloway**, *Environmental Sciences Department, University of Virginia, P.O. Box 400123, Charlottesville, VA 22904-4123 (USA)*, **J. Mphepya**, **K. Pienaar**, *School of Chemistry and Biochemistry, University for Christian Higher Education, 2520 Potchefstroom (South Africa)*, **L. Sigha**, *Centre de Recherches Hydrologiques BP 4110 Yaoundé (Cameroun)*, **V. Yoboué**, *Laboratoire de Physique de l'Atmosphère d'Abidjan, Université de Cocody, Abidjan, 04 BP 322 Abidjan 04, Côte d'Ivoire*.

## Introduction

This work is part of the IDAF (IGAC/DEBITS/Africa) program which began in 1995 with the establishment of 10 measurement sites representative of major African ecosystems (Figure 1). The objectives of the program are to study dry and wet deposition of important trace species, and more generally, the biogeochemical cycles of key nutrients. In support of these objectives, the IDAF program produces high quality measurements of atmospheric chemical data (gaseous, precipitation, and aerosol chemical composition) on a multi-year monitoring basis.

The atmosphere is a critical environment for the nitrogen cycle. In 1990, ~140 Tg N were converted from N<sub>2</sub> to reactive N (e.g., NO<sub>x</sub>, NH<sub>3</sub>) through worldwide energy and food production. A large portion of this N was emitted into the atmosphere as NO<sub>x</sub> (~34 Tg N) and NH<sub>3</sub> (~43 Tg N). All of the emitted NO<sub>x</sub> and NH<sub>3</sub> were deposited to the earth's surface, primarily to the continents (Galloway and Cowling, 2002). There are significant impacts when N is emitted into the atmosphere (Vitousek et al., 1997). There are also impacts of the N following its deposition, and there are additional impacts as N cascades along its biogeochemical pathway. The 'Nitrogen Cascade' (Galloway, 1998) can be characterized as the sequential transfer of reactive nitrogen through environmental systems. This results in environmental changes as N moves through or is temporarily stored within each system. For example, NO<sub>x</sub> is emitted to the atmosphere from soils, biomass burning and fossil fuel combustion. In sequence, an atom of N mobilized as NO in the atmosphere can first increase ozone concentrations, then decrease atmospheric visibility and increase concentrations of small particles, and finally

increase precipitation acidity. Following deposition to terrestrial ecosystems, that same N atom can increase soil acidity, decrease biodiversity, and either increase or decrease ecosystem productivity. When discharged into surface waters, the N atom can increase surface water acidity, and lead to coastal eutrophication. If the N atom is converted to N<sub>2</sub>O, and emitted back to the atmosphere, it can increase greenhouse warming potential, and decrease stratospheric ozone. A similar 'cascade' occurs for NH<sub>3</sub> emitted to the atmosphere. An important characteristic of the 'cascade' is that once it starts, the source of the N emitted to the atmosphere (e.g., biomass burning, fossil fuel combustion, fertilizer use, animal waste) becomes irrelevant.

DEBITS/AFRICA acknowledges the global importance of biomass burning, land use changes, and industrial activities associated with rapid population growth. These activities lead to important anthropogenic emissions and desertification which may produce atmospheric reactive carbon, nitrogen, sulphur and dust. Matson et al. (1999) suggest that the excess nitrogen in tropical systems might pre-dispose these regions to a rapid and negative response to increased nitrogen deposition. In this context, the IDAF program has provided the first atmospheric chemistry database focussed on atmospheric deposition on the African continent.

In this paper, our main objective is to present the first estimation of the atmospheric nitrogen deposition budget in Africa based on experimental measurements. To estimate atmospheric nitrogen deposition, including both wet and dry processes, we compiled the IDAF nitrogen data (gas, particles, rain) obtained from the network presented above for three consecutive years. In western and central Africa, we studied a transect going from dry savanna to humid savanna and forest. In South Africa, two very different IDAF sites were chosen to be representative of a rural, semi-arid savanna and of an industrialized area. Presenting the different components of nitrogen deposition on these sites, i.e. dry deposition in gaseous and particulate forms associated with wet deposition, this study will yield the relative contribution of dry and wet deposition processes to the total nitrogen deposition.

## Sampling and Chemical Analysis

The DEBITS committee has defined a set of experimental and analytical protocols to produce comparable measurements from all the DEBITS stations. The IDAF network has adopted these protocols as well.

**Sampling.** An automatic precipitation collector, specially designed for the IDAF network, has been installed at all network stations. A local operator collects water from each rainfall event in a Greiner tube (50 ml). Preserving the rainwater samples from contamination is an important issue since microbial input could modify its chemical composi-

tion. There are two techniques for preservation. The first technique is derived from procedures described by Gillett and Ayers (1991). Samples are refrigerated at 4°C and preserved with 15 mg of thymol biocide. Reference tubes are filled with 15 mg of thymol and de-ionized water and then analyzed by Ion Chromatography (IC) for blank values. In the second technique, samples are simply stored in a deep freeze environment.

Bulk particles were collected once per week on Teflon Millipore filters (1 µm pore size and 37 mm diameter). Sampling was performed at 10 m above ground level with an autonomous and mobile power pump unit consisting of a 12 V pump, a battery, and gas flow meter using an average sampling duration of 24 hours. The bulk aerosol sampler operated at a flow rate of approximately 500 L h<sup>-1</sup>. Each filter was preserved by refrigeration before and after exposure in sealed individual Millipore containers.

Gaseous measurements (NH<sub>3</sub>, HNO<sub>3</sub>, SO<sub>2</sub>, NO<sub>2</sub>, O<sub>3</sub>) were monthly integrated samples using passive sampling techniques following the work of Ferm (1994). This technique has been tested in different tropical and subtropical regions (Ferm and Rodhe, 1997, Carmichael et al, 2002).

All the samples from the six west-central African stations were brought to the Laboratory of Aerology (LA) in Toulouse, France for analysis. For the South African stations, rainwater analysis was performed at the ESKOM laboratory in Johannesburg and the passive sampler analysis was performed at Potchefstroom University.

**Chemical analysis.** Precipitation and aerosol dissolved content were determined by IC at the two IDAF Laboratories. For gas measurements, the impregnated filter of the passive samplers is also analyzed by IC. The IC system used in this study, as well as the main characteristics of the analytical parameters for the determination of mineral ions (Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, K<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>), total carbonate (HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup>) and organic ions (HCOO<sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup>, C<sub>2</sub>H<sub>5</sub>COO<sup>-</sup>, C<sub>2</sub>O<sub>4</sub><sup>2-</sup>), are detailed in Galy and Modi (1998) and Mphepya et al. (2001). International certified standards were used to calibrate minerals and organic ions.

The ESKOM and LA laboratories have participated in the annual international inter-calibration organized by the World Meteorological Organization (WMO) since 1996. Based on these tests, we estimated the analytical precision to be 5% or better for mineral ions, pH and conductivity. For organic ions, the analytical precision is about 10%. More information about sampling and analytical procedures for rain, aerosols and gases (including measurement

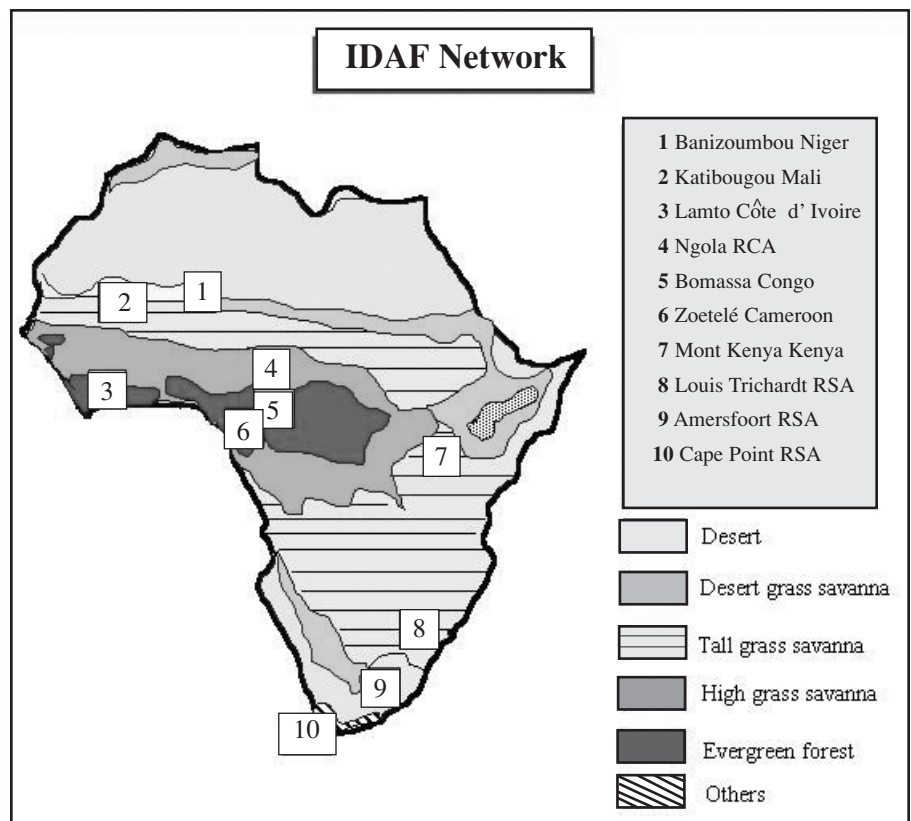
uncertainties) can be obtained from the IDAF Web Site: <http://medias.obs-mip.fr/idaf/>.

Finally, for each rainfall event and its chemical content, the data quality was determined by verifying the integrity of the ionic balance. The ionic balance is expressed by the ionic difference as specified by WMO recommendations.

## Atmospheric nitrogen deposition in west/central Africa

In Figure 1 the locations of the 10 IDAF specific stations existing in 2002 are displayed. The six stations in west-central Africa are maintained by the LA in France. They are paired in order to represent non perturbed areas of semi-arid savanna (Niger and Mali), of humid savanna (Ivory Coast and Central Republic of Africa), and of equatorial forest (Congo and Cameroon). To estimate atmospheric nitrogen deposition in west/central Africa, we compiled IDAF data obtained for three consecutive years: 1998, 1999 and 2000. We present here an estimated nitrogen atmospheric deposition for each type of ecosystem (dry savanna, wet savanna and forest). This estimation takes into account both dry deposition in gaseous and particulate forms and wet deposition.

**Wet deposition.** During the rainy season in tropical



**Figure 1 - Vegetation and location map for the 10 measuring stations in the IDAF Network in 2002.**

regions, convective clouds produce abundant rainfall which is an important sink of gases and particles emitted into the atmosphere. Recent studies indicate that the concentration of nitrogen, sulphur and organic compounds is increasing in tropical rainfall leading to increasingly acidic wet deposition. This is particularly true in Asia and South America (Ayers et al, 2000; Lara et al, 2001 ). There has been little research activity over the African continent. Contrary to many preconceptions, tropical Africa is not devoid of atmospheric pollution. A small number of limited studies of rainwater chemistry and wet deposition in Western and Central Africa showed that forest, savanna, and urban areas emitted substances such as nitrogenous compounds ( $\text{NO}_x$ ,  $\text{NH}_3$ , particles) and organic acids ( $\text{HCOOH}$ ,  $\text{CH}_3\text{COOH}$ ,  $\text{H}_2\text{C}_2\text{O}_4$  and  $\text{C}_2\text{H}_5\text{COOH}$ ) which contributed to changes in the tropospheric chemistry (FOS/DECAFE, 1991). These results instigated new studies by the IDAF network on rainwater chemistry, distributed by ecosystem types, over the African continent (Galy-Lacaux and Modi, 1998; Galy-Lacaux et al., 2001; Freydier et al., 1998; Mphepya 2001; Sigha et al., 2002). All these studies have demonstrated the importance of nitrogenous compounds to tropospheric chemistry in Africa among other results.

To calculate wet nitrogen deposition in Western Central Africa, we have compiled annual volume weighted mean concentrations of nitrate ( $\text{NO}_3^-$ ) and ammonium ( $\text{NH}_4^+$ ) from the precipitation collected at the 6 IDAF stations (1998 to 2000) (Table 1).  $\text{NO}_3^-$  and  $\text{NH}_4^+$  wet deposition rates were calculated based on mean annual rainfall for the 3-year period. The rainfall gradient from the semi-arid savanna of Niger to the forest of Congo ranges from about 500 mm yr<sup>-1</sup> to 2000 mm yr<sup>-1</sup>.  $\text{NO}_3^-$  and  $\text{NH}_4^+$  concentrations in precipitation in the forest, humid savanna and semi-arid ecosystems are relatively high, with values ranging from 10 to 20  $\mu\text{eq L}^{-1}$  of  $\text{NH}_4^+$  and 7 to 11  $\mu\text{eq L}^{-1}$  of  $\text{NO}_3^-$ .  $\text{NH}_4^+$  in precipitation is the result of the diffusion of gaseous ammonia and the transfer of particles containing  $\text{NH}_4^+$  into precipitating clouds. The highest concentrations of  $\text{NH}_4^+$  compounds in precipitation were measured in the semi-arid regions and have been attributed to strong sources of ammonia from domestic and pastoral animals during the wet season (Galy and Modi, 1998).  $\text{NO}_3^-$  in pre-

cipitation represents the end product of homogeneous and heterogeneous processes involving nitrogenous gases and particles in the atmosphere and cloud water. Nitric oxide (NO) is the primary nitrogen compound released from savanna soils during the non-burning season (Serça et al., 1997) and a large fraction of that NO is oxidized in the atmosphere, through photochemical reactions, into nitric acid ( $\text{HNO}_3$ ) or organic nitrates.  $\text{HNO}_3$  is extremely soluble in water and is easily scavenged by clouds. Galy-Lacaux et al. (2001) have demonstrated that heterogeneous processes involving  $\text{HNO}_3$  and mineral particles occur commonly all over the African continent. This mechanism is the best explanation for the declining removal of  $\text{HNO}_3$  along a gradient from the semi-arid regions to the forests. The mineral particles are readily scavenged by precipitation which explains the high  $\text{NO}_3^-$  concentration in precipitation and associated wet deposition in semi arid savannas.

Nitrogenous wet deposition is dominated by  $\text{NH}_4^+$  which accounts for around 60% of the total N flux (Table 1). Total nitrogen wet deposition in semi-arid savanna, humid savanna, and forested areas ranged from 2.1 to 3.5 kg N ha<sup>-1</sup> yr<sup>-1</sup>, 4.1 to 4.7 kg N ha<sup>-1</sup> yr<sup>-1</sup>, and 4.5 to 4.8 kg N ha<sup>-1</sup> yr<sup>-1</sup>, respectively. Figure 2 shows the contribution of wet deposition to total nitrogen deposition based on the mean of the experimental data for each ecosystem.

Typical mean  $\text{NO}_3^-$  precipitation concentrations in industrialized regions ranges from 15  $\mu\text{eq L}^{-1}$  (North America) to 35  $\mu\text{eq L}^{-1}$  (Europe) and  $\text{NH}_4^+$  concentrations range from 15 to 50  $\mu\text{eq L}^{-1}$  (Dovland and Pederson, 1996). Because industrial and transportation sources in west Africa are small, the nitrogenous compound content in precipitation from industrial activity is not as great as is found in some industrialized regions. However, it is comparable to the lower range of values measured in industrialized sites in the United States where deposition values range from 10 to 20 kg N ha<sup>-1</sup> yr<sup>-1</sup> (Bowen and Valiela, 2001).

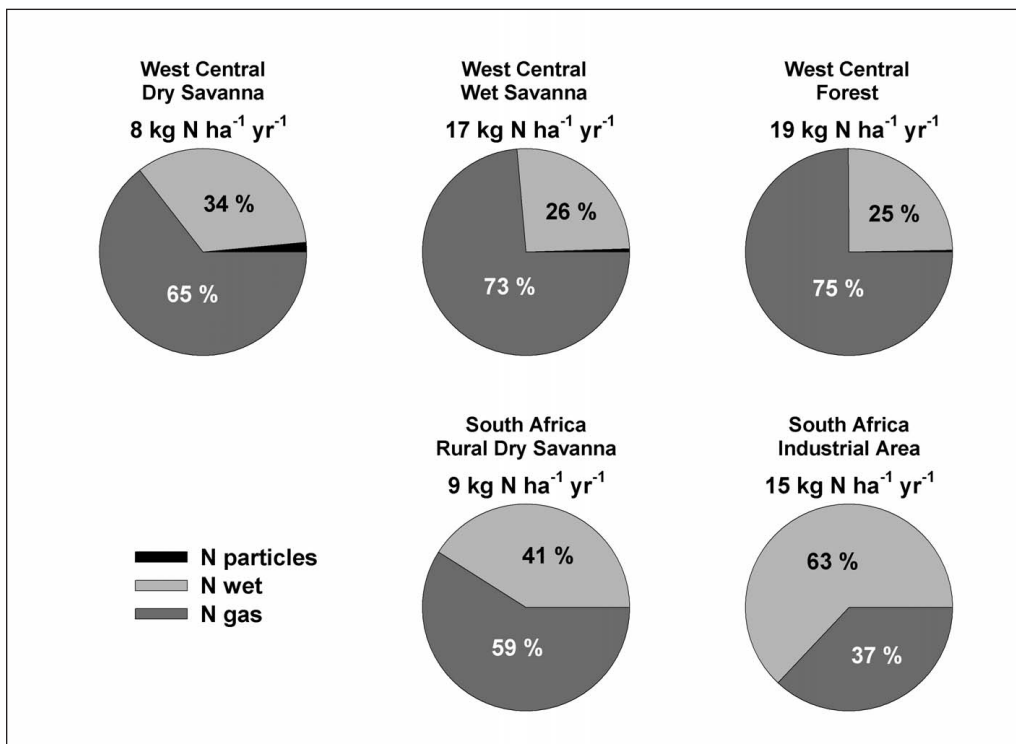
**Dry deposition.** The DEBITS program has chosen to indirectly infer dry deposition measurements because of the difficult nature of direct measurements. Dry deposition is estimated from continuous measurements of gaseous concentrations through passive gas sampling ( $\text{NO}_2$ ,  $\text{NH}_3$ ,  $\text{HNO}_3$ ), and on bulk air sampling for particulate species ( $\text{NH}_4^+$  and  $\text{NO}_3^-$ ).

	Banizoumbou	Katibougou	Lamto	Ngola	Zoétélé	Bomassa	Amersfoort	Louis Trischartdt
$\text{NH}_4^+$	18	19.3	16.5	10.4	10.5	9.4	22.3	9.7
$\text{NO}_3^-$	11.2	10	7.8	7.3	6.9	8.3	25	8
N- $\text{NO}_3^-$	0.8	1.2	1.3	1.9	1.9	2.3	5.5	2.1
N- $\text{NH}_4^+$	1.3	2.3	2.8	2.8	2.9	2.2	4.0	1.6

(Data from Galy and Modi, 1998; Sigha et al., 2002; Yoboué, pers. comm. 2002; Mphepya et al, 2001)

**Table 1 - Annual Volume Weighted Mean (VWM) of ammonium ( $\text{NH}_4^+$ ) and nitrate ( $\text{NO}_3^-$ ) concentration in precipitation ( $\text{NH}_4^+$  and  $\text{NO}_3^-$ ) ( $\mu\text{eq L}^{-1}$ ) and associated yearly wet deposition (N-  $\text{NO}_3^-$ , N-  $\text{NH}_4^+$ ) (kg N ha<sup>-1</sup> yr<sup>-1</sup>) at 9 IDAF stations.**





**Figure 2 - Wet and dry atmospheric nitrogen deposition in Africa.**

Dry deposition of particulate N was calculated from the particulate ammonium ( $p\text{NH}_4^+$ ) and nitrate ( $p\text{NO}_3^-$ ) concentrations in the water soluble content of the measured aerosols. We calculated annual mean concentrations values for the period 1998-2000. A dry particle deposition velocity value of  $0.15 \pm 0.05 \text{ cm s}^{-1}$  was used to estimate nitrogenous dry deposition flux (Whelpdale et al., 1996). The calculation shows that total dry deposition of  $p\text{NH}_4^+$  and  $p\text{NO}_3^-$  are of the same order of magnitude for all types of ecosystems with relatively low values. The mean annual deposition fluxes ( $p\text{NH}_4^+ + p\text{NO}_3^-$ ), in the semi-arid, humid savanna and forested ecosystems are  $0.12 \pm 0.01$ ,  $0.08 \pm 0.01$  and  $0.06 \pm 0.01 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ , respectively. It should be noted that particulate dry deposition of nitrogen is an order of magnitude smaller than wet deposition (Figure 2).

Gaseous dry deposition of nitrogen is calculated as the sum of the dry deposition fluxes of ammonia ( $\text{NH}_3$ ),  $\text{HNO}_3$ , and nitrogen oxide ( $\text{NO}_2$ ). The largest uncertainty in the estimation of dry deposition of trace gases is a result of the computation of the dry deposition velocity. The parameterization scheme is commonly described as a resistance analogy (Wesely and Hicks, 2000). The resistance is a function of wind speed variability, molecular diffusivity, and parameters describing surface vegetation. We have estimated the dry deposition velocities over the African ecosystems using two different models: the inferential model (Hicks et al., 1987) and the MesoNH-C model. Both models take into account the growth variability of the vegetation with more or less detailed processes and compute

results at different spatial and temporal scales. We used mainly values of dry deposition velocities calculated with the inferential model; this provides a smoothed temporal estimation in accordance with the sampling temporal scale of gaseous concentration measurements. Additionally, to compare and validate dry deposition velocities, a second modeling study was performed with the MesoNH-C model. This allowed us to take into account phenomena of different scales (from regional to 'leaf' scale) with various spatial and temporal resolutions. The MesoNH-C model uses initial physiographic data files containing 125 representative cover types at a 1 km resolution over the world

(Koeppel and De Long, 1998). Modelling results obtained with the inferential model and the MesoNH-C are of the same order of magnitude. They show that deposition velocities are highly dependent upon the spatial distribution of the vegetation. The highest dry deposition velocities (around  $1 \text{ cm s}^{-1}$ ) are encountered over the equatorial African forest vegetation type with high roughness length. We observed a deposition velocity gradient for all the gases that was proportional to the gradient of vegetation. Dry deposition velocities from the inferential model ranged from  $0.2$  to  $0.4 \text{ cm s}^{-1}$  for  $\text{NO}_2$ ,  $0.5$  to  $1.5 \text{ cm s}^{-1}$  for  $\text{NH}_3$  and  $0.7$  to  $1.7 \text{ cm s}^{-1}$  for  $\text{HNO}_3$ .

$\text{NO}_2$  dry deposition flux varies minimally among the African ecosystems studied with fluxes varying from  $0.8 \pm 0.01 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  in the dry savanna to  $1.3 \pm 0.05 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  in the forested ecosystem. However,  $\text{NH}_3$  and  $\text{HNO}_3$  dry deposition fluxes vary significantly with higher values in dry savanna despite lower dry deposition velocities related to the low vegetation cover.  $\text{NH}_3$  dry deposition fluxes range from  $3.1$  to  $5 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  in the dry savanna,  $9$  to  $12 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  in the humid savanna, and about  $12 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  in the forested ecosystem. Major sources of  $\text{NH}_3$  include bacterial decomposition of urea in animal excreta and emissions by natural or fertilized soils (Schlesinger and Hartley, 1992). In Africa, another significant source of ammonia is savanna fires and domestic fuelwood burning (Delmas et al., 1995). Dry deposition fluxes of  $\text{HNO}_3$  are very low compared to  $\text{NO}_2$  and  $\text{NH}_3$  with values ranging from  $0.5$  to  $0.9 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  for all the ecosystems. This result is correlated to very low  $\text{HNO}_3$  concen-

trations measured at all stations, ranging from 0.8 to 1  $\mu\text{g m}^{-3}$ .

Dry deposition fluxes, estimated for the three African ecosystems, were combined with the associated wet deposition fluxes to provide the first estimate in western-central Africa of annual nitrogen atmospheric deposition (Figure 2). The total nitrogen deposition is estimated to be 8 kg N  $\text{ha}^{-1} \text{yr}^{-1}$ , 17 kg N  $\text{ha}^{-1} \text{yr}^{-1}$ , and 19 kg N  $\text{ha}^{-1} \text{yr}^{-1}$ , respectively, over dry savanna, humid savanna, and the forest. In comparison, the total nitrogen deposition flux calculated for the Petit-Saut station in the Amazonian forest is about 6 kg N  $\text{ha}^{-1} \text{yr}^{-1}$ . However, these values should be accepted cautiously because the budget uncertainty is estimated to be approximately 30% compared to an estimated uncertainty of 10% for wet deposition. It is also important to note that our budget does not include all nitrogenous species, particularly organic nitrogen.

The importance of dry deposition processes in west central Africa is highlighted by this budget, especially for nitrogenous gaseous compounds. In dry savanna, the relative contribution of dry deposition is between 65 and 70%. In the humid savanna and forested ecosystems, this contribution increases to between 70 and 76%.

## Atmospheric nitrogen deposition in South Africa

Dry and wet deposition of nitrogen over southern Africa was examined using air and precipitation chemistry observations from two stations during the period 1996-1998. These sites represent industrial (Amersfoort) and rural (Louis Trichardt) environments in the savanna region of southern Africa. Amersfoort and Louis Trichardt are IDAF sites where both rain composition and gaseous measurements are performed as previously discussed. South Africa is one of the largest industrialized economies in the southern hemisphere and is the only heavily industrialized regional coal based energy producer on the African continent (Siversten et al., 1995). The regional climate is characterized by hot summers with afternoon thundershowers and cold dry winters with strong thermal stratification near ground level, particularly at night. Approximately 70% of the area is covered by grassland with the remainder used for crop cultivation and commercial forestry. The highly industrialized region comprising the Mpumalanga Highveld and the metropolitan areas of Gauteng (Johannesburg and Pretoria) accounts for about 90% of South Africa's regulated emissions including approximately 1 million tons year<sup>-1</sup> of  $\text{NO}_x$  and 0.3 million tons year<sup>-1</sup> of particulates (Wells et al., 1996).

Dry deposition rates were calculated from the product of the dry deposition velocities calculated from the inferential model (Hicks et al., 1987) and the ambient concentration of  $\text{NO}_2$  and  $\text{NH}_3$ . Wet deposition was calculated from the

measured mean  $\text{NH}_4^+$  and  $\text{NO}_3^-$  concentrations in precipitation (Table 1) and mean annual rainfall. Figure 2 shows that the total annual deposition of nitrogen varies from 15 kg N  $\text{ha}^{-1} \text{yr}^{-1}$  at Amersfoort (industrial area), to 9 kg N  $\text{ha}^{-1} \text{yr}^{-1}$  at Louis Trichardt (rural dry savannah). These values correspond well with that of Lowman and Scholes (2002) who estimated a deposition rate of 13.1 kg N  $\text{ha}^{-1} \text{yr}^{-1}$  for grasslands. At Amersfoort, situated close to major industrial emissions on the South African Plateau, wet deposition accounts for 63% of the total deposition of nitrogen and dry deposition accounts for 37% of the total deposition of nitrogen. At Louis Trichardt, 41% of the total nitrogen deposition is being delivered with the rain as is the case for dry savanna studied in west-central Africa. This large difference in total deposition load clearly illustrates the influence of industrial activities on the central Mpumalanga Highveld. It should be noted that nitrogen values reported here are based only on gaseous and precipitation measurements of  $\text{NO}_2$ ,  $\text{NH}_3$ ,  $\text{NO}_3^-$  and  $\text{NH}_4^+$ , and do not include species such as  $\text{HNO}_3$ , PAN and the dry deposition of N containing particles which could contribute significantly to the atmospheric burden of nitrogen (Barrie and Sirois, 1986), resulting in a possible underestimate of the values.

## Conclusion

The nitrogen atmospheric deposition presented for all the IDAF sites ranges from 8 to 19 kg N  $\text{ha}^{-1} \text{yr}^{-1}$ . Values from sites in the dry savanna of South Africa and West Africa lie within the low end of this range (around 8-9 kg N  $\text{ha}^{-1} \text{yr}^{-1}$ ). Measurements in the wet savanna and forests yield values in the upper end of this range (15 to 19 kg N  $\text{ha}^{-1} \text{yr}^{-1}$ ). The Amersfoort site, representative of an anthropogenically influenced savanna produces values also in the upper end of the range (15 kg N  $\text{ha}^{-1} \text{yr}^{-1}$ ). This study indicates that dry deposition is dominant in all the ecosystems and represents about 60-70% of the total nitrogen atmospheric deposition. The inverse is true for the anthropogenic South African site where wet deposition is dominant.

These new datasets enable us to estimate the nitrogen budget over the African continent for the first time. It is worth noting that the estimated range is similar to model results (Galloway and Cowling, 2002; F. J. Dentener, personal communication). The rates of inorganic N deposition to African biomes are a necessary component for the construction of a N budget for the African continent. Other important components are the input of N into the region (biological nitrogen fixation in unmanaged ecosystems,  $\text{NO}_x$  emissions from fossil fuel combustion, fertilizer consumption, cultivation-induced biological nitrogen fixation, commodity imports), loss of N from the region (emissions of  $\text{NO}_x$ ,  $\text{NH}_3$ , and organic N, atmospheric transport out of the region and riverine discharge of inorganic and organic N to the coastal zone), and changes in storage of N within the system (soils and biotic pools). To fully appreciate the

contribution of atmospheric deposition to the regional and global N cycles, it is important to quantify these other fluxes. Research and monitoring programs must be established to obtain the data where it is lacking and measurements within IDAF framework should continue in order to determine the long term trend of N deposition in Africa. Continuing IDAF measurements will also contribute significantly to the upcoming multidisciplinary project on mechanisms of the African monsoon, or AMMA (African Monsoon Multidisciplinary Analyses). For more information see <http://www.medias.obs-mip.fr/AMMA>.

## References

- Ayers, G. P., Leong Chow Peng, Lim Sze Fook, Cheah Wai Kong, R.W. Gillett and P.C. Manins Atmospheric concentrations and deposition of oxidised sulfur and nitrogen species at Petaling Jaya, Malaysia, 1993-1998, *Tellus B* 52 (2000) 60-73.
- Barrie, L. A., and Sirois, A., Wet and dry deposition of sulphates and nitrates in eastern Canada:1979-1982, *Water, Air and Soil Pollution*, 30, 303-310, 1986.
- Bowen J.L. and Valiela I., 2001. Historical changes in atmospheric nitrogen deposition to Cape Cod, Massachusetts, USA, *Atmospheric Environment*, 35, 1039-1051.
- Carmichael, G., M. Ferm, N.Thongboonchoo, et al., (2002) Measurements of Sulfur Dioxide, Ozone and Ammonia Concentrations in Asia, Africa, and South America Using Passive Samplers, *Atmospheric Environment*, in press.
- Delmas R., Lacaux J.P, Menaut J.C., Abbadie L., Leroux X., Helas G., and J. Lobert, Nitrogen compound emission from biomass burning in tropical African savanna, FOS/ DECAFE Experiment, *Journal of Atmospheric Chemistry*, 22, 175-194, 1995.
- Dovland H. and Pederson U., Acid deposition in Europe, in *Global acid deposition assessment*, World Meteorological Organization, Global Atmosphere Watch, Edited by D.M. Whelpdale and M.S. Kaiser, N° 106, 1996.
- Ferm, M., A. Lindskog, P. A. Svanberg, and C. A. Boström, New measurement technique for air pollutants (in Swedish), *Kem. Tidskr.*, 1, 30-32, 1994.
- Ferm, M., and H. Rodhe, Measurements of air concentrations of SO<sub>2</sub>, NO<sub>2</sub> and NH<sub>3</sub> at rural sites in Asia, *J. Atmos. Chem.*, 27, 17-29, 1997.
- FOS/DECAFE, special issue 1991 91 in *Journal of Atmospheric Chemistry*, 22, 1-239, 1995
- Freydier, R., Dupre, B., Lacaux, J.P. (1998). "Precipitation Chemistry in Intertropical Africa." *Atmos. Environ.* 32: 749-765.
- Galloway JN. 1998. The global nitrogen cycle: Changes and consequences. *Environmental Pollution* 102(S1): 15-24.
- Galloway, J. N., and E. B. Cowling, 2002. Reactive nitrogen and the world: 200 years of change, *Ambio*, 31, 64-71.
- Galy-Lacaux, C. and A.I. Modi, Precipitation chemistry in the Sahelian savanna of Niger, Africa, *J. Atmos. Chem.*, 30, 319-343, 1998.
- Galy-Lacaux C, G. R. Carmichael, C. H. Song, J.P. Lacaux and I. Modi, 2001. Heterogeneous processes involving nitrogenous compounds and Saharan dust inferred from measurements and model calculations Region. *J. of Geophys. Res.*, vol 106, D12pp 12559-12578.
- Gillett R.W. and G.P. Ayers. The use of thymol as a biocide in rain-water samples, *Atm. Env.*, 254A, 2677-2681, 1991.
- Hicks, B. B., Baldocchi, D. D., Meyers, T. P., Hosker Jr, R. P., and Matt, D. R., A preliminary multiple resistance routine for deriving dry deposition velocity from measured quantities, *Water, Air and Soil Pollution*, 36, 311-330, 1987.
- Lara, L.B.L.S., Artaxo, P.; Martinelli, L.A.; Victoria, R.L.; Camargo, P.B.; Krusche, A.; Ayers, G.P., Ferraz, E.S.B.; Ballester, M.V., Chemical composition of rainwater and anthropogenic influences in the Piracicaba river basin, Southeast Brazil. *Atmos. Env.*, 35, 4937-4945, 2001.
- Lowman G and Scholes M, Nitrogen deposition impacts on natural and forested ecosystems in Mpumalanga, South Africa. 7th Scientific Conference of the IGAC project, September 2002, Heraklion, Crète, Greece.
- Matson, P.A., W.H. McDowell, A.R. Townsend and P.M. Vitousek, 1999: The globalization of N deposition: ecosystem consequences in tropical environments. *Biogeochemistry*, 46, 67-83.
- J. N Mphepya, J.J Pienaar, C. Galy-Lacaux, G. Held and C.R Turner, 2002. Precipitation chemistry at a rural and an industrial site in South Africa, *J. of Atmos. Chem.*, in press.
- Koeppe, C. E. and De Long G. C., 1998: *Weather and Climate*. McGraw-Hill book company
- Schlesinger W.H. and A.E Hartley. A global budget for atmospheric NH<sub>3</sub>. *Biogeochemistry*, 15, 191-211, 1992
- Serça D., Delmas R., Le Roux X., Parsons D.A.B, Scholes M.C., Abbadie L., Lensi R. and L. Labroue. Variability of nitrogen monoxide emissions from African tropical ecosystems. *Glob. Biogeochem. Cycles*, 4, 637-645, 1998.
- L. Sigha-Nkamdjou, C. Galy-Lacaux, V. Pont, S. Richard, D. Sighomnou and J. P. Lacaux, 2002, Rainwater chemistry and wet deposition over the equatorial forested ecosystem of Zoéfé (Cameroon), *J. of Atmos. Chem.*, in press.
- Siversten, B., Matal, C., and Pereira, L. M. R., Sulphur emissions and trans-frontier air pollution in southern Africa., pp. 117, SADC ELMS, Lesotho, 1995.
- Vitousek, P.M.; Aber, J.D.; Howarth, R.W.; Likens, G.E.; Matson, P.A.; Schindler, D.W.; Schlesinger, W.H. and Tilman, D.G. Human alteration of the global nitrogen cycle: sources and consequences, *Ecol. Applic.* 7 (1997) 737-750.
- Wells, R. B., Lloyd, S. M., and Turner, C. R., National air pollution source inventory, in *Air pollution and its impacts on the South African Highveld*, edited by G. Held, Gore, B.J., Surridge, A.D., Tosen, G.R., Turner, C.R., and Walmsley, R., pp. 144, Environmental Scientific Association, Cleveland, 1996.
- Wesely, M.L and Hicks B.B, 2000. A review of the current status of knowledge on dry deposition, *Atmos. Environ.*, 34, 2261-2282.
- Whelpdale D.M. et al., *Global acid deposition assessment*, World Meteorological Organization, Global Atmosphere Watch, Edited by D.M. Whelpdale and M.S. Kaiser, N° 106, 1996.

# Dry and wet deposition in Amazonia: from natural biogenic aerosols to biomass burning impacts

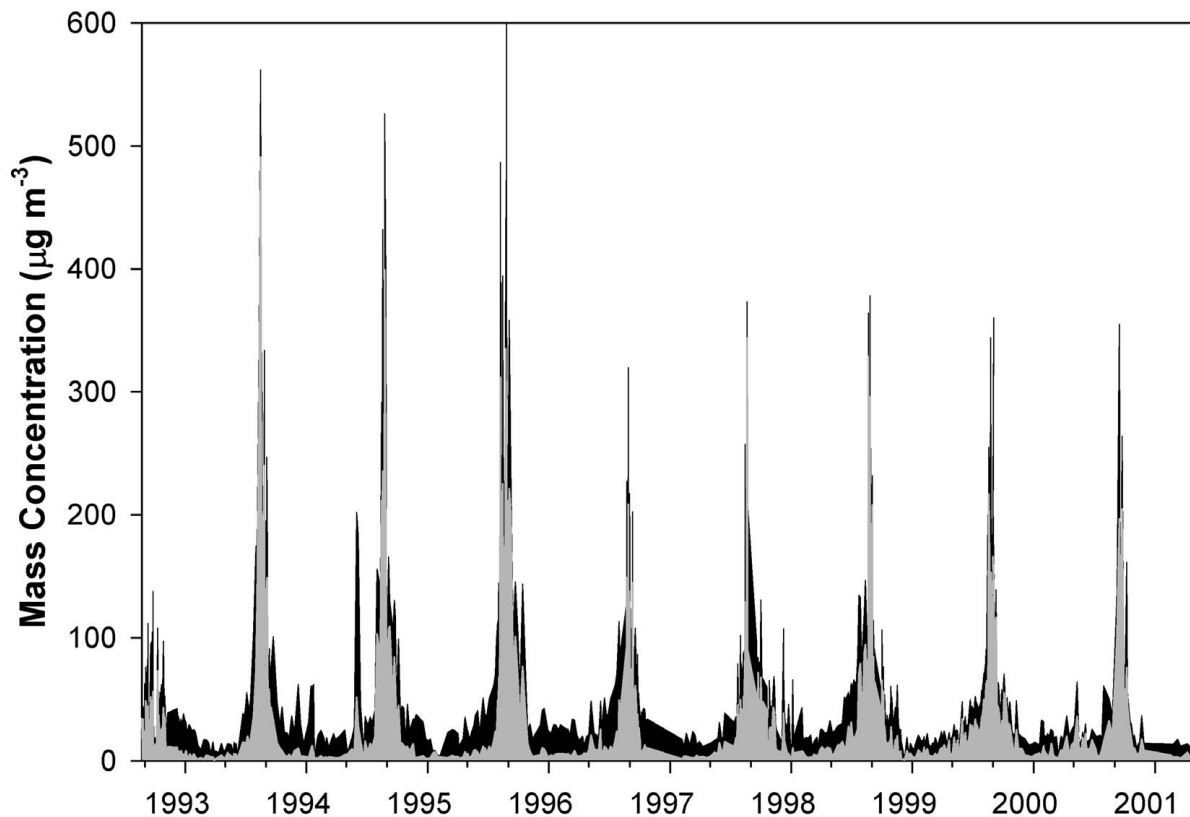
Contributed by **Paulo Artaxo** (artaxo@if.usp.br) and **Theotonio M. Pauliquevis**, Instituto Física, Universidade de Sao Paulo, Rua do Matao, Traverssa R – 187, CEP 05508-900, Sao Paulo, S.P., Brazil, **Luciene L. Lara**, (luciene@cena.usp.br), Laboratório de Ecologia Isotópica - CENA/USP, Av. Centenario, 303, CEP 13400-970, Piracicaba, SP, Brazil, **Sandrine Richard**, HYDRECO Laboratoire Environnement de Petit Saut BP823 97388 Kourou Cedex, French Guiana.

## Introduction

The Amazon Basin is a unique ecosystem, and one of the most important terrestrial ecosystems on the planet. There are several aspects of the Amazon Basin that make it very different from ecosystems elsewhere. The extensive vegetation cover plays a crucial role in determining aerosol and cloud condensation nuclei (CCN) concentrations, as well as water balances in the region. The aerosol particles emitted directly by the vegetation, or formed from the oxidation of gaseous volatile organic compounds, are efficient as

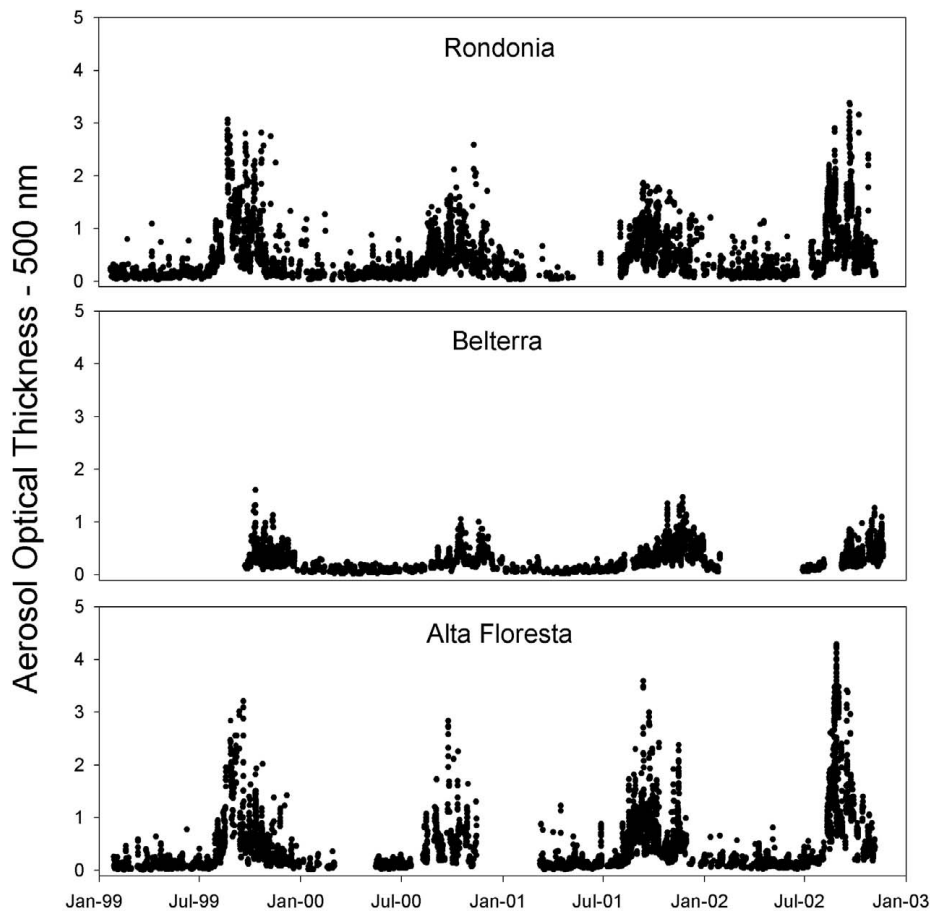
CCN. Thus, there are potential feedbacks between vegetation, aerosols, CCN and precipitation. These organic aerosols are an important (perhaps even controlling) factor in determining the microphysical characteristics of the clouds over the Amazon basin. Evapotranspiration from vegetation also represents a significant source of atmospheric water vapor in Amazonia. This means that the ecosystem itself controls some of the critical ingredients that make rain. Given the global importance of the region, it is necessary to more fully understand this complex system, especially the many potential feedbacks between the ecosystem and the physical and chemical climate of the region. DEBITS in Amazonia, an activity of the Large Scale Biosphere-Atmosphere Experiment in Amazonia (LBA), is investigating dry and wet deposition at several locations in the Amazon River basin. DEBITS is also examining deposition patterns in the industrialized Southern part of Brazil.

Amazonia has two very distinct “seasons” with extremely different aerosol concentrations.  $PM_{10}$  values in the wet season are about  $10 \mu\text{g m}^{-3}$ , whereas dry season values with



**Figure 1** - Time series of  $PM_{10}$  aerosol concentrations in the area of Alta Floresta from 1992 to 2002. In the wet season, natural biogenic aerosol dominates with  $PM_{10}$  concentrations of about  $10 \mu\text{g m}^{-3}$ , whereas in the dry season, very high  $PM_{10}$  concentrations up to  $600 \mu\text{g m}^{-3}$  dominates. Fine mode aerosol is in grey, coarse mode is in black.





**Figure 2** - Aerosol optical thickness (AOT) measured by AERONET sun-photometers for several sites in Amazonia from 1999 to 2002.

biomass burning emissions can reach extremely high  $PM_{10}$  concentrations of  $600 \mu\text{g m}^{-3}$ . Particle number concentration in natural conditions is about  $300 \text{ particles cm}^{-3}$ , but during the dry season it can reach  $30,000 \text{ particles cm}^{-3}$ . Such strong differences make cloud properties in the wet season resembles marine clouds, whereas in the dry season cloud structure is similar to industrial polluted regions.

Figure 1 presents a time series of aerosol mass concentrations in the area of Alta Floresta from 1992 to 2002. During the wet season, low biogenic aerosol  $PM_{10}$  concentrations are observed (on the order of  $10 \mu\text{g m}^{-3}$ ), but during the dry season (August–November), extremely high concentrations of biomass burning aerosols of up to  $600 \mu\text{g m}^{-3}$  are observed. This high aerosol concentration and the resulting high dry deposition rate has important ecosystem consequences. The transport and loss of key forest nutrients, such as phosphorus, occurs during this time because most of the aerosols are in the fine mode and have a high enough residence time to be transported and deposited over the Pacific and Atlantic Oceans. Another important aspect of this high aerosol loading is direct radiative forcing that can reach  $200\text{--}250 \text{ watts m}^{-2}$  over large areas, affecting

plant productivity and photosynthetic rate (Artaxo et al., 2002). The indirect effect is also important, because the amount of CCN under natural conditions is very low, on the order of  $200\text{--}300 \text{ CCN cm}^{-3}$ . Very low CCN concentration results in clouds with large ( $20\text{--}25 \mu\text{m}$ ) droplets, that are normally shallow ( $3\text{--}4 \text{ km}$ ), making mostly very efficient warm precipitation (Artaxo et al. 2001). This efficient natural mechanism for rain production contrasts sharply with the clouds that are present during periods of high biomass burning. Under these high CCN conditions (more than  $10,000 \text{ CCN cm}^{-3}$ ) cloud droplets are small ( $5\text{--}12 \mu\text{m}$ ) and the cloud structure forces the droplets to heights up to  $16\text{--}18 \text{ km}$ , with most of the precipitation initiated in the ice phase. These biomass-burning affected clouds produce precipitation much less efficiently than natural clouds. Similar effects have been observed over polluted clouds in other parts of the world (Rudich, 2002).

One very important and interesting feature of the natural biogenic aerosol, from the point of view of dry deposition, is the total aerosol and phosphorus distribution through the forest canopy in the wet season. Measurements of phosphorus concentrations at three levels ( $1.5$ ,  $28$ , and  $55 \text{ m}$ ) at several LBA towers, shows that the fine particle concentrations are virtually identical for the three levels with no evidence of production or deposition. However, a strong coarse mode aerosol concentration gradient was observed with the highest concentrations at the bottom of the tower (Artaxo, 2001). This is evidence that internal forest canopy processes could be responsible for a large fraction of the aerosol concentration in pristine forest sites. This enhancement of aerosols at ground level is more sharply pronounced during nighttime. The coarse mode phosphorus concentration increases from  $16 \text{ ng m}^{-3}$  at the top of the tower during the day to  $68 \text{ ng m}^{-3}$  under the canopy at night. It is unclear which biogenic mechanism could be responsible for this nighttime coarse mode phosphorus enhancement. Similar patterns were also observed at several other LBA towers. This phenomenon is even more significant when we consider that P is the limiting nutrient for

the Amazonian forest and that P is not present at concentrations above 1 ppb in Amazonian precipitation. Phosphorus is exchanged in the ecosystem exclusively in the aerosol phase and mostly for coarse mode particles and during nighttime (Artaxo, 2001).

Figure 2 shows the spatial distribution of the aerosol optical thickness (AOT) measured by AERONET sun-photometers. The AOT is a measurement of the total aerosol column amount at a given wavelength. In the wet season very low AOT are observed, on the order of 0.05 to 0.1 at 550 nm. In the dry season, the AOT values observed over Amazonia are the highest observed anywhere by AERONET on 5 continents. Remote sensing measurements using MODIS, GOES and MISR show that the high aerosol loading extends over 4-5 millions square kilometers, about half the area of South America, having important effects on cloud formation and radiative forcing over most of the South American continent.

## Wet deposition in Amazonia

Rainfall amount and its composition are determining factors in the functioning of a tropical forest ecosystem. The volume weighted mean (VWM) concentrations of ionic constituents in rainwater from Rondonia, Balbina, Central Amazon (Williams et al., 1997), French Guiana (Richard et al., 2002) and the Piracicaba Basin in Southeast Brazil (Lara et al., 2001) are presented in Table 1. At all sampling sites the most abundant ion was H<sup>+</sup> except French Guiana where Cl<sup>-</sup> was dominant due to the presence of sea-salt. The average acidity of the French Guiana precipitation (VWM pH 5.1) is similar to values from the other Amazon sites during the wet season (Rondonia, Balbina and Central Amazon), with the hydrogen ion concentration ranging from 8.2 to 11.2 µeq L<sup>-1</sup>. The acidity of Precipitation from sites located in industrialized Southern Brazil has signifi-

	Amazon Basin		Central Amazon*			Southeast Brazil	
	Rondonia	Balbina	Wet	Dry	Annual	French Guiana**	Piracicaba Basin***
pH	5.1	5.1	5.0	4.5	4.7	5.1	4.5
H <sup>+</sup>	8.2	8.7	11.2	31.7	17.0	8.2	34.7
Na <sup>+</sup>	3.9	1.7	2.1	3.4	2.4	23.8	3.1
NH <sub>4</sub> <sup>+</sup>	-	2.5	1.2	7.4	3.0	4.4	16.4
K <sup>+</sup>	2.2	0.6	0.7	1.2	0.8	2.5	3.1
Ca <sup>2+</sup>	1.2	0.4	2.4	2.4	2.4	4.6	4.8
Mg <sup>2+</sup>	0.8	0.4	1.0	0.6	0.9	7.1	1.8
Cl <sup>-</sup>	2.8	1.6	4.6	4.5	4.6	25.9	6.7
NO <sub>3</sub> <sup>-</sup>	5.1	1.2	3.3	6.4	4.2	5.6	15.8
SO <sub>4</sub> <sup>2-</sup>	0.7	1.0	1.6	2.8	2.0	6.7	16.9
PO <sub>4</sub> <sup>3-</sup>	-	-	0.02	0.06	0.03	-	-
HCOO <sup>-</sup>	-	3.9	-	-	2.9	5.8	-
CH <sub>3</sub> COO <sup>-</sup>	-	2.5	-	-	9.3	3.3	-
C <sub>2</sub> O <sub>4</sub> <sup>-</sup>	-	0.1	-	-	-	0.4	-
DEF <sup>a</sup>	7.0	2.8	9.1	32.9	15.7	7.5	22.2
DOC <sup>b</sup>	118	-	-	-	154	-	70.2
DIC <sup>b</sup>	41.6	-	-	-	-	-	48.1

Data from:\* Williams et al., 1997; \*\* Richard et al., 2002; \*\*\* Lara et al., 2001. DOC is the Dissolved Organic carbon, DIC is the Dissolved Inorganic Carbon.

a: DEF = (Σcations - Σanions), deficit of anions observed for all sites. b: DOC and DIC concentrations expressed in µM L<sup>-1</sup>.

**Table 1** - Average volume weighted mean (VWM) concentrations in the rainwater for Rondonia, Balbina, Central Amazon, French Guiana and Piracicaba Basin. Values are expressed in µeq L<sup>-1</sup>, except for DOC and DIC which are expressed in µM L<sup>-1</sup>.

	Amazon Basin Central Amazon *	French Guiana**	Southeast Brazil Piracicaba Basin***
H <sup>+</sup>	46.8	25.5	39.6
Na <sup>+</sup>	6.7	74.1	3.6
NH <sub>4</sub> <sup>+</sup>	8.2	13.7	16.5
K <sup>+</sup>	2.3	7.8	2.9
Ca <sup>2+</sup>	6.6	14.3	5.8
Mg <sup>2+</sup>	2.5	22.1	2.0
Cl <sup>-</sup>	12.6	80.6	7.4
NO <sub>3</sub> <sup>-</sup>	11.5	17.4	18.5
SO <sub>4</sub> <sup>2-</sup>	5.4	10.4	20.0
HCOO <sup>-</sup>	8.0	25.6	-
CH <sub>3</sub> COO <sup>-</sup>	18.1	10.3	-
C <sub>2</sub> O <sub>4</sub> <sup>-</sup>	-	1.2	-
DOC <sup>a</sup>	437.9	-	80.0
DIC <sup>a</sup>	-	-	54.9
Rainfall (mm)	2754	3113	1141

Data from:\* Williams et al., 1997; \*\* Richard et al., 2002; \*\*\* Lara et al., 2001.

a: For DOC and DIC the deposition rate is expressed as mmol.m<sup>-2</sup>.yr<sup>-1</sup>.

**Table 2** - Annual deposition rates (meq m<sup>-2</sup> yr<sup>-1</sup>) for Central Amazon, French Guiana and Southern Brazil.

cantly higher acidity (VWM pH 4.5), with a hydrogen ion concentration of 34.7 µeq L<sup>-1</sup> due to anthropogenic activities such as urbanization, industrialization and intensive agricultural practices.

Typically, an excess of cations relative to anions was observed. VWM ion deficit (DEF = ∑ cations - ∑ anions) yielded an anion deficit ranging from 3.0 µeq L<sup>-1</sup> to 33 µeq L<sup>-1</sup> (Table 1), with significantly higher values found during the dry season. The unaccounted for free acidity is attributable to organic acids which were not measured in the samples from Rondonia and Piracicaba. But, even in the places where the main organic anions (acetate, formate and oxalate) were measured (French Guiana, Central Amazon and Balbina) there was still an anion deficiency, indicating that there could be other organic components present in the rainwater in the Amazon. In tropical and sub-tropical South America there are several unidentified organic compounds (Williams et al., 1997, Lara et al., 2001) which could be interacting and may be responsible for the anion deficit. In Rondonia and Piracicaba, a significant correlation (p<0.05) was observed between dissolved organic carbon (DOC) and DEF, and H<sup>+</sup> and DEF, suggesting that the free acidity is correlated to missing organic acids. Generally, the VWM ion concentrations of rainwater in Rondonia were in good agreement with the wet season values in the Central Amazon. The exceptions were K<sup>+</sup> and NO<sub>3</sub><sup>-</sup> which were

higher in Rondonia while SO<sub>4</sub><sup>2-</sup> and Ca<sub>2</sub><sup>+</sup> concentrations were smaller. These differences can be attributed to anthropogenic activities and land-use changes which are much more prevalent in Rondonia than in the Central Amazon. In Balbina, concentrations were smaller compared to other sites. In French Guiana, high concentrations of Na<sup>+</sup>, Mg<sub>2</sub><sup>+</sup>, and Cl<sup>-</sup> are associated with sea-salt influences. The high concentrations found in Southern Brazil are attributable to emissions related to anthropogenic activities (Lara et al., 2001).

The relationship between H<sup>+</sup> and other inorganic anions was examined to estimate the possible sources of acidity. In Rondonia, the significant correlation (r<sup>2</sup> = 0.78) of the main sources of strong acids (NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and Cl<sup>-</sup>) and H<sup>+</sup> suggests that the dilute mineral acids of nitrogen, sulfur and chloride compounds are significant sources of H<sup>+</sup>. However, gaseous sulfuric and nitric acids can be partially neutralized by gaseous NH<sub>3</sub> to form NH<sub>4</sub>NO<sub>3</sub> and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, and significant contribution from organic acids could raise the free acidity. At the same time, the significant correlation between DOC and H<sup>+</sup> (r<sup>2</sup> = 0.72) indicates that there is a combination of inorganic and organic sources of acidity in Rondonia, as well as in the Central Amazon (Williams et al., 1997) and the Piracicaba Basin (Lara et al., 2001). DOC usually arises from organic aerosol emissions from vegetation and the oxidation of biogenic com-

pounds contributes to the presence of organic acids such as formic, acetic and pyruvic acids. Marine aerosol appears to be another minor source of some solutes in precipitation in the Amazon Basin. However, the low concentrations of  $\text{Cl}^-$ ,  $\text{Ca}^{2+}$ , and  $\text{K}^+$ , compared to those in French Guiana, suggests that these compounds could have anthropogenic or terrigenous origins. In fact, the Spearman correlation of  $\text{K}^+$  and  $\text{Cl}^-$  was positive ( $r^2=0.96$ ) and significant ( $p<0.01$ ) indicating that biomass burning is influencing the chemical composition of precipitation in Rondonia, even during the wet season. This is the result of the release of KCl from burning biomass.

Annual deposition of  $\text{H}^+$ ,  $\text{NO}_3^-$ , and  $\text{NH}_4^+$  is highest in French Guiana and in the Piracicaba Basin in Southern Brazil (Table 2). But the high deposition rate in French Guiana is more a result of the high annual rainfall rate than of the concentration values in rainwater. Sulfate annual deposition was smaller and varied from 5 to 20 meq  $\text{m}^{-2}$  (Table 2).  $\text{Na}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  deposition values are higher in French Guiana than in the Central Amazon and Piracicaba Basin, probably due to the influence of sea-salt and the high rainfall rate. Cation deposition values in the Piracicaba Basin and the Central Amazon are between values observed in remote and polluted areas of the Northern Hemisphere. Annual wet deposition of total N in the Central Amazon (2.8  $\text{g m}^{-2}$ ) is smaller than in French Guiana (4.3  $\text{g m}^{-2}$ ) but similar to those values (3.1  $\text{g m}^{-2}$ ) found in Asia (Granat et al., 1996). On the other hand, the annual N deposition in the Piracicaba Basin (5.4  $\text{g m}^{-2}$ ) is similar to that observed in polluted regions of North America (6.3-7.1  $\text{g m}^{-2}$ ). Indeed, 26% of the total nitrogen deposition in the Piracicaba Basin comes from wet deposition (Lara et al., 2001).

## Final observations

Amazonia is one of the few terrestrial ecosystem on Earth where, during the wet season, it is still possible to observe the functioning of an ecosystem relatively unperturbed by anthropogenic activities. The cloud structure over Amazonia is unique among all terrestrial ecosystems (Artaxo *et al.*, 2001). It is actually similar to remote marine clouds, indicating that in fact only two cloud “types” exist: a natural type over unperturbed marine and terrestrial ecosystems, and clouds influenced by anthropogenic emissions with smaller cloud droplets and a much higher number of CCN.

A primary goal of the LBA experiment is to understand this tightly coupled biosphere-atmosphere interaction (Artaxo, 2001). LBA is using a multidisciplinary research agenda aimed at characterizing the Amazonian ecosystem with a long term objective of determining how to manage sustainable development in such a complex ecosystem.

## References

- Artaxo, P., The atmospheric component of biogeochemical cycles in the Amazon basin, In: The biogeochemistry of the Amazon basin. Ed. by Michael E. McClain, Reynaldo Victória, Jeffrey E. Richey. Oxford University Press, 42-52, 2001.
- Artaxo, P., M. O. Andreae, A. Guenther, and D. Rosenfeld, LBA Atmospheric Chemistry: Unveiling the lively interactions between the biosphere and the Amazonian atmosphere. IGBP Global Change Newsletter, LBA Special Issue, 12-15, 2001.
- Artaxo, P., J. V. Martins, M. A. Yamasoe, A. S. Procópio, T. M. Pauliquevis, M. O. Andreae, P. Guyon, L. V. Gatti, and A. M. C. Leal. Physical and chemical properties of aerosols in the wet and dry season in Rondonia, Amazonia. Journal of Geophysical Research, in press, 2002.
- Granat, L., Suksomsankh, K., Simachaya, S., Tabucanon, M., Rhode, H., Regional background acidity and chemical composition of precipitation in Thailand. Atmospheric Environment 30, 1589-1596, 1996.
- Keene, W.C., Galloway, J.N. Considerations regarding sources for formic and acetic acids in the troposphere. Journal of Geophysical Research 91, 14466-14474, 1986.
- Lara, L.B.L.S., Artaxo, P.; Martinelli, L.A.; Victoria, R.L.; Camargo, P.B.; Krusche, A.; Ayers, G.P., Ferraz, E.S.B.; Ballester, M.V., Chemical composition of rainwater and anthropogenic influences in the Piracicaba river basin, Southeast Brazil. Atmospheric Environment. 35, 4937-4945, 2001.
- Rodhe, H., Dentener, F., Schulz, M., The Global Distribution of Acidifying Wet Deposition, Environmental Science and Technology, 36, 4382-4388, 2002.
- Rudich, Y., D. Rosenfeld and O. Khersonsky, Treating clouds with a grain of salt, Geophysical Research Letters, in press, 2002.
- Williams, M.R., Fisher, T.R., and Melack, J.M. (1997) Chemical composition and deposition of rain in the central Amazon, Brazil. Atmospheric Environment 31, 207-217.
- Richard et al., 2002, Personal communication from Sandrine Richard, e-mail: hydreco-labops@wanadoo.fr, HYDRECO Laboratoire Environnement de Petit Saut BP823 97388 Kourou Cedex, French Guiana (France).



# Acid wet deposition in the Tropics: two case studies using DEBITS measurements

Contributed by **Jean-Pierre Lacaux** (lacaux@medias.cnes.fr), *MEDIAS-France, 18 avenue E. Belin, 31401 Toulouse Cedex 4, France, J.P. Tathy, Délégation Générale de la Recherche Scientifique et Technologique (DGRST), B.P. 2499 Brazzaville, Congo, and L. Sigha, Centre de Recherches Hydrologiques BP 4110 Yaoundé, Cameroun.*

## Introduction

Acid wet deposition delivers acids and acidifying compounds to the Earth's surface which invade soil, vegetation and continental waters. New results show that some ecosystems cannot neutralize these acidic compounds. Moreover, ammonium can be transformed into nitrates in terrestrial ecosystems saturated by nitrogen compounds, thus increasing soil acidity through release of hydrogen ions.

Tropical forest ecosystems are sensitive to acid deposition. We illustrate that here in two case studies using DEBITS data. The first case study takes place in African and Amazonian equatorial forests. By comparing rainfall chemistry from these two forests, we demonstrate that biomass burning alters the overall chemical composition of rainfall, including acidity.

The second case study examines other terrestrial ecosystems, using DEBITS measurements within the tropical belt. In these ecosystems, measured acid deposition is compared to the maximum buffering capacity of the soils.

## Precipitation chemistry in equatorial forests

Table 1 presents data of precipitation chemistry and associated wet deposition from several sampling sites located in the equatorial forests. The mean yearly chemical com-

position of this rainwater shows that hydrogen ion is abundant at all sites, thus indicating an acidic character generally found in equatorial precipitation. This acidity results from a mixture of mineral acids ( $\text{HNO}_3$ ,  $\text{HSO}_4$ , etc.) and organic acids (formic, acetic, propionic and others). (Andreae et al., 1994, Lacaux et al., 1992, Ayers et al., 1988, Galloway et al., 1982, Williams et al., 1997). In African forests, the acidity contributed by organic acids (40 - 60%) is equivalent to that of mineral acids (~40%). This equivalence is characteristic of the rainwater collected in equatorial Africa. The Amazonian composition is very different, with organic acids accounting for 80 - 90% of the total acidity. In the rainwater collected in several remote places of the Northern Territory of Australia, Gillet et al. (1990) found a Volume Weighted Mean (VWM) pH for all samples of 4.89, with organic acids contributing about 50% of the free acidity; the remainder being  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$ .

During the dry season, biomass burning has a drastic influence on rainwater composition. To get a rough estimate of the contribution of some chemical compounds by the vegetation fire source, we compared the chemical content of rainwater from Amazonia (ABLE-2A, wet season) and African equatorial sites (Dimonika, Congo, and Zoétélé, Cameroon) (Table 2). For Amazonia, we assumed that the precipitation chemistry was essentially due to the influence of biogenic sources, soils and vegetation, and little influenced by biomass burning emissions. Therefore, the mean contribution from the vegetation burning source was estimated, for the two African sites, to be about 60 to 70% of the  $\text{NO}_3^-$ ,  $\text{NH}_4^+$  and acidity contents. The two sites in Africa, Dimonika and Zoetélé, located on both sides of the Equator, are alternatively affected by the influence of the savannah burning sources from the Southern and Northern Hemisphere. The higher concentration of  $\text{NO}_3^-$ ,  $\text{NH}_4^+$  and  $\text{H}^+$  may be explained by the transport of the northeast flow of gases and particles produced by the savannah burning in the Northern hemisphere. A similar atmospheric transport mechanism occurs in the opposite direction during the Southern hemispheric savannah burn-

Location	Reference	pH	H <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	Ca <sub>2</sub> <sup>+</sup>	Mg <sub>2</sub> <sup>+</sup>	NO <sub>3</sub> <sup>+</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	HCOO <sub>T</sub>	CH <sub>3</sub> COO <sub>T</sub>
Dimonika (Congo)	Laucaux et al (1992)	4.74	18.1	11.1	2.0	6.4	9.3	-	8.6	13.3	10.5	6.6	3.0
Zoétélé	Lacaux (1991)	4.83	14.8 (23.7)	1.7 (2.7)	3.6 (6.5)	9.6 (15.4)	6.3 (10.2)	1.9 (3.2)	7.0 (11.6)	2.2 (3.7)	5.0 (8.2)	8.1 (13.1)	5.3 (8.4)
Central Amazon	Andreae et al (1994)	4.91	12.2 (29.4)	4.0 (9.5)	1.8 (4.2)	4.0 (9.6)	4.2 (10.0)	-	2.1 (5.0)	4.7 (11.3)	3.5 (8.2)	6.3 (15.1)	4.3 (10.3)
Central Amazon	Williams et al (1997)	4.70	17.0 (46.8)	2.4 (6.7)	0.8 (2.3)	3.0 (8.2)	2.4 (13.2)	0.9 (5.0)	4.2 (11.5)	4.6 (12.6)	2.0 (10.8)	2.9 (8.0)	9.3 (25.6)

**Table 1** - Weighed volume mean concentration in  $\mu\text{eq L}^{-1}$  and wet deposition in  $\text{meq m}^{-2} \text{yr}^{-1}$  for precipitation collected in sites located in equatorial forests.

ing season.

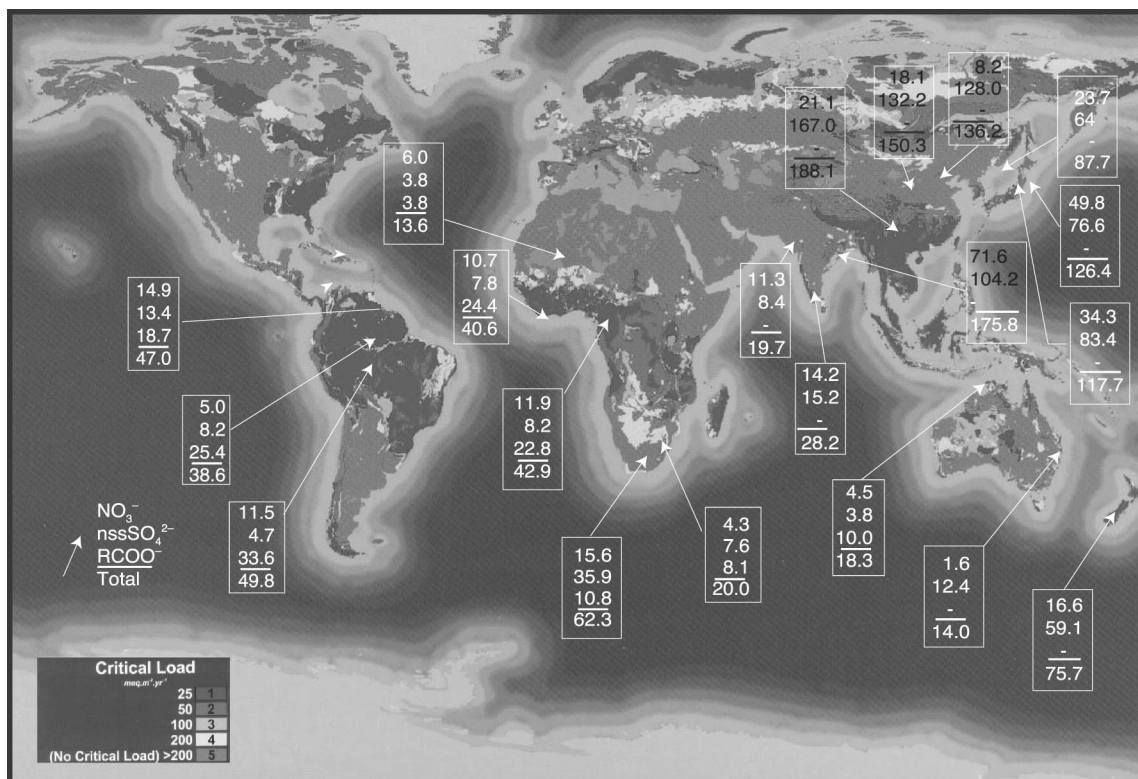
The potential for acid wet deposition is high in the semi arid and humid savannas surrounding the forested ecosystems. For example, Galy and Modi (1998) have shown that the arid savanna precipitation is characterized by a weak acidity ( $H^+=2 \mu\text{eq L}^{-1}$ ) in spite of a high potential acidity ( $\text{NO}_3^- + \text{HCOO}_D + \text{CH}_3\text{COO}_D = 22 \mu\text{eq L}^{-1}$ ). This result is explained by heterogeneous interactions occurring between alkaline soil dust particles and acidic gases. Moreover, recent experimental and modeling studies (Dentener et al, 1996; Carmichael et al, 1996; 1997) have emphasized the importance of heterogeneous processes in atmospheric chemistry. These processes may significantly affect the cycles of nitrogen, sulfur, and atmospheric oxidants including the last step of these cycles: deposition.

In the tropics, high concentrations of organic aerosols (biomass burning and condensation of biogenic hydrocarbons) and mineral dust (deserts and arid areas) could promote intense heterogeneous atmospheric chemistry. Understanding heterogeneous and multiphase processes is a high priority for future research in the assessment of the atmospheric chemistry. The DEBITS program, simultaneous measurements of gas, particles and precipitation chemistry, is well adapted to study gas/particle interactions and to identify the main mechanisms in regulating atmospheric deposition. Moreover, DEBITS will provide the quality controlled data required to study the long term evolution trends in atmospheric chemical composition.

## Effect of wet deposition on tropical terrestrial ecosystems

Acidification effects are mainly due to deposition of mineral sulphur and nitrogen compounds. In tropical regions, organic acid deposition may account for as much as 8% of total acidity. However, these acids are oxidized in soils and will not participate directly in soil acidification. Soil particles exchange alkaline cations with  $H^+$  and the concentration of alkaline ions determine the soil base saturation. When base saturation is low, acids may release ions from soil particles, for example aluminium ions. In spite of limitations, the critical load concept, characterizing ecosystem sensitivity to acidic deposition, has been adopted as a tool for estimating potential impacts on ecosystems. In order to facilitate the development of strategies to control pollution in tropical countries, the Stockholm Environment Institute (SEI) has recently proposed a global assessment of terrestrial ecosystem sensitivity to acidic deposition (S. Cinderby et al, 1998). This assessment depends on the buffering capacity of the base saturation to identify the weathering rate and cation exchange capacity of soils to quantify the capacity of a soil to buffer acidity.

Figure 1 shows a global map prepared by SEI, with five classes of sensitivity to acidic deposition, from a critical load of  $200 \text{ meq m}^{-2} \text{ yr}^{-1}$  for the insensitive class, to a critical load of  $25 \text{ meq m}^{-2} \text{ yr}^{-1}$  for the most sensitive class.



**Figure 1** - Wet deposition measurements of nitrate, non sea-salt sulfate and organic acids compared with ecosystem sensitivity to acidic deposition. References: Wet deposition [Asia and Oceania (Ayers et al., 1996); Africa (Galy and Modi, 1998, Turner et al., 1996); Amazonia (Andreae et al., 1994, William et al., 1997)] and Ecosystem sensitivity to acidic deposition (S. Cinderby et al., 1998)

	Amazonia	Equatorial Africa			
	ABLE-2A Biogenic reference	South Equator Dimonika Congo		North Equator Zoétélé	
	$\mu\text{eq L}^{-1}$	$\mu\text{eq L}^{-1}$	Biomass Buning contribution	$\mu\text{eq L}^{-1}$	Biomass Buning contribution
H <sup>+</sup>	5.8	18.1	68%	14.8	61%
pH	5.24	4.74		4.83	
NO <sub>3</sub> <sup>-</sup>	1.1	8.6	87%	7.0	84%
Organic acids	5.2	7.4	30%	13.4	61%
NH <sub>4</sub> <sup>+</sup>	1.9	6.4	70%	9.6	80%

**Table 2** - Biomass burning contribution to chemical precipitation in African rainforests.

Some selected wet deposition measurements of non sea – salt sulphate, nitrate and organic acids, mainly obtained in the DEBITS project, are also presented.

An examination of this map, along with wet deposition, provides an overall impression of tropical regions where a potential risk of acidification is important. All the equatorial rainforests of South America, Africa and Asia are classified in the most sensitive classes. For South American soils, with a level of mineral acidity deposition of about 10 to 20 meq m<sup>-2</sup> yr<sup>-1</sup>, future acidification problems may become severe if land use change and industrial activities continue to increase in these regions. For tropical Africa, due to the high contribution of mineral acidity to wet deposition as a result of biomass burning sources, the critical load is nearly exceeded in many areas. For Asia, in some parts of China, Japan and other industrialized and populated zones, the critical load has already been reached. This comparison of acidic wet deposition and sensitivity represents only one part of the risk estimation. In some areas, dry deposition is at least as important as wet processes and must be considered in the calculation of total deposition.

Acidic gaseous dry deposition is toxic to many soil organisms and plants. High concentrations of sulphur, nitrogen dioxide, and nitric and sulphuric acid may increase acidification processes. In many arid or semiarid regions there is significant transport and deposition of alkaline soil particles to adjacent ecosystems. The base cation deposition of particles partially mitigates wet and dry deposition of acidic compounds.

## References

Andreae M.O., Talbot R.W., Berresheim H. and Beecher K.M., 1994 – Precipitation chemistry in central Amazonia, *J. Geophys. Res.* 95, 16, 987 – 17,000.

Ayers G.P., Gillett R.W., 1988 – Acidification in Australia, in H. Rodhe and R. Herera (eds), *acidification in tropical countries*, John Wiley, New York, pp 347 – 402.

Ayers G. Gillet R. and H. Hara, 1996 – Acidic deposition in east Asia and Oceania in *Global acid deposition assessment WMO n° 106*, pp 107-134.

Carmichael G.R., Zhang Y. Chen L.L., Hong M.S. and Ueda H., 1996 – Seasonal variation of aerosol composition at Cheju Island, Korea – *Atmospheric Environment* 30, 2407-2416.

Carmichael G.R., Hong M.S., Ueda H. Chen L.L., Murano K., Park J.K., Kang C. and Shim S., 1997 – Aerosol composition at Cheju Island, Korea – *Journal of Geophysical research* 102? 6047-6061.

Cinderby S, Cambridge H.M., Herrera R., Hicks W.K., Kuylenstierna J.C.I., Murray F. and Olbrich K., 1998 - *Global assessment of ecosystem sensitivity to acidic deposition - SEI edition*, pp 1 – 18.

Dentener F.J., Carmichael G.R., Zhang, Lelieved Y.J. and Crutzen P.J., 1996 – Role of mineral aerosol as a reactive surface in the global troposphere, *J. Geophys. Res.* 101, 22,869 – 22,889.

Galloway J.N., Likens G.E., Keene W.C. and Miller J.M., 1982 – The composition of precipitation in remote areas of the world, *J. Geophys. Res.* 87, 8771 – 8786.

Galy C. and Modi A.I., 1998 - Precipitation chemistry in the sahelian savanna of Niger, Africa - *Journal of Atmospheric Chemistry*, 30, 319-343.

Gillet R.W., Ayers G.P. and Noller B.N., 1990 - Rainwater acidity at Jabiru, Australia in the wet season 1983/84 - *The science of Total Environment*, 92, 122-144.

Lacaux J.P., Delmas R. Kouadio G., Cros B. and Andreae M.O., 1991 – Precipitation chemistry in the Mayombé forest of equatorial Africa, *J. Geophys. Res.* 97, 6195-6206.

Lacaux J.P., 1999 - DEBITS activity in Africa: Atmospheric deposition in northern hemisphere of Tropical Africa - *Proceeding IGAC 99 Conference*, Bologna.

Turner C.R., Wells R.B. and Olbrich K.A., 1996 – Deposition chemistry in South-Africa – Air pollution and its impacts on the South African Highveld Cleveland, pp 80-85.

Williams M.R., Fischer T.M. and Melack J.M., 1997 – Chemical composition and deposition of rain in the Central Amazon, Brazil, *Atmos. Environ.* 31, 207-217.



# Heterogeneous processes involving nitrogenous compounds and Saharan dust inferred from in-situ measurements and model outputs

Contributed by **Corinne Galy-Lacaux** (lacc@aero.obs-mip.fr), *Laboratoire d'Aérodologie, UMR Université Paul Sabatier/CNRS 5560, Observatoire Midi-Pyrénées Toulouse, France*, **Gregory Carmichael**, *Department of Chemical & Biochemical Engineering, Center for Global & Regional Environmental Research, University of Iowa, Iowa City, IA USA*, and **A. I. Modi**, *Département de Physique ENS, Université de Niamey, Niger*

## Introduction

We present here a synthesis of studies using data collected in the Sahelian region within the framework of the IDAF (IGAC DEBITS AFRICA) Network. Galy-Lacaux and Modi (1998) and Galy-Lacaux et al. (2001) have analyzed data covering the entire wet and dry seasons, during 1996 and 1998, in the semi-arid savanna of the Sahelian region in Niger (station of Banizoumbou). These data include precipitation and aerosol chemistry, as well as gaseous concentrations. These results were intended to:

- determine the general patterns of the chemical composition of rainfall and aerosols collected in a rural area within the semi arid savanna of Sahel
- identify potential atmospheric sources of gas and particulates which may control deposition flux rates in the desert and the semi-arid savanna
- emphasize the major role of heterogeneous chemical processes in determining the composition of aerosols and rainwater in this region.

The overall understanding and the interpretation of wet deposition and precipitating chemical compounds depends upon our ability to comprehend transfer and multi-phase reactions which occur between atmospheric gases and particles, and between gases, particles, and cloud droplets.

## Chemical composition of precipitation and aerosols

The influence of atmospheric gases and particle sources on precipitation, aerosol chemical content, and gaseous concentrations is examined. The relative influence of marine, terrigenous, and biogenic sources in the Sahelian region is also highlighted. The terrigenous signature, related to Sahelian soil erosion, dominates with high calcium content in precipitation ( $31.2 \mu\text{eq L}^{-1}$ ) and in aerosols ( $1.8$

$\mu\text{g m}^{-3}$ ). In addition, relatively high nitrogenous (ammonium and nitrate) and organic (formate and acetate) concentrations were observed in precipitation and aerosol. The release of ammonia from domestic animal excreta in Niger is believed to be the source of ammonium ( $12.9 \mu\text{eq L}^{-1}$ ) in rainfall and natural emissions from semi-arid savanna soils, perturbed by wild or domestic animal grazing is believed to be the primary source of nitrate ( $12.3 \mu\text{eq L}^{-1}$ ). In spite of a high potential acidity from nitrate, formate and acetate, a weak acidity ( $\text{H}^+ = 2.1 \mu\text{eq L}^{-1}$ ) with an average pH of 5.67 has been measured. Moreover, it has been shown that precipitation acidity originates mainly from organic acid produced by biogenic emissions.

A statistical analysis of the aerosol chemical composition clearly indicates that nitrates are strongly correlated at the 1% level with terrigenous ions (i.e.  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  [ $0.95 < r < 1$ ]). We observed a similar relationship between all terrigenous ions and nitrate in precipitation. In the Sahelian region, alkaline soil dust representative of the terrigenous contribution interacts with gaseous nitrogen leading to the neutralization of acid gases and subsequent weakening of acidity in precipitation. Taking into account the main chemical characteristics of Banizoumbou precipitation and aerosol and important heterogeneous and multi-phase chemical processes, we proposed a conceptual model of the atmospheric chemistry for the Sahelian region (Figure 1).

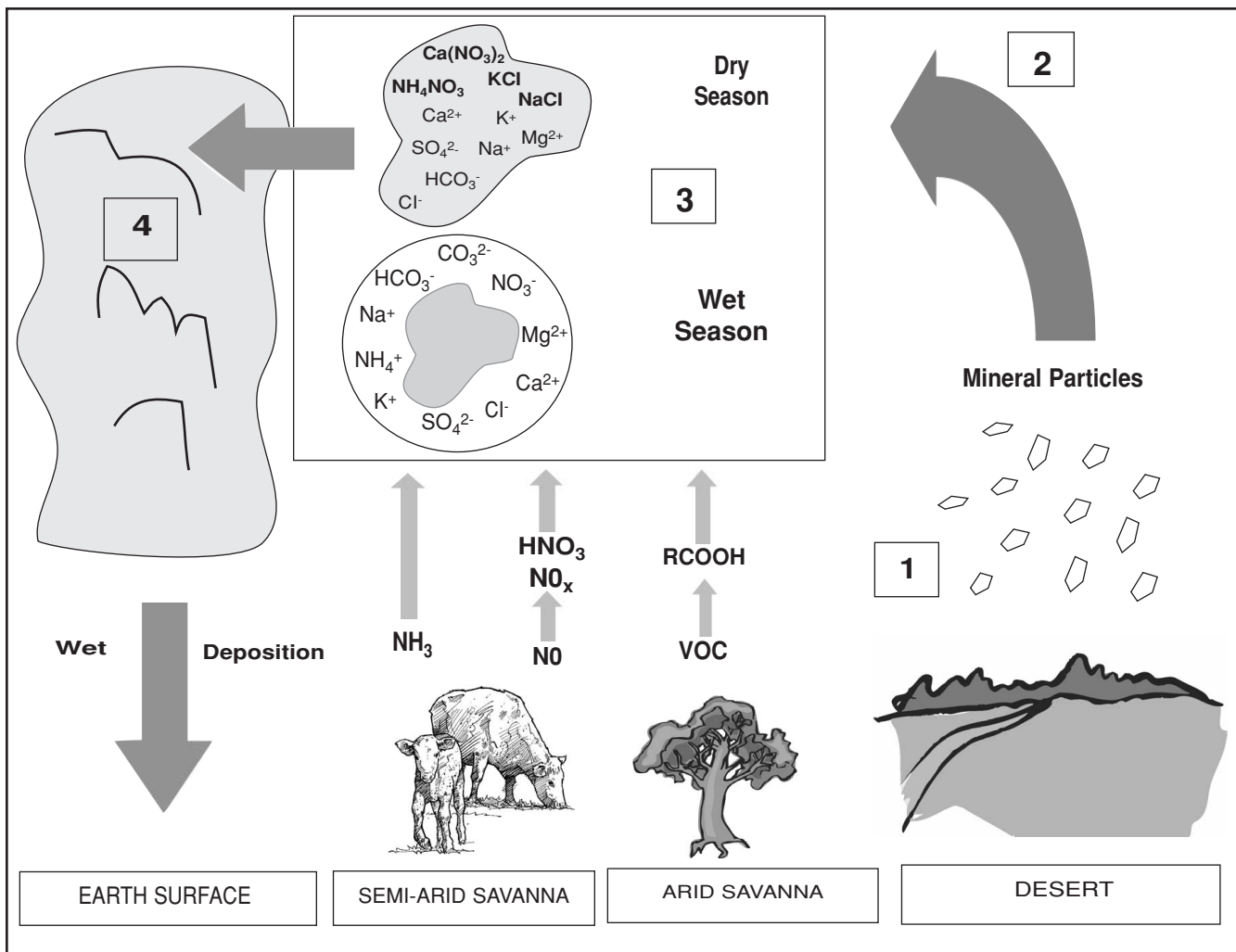
## Conceptual model of atmospheric chemistry in Sahelian region

The conceptual model of atmospheric chemistry in the Sahelian region is presented in Figure 1 and can be described by the following 4 steps.

**Step one** identifies all emissions of trace gases and atmospheric particles prevalent in the Sahelian region. They are emitted to the atmosphere from savanna soils, biomass burning (during dry season), animals, natural or fertilized soils, and eolian erosion which forms mineral aerosol. Significant specific sources include the release of NO from soils which is transformed into  $\text{HNO}_3$ ,  $\text{NH}_3$  emitted during biomass burning, and VOC released by vegetation that is oxidized to form RCOOH;

**Step two** concerns the behavior of terrigenous aerosol at different degrees of relative humidity. When relative humidity is low (20 to 30%), associated with Harmattan flow, gases may interact directly with the surface of the





**Figure 1** - Conceptual model of atmospheric chemistry in the Sahelian region. The enlargement at the top of the figure shows the heterogeneous processes between gas and particles during the wet and dry seasons. Chemical species in bold are in the solid phase, while other species are in ionic form (Galy-Lacaux and Modi, 1998; Galy-Lacaux et al, 2001).

particle. When relative humidity is high (50 to 80%), such as within the summer monsoon layer, soil particles incorporate water vapor to provide a water shell adsorbed on the particle. This forms a concentrated chemical environment for chemical reaction processes.

**Step three** describes heterogeneous and multiphase interactions between gases (H<sub>2</sub>O, HNO<sub>3</sub>, NH<sub>3</sub>, RCOOH, HCHO, N<sub>2</sub>O<sub>5</sub>, NO<sub>x</sub>) and mineral particles. Highly soluble atmospheric gases like NH<sub>3</sub> and HNO<sub>3</sub> will be dissolved in the water shell to form a reactive solution around the dust soil particle. The dissolution of organic acid (RCOOH) or H<sub>2</sub>O<sub>2</sub> is also likely. Non-soluble species could then react on the water layer surface. These processes result in a complex gas/particle as shown in the figure.

**Step four** is the deposition of particles and gases. Dry deposition of particles and/or gases may occur at each step of this schematic cycle (not represented). On the other hand, modified particles could be scavenged efficiently

during cloud formation and act as cloud condensation nuclei (CCN), which are then incorporated into cloud droplets. The hydrophilic character of the particle will promote this process. Aerosol particles and gases could be also scavenged by raindrops as they fall between the cloud base and the ground or be incorporated into cloud droplets.

## Modeling analysis with SCAPE

The analysis of the aerosol and precipitation chemical composition and gas phase concentrations indicates that the Sahel is characterized by significant quantities of mineral dust and nitrogenous compounds throughout the year. The data further suggest that the presence of mineral aerosol affects the partitioning of the nitrogenous compounds between the gas and aerosol phases. To further

investigate the nature of these interactions, the data from the Sahelian region were studied using the Simulating Composition of Atmospheric Particles at Equilibrium (SCAPE) model (Kim and Seinfeld, 1995). The thermodynamic SCAPE model 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 provide a better understanding of the heterogeneous processes involved in the mechanisms of wet and dry deposition in the Sahelian region. This model has been widely and successfully used in an urban environment (Los Angeles) and is beginning to be used in other regions, especially in Asia, to interpret experimental data (Carmichael et al., 1996, 1997). In this work, it has been applied for the first time to African data.

We found that the model accurately represents the mean aerosol and gas chemical composition of the Sahelian region during the dry and the wet seasons. The model prediction accurately simulated the interactions between  $\text{HNO}_3$  and terrigenous compounds. Non-volatile cation species ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ) were found to neutralize gaseous  $\text{HNO}_3$  in the two modes and were identified as the key parameter to retain nitrate in the aerosol phase for both seasons. In the Sahelian region, non volatile cations species are sufficient to entirely neutralize gaseous  $\text{HNO}_3$ .

Our analysis indicates that the SCAPE model can provide a valuable assessment of the equilibrium gas-aerosol representative of the semiarid savanna. These numerical calculations provide the first successful analysis of heterogeneous processes between gas and particles from the IDAF African Network. The model provides a better understanding of the chemical reactions involved in the neutralization process between  $\text{HNO}_3$  and mineral particles during the dry and the wet seasons. Our conceptual model of atmospheric chemistry in the Sahelian region is represented by Step 3 in Figure 1. 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. In the dry season, gas/particle interactions occur both in ionic and solid form. The most important result shows that the neutralization of  $\text{HNO}_3$  is primarily performed by calcium to form the solid  $\text{Ca}(\text{NO}_3)_2$ .

## Conclusion

Our results point out the major role of heterogeneous processes in the Sahelian region in regulating atmospheric chemical composition (gas and particles) and affecting wet and dry deposition chemical characteristics. In Africa and other tropical regions, understanding gas/particles interactions, i.e. heterogeneous and multiphase reactions, is essential in assessing the atmospheric chemistry. This assump-

tion has been emphasized previously by Dentener et al. (1996); Andreae and Crutzen (1997), Galy-Lacaux and Modi (1998). The African atmosphere is an excellent medium for studying these interactions. This study demonstrates that IDAF measurements are ideal, both experimentally and numerically, for studying heterogeneous processes in Africa. There is a clear need to perform additional sampling in the tropics with simultaneous measurements of gas, aerosol, and precipitation chemistry. The goal of the IDAF Project is to collect these data on a long-term basis, to identify trends, and determine the mechanisms that modulate atmospheric chemistry in the tropics.

## References

- Andreae M.O. and P.J. Crutzen (1997). Atmospheric aerosols: biogeochemical sources and role in atmospheric chemistry, *Science*, 276, 1052-1057.
- Carmichael G. R., Hong M.S., Ueda H., Chen L.L., Murano K., Park J.K. Kang C. and Shim S. (1997). Aerosol composition at Cheju Island, Korea. *J. Geophys. Res.*, 102, 6047-6061.
- Dentener, F. J., G. R. Carmichael, Y. Zhang, J. Lelieveld, and P. J. Crutzen (1996). Role of mineral aerosol as a reactive surface in the global troposphere, *J. Geophys. Res.*, 101, 22, 869-22,889.
- Galy-Lacaux C. and Modi A.I. (1998). Precipitation chemistry in the Sahelian savanna of Niger, Africa, *J. Atm. Chem.*, 30, 319-343.
- C. Galy-Lacaux, G. R. Carmichael, C. H. Song, J.P. Lacaux and I. Modi, 2001. Heterogeneous processes involving nitrogenous compounds and Saharan dust inferred from measurements and model calculations Region. *J. Geophys. Res.*, 106, D12, 12559-12578.
- Kim Y. P. and Seinfeld J. H. (1995) Atmospheric gas-aerosol equilibrium: III. Thermodynamics of crustal elements  $\text{Ca}^{2+}$ ,  $\text{K}^+$ , and  $\text{Mg}^{2+}$ . *Aerosol Sci. Technol.* 22, 93-110.

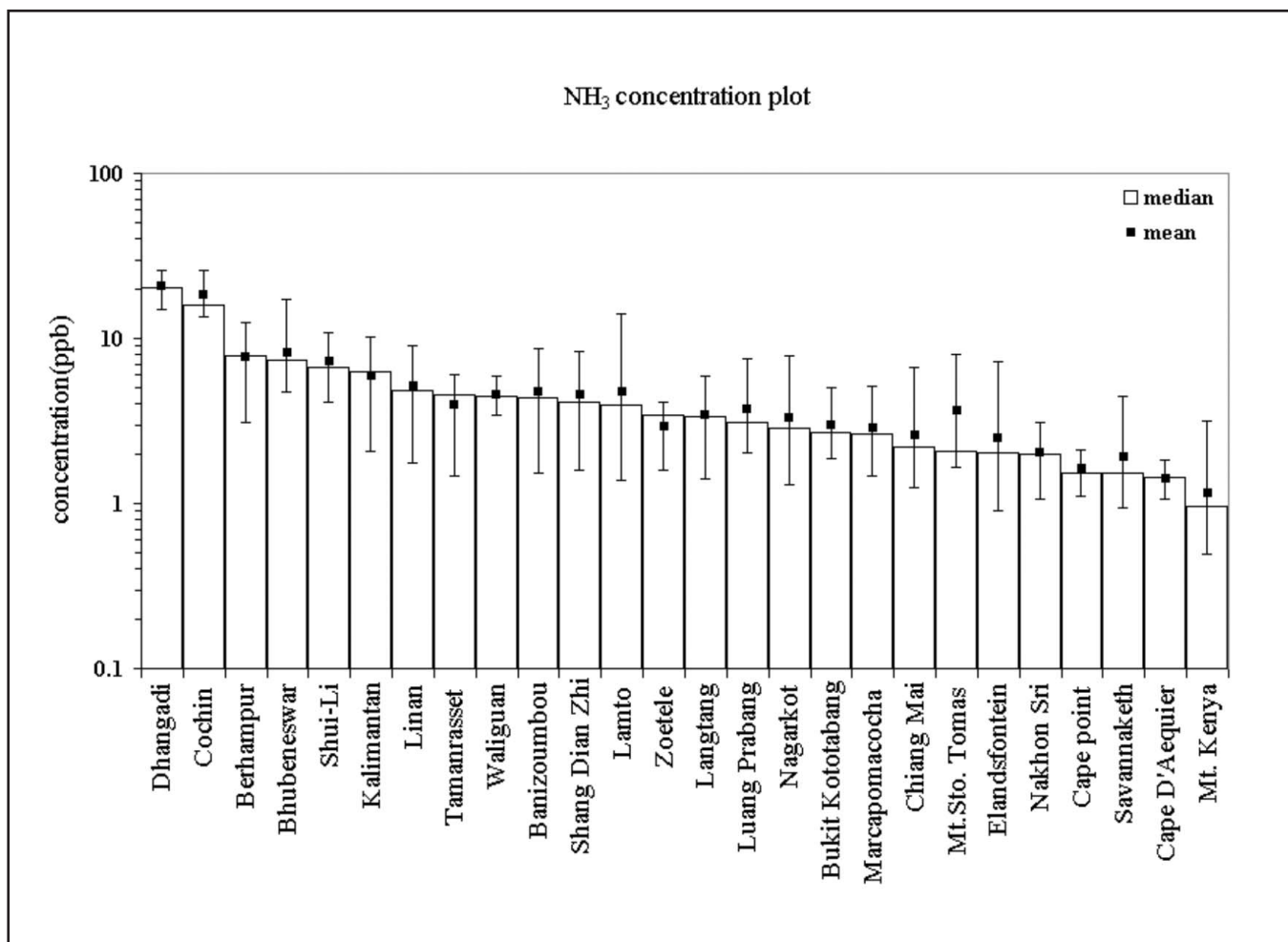
# Measurements of sulfur dioxide, ozone and ammonia concentrations in Asia, Africa, and South America using passive samplers

Contributed by **Martin Ferm**, IVL Swedish Environmental Research Institute, and **Gregory Carmichael**, Department of Chemical & Biochemical Engineering, Center for Global & Regional Environmental Research, The University of Iowa, Iowa City, IA USA

Measurement programs play a critical role in air pollution and atmospheric chemistry studies. Pressures of costs and changing priorities often make it difficult to maintain and expand long terms measurement programs. In some cases environmental planning activities are severely hampered by the lack of information on the ambient levels of pollutants. Yet this information is needed to improve our understanding of the behavior of the atmosphere and its interac-

tions with oceans and the biosphere and to better anticipate the future states of the earth-atmosphere system. One challenge facing the community is the need to expand its activities to include measurements in each principal climatic zone and each biome, and to continue to add important species to the list of observed parameters. Passive samplers present a means of addressing many measurement issues in air pollution and atmospheric chemistry, in that they provide a cost effective way to monitor specific species at urban, regional and global scales, and offer broad capacity building opportunities.

To demonstrate the expanded use of passive samplers in air quality studies a pilot measurement program was initiated as a key component of the newly established



**Figure 1** - Measured NH<sub>3</sub> concentrations at various regional sites. The bars indicate maximum, minimum and mean values, and the solid box designates the median values.

WMO/GAW Urban Research Meteorology and Environment (GURME) project. This passive sampler project was done in collaboration with, and as a component of, the IGAC-DEBITS program. The pilot network consisted of stations from previous studies in Asia and from existing GAW stations, along with newly established sites. In total, 50 stations in twelve Asian countries (China, India, Indonesia, Japan, Korea, Malaysia, Nepal, Philippines, Singapore, Thailand, Laos and Vietnam), seven African countries (Algeria, Cameroon, Ivory Coast, Niger, Morocco, Kenya and South Africa), five South American countries (Argentina, Brazil, Chile, Peru, and French Guyana) and a European country (Turkey). At these sites sulfur dioxide (SO<sub>2</sub>), ammonia (NH<sub>3</sub>) and ozone (O<sub>3</sub>) were monitored monthly at the rural sites and with short sampling periods at the urban sites. At the urban sites weekly samples of NO, NO<sub>2</sub>, HCOOH, CH<sub>3</sub>COOH, benzene, ethyl benzene, toluene, and xylenes were also obtained.

The samplers used are of badge type, 10 mm long and 20 mm internal diameter. A membrane is mounted at the inlet to prevent wind-induced turbulent diffusion. The membrane is protected from mechanical damage by a stainless steel mesh. The detection limit was estimated from a sampled amount corresponding to three times the standard deviation of the average field blanks using the actual exposure time. For exactly one month sampling this corresponded to 0.03 ppb SO<sub>2</sub>, 1.0 ppb NH<sub>3</sub>, and 0.6 ppb O<sub>3</sub>. The SO<sub>2</sub> and NO<sub>2</sub> samplers have been compared to active sampling within a routine network (Ferm and Svanberg 1998). Additional information on the use of these samplers and their comparison with active sampling results can be found in Ayers et al. (1998). The NH<sub>3</sub> sampler was tested in an intercomparison (Kirchner et al., 1999). The O<sub>3</sub> sampler was compared to results from a UV-instrument (Sjöberg et al., 2001). The O<sub>3</sub> sampler has also been validated for use in workplace atmospheres (Ferm 2001). All the samplers are also undergoing intercomparisons within CEN.

Results for measured NH<sub>3</sub> at the regional sites are presented in Figure 1. Annual median NH<sub>3</sub> concentrations range from 20 ppb at Dhangadi, India to less than 1 ppb for nine stations. At 27 of regional stations, the sampled ambient NH<sub>3</sub> levels exceeded 1 ppb. The observed SO<sub>2</sub> concentrations varied from a high of 13 ppb at Linan, China to less than 0.03 ppb for four stations. At 30 of 36 regional stations the observed mean annual concentrations of SO<sub>2</sub> were less than 1.0 ppb. The median O<sub>3</sub> concentrations varied from a maximum of 45 ppb at Waliguan Mountain to 8 ppb at Petit Saut, French Guiana. In general, the highest O<sub>3</sub> values were found in the mid latitudes with the Northern hemisphere mid-latitude values exceeding the Southern hemisphere mid-latitude levels. The lowest values were found in the tropical regions.

Results from this study help to demonstrate that diffusive samplers are ideal for measurements at remote sites, for

checking transport models, screening studies, mapping concentrations in cities, siting of more advanced stations, personal monitoring, etc. The main advantages are: the samplers are small, silent, do not need electricity; the measurements are made *in situ* (without inlet tubing); the measurement range is very large; technical personnel are not needed at the sampling site; field calibration is not needed; 100% time coverage can be obtained; and they are simple to deploy and mail. The drawbacks are that only gases can be monitored, that the results are not obtained immediately, and peak values of short duration are not resolved.

Finally, these results demonstrate that passive samplers offer a low cost means of obtaining high quality measurements, covering large regions, while engaging many scientists around the world. Further details of this study can be found in Carmichael et al., (2002) and at (<http://www.cgrer.uiowa.edu/people/nthongbo/Passive/pasmain.html>).

## References

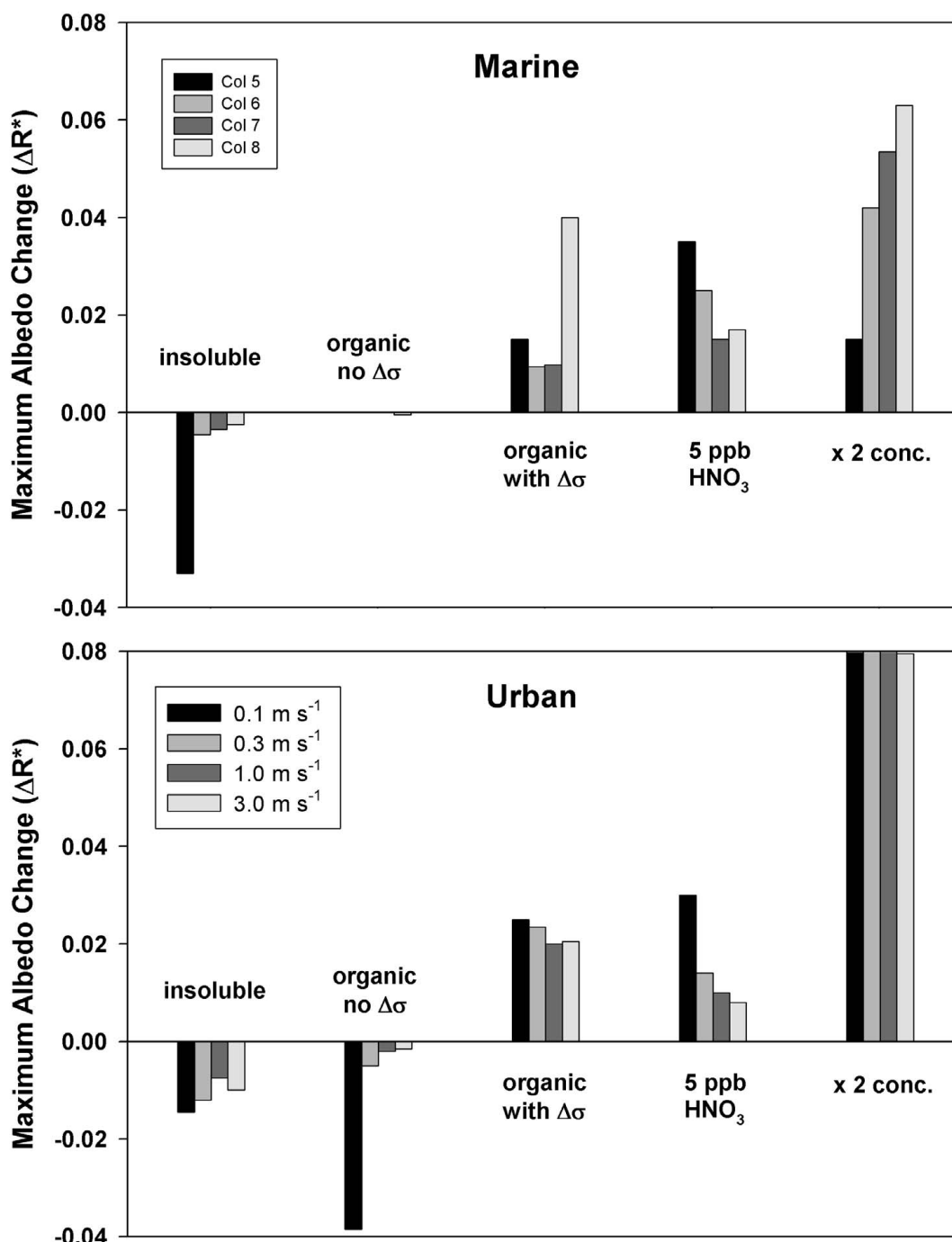
- Ayers G.P., Keywood M.D., Gillet R.W., Manins P.C., Malfroy H. and Bardsley T. (1998) Validation of passive diffusion samplers for SO<sub>2</sub> and NO<sub>2</sub>, *Atmos. Environ.*, 32, 3593-3609.
- Carmichael, G., M. Ferm, N.Thongboonchoo, et al., (2002) Measurements of Sulfur Dioxide, Ozone and Ammonia Concentrations in Asia, Africa, and South America Using Passive Samplers, *Atmospheric Environment*, in press.
- Ferm M. (2001b). Validation of a diffusive sampler for ozone in workplace atmospheres according to EN838. Proc. from International Conference Measuring Air Pollutants by Diffusive Sampling, Montpellier, France 26-28 September 2001. 298-303.
- Ferm M. and Svanberg P.A. (1998). Cost-efficient techniques for urban- and background measurements of SO<sub>2</sub> and NO<sub>2</sub>. *Atmospheric Environment*, 32, 1377-1381.
- Kirchner M., Braeutigam S., Ferm M., Haas M., Hangartner M., Hofschreuder P. Kasper-Giebl A., Römmelt H., Striedner J., Terzer W., Thöni L., Werner H. and Zimmerling R. (1999). Field intercomparison of diffusive samplers for measuring ammonia. *J. Environmental Monitoring*, 1, 259-265.
- Sjöberg K., Lövblad G., Ferm M., Ulrich E., Cecchini S. and Dalstein L. (2001) Ozone measurements at forest plots using diffusive samplers. Proc. from International Conference Measuring Air Pollutants by Diffusive Sampling, Montpellier, France 26-28 September 2001. 116-123.



# Correction

From June 2002 Issue — *Clouds, Atmospheric Chemistry and Climate* by Maria Cristina Faccini

**Figure 3** - Maximum albedo difference, with respect to the baseline simulation, for a convective marine cloud and a convective urban cloud. “*insoluble*”: CCN containing insoluble material (10% by mass for marine, 50% for urban); “*organic no  $\Delta\sigma$* ”: CCN containing water soluble organic carbon (10% by mass for marine, 50% for urban) and no surface tension effects; “*organic with  $\Delta\sigma$* ”: CCN containing water soluble organic carbon (10% by mass for marine, 50% for urban) and with surface tension effects; “*5 ppb  $\text{HNO}_3$* ”: completely soluble inorganic aerosol, with 5 ppb initial gas-phase  $\text{HNO}_3$ ; “*x 2 conc.*” completely soluble inorganic aerosol with concentration doubled. The organic fraction is assumed to be composed (by mass) of 18% levoglucosan, 41% succinic acid, and 41% fulvic acid.



# Announcements

## Biosphere-atmosphere exchange of reactive trace gases, Session AS3.04, EGS-AGU-EUG Joint Assembly Nice, France, 06-11 April 2003

The biosphere is both a major source and sink of reactive gases (e.g., ozone, NO, isoprene). There are major uncertainties associated with descriptions of the processes controlling surface-atmosphere trace gas exchange. This limits our ability to predict the fluxes that are needed for regional and global chemistry and transport modeling. New methods for measuring trace gas exchange are being developed and applied and are improving our understanding of magnitude and variability of these fluxes.

The session is open to all contributions related to reactive trace gas exchange studies at various spatial and temporal scales using e.g. enclosure, turbulent flux, and boundary layer profiling techniques. This includes both measurement and modeling investigations of biosphere atmosphere exchange. Especially welcome are contributions associated with the interactions between reactive carbon and nitrogen trace gases (e.g., isoprene, NO and isoprene nitrates) within and near vegetation canopies, up-scaling of trace gas exchange measurements, and the impact of climate and land use change on reactive trace gas exchange.

We encourage you to present your work on this subject and submit your abstract by 15 January 2003 to session AS3.04 at the forthcoming EGS-AGU-EUG Joint Assembly, Nice, France, 06-11 April 2003.

### IMPORTANT DEADLINES

- 1) "Early Bird" Registration: 31 December 2002 (Savings of 30-60 Euro)
- 2) Deadline for Receipt of Abstracts: 15 January 2003  
See the following website for more information:  
[http://www.copernicus.org/EGS/egsga/nice03/abstract\\_submission\\_txt\\_new.htm](http://www.copernicus.org/EGS/egsga/nice03/abstract_submission_txt_new.htm)
- 3) Deadline for Pre-Registration: 07 March 2003 (Savings of 15-30 Euro)
- 4) Deadline for Hotel Accommodation: March 7, 2003  
See the following website for more information:  
[http://www.copernicus.org/EGS/egsga/nice03/hotel\\_booking.html](http://www.copernicus.org/EGS/egsga/nice03/hotel_booking.html)

Please help us keep our mailing list up to date:

\_\_\_\_\_ Please note my new address

\_\_\_\_\_ Please also send IGAC*tivities* to my colleague



Name: \_\_\_\_\_ Organization \_\_\_\_\_

Street address: \_\_\_\_\_

City: \_\_\_\_\_ State: \_\_\_\_\_ Zip: \_\_\_\_\_ Country: \_\_\_\_\_

Telephone: \_\_\_\_\_ Fax: \_\_\_\_\_ E-Mail: \_\_\_\_\_

Please return by mail to:

Peter Czepiel/IGAC

Morse Hall, University of New Hampshire

39 College Rd., Durham, NH 03824-3575

or e-mail to: [igac.cpo@unh.edu](mailto:igac.cpo@unh.edu)

# The 8th Scientific Conference of the International Global Atmospheric Chemistry Project (IGAC)

To be held in Christchurch,  
New Zealand in  
September 2004.

Check the IGAC  
web site for details.

# Joint SPARC/IGAC workshop on Climate-Chemistry Interactions

April 3-5, 2003,  
Giens, France

For further information  
contact A. Ravishankara  
(ravi@al.noaa.gov)  
or Shaw Liu  
(shawliu@earth.sinica.edu.tw)



## *activities* Newsletter

Published by The IGAC Core Project Office  
CCRC/Morse Hall, University of New Hampshire  
39 College Road, Durham, NH 03824-3575 USA

Editor: Peter Czepiel  
Layout and Proofreading: Virginia Moore  
IGAC logo: Linda Kubrick



Tel: (+1-603) 862-4520, Fax: (+1-603) 862-3875  
E-mail: igac.cpo@unh.edu

IGAC was initiated by the Commission on Atmospheric Chemistry and Global Pollution (CACGP) and is a Core Project of the International Geosphere-Biosphere Programme (IGBP). The IGAC Core Project Office is currently supported by the National Science Foundation (NSF), National Aeronautics and Space Administration, and National Oceanic and Atmospheric Administration of the United States of America through NSF Grant No. ATM 99-08980. Any opinions, findings and conclusions, or recommendations expressed in this newsletter are those of the individual author(s) and do not necessarily reflect the views of the NSF or other agencies.



# *Activities* Newsletter

Morse Hall  
University of New Hampshire  
39 College Road, Durham, NH  
03824-3575 USA

NON-PROFIT ORG:  
U.S. POSTAGE  
PAID  
Durham, NH 03824  
Permit No. 2



Printed on Recycled Paper  
Please Recycle after Use!