Atmos. Chem. Phys. Discuss., 10, 4407–4461, 2010
www.atmos-chem-phys-discuss.net/10/4407/2010/

Atmospheric Chemistry and Physics Discussions

This discussion paper is/has been under review for the journal Atmospheric Chemistry and Physics (ACP). Please refer to the corresponding final paper in ACP if available.

Long term measurements of sulfur dioxide, nitrogen dioxide, ammonia, nitric acid and ozone in Africa using passive samplers

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Received: 18 December 2009 – Accepted: 11 January 2010 – Published: 12 February 2010

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Published by Copernicus Publications on behalf of the European Geosciences Union.

Abstract

In this paper, we present the long term monitoring of ambient gaseous concentrations within the framework of the IDAF (IGAC-DEBITS-AFRICA) program. This study proposes for the first time to study long term gases concentrations (1998–2007) by determining the ambient concentration of the inorganic gases, i.e., SO_2, NO_2, HNO_3, NH_3 and O_3 using passive samplers at seven remote sites in West and Central Africa. Sites are representative of a great African ecosystem and are located according a transect: dry savannas-wet savannas-forests with Banizoumbou (Niger), Katibougou and Agoufou (Mali), Djougou (Benin), Lamto (Cote d'Ivoire), Zoetele (Cameroon) and Bomassa (Congo). The validation and inter-comparison studies conducted with the IDAF passive samplers assure the quality and the control of the measurement technique to show the accuracy of the measurements. For each type of African ecosystems, we have studied the long term data series to document the levels of gaseous surface concentrations and the seasonal and interannual variations analyzed as a function of emission sources variations. We have tried to compare West and Central African gases concentrations to the results obtained in other parts of the world. Results show that the annual mean concentrations of NO_2, NH_3, HNO_3 measured in dry savannas are higher than those measured in wet savannas and forests that have quite similar concentrations. Annual mean NO_2 concentrations vary from 0.9±0.2 in forests to 2.4±0.4 ppb in the dry savannas, NH_3 from 3.9±1.4 to 7.4±0.8 ppb, HNO_3 from 0.2±0.1 to 0.5±0.2 ppb. Annual mean O_3 and SO_2 concentrations are lower for all the ecosystems and range from 4.0±0.4 to 14.0±2.8 and from 0.3±0.1 to 1.0±0.2 ppb, respectively. A focus on dry savannas processes involved in gases emission is presented in this work, explaining the high concentrations of all gases measured on the three dry savannas sites. For all gases, seasonal concentrations are higher in the wet season of dry savannas. Conversely, concentrations are higher in the dry season of wet savannas. In forest, we measure no significant difference between wet and dry seasons. This unique database of long term gases concentrations monitoring is available at: http://www.obs-mip.fr/idaf/.

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1 Introduction

Measurement programs play a critical role in air pollution and atmospheric chemistry studies. Moreover, long term measurements programs are crucial to document changes in the atmospheric composition. Long term monitoring allows to characterize seasonal and interannual variations. It is particularly important in tropical regions where seasonal cycles related to natural and anthropogenic emissions sources of gases and particles are well marked, i.e. biomass burning, soils and vegetation emissions.

The international program DEBITS (Deposition of Biogeochemically Important Trace Species) was initiated in 1990 as part of IGAC/IGBP (International Global Atmospheric Chemistry/International Geosphere-Biosphere Programme) "core project" in order to study wet and dry atmospheric deposition in tropical regions (Lacaux et al., 2003). In 2004, DEBITS activities have been positively assessed and are continuing in the new IGAC II structure (task DEBITS II, Pienaar et al., 2005; Bates et al., 2006). In 2009, the DEBITS network includes about twenty five long term measuring stations evenly distributed within the tropical belt in Africa, Asia and South America. For tropical Africa, the IDAF (IGAC/DEBITS/AFRICA) project started in 1994. Since this date, the IDAF program is recognized by INSU (Institut National des Sciences de l'Univers, in France) and the CNRS (Centre National de la Recherche Scientifique, in France) as a member of the Environmental Research Observatory (ORE, in France) network. The ORE IDAF has been given the mission of establishing a long-term measuring network to study the atmospheric composition in Africa. Since 2005, the IDAF program is associated to the AMMA LOP (African Monsoon Mutidisciplinary Analyses/Long Observation Program, Lebel et al., 2007). Within the framework of IDAF, several studies of precipitation chemical composition representative of great African ecosystems have been recently published. These studies have helped to quantify wet depositions of important biogeochemical elements and to estimate the contributions of different atmospheric sources (Galy-Lacaux and Modi, 1998; Galy-Lacaux et al., 2001, 2009; Sigha et al., 2003;

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Yoboue et al., 2005; Mphepya et al., 2004, 2006). To complement these studies, it is appropriate to study and quantify dry deposition fluxes. Dry deposition is estimated on the one hand from measurements of gaseous and particulate species based on continuous measurements of gaseous concentrations and on bulk air sampling (ammonium and nitrate particulate content). On the other hand, realistic dry deposition velocity according to the site and the species needs to be calculated in order to estimate dry deposition fluxes.

In this paper, we present the long term monitoring of ambient gaseous concentrations in the IDAF program. In a second step, dry gaseous deposition fluxes will be estimated and results will be subject of a separate paper. Our study presents an original database based on ten years of measurements of five important atmospheric gases on the IDAF African network composed of seven sites in West and Central Africa. Martins et al. (2007) have already published the long term monitoring of gases at the three IDAF sites located in South Africa. All the monitored gases play a major role in the chemistry of the atmosphere and they were included in the measurement program of the atmospheric chemistry international network DEBITS/IGAC. The monitored compounds are sulfur dioxide (SO_2), nitrogen dioxide (NO_2), nitric acid (HNO_3), ammonia (NH_3) and ozone (O_3).

It is known that atmospheric releases of acidic pollutants, which include sulfur and nitrogen compounds, can cause adverse health effects and have the potential to cause other environmental damage (e.g. acid rain) (Brimblecombe et al., 2007). The deposition of atmospheric compounds containing these species are thus of major importance in atmospheric studies. The oxides of nitrogen, NO_X ($NO+NO_2$) mainly emitted into the atmosphere as NO, which is subsequently transformed into NO_2 and other nitrogenous species (collectively known as NO_y) play important roles in controlling the oxidative chemistry of the lower atmosphere, including regulation of the photochemical production of ozone, nitric acid and organic nitrates. Nitric acid is the most important transformation product of NO_x. The measurement of HNO_3 in ambient air is of great importance because of its significance in the acidification of the atmosphere and its

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control of the levels of photooxydants. Ammonia is also an important atmospheric pollutant, with a wide variety of impact. In the atmosphere, NH_3 neutralizes a great portion of the acids produced by oxides of sulfur and nitrogen. Essentially, all emitted NH_3 is returned to the surface by deposition, which is known to be one of the causes of soil acidification since the early 1980s (Sutton et al., 2009). Sulfur dioxide (SO_2) is the primary cause of acid precipitation, which adversely affects natural systems, agriculture and building materials (Smith et al., 2001). The sulfate aerosol particles formed as a consequence of these emissions impair visibility and affect human health (Chestnut, 1995). Tropospheric ozone (O_3) is also a major environmental concern because of its adverse impacts on human health (Mc Granaham and Murray, 2003), its impact on crops and forest ecosystems (NRC, 1991; Mauzerall and Wang, 2001) and its greenhouse gas effect responsible for climate change (Hansen et al., 2002).

In the IDAF program, SO_2, NO_2, HNO_3, NH_3 and O_3 have been measured using the passive sampler technique. Passive samplers present a good mean of addressing many measurement issues in air pollution and atmospheric chemistry. They provide a cost-effective way to monitor specific species at rural, regional and global scales. Passive samplers have been extensively tested in various international studies (Ferm and Rodhe, 1997; Ferm et al., 2005; Carmichael et al., 1996; Martins et al., 2007). In the framework of the IDAF project, we have developed a set of passive samplers at the Laboratory of Aerology in Toulouse.

In this paper, it is proposed for the first time to study long term gases concentrations (1998–2007) by determining the ambient concentration of the inorganic gases, i.e., SO_2, NO_2, HNO_3, NH_3 and O_3 using passive samplers at seven remote sites in West and Central Africa. We will first present the validation of the IDAF passive samplers measurements. Then, it is an attempt to report and analyze the long-term data series of NO_2, HNO_3, NH_3, SO_2 and O_3 according a regional representative transect of the great Africa ecosystems: dry savanna/wet savanna/forest. The objectives are: (1) to characterize the levels of gaseous surface concentrations in order to give a representative order of magnitude at the regional scale of the African ecosystems, and

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(2) to establish the linkages between seasonal cycle and interannual variability according to the atmospheric emission sources of each studied gas. Results for West and Central African sites can then be compared to the gases concentrations measured on Southern African sites (Martins et al., 2007).

2 Experimental design

2.1 Sampling sites

In the framework of the IDAF project, 10 specific sites to constitute a long term monitoring network have been initiated. All are representative of remote sites. Three types of ecosystems over West and Central Africa are each monitored by multiply sites (2 pairs and 1 group of 3): dry savanna (Niger and Mali), wet savanna (Cote d'Ivoire and Benin), and equatorial forest (Congo and Cameroon). In South Africa, three long-term sites have been chosen to be regionally representative of specific Southern African ecosystems (Martins et al., 2007). Figure 1 shows the location of the 10 IDAF sites operating and monitoring ambient gases concentrations in 2007. For the Western Central Africa sites, of interest in this study, we present the geographic and ecologic characteristics in the Table 1.

In general, the West and Central African climate (and its variability) is a function of the position of the Inter Tropical Convergence Zone (ITCZ) which separate hot and dry continental air coming from the Sahara desert (Harmattan) and cooler and humid maritime air masses (Monsoon) coming from the equatorial Atlantic Ocean. Extreme latitudinal positions of the ITCZ are in January (around 5° N) and August (around 22° N). Taking into account the position of ITCZ and based on monthly mean recorded rainfall, we have determined the mean dry and wet season of each studied stations (1998–2007) (Table 2). The table indicates the variation of season duration according the site and the ecosystem. The rainfall gradient extends from 358 mm in the dry savanna to 1588 mm in the forest.

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To briefly describe the IDAF monitoring stations:

Banizoumbou is located in a rural and agro pastoral area of the Sahelian region of Niger, approximately 60 km east-ward of Niamey in the southwest Niger. The climate of the studied region is typically Sahelian. The annual rainfall varies from 402 mm in 2002 to 699 mm in 1998 with a mean annual rainfall during the ten year studied period of 486 mm. More information is available in Galy-Lacaux and Modi (1998) and Galy-Lacaux et al. (2001). Katibougou is located in the Koulikoro region, in the IPR center (Institut Polytechnique Rural) approximatly 60 km northeast of Bamako. It is representative of the Sudano-Sahelian zone. The annual rainfall varies from 585 to 1039 mm with an average of 771 mm. Agoufou is part of the gourma meso scale site in the AMMA (African Monsoon Multidisciplinary Analysis) CATCH (Couplage de l'Atmosphere Tropicale et du Cycle Hydrologique) observatory. It is situated towards the northern limit of the area reached by the West African monsoon. The mean annual precipitation amount from 2005 to 2007 is 348 mm. A comprehensive description of the station can be found in Mougin et al. (2009). Lamto is located, in the "V-shaped Baoule" region, 120 km north of Abidjan and it belongs to the wet savanna region of Cote d'Ivoire. The Lamto Reserve covers approximately 2600 ha and is essentially made up of wet savanna with the, so-called, Gallery Forest along the Bandama river (Gautier, 1990). At Lamto station, the mean annual rainfall amount is about 1269 mm (Yoboue et al., 2005). Djougou station is located in northern Benin at 450 km of Cotonou. The site is one of the sites forming the AMMA Oueme mesoscale. It is located in a clearing surrounded by secondary woodland, cultivated crops and fallow that had been subjected to some small-scale vegetation burning during the five last years. It lies within a southern Sudanian vegetation-type zone characterized by woodland savanna. The mean annual rainfall is 1205 mm from 2005 to 2007. Zoetele is located in the rainforest of Southern Cameroon, at 120 km south of Yaounde. A dense evergreen forest called the "Congo Forest" covers the whole region. Agriculture remains the dominant regional activity. At Zoetele, the average annual rainfall amount is of 1479 mm (1998–2007) with a maximum of 2162 mm in 1999 (Sigha et al., 2003). Bomassa is located in

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the natural park of Nouabale Ndoki (3°32′12″ N–0°40′29″ N; 15°28′26″ E–17°34′8″ E) which extends from north Congo to Central African Republic. The site is located in the North West Congolese equatorial forests. The altitude varies from 330 to 600 m and the mean annual precipitations between 1450 and 1600 mm.

Banizoumbou, Katibougou, Lamto, Zoetele and Bomassa began monitoring gases in 1998. Djougou and Agoufou, part of the Long term Observation Period of the AMMA program, started operating in 2005. NO_2, NH_3 and HNO_3 have been monitored since 1998. Ozone starts in 2001 and SO_2 in 2002. All the measurements are still continuing in all the IDAF sites.

2.2 Description and preparation of the passive sampler

In the framework of the IDAF project, we have developed a set of passive samplers at the Laboratory of Aerology in Toulouse. These samplers have been developed according to the DEBITS procedures based on the work of Ferm (1991, 1994).

The functioning of the diffusive samplers is based on both, a chemical and a physical process (i.e. a chemical reaction and laminar diffuse, respectively). The rates at which gaseous pollutants in ambient air diffuse into the sampler are controlled by the diffusion coefficients of the respective gases. At the opposite side of the inlet sampler, the gases impinge on a paper disk that has been impregnated with a specific chemical reactant able to trap the pollutant of interest. Since this solid support is impregnated with a small amount of sorbent material dissolved in a volatile solvent, the gases that come into contact with it impact against a high surface area and are trapped efficiently.

The Fig. 2 presents the typical design of the IDAF passive sampler showing series of caps, rings and filters; each with a specific function within the sampler. To minimize internal turbulent diffusion and particle interference, a Teflon membrane (pore 1 µm, diameter 25 mm) was used in the air inlet. The membrane was protected from mechanical damage by a stainless steel screen (thread diameter 0.08 mm and mesh size 0.125 mm). The concentration of the net flux of the gas through the sampler itself and trapped on the sorbent is calculated using Fick's first law of diffusion (Ferm,

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2001). Following this law, the average concentration C_{avg} in µmol m^{-3} is calculated from Eq. (1).

$$C_{avg} = \left[(L/A)\cdot X\right]/(t\cdot D) \quad (1)$$

Where X (µmol) is the amount of gas pollutant trapped on paper disk (corrected for the blank) after exposure time (s), (m^2 s^{-1}) is the diffusion coefficient of the gas in air, (m) is the diffusion path length, and (m^2) is the cross sectional area of diffusion path.

The average concentration can be expressed in ppb using the Eq. (2).

$$C_{avg}(\text{ppb}) = \left[(L/A)\cdot X\cdot R\cdot T\right]/(t\cdot D\cdot P) \quad (2)$$

Where T is the average temperature during the sampling period (K), R is the ideal gas constant (R=0.08206 l atm k^{-1} mol^{-1}) and P is the mean atmospheric pressure during the sampling period (P = 1 atm). L/A is the coefficient of air resistance and depends on the sampler geometry and size.

In the IDAF network we define three samplers which differ by their color and their coating solutions: grey for nitrogen dioxide (NO_2), black for nitric acid (HNO_3) and sulfur dioxide (SO_2), white for ammonia (NH_3), black and grey for ozone (O_3).

Samplers were prepared in our lab in the following manner: 25 mm diameter cellulose filters (whatman 40) were cut to fit into the sampler bottom and were submitted to three washings with deionised water in an ultrasonic bath, and one with methanol (15 min each). After drying in a stove at 50 °C, the filters were impregnated with the different coating solutions, for 2 h, and dried again before being put into the samplers (Table 3). All other components of the passive sampler used for storing and transport, underwent a similar cleaning treatment. Rubber gloves were used to handle passive samplers and avoid contamination.

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2.3 Sampling and analysis

2.3.1 Sampling procedure

In the IDAF measuring network, the Laboratory of Aerology is in charge of the preparation and the analysis of passive samplers of the seven Western and Central African sites. Initially, the passive samplers are supplied ready for use in a sealed container, loaded with a filter treated for a nominated pollutant gas. Each two months, they are sent to the stations with a technical sheet (dates of installation/removal, temperature during exposition, etc.) to local operators. Passive gas samplers were exposed for a one month period at the remote rural African sites of the network. They were mounted under a plastic plate support to avoid direct effect of wind transport and splashing from precipitation. The support was attached to a pole at a minimum height of 1.5 m. All the samplers are exposed in pairs to ensure the reproducibility of results and to reduce data loss if a sampler suffers interference (Fig. 2). For each set of samplers, blank samples are kept sealed in the film container as a field blank and also returned for analysis. After exposure, passive samplers are sent back to the Laboratory of Aerology and stored in a fridge (4 °C) before analysis. The impregnated filter is removed from the sampler and is prepared for analysis by ionic chromatography. Then, in the long term measurement network, samplers are recycled. All the parts are cleaned and supports were reloaded with a freshly impregnated filter before being mailed again to the site operators. The Laboratory of the School for Chemistry and Biochemistry of the North-West University in South Africa is tasked with the preparation and the analysis of the passive samplers used on the three IDAF sites of South Africa (Martins et al., 2007).

2.3.2 Chemical analysis

Inorganic anions and cations, i.e., sulfate, nitrate, nitrite and ammonium captured on impregnated filters of the gas passive samplers are determined by ionic

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chromatography (see chemical reactions in Table 3). Filters were extracted in 10 mL of 18 MΩ water by ultrasonic stirring (15 min). The laboratory is equipped with a DIONEX DX500 and ICS 1000 ionic chromatograph (IC) with two automatic samplers (AS50). The determination of anions on the DX500 used a gradient pump (GP40), with a conductivity detector (CD20), and a DIONEX Ionpac AS-11 and AG-11 as pre-column. For cations detection, the ICS 1000 in an isocratic mode with CG12A and CS12A as pre-column and column, was used. The eluents were NaOH and MSA for anions and cations, respectively. Certified ionic standards were used for IC calibration. The quality does not depend only on the sampler, but also on the analysis (Galy-Lacaux and Modi, 1998) and the standardized and accredited procedures. Since 1996 the analytical Laboratory of Aerology has participated in the quality control inter-comparison program organized twice a year by the World meteorological Organization Center (WMO). According to our results of the quality assurance program, analytical precision is estimated to be 5% or better for all ions, within the uncertainties of all measured values presented here. All the results for our lab referenced as the participant number 700106 are available at: http://qsac-americas.org/.

A field blank is included with each set of samplers deployed. Over the studied period, 23 analytical series of measurements have been performed in IC and a total of 230 blanks for each gas have been analyzed. Detection limits for each trace gas were calculated from field blanks and found to be 0.07±0.03 ppb for HNO_3, 0.2±0.1 ppb for NO_2, 0.7±0.2 ppb for NH_3, 0.05 ±0.03 ppb for SO_2 and 0.1±0.1 ppb for O_3. The analysis of our database shows that 12% of HNO_3, 4% of NO_2 and 13% of SO_2 measurements were below the detection limit. Data below detection limits were removed from the final database.

All samples were collected in duplicate. The average of the two duplicate samples was used in all cases except when contamination of one of the samples was suspected (it happens in less then 5% of all data). To give an indication of the precision of this sampling technique, the covariance of all duplicate samples were calculated for the ten year period (1998–2007). The reproducibility was found to be 20%, 9.8%, 14.3%,

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16.6% and 10% for HNO_3, NO_2, NH_3, SO_2 and O_3, respectively. These results compare well with those reported by Martins et al. (2007), at the Southern Africa sites, for the same pollutants (20%, 8.3%, 15.3%, 16.6% and 2.4% for HNO_3, NO_2, NH_3, SO_2 and O_3, respectively). These results are also in accordance with the variations found between different laboratories for duplicate analysis equal to ± 25%, which is acceptable for indicative monitoring (Stevenson et al., 2001).

2.4 Validation of IDAF passive samplers

The use of passive samplers in the IDAF network has been preceded by several tests and validations.

2.4.1 Determination of the *L/A* parameter

We have first optimized the determination of the *L/A* ratio (Eq. 2) dependant of the sampler geometry. *L/A* is defined by the following sum:

$$L/A = \left(L_a/A_a + L_f/A_f + L_g/A_g + L_c/A_t\right) \quad (3)$$

where L_a is the ring lenght (10^{-2} m), A_a the surface of the ring section (3.46×10^{-4} m^2), L_f the thickness of the teflon filter (175×10^{-6} m), A_f the teflon filter area permeable to air (2.27×10^{-4} m^2), L_g is the thickness of the stainless steel grid (90×10^{-6} m), A_g is the grid surface permeable to air (9.9×10^{-5} m^2), L_c the thickness of the laminar boundary layer and A_t is the surface of the inlet hole (2.84×10^{-4} m^2). L_c is a key parameter in the calculation of the gas concentration in the atmosphere. In the IDAF validation phase, we have experimentally determined the L_c value for our passive samplers. For a specific gas, two passive samplers were mounted and exposed at the same moment: one with the impregnated filter normally mounted at the bottom of the sampler and one with the impregnated filter directly at the inlet of the sampler. The analysis of the two samplers allow the calculation of L_c and thus the final determination of *L/A*. A total of two

hundred samplers have been exposed, about 50 for each color and gases. A synthesis of all the results is presented in Table 4. The *L/A* value for the IDAF passive samplers is estimated to be 47.5±1.6 m^{-1} with an uncertainty of 3.4%. The corresponding thickness value of the laminar boundary layer (L_c) is equal to 4.8±0.5 mm.

2.4.2 Inter-comparison and quality control for passive samplers

To ensure that the western central Africa passive samplers monitoring network delivers reliable results, a number of inter-comparison and tests studies were performed within the IGAC-DEBITS program. Also some comparisons were initiated in collaboration with the IVL (Swedish Environmental Research Institute) (accredited lab). In order to assess the performance and reliability of IDAF passive samplers, a study was undertaken at different sites in Toulouse, France (1998–2000). The accuracy of the IDAF passive samplers measurements was determined during a two week experiment, in the city, by comparison to readings performed by a set of MEGATEC continuous analyzer for NO_2, O_3 and SO_2. Figure 3a–c presents the comparisons of gases concentrations measured by passive samplers (integration over 15 days) and active analyzers. All the gases showed a good correlation between the two methods of measurements. NO_2, SO_2 and O_3 have a mean comparative ratio of 1:0.9, 1:0.8 and 1:0.7, respectively, between passive and active sampling methods. The correlations are high with R^2=0.95 for NO_2, R^2=0.8 for O_3 and R^2=0.9 for SO_2. The lower correlation is for O_3 and can be explained by the indirect O_3 determination using the passive sampler method but rather the overall oxidation potential of the atmosphere.

In a second phase of validation, the IDAF passive samplers have participated in the pilot measurement program initiated by WMO/GAW Urban Meteorology and Environment (GURME) project. This passive sampler project was done in collaboration and as a component the IGAC DEBITS program. Banizoumbou (Niger), Zoetele (Cameroon), Lamto (Cote d'Ivoire) and Cape Point (South Africa) have participated to this test from 1998 to 2000 (Carmichael et al., 2003). On these sites, the IVL samplers were exposed for one month in parallel to the IDAF samplers (Ferm and Rodhe, 1997; Carmichael et

al., 2003). IVL samplers were analyzed in the IVL accredited laboratory. IDAF samplers were analyzed in the Analytical Laboratory of Aerologie. This study allowed the comparison of SO_2, NH_3 and O_3 measurements with about 35 samples for each gas. The IVL and the IDAF measurements compare well with acceptable correlation coefficient according to the measurement uncertainties. Figure 4 details the NH_3 results and shows the good linear relation between the two passive samplers (R^2=0.76).

Moreover, the literature indicates that these samplers have been extensively tested in various international studies. Several tests were carried out to compare absorption efficiency and select the most adequate solution to impregnate the filters, used in the passive sampler that would be exposed under conditions of relative temperature and humidity present in typically tropical air. For HNO_3, SO_2, NO_2, NH_3, we can cite Ferm and Rodhe (1997) and Ferm et al. (2005). Cruz et al. (2004) validate SO_2 passive samplers for tropical industrial and urban air in South America. Passive samplers have been also extensively used in tropical Asia and South America (Carmichael et al., 1996, 2003; Gupta et al., 2003; Tidblad et al., 2007, Rondon et al., 1993). In Africa, first studies mainly concerning the South African passive sampler network have been recently published (Zunckel et al., 2004, Martins et al., 2007, Josipovic et al., 2007).

Diffusive samplers have many advantages in the field such as: no need for calibration, sampling tubing, electricity or technicians. The samplers are small, light, reusable, cost-efficient and soundless. The outcome of the above mentioned validation and intercomparison studies of passive sampling assures the quality and control of its sampling and analytical protocols to make it a viable means of obtaining credible atmospheric data at remote sites on a long-term base.

3 Results and discussion

Atmospheric concentrations of NO_2, HNO_3, NH_3, SO_2 and O_3 are measured on the IDAF network on a monthly basis. Passive samplers observations on the West and Central African sites have been deployed over a ten year period from 1998 to 2007.

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Table 5 presents a synthesis of the mean annual gas concentrations for all the IDAF network. For South African IDAF sites measurements have been performed from 1995 to 2005 (Martins et al., 2007). Results were calculated using only the approved data points (in brackets in Table 5). Considering the whole database, we found that less than 10% of the returned samplers were below the detection limit.

In our study, we present monthly, seasonal, annual and interannual variations for each gas as a function of the site representative of one ecosystem. The analysis of the global database should provide for the first time the levels of important trace gas concentrations for remote African sites on a long term basis. The seasonal and annual cycles of gas concentrations will be discussed in relation with climatology and gases emissions sources. Comparative studies along the ecosystems transect, i.e., dry savannas-wet savannas-forests will highlight the predominant atmospheric processes in terms of gaseous atmospheric sources on each ecosystem.

3.1 Nitrogen dioxide (NO_2)

Figure 5 presents the monthly NO_2 evolution measured in the dry savannas of Niger and Mali (Fig. 5a: Banizoumbou, Katibougou, Agoufou), in wet savannas of Cote d'Ivoire and Benin (Fig. 5b: Lamto, Djougou) and in equatorial forests of Cameroon and Congo (Fig. 5c: Zoetele, Bomassa). Vertical bars indicate standard deviation calculated from the studied period (1998–2007). Decadal monthly evolution of pluviometry is superimposed on the monthly NO_2 concentrations.

For the first time, this study reports the well marked seasonal cycle of NO_2 surface concentrations in arid and semi arid African areas (Fig. 5a). It allows quantifying concentrations levels with a strong level of confidence, according the mean calculated from 10 years of measurements on two of these Sahelian sites. The dry savannas are characterized by a dry season from October to May and a wet season from June to September. The month of May represents the transition between the dry and the wet season. Monthly mean NO_2 concentrations over the ten years of measurements, respectively range between 0.9±0.3 ppb and 4.3±1.0 ppb in Banizoumbou, 1.2±0.5 ppb

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and 3.1±0.9 ppb in Katibougou, 0.9±0.3 ppb and 3.5±1.2 ppb in Agoufou (3 years of measurements). Variations of monthly NO_2 concentrations present the same pattern at the three sites of dry savannas. As a matter of fact, monthly concentrations begin to increase significantly from April, the month of the first rain events of the wet season. A first maximum is obtained in May/June. This maximum is consistent with the emission of inorganic nitrogen that accumulated in soils during the long dry season from traditional agricultural practices such as grazing, manure application and decomposition of crop residues, followed by rain on the sandy soils of this area (Jaegle et al., 2004). In fact, after the first rains occurring in April–May announcing the wet season, the bacterial nitrification is activated and lead to the nitrogen consumption and consequently to the release of large pulses of NO (Davidson, 1992; Laville et al., 2005; Ludwig et al., 2001; Williams et al., 1992; Yienger and Levy, 1995). NO is then rapidly converted in NO_2 in the atmospheric oxidative processes. After the excess nitrogen is consumed, wet season NO emissions decrease but remain at relatively high levels compared to the dry season (Serça et al., 1998). A second maximum is obtained at the beginning of the dry season in October–November in Katibougou and Banizoumbou. It is correlated to the biomass burning sources active in the Northern Hemisphere at this period (Jaegle et al., 2004). In Agoufou (Mali), a second maximum is measured in September. According to the high latitude of this site, we assume that the biomass burning has a lower influence than for the other dry savannas sites. This second peak could be correlated to the return of some rain events occurring after several days of a dry period.

In the dry savannas, mean seasonal concentrations are 3.1±0.6 ppb, 2.1±0.5 ppb and 2.5±0.7 ppb in the wet season; and 1.9±0.5 ppb, 1.8±0.2 ppb and 1.4±0.4 ppb in the dry season for Banizoumbou, Katibougou and Agoufou sites, respectively. Monthly concentrations are higher in the wet season. Mean annual NO_2 concentrations are 2.4±0.4 ppb, 1.9±0.3 ppb and 1.8±0.4 ppb in Banizoumbou, Katibougou, and Agoufou, respectively (see Table 5). The interannual variability for the ten year period is about 19%, 15% and 24% for the three Sahelian sites. No specific trend in the variability is

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observed. The analysis of interannual variability reflects clearly the potential variation of the intensity of atmospheric sources associated to a second important factor, i.e. the variation of the annual rainwater depth. The amount of water and its temporal variation is determinant of NO_x soil emission (Johansson and Sanhueza, 1988; Davidson, 1992; Scholes et al., 1997). In the AMMA program (African Monsoon Multidisciplinary Analysis), Delon et al. (2008) and Stewart et al. (2008) have studied NO_x soil emission variation as a function of spatial patterns of rainfall during the month of August 2006 in the Sahelian region. Modeling studies and measurements presented in these papers clearly show strong NO_x emissions in the Sahel during the wet season, strongly dependent on soil moisture and on the temporal distribution and rates of precipitation. The analysis of rainfall in the Sahel shows a strong spatial and temporal variability (Balme et al., 2006) which will influence the interannual variability of NO_2 concentration. However, the weight of each process is somewhat difficult to estimate. Jaegle et al. (2004) show that monthly top down GOME soil NO_x emissions allow a good representation of the temporal variation with a maximum in June–July. Delon et al. (2008) and Stewart et al. (2008) with other methods confirm the strong potential for semi arid areas to emit large amount of NO_x. In vast areas covered by dry ecosystems, the long term monitoring of the IDAF sites in Mali and Niger provides evidence of the large influence of microbial soil emissions of NO_x.

Monthly mean NO_2 concentrations in wet savannas range from 0.4±0.1 ppb to 2.0±0.7 ppb in Lamto (mean for 10 years of measurements) and from 0.4±0.1 ppb to 3.6±0.2 ppb in Djougou (mean for 3 years of measurements) (Fig. 5b). In a general way, atmospheric NO_2 concentrations slowly decrease between January and October. Then, monthly mean concentrations increase until a maximum in December. Djougou site in Benin shows strong concentrations in November–December, Lamto in January–February. This result is explained by the biomass burning NO_x source. African fires have a well known seasonality with a northern fire belt in November–February and a southern fire belt in June–October (Hao and Liu, 1994; Cooke et al., 1996). Galanter et al. (2000) have shown that more than 75% of the NO_x at the surface near equatorial

Africa was a result of biomass burning during December, January and February. Menaut et al. (1991) assumed that 5–15% of the Sahelian savanna (dry savanna), 25–50% of the Sudanian savanna, and 60–80% of the Guinean savannas (wet savanna) were burned every year. Seasonal NO_2 concentrations in Lamto are twice as high in the dry season (1.4±0.4 ppb) than in the wet season (0.7±0.2 ppb). In Djougou (Benin), concentrations in the dry season are four times higher (2.2±0.8 ppb) than in the wet season (0.5 ppb). During the 2005–2006 enhanced observation period of the AMMA experiment, NO_x measurements have been done using an active analyzer (42i-TL Megatec). Between October 2005 and September 2006, mean concentration in the dry season (3.2±1.6 ppb) is eight times higher than in the wet season (0.4±0.2 ppb). These values are of the same order of magnitude and confirm IDAF passive samplers measurements in Djougou. In the wet savanna of Lamto, Serça et al. (1998) have measured low NO biogenic fluxes, ranging from 0.11 ng NO-N m^{-2} s^{-1} at the end of the dry season to 0.56 ng NO-N m^{-2} s^{-1} (mean) during the wet season. NO fluxes measured during the wet season were significantly higher (≈ 5 times higher) than fluxes measured during the dry season. Interestingly, the relatively high NO_x concentrations encountered at Lamto (during the dry season) are not explained by the very low NO emissions from savanna soils but by remote biomass burning emissions at the regional scale (Abbadie et al., 2006). Opposite to dry savannas, monthly mean NO_2 concentrations are higher in the dry season (November–March) compared to the wet savannas. Annual mean concentrations are 1.0±0.3 ppb (NO_2) in Lamto and 1.2±0.1 ppb in Djougou with an interannual variability of 29% and 10%, respectively. The interannual variability is more representative in Lamto with 10 years of measurements (3 years in Djougou) and is attributed to spatio temporal variations of savannas fires. In 1990–1991, Ferm and Rodhe (1997) have performed first passive sampler measurements in Lamto. NO_2 concentrations of 0.5 ppb measured in September–October 1990 and 2 ppb in February are coherent with IDAF measurements. IDAF measurements tend to demonstrate that biomass burning in the dry season of wet savannas and soil biogenic NO_x emissions in the wet season of the dry savannas have a comparable contribution: 1.4–2.2 ppb

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of NO_2 for biomass burning and 2.1–3.1 ppb of NO_2 for NO emission from soils. This result confirms the conclusion given by Jaegle et al. (2004, 2005) with a comparable contribution of soils and biomass burning to the NO_x budget at the scale of the African continent.

In forests, monthly mean NO_2 concentrations range between 0.5±0.3 ppb–1.5±0.5 ppb in Zoetele (ten years of measurements) and 0.8±0.3 ppb–2.4±1.3 ppb in Bomassa (eight years of measurements) (Fig. 5c). Monthly mean concentrations increase slowly during the dry season (December–February). Seasonality is the same for the two sites with maxima registered in February–March. NO_2 enhancements correspond to the biomass burning season (Cros et al., 1992; Cooke et al., 1996; Galanter et al., 2000). In the Mayombe equatorial rain forest of Congo, Serça et al. (1998) have measured NO emissions from soils. NO fluxes in the wet season (4.41 ng NO-N m^{-2} s^{-1}) were 3 times higher than those of the dry season (1.54 ng NO-N m^{-2} s^{-1}). Even if NO fluxes are high, NO is rapidly transformed into NO_2, and a large part of NO_2 is captured by the leave plant density (Jacob and Bakwin, 1991; Sparks et al., 2001). In the forested ecosystems, seasonal concentrations are comparable: 1.1±0.2 ppb and 0.9±0.3 ppb in Zoetele and 1.6±0.5 ppb and 1.4±0.5 ppb in Bomassa, respectively in dry and wet seasons. However, wet season values remain a little bit higher. These measurements tend to assume that the biomass burning source in the dry season is equivalent to soil emissions buffered by canopy uptake in forests during the wet season. Mean annual concentrations are 0.9±0.2 ppb in Zoetele and 1.4±0.4 ppb in Bomassa with interannual variations equal to 23% and 31%, respectively.

As a comparison to West and Central Africa, NO_2 concentrations, monitored in other tropical regions are given here as examples. In the Indian semi arid site of Rampur, annual NO_2 concentration is about 7 ppb (Gupta et al., 2003). In South Africa, Louis Trischardt, a non perturbed rural dry savanna and Cape Point the preserved continental coastal site present annual mean concentrations of 0.7–1.2 ppb, respectively. These values are closed to concentrations observed in West and Central wet savannas and forests (Table 5). Levels of annual NO_2 concentrations measured in Amersfoort

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(2.5 ppb), the South African dry savanna influenced by industrial emissions, are comparable to those observed in Western African dry savannas (1.8–2.4 ppb) (Martins et al., 2007). As a partial conclusion, we assume that NO_2 concentrations are higher in dry savannas compared to wet savannas and forests.

3.2 Nitric acid (HNO_3)

HNO_3 monthly mean concentrations range between 0.1±0.1 ppb and 1.4±0.4 ppb in dry savannas, 0.2±0.1 ppb and 0.7±0.3 ppb in wet savannas and 0.1±0.1 ppb and 0.5±0.3 ppb in equatorial forests (Figs. 6a–c). The minima values measured are the same for all the ecosystems and represent two to four times the detection limit value. The maxima present a negative gradient from the dry savannas (1.4 ppb) to the forest (0.5 ppb). Results show that monthly HNO_3 evolution is highly comparable to NO_2 monthly evolution, and thus follow the same gradient. If we consider the seasons, mean HNO_3 concentrations on the transect are 0.8±0.2 ppb, 0.3±0.1 ppb and 0.2±0.1 ppb during the wet season and 0.2±0.1 ppb, 0.5±0.2 ppb and 0.4 ±0.1 ppb during the dry season, respectively for dry savannas, wet savannas and forests.

The highest HNO_3 concentrations are measured in the wet season of the arid Sahelian ecosystems, opposite to the wet savannas and forests. These results are consistent with the measured NO_2 seasonal cycle, which is maximal during the rainy season in dry ecosystems. Higher concentration of HNO_3 in the wet season can be explained by increased production of HNO_3 from gaseous precursors during photochemical activity. This mechanism is particularly active in tropical regions with high humidity and photochemical activity, leading to maximum production of hydroxyl radicals (OH) (Graedel and Crutzen, 1993). For NO_2, arid savannas present a second maximum during the dry season (October–November) that is not observed for HNO_3. The dry season is characterized by high load of atmospheric dust particles and also lower NO_x precursor emissions. Thus, mineral dust captures gaseous HNO_3 and neutralizes acidity with carbonates of Ca^{2+} or Mg^{2+}. Carmichael et al. (1997) or Dentener et al. (1996) have shown that dust particles can significantly influence trace gas cycles in the atmosphere

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such as HNO_3, especially in tropical areas. In African ecosystems, heterogenous processes leading to acidity neutralization with alkaline particles have been also clearly emphasized in the wet season to explain the low pH of precipitation in semi arid savannas (Galy-Lacaux et al., 2009; Galy-Lacaux and Modi, 1998). In wet savannas and forested ecosystems, lower HNO_3 concentrations are directly correlated to lower levels of measured NO_2 concentrations (Serça et al., 1998; Jaegle et al., 2004), and can also be attributed to the very high HNO_3 solubility in water and thus easily scavenged by clouds and rain (Sigha et al., 2003; Yoboue et al., 2005). In a tropical forested savanna site of South America, very low concentrations of HNO_3 (0.04 ppb) have been reported by Rondon and Sanhueza, 1990.

Our work estimates for the first time an order of magnitude for HNO_3 concentrations representative of different African ecosystems in West Africa (Table 5). Based on the 10 years period, mean annual HNO_3 concentrations are 0.5 ±0.2 ppb in dry savannas and 0.3±0.1 ppb in wet savannas and forests.

Measurements of ambient HNO_3 levels are very few, especially in tropical areas. An original paper from Ferm et al. (2005) related to corrosion studies presents acid nitric measurements during two years using diffusive sampler for 11 rural and 23 urban sites in Northern Europe. Higher values are measured in Milan, Athens and London with annual average results varying from 0.16 to 2.5 $\mu g/m^3$ (0.05–1 ppb). In rural Northern European sites, monthly HNO_3 concentrations range between 0 and 0.5 $\mu g/m^3$ (0–0.2 ppb). In the tropics, a project of corrosion studied in the frame of the RAPIDC program (http://www.sei.se/rapidc/pdfs/corrsion.PDF) reports HNO_3 concentrations from 14 stations of Africa and Asia in tropical or sub tropical area. The average HNO_3 concentrations show a rather uniform distribution, with monthly mean concentrations between 0.4 and 0.6 ppb (Tidblad et al., 2007). This study also reports annual HNO_3 concentrations varying from 0.1 ppb in Mytho (Ho Chi Minh Branch of the Environmental Institute of Materials science) to 1.5 ppb in Kuala Lumpur (Malaysia). Gupta et al. (2003) presents HNO_3 measurements at an Indian rural site (Rampur) with an annual mean of 0.3 ppb. This level is quite comparable to HNO_3 concentrations obtained

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for African ecosystems in this work. Concentrations are around 0.5 ppb, with a maximum in Amersfoort (South Africa, industrialized dry savanna) of 0.9 ppb and a minimum of 0.2 ppb in the remote South African site of Louis Trischardt and in Zoetele (forest in Cameroon).

3.3 Ozone (O_3)

Monthly mean ozone surface concentrations range between 4.4±0.5 ppb and 21±4.5 ppb in dry savannas, between 6.9±1.0 ppb and 17.3±5.0 ppb in wet savannas and between 2.8±0.8 ppb and 7.3±1.7 ppb in forested ecosystems (Figs. 7a–c). Along the ecosystem transect, the seasonal trend in ozone is comparable to NO_2 seasonal evolution. In dry savannas, mean seasonal concentrations in the wet season (16.8±5.2 ppb in Banizoumbou, 14.8±3.9 ppb in Katibougou and 16.4±4.8 ppb in Agoufou) are twice higher than in the dry season (7.9±1.9 ppb in Banizoumbou, 10.2±1.7 ppb in Katibougou and 7.4±1.6 ppb in Agoufou). In wet savannas, mean concentrations in the dry season (13.2±2.5 ppb in Lamto and 16.5±5.0 in Djougou) are comparable to dry savannas in the wet season. In the wet season, Lamto and Djougou ozone concentrations are 9.1±1.1 ppb and 12.8±3.0, respectively. In the two sites of forests, there is no or small seasonal difference in ozone concentrations. For the Congolese forest of Bomassa, concentrations are 4.0±0.8 ppb and 4.0±0.4 ppb in wet and dry seasons. For Zoetele in Cameroon, we measure 7.2±1.1 ppb in the dry season and 4.1±0.9 ppb in the wet season. Annual mean concentrations are around 11–14 ppb in dry and wet savannas (11.9±2.3 ppb in Banizoumbou, 12.6±2.2 ppb in Katibougou and 12.2±2.6 ppb in Agoufou, 10.9±1.8 ppb in Lamto and 14.0±2.8 ppb in Djougou) and 4–5 ppb in forests (4.8±1.0 ppb in Zoetele and 4.0±0.4 in Bomassa). The interannual variability is about 10% in Bomassa, 21% in Zoetele and Agoufou, 19% in Banizoumbou, 17% in katibougou, 16% in Lamto and 20% in Djougou. Spatiotemporal evolution of ozone concentration distributions will depend on various processes as ozone production is non linearly driven by the supply of nitrogen oxides and VOC from biomass burning, fossil fuel combustion, biogenic sources and soils (Jacob et al., 1990,

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1991, 1995). In the tropics, in the absence of anthropogenic biomass burning, the seasonal variation of O_3 in the boundary layer is mainly a consequence of photochemical processes and the exchange with free troposphere and terrestrial surfaces.

In the semi arid savannas, the seasonality trend is clear with a maximum in June–July, the heart of the wet season. This is the result of active photochemical production of ozone in the boundary layer correlated to large NO_x concentrations. In the wet season in the Sahel during the AMMA experiment, Stewart et al. (2008) have estimated a production of ozone at a rate of 1 ppb h^{-1} as the result of large NO_x concentrations in the boundary layer. Moreover, the measurements of NO_x and ozone concentrations during the low level transects of the AMMA flights present a good correlation. The same correlation is found in IDAF measurements. The Sahelian region is an original case in atmospheric chemistry where ozone production is mainly related to natural biogenic precursor sources. IDAF gas concentrations monitoring confirms this result.

In the wet savannas of Lamto, NO_x are well correlated to O_3 concentrations (R^2=0.7). Lamto is strongly influenced by biomass burning of West and Central Africa from December to February (Lacaux et al., 1995), far enough from anthropogenic sources of emissions so that ozone production is driven by NO_x limited regime. In Lamto (wet savanna), the fire generally occurs in January, i.e., in the heart of the dry season and around 80% of the savanna soil surface is burned yearly (Abbadie et al., 2006). Thus biomass burning could significantly contribute to ozone production through the emissions of precursors (NO_x and CO). Indeed Liu et al. (1987) have shown higher ozone production efficiency for lower NO_x mixing ratios at rural stations. Galanter et al. (2000) have shown that from December to February, biomass burning contributes indirectly to 30 to 40% to the O_3 concentration over equatorial and Northern Africa at 940 hPa.

For African forested ecosystems, ozone concentrations are lower. The mean annual concentrations are around 4 ppb. This result is consistent with measurements done by Cros et al. (1987) in the Mayombe forest of Congo. Under the canopy at an altitude of 3 m, the O_3 levels were always very low in the Mayombe forest (Congo) and never going over 5 ppb. We observe in the two forests that the maximum of ozone occurs

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during the biomass burning season in these ecosystems. It is consistent with Cros et al. (1992) observations. Several studies have shown that tropical forests appear to be a major O_3 sink, i.e., ground and foliage deposits and loss through chemical reactions with hydrocarbons and nitrogen oxides (Rummel at al., 2007; Jacob and Wofsy, 1990; Bakwin et al., 1990; Kaplan et al., 1988). Hence, in forests, all the strata of the vegetation may participate in the destruction of ozone by dry deposition and chemical reactions (Cros et al., 1992). Mean ozone deposition velocity have been measured to be very high in equatorial Africa in Northern Congo (Cros et al., 1992; Andreae et al., 1992) and in Republic of Central Africa (Cros et al., 2000). Saunois et al. (2009) have shown from measurements of FAAM BAe-146 aircraft that there is a strong ozone gradient between forest and bare soil in the boundary layer in West Africa during AMMA wet season campaign. They observed the increase of the ozone mixing ratios from 25 ppbv over the forested area up to 40 ppbv over the Sahelian area in the West African lower troposphere. And they found that the lower values of ozone over vegetation are essentially controlled by dry deposition over trees and that the ozone maximum is clearly a consequence of higher NO_x mixing ratios north of 12° N. IDAF surface measurements tend to confirm this strong ozone gradient between forests (seasonal mean concentration around 4 ppb) and dry savannas (around 16 ppb) in wet season. IDAF measurements have also been performed in the Amazonian forest of French Guyana (Petit Saut Site). Ozone measurements indicate low concentrations with an annual mean of 4.6±0.7 ppb (from 2001–2007).

A few observational studies on surface O_3 are available over tropical areas. In the Indian region, Naja and Lal (2002) reported that monthly average O_3 concentrations range from 18.1±10.8 ppbv (October) to 33.6±20.6 ppb (March) at the rural site of Gadanki (13.5° N, 79.2° E) during the period from 1993 to 1996. Also, in a tropical rural coastal site of Southeast India, from May 1997 to October 2000, Debaje et al. (2003) reported the average O_3 concentrations from 17±7 ppbv (October) to 23±9 ppbv (May) at Tranquebar (11° N, 79.9° E). The increase in O_3 is attributed to the increase in NO_x and other precursor emissions by different sources in the proximity of this site. These

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monthly average O_3 concentrations, in the Indian rural sites, are higher than those reported in African rural sites (2.8±0.8 ppb to 21±4.5 ppb on the transect of ecosystems). Annual mean ozone concentrations in South Africa (27±8.3 ppb in Amersfoort and Cape Point, 35±8.6 ppb in Louis Trichardt) are two and a half higher than in Western and Central African dry and wet savannas (12 ppb) and forests (4 ppb). The industrial pollution affects directly all the South African sites because of the air masses recirculation. Higher ozone level in the remote dry savanna of Louis Trischardt is probably due to a large intercontinental mixing zone of ozone precursor gases (namely: volatile organic compounds from biomass burning from Zambia and Zimbabwe and NO_2 from the industrial activities in South Africa) (Martins et al., 2007).

3.4 Ammonia (NH_3)

Monthly mean NH_3 concentrations range from 3.2±1.6 ppb to 10.6±1.8 ppb in dry savannas; from 2.0±0.2 ppb to 8.4±1.9 ppb in wet savanna and from 2.9±1.0 ppb to 7.2±4.3 ppb in the forests (Figs. 8a–c). In dry savannas, mean concentrations in the wet season are: 7.7±2.5 ppb in Banizoumbou, 8.1±1.9 ppb in Katibougou and 8.4±1.2 ppb in Agoufou. In the dry season lower concentrations are measured: 5.3±1.6 ppb in Banizoumbou, 5.5±1.1 ppb in Katibougou and 5.7±0.5 ppb in Agoufou. In wet savannas, the phenomenom is inversed, i.e. we measured lower mean concentrations in the wet season (3.0±1.0 ppb in Lamto and 3.1±1.3 ppb in Djougou) and higher mean concentrations in the dry season (5.2±1.5 ppb in Lamto and in Djougou). In the forests, no significant difference between wet and dry season exists. Concentrations are 4.1±1.0 ppb and 4.4±1.4 ppb in Zoetele and 4.6±1.6 ppb and 5.1±2.2 ppb in Bomassa, in the wet and the dry season, respectively. Annual mean concentrations of ammonia in the dry savannas are 6.3±2.0 ppb in Banizoumbou, 6.6±1.0 ppb in Katibougou and 7.4±0.8 ppb in Agoufou (Table 5) (with interannual variations equal to 31%, 15% and 10%, respectively). These values are higher than those measured in the other ecosystems: 4.0±1.2 in Lamto, 3.9±1.4 ppb in Djougou, 4.2±0.9 ppb in Zoetele and 4.7±1.7 in Bomassa (Table 5). The interannual variability on the ten years

is about 29%, 22% and 35% for Lamto, Zoetele and Bomassa, respectively and 35% for Djougou over three years. No specific trend in the variability is observed. It is noticeable that wet savannas and forests present seasonal and mean annual NH_3 concentrations of the same order of magnitude. From January to March (dry season), monthly atmospheric concentrations of NH_3 in wet savannas and forests are higher than 4 ppb (5–8 ppb). At the same period, NH_3 concentrations are lower in dry savannas and around 4 ppb. Then, from May to the end of the wet season, we observed high NH_3 concentrations in dry savannas from 5 to 10 ppb. In 1990–1991, NH_3 concentrations in Lamto have been measured by Ferm and Rodhe (1997). NH_3 concentrations of 2–3 ppb measured in September–October 1990 and 5–7 ppb in January–February are coherent with IDAF measurements.

Major sources of NH_3 include bacterial decomposition of urea in animal excreta and emission by natural or fertilized soils (Schlesinger and Hartley, 1992; Bouwman et al., 2002). In tropical regions, another significant source of ammonia is produced by savanna fires and domestic fuelwood burning (Lobert et al., 1990; Delmas et al., 1995; Brocard et al., 1996). For the remote sites of the IDAF network, neither industrial N sources nor N emissions from synthetic fertilization have to be considered. In wet savannas and forests, the NH_3 concentrations represent a combination of all these natural sources with the largest contribution from biomass burning sources as shown by the highest concentration observed in the dry season. In a rural site of the Amazon basin, Trebs et al. (2004) have measured a mixing ratio of NH_3 of 8 ppb in the burning season, 3 times higher than in the wet season. This result is quite comparable to concentrations recorded in the dry season of the West and Central African wet savannas and forests. In the Sahelian region during the wet season, the burning of the savanna is improbable and the main source of ammonia is certainly the hydrolysis of urea from animal urine deposited in pasture grazing areas. High densities of domestic animals are concentrated on the fresh natural pastures greening during the rainy season. Mc Calley et al. (2008) have measured NO and NH_3 emission from the Mojave desertic soils. Results indicate that seasonal changes in temperature and precipitation are driving the

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emissions with maximum fluxes in the wet season around 0.9 to 10 ng N m^{-2} s^{-1} (from 0.3 to 3 kg N ha^{-1} yr^{-1}). In Niger, Modi et al. (1995) estimated the NH_3 emission to be 0.5 kg ha^{-1} yr^{-1}, representing a flux of 3.1 mmol m^{-2} yr^{-1}. Ammonium wet deposition of 6.3 mmole m^{-2} yr^{-1} in 1996 at Banizoumbou confirms the intense source of ammonia in this semi arid savanna (Galy-Lacaux and Modi, 1998). Atmospheric ammonia fluxes have been estimated in the Sahel and more generally in Africa (Schlecht et al., 1998; Bouwman et al., 2002). In the Sahelian zone, the agropastoralism appears to be very important, representing 25 to 30% of the GDP (Gross Production Product). Pastoralism contributes to 10 to 15% of the GDP of Mali and Niger for example. It is important to note that the pastoralism is mainly nomad. Recently Delon et al. (2009) have developed a specific NH_3 emission inventory for 23 countries of West Africa where grazing related to the number of heads of cattle seems to be the most important source of NH_3. The N quantity released by livestock is calculated from Schlecht et al. (1998), in g N $head^{-1}$ day^{-1}, for cows, sheep and goats. This estimate is multiplied by the number of animals per km^2 in each region of each concerned country, information found in the FAO (Food and Agriculture Organization) GLiPHA (Global Livestock Production and Health Atlas) database. The mean total N input from animal manure is estimated to be 23 kg N ha^{-1} yr^{-1} in Agoufou, 25 kg N ha^{-1} yr^{-1} in Banizoumbou, 11 kg N ha^{-1} yr^{-1} in Katibougou. Better conditions are encountered in Sahel regions to favor NH_3 volatilization, i.e. high temperatures, low soil moisture and bare soil surfaces. As a consequence, 30–50% of loss rate has been applied to the input of N by animal manure previously calculated. This leads to a N-NH_3 volatilization estimated ranging from 3 to 6 kg N ha^{-1} yr^{-1} at Katibougou, and from 7 to 12 kg N ha^{-1} yr^{-1} at Agoufou and Banizoumbou, depending on the loss rate. The rest of the N input remains in the soil and is further used for the release of biogenic NO.

To try to have a rough estimation of the comparison between emission fluxes and surface concentrations, (without taking into account the compensation point of NH_3) we suppose that essentially, all emitted NH_3 (in arid region) is returned to the surface by deposition (wet and dry) (Bouwman et al., 2002) and we use the relation between

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deposition flux and concentration defined by Eq. (4):

$$C_z = F/V_d \quad (4)$$

where F is the deposition flux of the trace gas (molecules $m^{-2} s^{-1}$), V_d is the deposition velocity ($m s^{-1}$), C_z is the concentration of the gas (molecules m^{-3}) at reference height z. The concentration C_z is converted to ppb afterwards. Taking account dry deposition velocity around 0.4 cm^{-1} (Trebs et al., 2006; Zhang et al., 2003b), and a 30% loss rate of N input, mean NH_3 calculated concentrations are 8.9 ppb in Agoufou and Banizoumbou. These values are comparable to those obtained with IDAF passive samplers (7.4 ppb in Agoufou and 6.3 ppb in Banizoumbou) and we assume that animals represent the main NH_3 sources for these African arid and semi arid ecosystems. These concentrations are five times higher than in South Africa (1.2±0.7 ppb in Amersfoort and in Louis Trichardt, 1.5±0.7 ppb in Cape Point) (Table 5). Mean annual concentrations also remains high in wet savannas and forests (around 4 ppb). Carmichael et al. (2003) have already noticed that ambient ammonia levels are high in the Indian sub continent, Southeast and South Asia and Africa. These concentrations reflect the high NH_3 emission from agricultural activities, livestock and the use of biofuels (as animal dung) as domestic fuel.

3.5 Sulfur dioxide (SO_2)

In general, we measure low SO_2 concentrations in all West and Central African sites. This result is true for Southern African sites except Amersfoort (Table 5). For the West and Central African sites, the annual mean SO_2 concentrations are of the same order of magnitude in dry savannas (0.6±0.2 ppb in Banizoumbou and Katibougou, 1.0±0.2 ppb in Agoufou) and wet savannas (0.5±0.2 ppb in Lamto and 0.8±0.3 ppb in Djougou). For forested ecosystems, annual mean SO_2 concentrations are twice as low (0.3±0.1 ppb in Zoetele and 0.4±0.2 ppb in Bomassa). The high annual mean SO_2 concentration measured in Amersfoort (2.8±1.1 ppb) is related to the fact that for most of the time, the site downwind the industrial activities in the vicinity (Martins et al., 2007).

If we consider the seasons, mean SO_2 concentrations on the transect are 0.9±0.3 ppb, 0.6±0.2 ppb and 0.3±0.2 ppb in the wet season and 0.6±0.2 ppb, 0.7±0.4 ppb, 0.4±0.2 ppb in the dry season, respectively for dry savannas, wet savannas and forests. We observe the same order of magnitude of SO_2 in dry and wet seasons in each ecosystem with a higher value in wet season for dry savannas. This suggests a proportional contribution of soil emission and biomass burning sources. On the other hand, soils have long been recognized as SO_2 sink (Garland, 1977), but it has been suggested that acid sulfate soils may emit SO_2 (Van Breemen, 1982, 1993). SO_2 can be also generated through reactions involving dissolved sulfite (SO_3^{2-}) (Barnett and Davis, 1983) which occurs naturally in soils. Macdonald et al. (2004) have shown that partially oxidized sulfide-containing acid sulfate soils are a source of atmospheric SO_2 and the evolution of SO_2 appears to be linked to surface soil evaporation. Moreover, biomass burning (burning of forest, grassland, and agricultural wastes) is a significant source of SO_2 to the atmosphere (Bates et al., 1992; Arndt et al., 1997). However, the content of vegetation in sulfur is quite low and emission factors of SO_2 are lower than for carbonaceous or nitrogenous species in the combustion processes (Lacaux et al., 1995).

SO_2 and ammonia play important roles in aerosol processes, and in influencing the acidity of precipitation. It is interesting to note that the NH_3/SO_2 mixing ratio exceeds 10 at forested ecosystems (14 at Zoetele, 12 at Bomassa) and dry savannas (11 at Banizoumbou and Katibougou) except Agoufou (7). A ratio of 8 and 5 is observed at Lamto and Djougou, respectively (Wet savannas). These results are consistent with those reported by Carmichael et al. (2003) for 24 remote sites world wide at which the ratio at 15 sites exceeds 10 and a ratio <1 was not observed at any of the sites. For the Southern African sites, we note that a rather low NH_3/SO_2 mixing ratio of 1.46 and 2.73 is observed at Louis Trichardt and Cape Point, respectively while a ratio of 0.42 is observed at Amersfoort (Martins et al., 2007).

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4 Conclusions

The present study reports for the first time measurements of gaseous NO_2, HNO_3, NH_3, O_3, and SO_2 at seven remote sites in West and Central Africa within the framework of the IDAF network. The sites are located to represent a transect of the great African ecosystems, i.e., dry savanna-wet savanna-forest. Monthly measurements were obtained using the set of IDAF passive samplers over a ten year period from 1998 to 2007. The validation and inter-comparison studies conducted with the IDAF passive samplers, presented in Sect. 2, assure the quality and the control of the technique and show the accuracy of the measurements. The IDAF database of gases is available at: http://www.obs-mip.fr/idaf/. The reproducibility of IDAF passive samplers was found to be 9.8%, 20%, 14.3%, 10% and 16.6% for NO_2, HNO_3, NH_3, O_3, and SO_2, respectively. For each type of African ecosystems, we have studied the long term data series (1) to characterize for the first time the levels of gaseous surface concentrations, and (2) to document the seasonal cycles according to the atmospheric sources of gases. We have tried to compare West and Central African gas concentrations with the results obtained in other parts of the world such South Africa, Asia and India. We found that for all the gases, seasonal concentrations are higher in the wet season of the dry savannas. Conversely, concentrations are higher in the dry season of the wet savannas. In forests, we measure no significant difference between wet and dry seasons. Along the transect of ecosystems, NO_2 variability emphasizes the importance of two main NO_x sources, i.e., biomass burning and biogenic soil emissions. IDAF measurements tend to demonstrate that biomass burning in the dry season of the wet savannas and forested ecosystems lead to 1.1–2.2 ppb NO_2 concentrations. These concentrations are of the same order of magnitude as the soil biogenic NO_x source in the wet season of arid and semi arid savannas (2.1–3.1 ppb of NO_2). Monthly HNO_3 evolution is highly comparable to NO_2 monthly evolution, and thus follows the same gradient. Higher concentrations of HNO_3 in the wet season of dry savannas (0.5–1 ppb) can be explained by increased production of HNO_3 from gaseous precursors (NO_x) during photochemical activity. IDAF measurements emphasize that O_3 concentrations during the wet season

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of dry savannas that vary from 14.8±3.9 to 16.8±5.2 ppb are of the same order of magnitude as those during the dry season of wet savannas which range from 13.2±2.5 to 16.5±5.0 ppb. The clear seasonality measured with IDAF passive samplers in the semi arid savannas allows us to argue in favor of ozone production related to NO_x. Biogenic emission could mainly contribute to ozone production through the emissions of NO_x as precursors during the wet season of dry savannas and biomass burning during the dry season of wet savannas. In forested ecosystems, the lower O_3 concentrations measured in both dry and wet seasons (4–7 ppb) show that tropical forests appear to be a major O_3 sink. For NH_3, the higher concentrations measured in the wet season of the semi arid savannas (7.5–8.5 ppb) is mainly due to the hydrolysis of urea from animal excreta deposited in pasture grazing area. It is noticeable that the transect of ecosystems present a comparable seasonal mean of NH_3 concentration around 5 ppb in the dry season. The annual mean concentrations of NH_3, NO_2, HNO_3 measured in dry savannas are higher than those measured in wet savannas and forests that have quite similar concentrations. NH_3 concentrations are around 6–7.5 ppb in dry savannas and 4–5 ppb in wet savannas and forests. Annual NO_2 concentrations are around 2–2.5 ppb in dry savannas and 1 ppb in wet savannas and forests and HNO_3 around 0.5 ppb in dry savannas and 0.3 ppb in wet savannas and forests. Annual O_3 and SO_2 concentrations are low for all the African ecosystems studied. Annual mean O_3 concentrations are around 11–14 ppb in dry and wet savannas and 4–5 ppb in forests and SO_2 around 0.5–1 ppb in dry and wet savannas and 0.3 ppb in forests.

Results from this study have demonstrated that passive samplers are ideal for measurements at remote sites with low cost means to obtain high quality data covering large regions unexplored in the world. The IDAF remote sites are not yet impacted by anthropogenic sources of gases and particles. However, industrial pollution and traffic increase rapidly in African urban cities. Moreover, according to the United Nation, the present urban population of 3.2 billion individuals will rise to almost 5 billion from now to 2030. This increase will result in most dramatic consequences in developing countries. This is particularly true for West Africa with the rapid development of

megacities (Lagos, Accra, Abidjan, Bamako ...). Concerning effects on atmospheric chemistry, this signifies an inordinate surge in particle and gas emissions into the atmosphere with large impacts on populations health and climatic impacts on local and regional scales. These impacts are still unknown. To begin to study the pollution of future African megacities, we have launched the POLCA pilot program (POLlution des Capitales Africaines). We have performed in the 2004 dry season some gaseous concentrations measurements in eight African capitals. The preliminary results reveal that the atmospheric concentrations of SO_2, NO_2, HNO_3, NH_3 and O_3 are very high and comparable to those measured in industrialised countries of the Northern Hemisphere. An example is given by the 50 ppb of NO_2 measured in Bamako, Abidjan and Dakar (personal communication, Yoboue et al., 2009). Finally, to extend the results presented in this paper, we have proposed for 2010 a new IDAF scientific plan to include gaseous and particulate pollution measurements in two African capitals, i.e., Yaounde and Bamako in comparison to the actual remote IDAF sites.

Acknowledgement. This work is part of the IDAF (IGAC/DEBITS/AFRICA) project; and was funded by INSU/CNRS "Institut National des Sciences de l'Univers/Centre National de Recherche Scientifique" and the API "African Monsoon Multidisciplinary Analyses" (AMMA in 2005). The authors are grateful to all the field technicians of the IDAF network: Alfari Zakou for Banizoumbou in Niger, Raphael Zouzou for Lamto in Cote d'Ivoire, Mathieu Zang for Zoetele in Cameroon, Hama Maïga for Agoufou in Mali, Celestin Darakpa for Djougou in Benin and Kanoute Cheick for Katibougou in Mali.

References

Abbadie, L., Gignoux, J., Le Roux, X., and Lepage, M.: Lamto: Structure, Functioning, and Dynamics of a Savanna Ecosystem, Ecological Studies, Springer, New York, 179, 455 pp., 2006.

Andreae, M. O., Chapuis, A., Cros, B., Fontan, J., Helas, G., Justice, C., Kaufman, Y. J., Minga, A., and Nganga, D.: Ozone and Aitken nuclei over Equatorial Africa: airborne observations during DECAFE 88, J. Geophys. Res., 97, 6137–6148, 1992.
Arndt, R., Carmichael, G. R., Streets, D. G., and Bhatti, N.: Sulfur dioxide emissions and sectorial contributions to sulfur deposition in Asia, Atmos. Environ. 31, 1553–1572, 1997.
Bakwin, P. S., Wofsy, S. C., and Fan, S.-M.: Measurements of reactive nitrogen oxides (NO_y) within and above a tropical forest canopy in the wet season, J. Geophys. Res., 95, 16765–16772, 1990.
Balme, M., Vischel, T., Lebel, T., Peugoet, C., and Galle, S.: Assessing the water balance in the sahel: impact of small scale rainfall variability on runoff, part 1: Rainfall variability analysis, J. Hydrol., 331(1–2), 336–348, 2006.
Barnett, D. and Davis, E. G.: A GC method for the determination of sulphur dioxide in food headspaces, J. Chromatogr. Sci., 21, 205–208, 1983.
Bates, T., Scholes, M., Doherty, S., and Young, B.: IGAC Science Plan and Implementation Strategy IGBP Report 56, IGBP Secretariat, Stockholm, Sweden, 44 pp., 2006.
Bates, T. S., Lamb, B. K., Guenther, A., Dignon, J., and Stoiber, R. E.: Sulfur emissions to the atmosphere from natural sources, J. Atmos. Chem., 14, 315–317, 1992.
Bouwman, A. F., Boumans, L. J. M., and Batjes, N. H.: Estimation of global NH_3 volatilization loss from synthetic fertilizers and animal manure applied to arable lands and grasslands, Global Biogeochem. Cy., 16(2), 1024, doi:10.1029/2000GB001389, 2002.
Brimblecombe, P., Hara, H., Houle, D., and Novak, M.: Acid Rain - Deposition to Recovery, Springer edition, Reprinted from Water Air Soil Pollut.: Focus, 7(1–3), VIII, 420 pp., Hardcover, ISBN: 978-1-4020-5884-4, 2007.
Brocard, D., Galy-Lacaux, C., Lacaux, J. P., Kouadio, G., and Yoboué, V.: Emissions from the combustion of biofuels in Western Africa, in: Global Biomass Burning, edited by: Levine, J. S., MIT Press, Cambridge, MA, 350–360, 1996.
Carmichael, G. R., Ferm, M., Thongboonchoo, N., Woo, J.-H., Chan, L. Y., Murano, K., Viet, P. H., Mossberg, C., Bala, R., Boonjawat, J., Upatum, P., Mohan, M., Adhikary, S. P., Shrestha, A. B., Pienaar, J. J., Brunke, E. B., Chen, T., Jie, T., Guoan, D., Peng, L. C., Dhiharto, S., Harjanto, H., Jose, A. M., Kimani, W., Kirouane, A., Lacaux, J. P., Richard, S., Barturen, O., Cerda, J. C., Athayde, A., Tavares, T., Cotrina, J. S., and Bilici, E.: Measurements of sulfur dioxide, ozone and ammonia concentrations in Asia, Africa, and South America using passive samplers, Atmos. Environ., 37, 1293–1308, 2003.

Carmichael, G. R., Hong, M. S., Ueda, H., Chen, L. L., Murano, K., Kang, C., and Shim, S.: Aerosol composition at Cheju Island, Korea, J. Geophys. Res., 102, 6047–6061, 1997.
Carmichael, G. R., Zhang, Y., Chen, L. L., Hong, M. S., and Ueda, H.: Seasonal variation of aerosol composition at Cheju Island, Korea, Atmos. Environ., 30, 2407–2416, 1996.
Chestnut, L. G.: Human Health Benefits From Sulfate Reductions Under Title IV of the 1990 Clean Air Act Amendments, Final Report, US EPA, Office of Atmospheric Programs, Acid Rain Division, 1995.
Cooke, W. F., Koffi, B., and Grégoire, J.-M.: Seasonality of vegetation fires in Africa from remote sensing data and application to a global chemistry model, J. Geophys. Res., 101, 21051–21065, 1996.
Cros, B., Delmas, R., Clairac, B., Loemba-Ndembi, J., and Fontan, J.: Survey of ozone concentrations in an equatorial region during the rainy season, J. Geophys. Res., 92, 9772–9778, 1987.
Cros, B., Delon, C., Affre, C., Marion, T., Druilhet, A., Perros, P. E., and Lopez, A.: Sources and sinks of ozone in savanna and forest areas during EXPRESSO: airborne turbulent flux measurements, J. Geophys. Res., 105, 29347–29358, 2000.
Cros, B., Fontan, J., Minga, A., Helas, G., Nganga, D., Delmas, R., Chapuis, A., Benech, B., Druilhet, A., and Andreae, M. O.: Vertical profiles of ozones between 0 and 400 meters in and above the African equatorial forest, J. Geophys. Res., 97, 12877–12887, 1992.
Cruz, L. P. S., Campos, V. P., Silva, A. M. C., and Tavares, T. M.: A field evaluation of a SO_2 passive sampler in tropical industrial and urban air, Atmos. Environ., 38, 6425–6429, 2004.
Davidson, E. A.: Pulses of nitric oxide and nitrous oxide flux following wetting of dry soil: an assessment of probable sources and importance relative to annual fluxes, Ecol. Bull., 42, 149– 155, 1992.
Debaje, S. B., Jeyakumar, S. J., Ganesan, K., Jadhav, D. B., and Seetaramayya, P.: Surface ozone measurements at tropical rural coastal station Tranquebar, India, Atmos. Environ., 37, 4911–4916, 2003.
Delmas, R. A., Lacaux, J. P., Menaut, J. C., Abbadie, L., Le Roux, X., Helas, G., and Lobert, G.: Nitrogen compound emission from biomass burning in tropical African savanna, FOS/DECAFE 91 Experiment (Lamto, Ivory Coast), J. Atmos. Chem., 22, 175–194, 1995.
Delon, C., Reeves, C. E., Stewart, D. J., Serça, D., Dupont, R., Mari, C., Chaboureau, J.-P., and Tulet, P.: Biogenic nitrogen oxide emissions from soils – impact on NO_x and ozone over West Africa during AMMA (African Monsoon Multidisciplinary Experiment): modelling study,

Atmos. Chem. Phys., 8, 2351–2363, 2008, http://www.atmos-chem-phys.net/8/2351/2008/.
Delon, C., Galy-Lacaux, C., Boone, A., Liousse, C., Serça, D., Adon, M., Diop, B., Akpo, A., Lavenu, F., Mougin, E., and Timouk, F.: Atmospheric nitrogen budget in Sahelian dry savannas, Atmos. Chem. Phys. Discuss., 9, 14189–14233, 2009, http://www.atmos-chem-phys-discuss.net/9/14189/2009/.
Dentener, F. J., Carmichael, G. R., Zhang, Y., Lelieveld, Y. J., and Crutzen, P. J.: Role of mineral aerosols as a reactive surface in the global troposphere, J. Geophys. Res., 101, 22869–22889, 1996.
Ferm, M. and Rodhe, H.: Measurements of air concentrations of SO_2, NO_2 and NH_3 at rural and remote sites in Asia, J. Atmos. Chem., 27, 17–29, 1997.
Ferm, M., De Santis, F., and Varotsos, C.: Nitric acid measurements in connection with corrosion studies, Atmos. Environ., 39, 6664–6672, 2005.
Ferm, M., Lindskog, A., Svanberg, P.-A., and Boström, C.-A.: New measurement technique for air pollutants, Kem. Tidskr., 1, 30–32, 1994 (in Swedish).
Ferm, M.: A sensitive Diffusional Sampler. IVL publication B – 1020, Swedish Environmental Research Institute, 40258 Gotebory, Sweden, 1–12, 1991.
Ferm, M.: The theories behind diffusive sampling. Proceedings from the International Conference on Measuring Air Pollutants by Diffusive Sampling, Montpellier, France, 31–40, 26–28 September 2001.
Galanter, M., Levy II, H., and Carmichael, G. R.: Impacts of biomass burning on tropospheric CO, NO_x, and O_3, J. Geophys. Res., 105, 6633–6653, 2000.
Galy-Lacaux, C. and Modi, A. I.: Precipitation chemistry in the Sahelian Savanna of Niger, Africa, J. Atmos. Chem., 30, 319–334, 1998.
Galy-Lacaux, C., Carmichael, G. R., Song, C. H., Lacaux, J. P., and Modi, I.: Heterogenous processes involving nitrogenous compounds and Saharan dust inferred from measurements and model calculations region, J. Geophys. Res., 106, 12559–12578, 2001.
Galy-Lacaux, C., Laouali, D., Descroix, L., Gobron, N., and Liousse, C.: Long term precipitation chemistry and wet deposition in a remote dry savanna site in Africa (Niger), Atmos. Chem. Phys., 9, 1579–1595, 2009, http://www.atmos-chem-phys.net/9/1579/2009/.
Garland, J. A.: The dry deposition of sulphur dioxide to land and water surfaces, P. Roy. Soc. Lon. Ser. A, 354, 245–268, 1977.

Gautier, L.: Contact forêt-savane en Côte d'Ivoire centrale: évolution de la surface forestière de la réserve de Lamto (sud de V-Baoulé), Candoella, 45, 627–641, 1990.
Graedel, T. E. and Crutzen, P. J.: Atmospheric Change: An Earth System Perspective, W. H. Freeman and Company, New York, p. 446, 1993.
Gupta, A., Kumar, R., Kumari, K. M., and Srivastava, S. S.: Measurement of NO_2, HNO_3, NH_3 and SO_2 and related particulate matter at a rural site in Rampur, India, Atmos. Environ., 37, 4837–4846, 2003.
Hansen, J., Sato, M., Nazarenko, L., Ruedy, R., Lacis, A., Koch, D., Tegen, I., Hall, T., Shindell, D., Santer, B., Stone, P., Novakov, T., Thomason, L., Wang, R., Wang, Y., Jacob, D., Hollandsworth, S., Bishop, L., Logan, J., Thompson, A., Stolarski, R., Lean, J., Willson, R., Levitus, S., Antonov, J., Rayner, N., Parker, D., and Christy, J.: Climate forcings in Goddard Institute for Space Studies SI2000 simulations, J. Geophys. Res., 107, 4347, doi:10.1029/2001JD001143, 2002.
Hao, W. M. and Liu, M.-H.: Spatial and temporal distribution of tropical biomass burning, Global Biogeochem. Cy., 8, 495–503, 1994.
Jacob, D. J. and Bakwin, P. S.: Cycling of NO_x in tropical forest canopies, in: Microbial Production and Consumption of Greenhouse Gases: Methane, Nitrogen Oxides, and Halomethane, edited by: Rogers, J. E. and Whitman, W. B., Am. Soc. Microbiol., Washington DC, Chap. 13, 237–253, 1991.
Jacob, D. J. and Wofsy, S. C.: Budgets of reactive nitrogen, hydrocarbons, and ozone over the Amazon-Forest during the wet season, J. Geophys. Res., 95, 16737–16754, 1990.
Jacob, D. J., Heikes, B. G., Dickerson, R. R., Artz, R. S., and Keene, W. C.: Evidence for a seasonal transition from NO_x- to hydrocarbon-limited ozone production at Shenandoah National Park, Virginia, J. Geophys. Res., 100, 9315–9324, 1995.
Jaegle, L., Martin, R. V., Chance, K., Steinberger, L., Kurosu, T. P., Jacob, D. J., Modi, A. I., Yoboué, V., Sigha-Nkamdjou, L., and Galy-Lacaux, C.: Satellite mapping of rain-induced nitric oxide emissions from soils, J. Geophys. Res., 109, D21310, doi:10.1029/2004JD004787, 2004.
Jaegle, L., Steinberger, L., Martin, R. V., and Chance, K.: Global partitioning of NO_x sources using satellite observations: relative roles of fossil fuel combustion, biomass burning and soil emissions, Faraday Discuss., 130, 407–423, doi:10.1039/b502128f, 2005.
Johansson, C. and Sanhueza, E.: Emissions of NO from savannah soils during rainy season, J. Geophys. Res., 93, 14193–14198, 1988.

Josipovic, M., Annegarn, H., Kneen, M., Piketh, S., and Pienaar, J.: A regional passive monitoring Study of SO_2, NO_2 and Ozone in South Africa, IGACtivities Newsletter No. 36, July 2007.
Kaplan, W. A., Wofsy, S. C., Keller, M., and Da Costa, J. M.: Emission of NO and deposition of O_3 in a tropical forest system, J. Geophys. Res., 93, 1389–1395, 1988.
Lacaux, J. P., Brustet, J. M., Delmas, R., Menaut, J. C., Abbadie, L., Bonsang, B., Cachier, H., Baudet, J. G. R., Andreae, M. O., and Helas, G.: Biomass burning in the tropical savannas of Ivory Coast: an overview of the field experiment Fire of Savannas (FOS/DECAFE 91), J. Atmos. Chem., 22, 195–216, 1995.
Lacaux, J. P., Tathy, J. P., and Sigha, L.: Acid wet deposition in the tropics: two case studies using DEBITS measurements, IGACtivities Newsletter of the International Global Atmospheric Chemistry Project, DEBITS Special 2, 13–18, 2003.
Laville, P., Hénault, C., Gabrielle, B., and Serça, D.: Measurement and modelling of NO fluxes over maize and wheat crops during their growing seasons: effect of crop management, Nutr. Cycl. Agroecosyst. 72, 159–171, 2005.
Lebel, T., Parker, D. J., Bourlès, B., Diedhiou, A., Gaye, A., Polcher, J., Redelsperger, J.-L., and Thorncroft, C. D.: AMMA field campaigns in 2005 AND 2006, Gewex News, 1, 4–6, 2007.
Liu, S. C., Trainer, M., Fehsenfeld, F. C., Parrish, D. D., Williams, E. J., Fahey, D. W., Hubler, G., and Murphy, P. C.: Ozone production in the rural troposphere and the implications for regional and global ozone distributions, J. Geophys. Res., 92, 4191–4207, 1987.
Lobert, J. M., Scharffe, D. H., Hao, W. M., and Crutzen, P. J.: Importance of biomass burning in the atmospheric budgets of nitrogen containing gases, Nature, 346, 552–524, 1990.
Ludwig, J., Meixner, F. X., Vogel, B., and Forstner, J.: Soil-air exchange of nitric oxide: an overview of processes, environmental factors, and modelling studies, Biogeochemistry, 52, 225–257, 2001.
Macdonald, B. C. T., Denmead, O. T., White, I., and Melville, M. D.: Natural sulfur dioxide emissions from sulfuric soils, Atmos. Environ., 38, 1473–1480, 2004.
Martins, J. J., Dhammapala, R. S., Lachmann, G., Galy-Lacaux, C., and Pienaar, J. J.: Long-term measurements of sulphur dioxide, nitrogen dioxide, ammonia, nitric acid and ozone in Southern Africa using passive samplers, S. Afr. J. Sci., 103(7–8), 336–342, 2007.
Mauzerall, D. L. and Wang, X. P.: Protecting agricultural crops from the effects of tropospheric ozone exposure: reconciling science and standard setting in the United States, Europe, and Asia, Annu. Rev. Energ. Env., 26, 237–268, 2001.

McCalley, C. K. and Sparks, J. P.: Controls over nitric oxide and ammonia emissions from Mojave Desert soils, Oecologia, 156, 871–881, 2008.
McGranaham, G. and Murray, F.: Air Pollution and Health in Rapidly Developing Countries, Edition SEI Earthscan, London, 1–227, 2003.
Menaut, J. C., Abbadie, L., Levanu, F., Loudjani, P., and Podaire, A.: Biomass burning in West African Savannas, in: Global Biomass Burning: Atmospheric, Climatic, and Biospheric Implications, edited by: Levine, J. S., MIT Press, Cambridge, MA, 133–142, 1991.
Mphepya, J. N., Galy-Lacaux, C., Lacaux, J. P., Held, G., and Pienaar, J. J.: Precipitation chemistry and wet deposition in Kruger National Park, South Africa, J. Atmos. Chem., 53, 169–183, 2006.
Mphepya, J. N., Pienaar, J. J., Galy-Lacaux, C., Held, G., and Turner, C. R.: Precipitation chemistry in semi-arid areas of Southern Africa: a case study of a rural and an industrial site, J. Atmos. Chem., 47, 1–24, 2004.
Modi, A. I., Lacaux, J. P., Labroue, L., and Baudet, J. G. R.: Chimie des aérosols et des pluies dans la savane semi-aride du Niger pendant la saison humide 1989, Sécheresse, 6, 331–335, 1995.
Mougin, E., Hiernaux, P., Kergoat, L., Grippa, M., De Rosnay, P., Timouk, F., Le Dantec, V., Demarez, V., Arjounin, M., Lavenu, F., Soumaguel, N., Ceschia, E., Mougenot, B., Baup, F., Frappart, F., Frison, P. L., Gardelle, J., Gruhier, C., Jarlan, L., Mangiarotti, S., Sanou, B., Tracol, Y., Guichard, F., Trichon, V., Diarra, L., Soumaré, A., Koité, M., Dembélé, F., Lloyd, C., Hanan, N. P., Damesin, C., Delon, C., Serça, D., Galy-Lacaux, C., Seghiéri, J., Becerra, S., Dia, H., Gangneron, F., and Mazzega, P.: The AMMA-CATCH Gourma observatory site in Mali: Relating climatic variations to changes in vegetation, surface hydrology, fluxes and natural resources, J. Hydrol., 375(1–2), 14–33, doi:10.1016/j.jhydrol.2009.06.045, 2009.
National Research Council (NRC), Committee on Tropospheric Ozone Formation and Measurement: Rethinking the Ozone Problem in Urban and Regional Air Pollution, National Academy Press, Washington, 1991.
Naja, M. and Lal, S.: Surface ozone and precursor gases at Gadanki (13.5° N, 79.2° E), a tropical rural site in India, J. Geophys. Res., 107, 4197, doi:10.1029/2001JD000357, 2002.
Pienaar, J. J.: Proposal of a new IGAC II task: DEBITS II (Deposition of Biogeochemically Important Trace Species), http://www.igac.noaa.gov/DEBITS.php, 2005.
Rondon, A. and Sanhueza, E.: Seasonal variation of gaseous HNO_3 and NH_3 at a tropical savannah site, J. Atmos. Chem., 11(3), 245–254, 1990.

Rondon, A., Johansson, C., and Sanhueza, E.: Emission of nitric oxide from soils and termite nests in a trachypogon savanna of the Orinoco Basin, J. Atmos. Chem., 17, 293–306, 1993.
Rummel, U., Ammann, C., Kirkman, G. A., Moura, M. A. L., Foken, T., Andreae, M. O., and Meixner, F. X.: Seasonal variation of ozone deposition to a tropical rain forest in Southwest Amazonia, Atmos. Chem. Phys., 7, 5415–5435, 2007, http://www.atmos-chem-phys.net/7/5415/2007/.
Saunois, M., Reeves, C. E., Mari, C. H., Murphy, J. G., Stewart, D. J., Mills, G. P., Oram, D. E., and Purvis, R. M.: Factors controlling the distribution of ozone in the West African lower troposphere during the AMMA (African Monsoon Multidisciplinary Analysis) wet season campaign, Atmos. Chem. Phys., 9, 6135–6155, 2009, http://www.atmos-chem-phys.net/9/6135/2009/.
Schlecht, E., Fernandez-Rivera, S., and Hiernaux, P.: Timing, size and N-concentration of faecal and urinary excretions in cattle, sheep and goats – can they be used for better manuring of cropland?, in: Soil fertility Management in West African Land Use Systems, edited by: Renard, G., Neef, A., Becker, K., and von Oppen, M., Margraf Verlag, Weikersheim, Germany, 361–368, 1998.
Schlesinger, W. H. and Hartley, A. E.: A global budget for NH_3, Biogeochemistry, 15, 191–211, 1992.
Scholes, M., Martin, R., Scholes, R. J., Parsons, D., and Winstead, E.: NO and N_2O emissions from savanna soils following the first simulated rains of the season, Nutr. Cycl. Agroecosys. 48, 115– 122, 1997.
Serça, D., Delmas, R., Le Roux, X., Parsons, D. A. B., Scholes, M. C., Abbadie, L., Lensi, R., Ronce, O., and Labroue, L.: Comparison of nitrogen monoxide emissions from several African tropical ecosystems and influence of season and fire, Global Biogeochem. Cy., 12, 637–651, 1998.
Sigha-Nkamdjou, L., Galy-Lacaux, C., Pont, V., Richard, S., Sighoumnou, D., and Lacaux, J. P.: Rainwater chemistry and wet deposition over the equatorial forested ecosystem of Zoétélé (Cameroon), J. Atmos. Chem., 46, 173–198, 2003.
Smith, S. J., Pitcher, H., and Wigley, T. M. L.: Global and regional anthropogenic sulfur dioxide emissions, Global Planet. Change, 29, 99–119, 2001.
Sparks, J. P., Monson, R. K., Sparks, K. L., and Lerdau, M.: Leaf uptake of nitrogen dioxide (NO_2) in a tropical wet forest: implication for tropospheric chemistry, Oecologia, 127, 214–221, 2001.

Stevenson, K., Bush, T., and Mooney, D.: Five years of nitrogen dioxide measurement with diffusion tube samplers at over 1000 sites in the UK, Atmos. Environ., 35, 281–287, 2001.
Stewart, D. J., Taylor, C. M., Reeves, C. E., and McQuaid, J. B.: Biogenic nitrogen oxide emissions from soils: impact on NO_x and ozone over West Africa during AMMA (African Monsoon Multidisciplinary Analysis): observational study, Atmos. Chem. Phys., 8, 2285–2297, 2008, http://www.atmos-chem-phys.net/8/2285/2008/.
Sutton, M., Reis, S., and Baker, S. M. H.: Atmospheric Ammonia, detecting emission changes and environmental impacts. Results of an expert workshop under the convention of long range transboundary air pollution, Springer Edition, New York, ISBN 978-1-4020-9120-9, 2009.
Tidblad, J., Kucera, V., Samie, F., Das, S. N., Bhamornsut, C., Peng, L. P., Lung So, K., Dawei, Z., Hong Lien, L. T., Schollenberger, H., Lungu, C. V., and Simbi, D.: Exposure programme on atmospheric corrosion effects of acidifying pollutants in tropical and subtropical climates, Water Air Soil Pollut., 7, 241–247, 2007.
Trebs, I., Lara, L. L., Zeri, L. M. M., Gatti, L. V., Artaxo, P., Dlugi, R., Slanina, J., Andreae, M. O., and Meixner, F. X.: Dry and wet deposition of inorganic nitrogen compounds to a tropical pasture site (Rondônia, Brazil), Atmos. Chem. Phys., 6, 447–469, 2006, http://www.atmos-chem-phys.net/6/447/2006/.
Trebs, I., Meixner, F. X., Slanina, J., Otjes, R., Jongejan, P., and Andreae, M. O.: Real-time measurements of ammonia, acidic trace gases and water-soluble inorganic aerosol species at a rural site in the Amazon Basin, Atmos. Chem. Phys., 4, 967–987, 2004, http://www.atmos-chem-phys.net/4/967/2004/.
Van Breemen, N.: Acid Sulfate Weathering, Soil Science Society of America, Madison, WI, USA, 95–108, 1982.
Van Breemen, N.: Selected Papers of the Ho Chi Minh City Symposium on Acid Sulphate Soils, ILRI Pub No. 53, ILRI, Wageningen, The Netherlands, 391–401, 1993.
Yienger, J. J. and Levy II, H.: Empirical model of global soil biogenic NO_x emissions, J. Geophys. Res., 100, 1447–1464, 1995.
Yoboue, V., Galy-Lacaux, C., Lacaux, J. P., and Silue, S.: Rainwater chemistry and wet deposition over the Wet Savanna ecosystem of Lamto (Côte d'Ivoire), J. Atmos. Chem., 52, 117–141, 2005.
Williams, E. J., Guenther, A., and Fehsenfeld, F. C.: An inventory of nitric oxide emissions from soils in the United States, J. Geophys. Res., 97, 7511–7519, 1992.

Zhang, L., Brook, J. R., and Vet, R.: A revised parameterization for gaseous dry deposition in air-quality models, Atmos. Chem. Phys., 3, 2067–2082, 2003b, http://www.atmos-chem-phys.net/3/2067/2003/.

Zunckel, M., Venjonoka, K., Pienaar, J. J., Brunke, E.-G., Pretorius, O., Koosailee, A., Raghunandan, A., and van Tienhoven, M. A.: Surface ozone over Southern Africa: synthesis of monitoring results during the cross border air pollution impact assessment project, Atmos. Environ., 38, 6139–6147, 2004.

Table 1. Geographic and ecologic characteristics of the Western and Central Africa IDAF sites.

Ecosystem	Station	Latitude	Longitude	Elevation/m	Country
Dry savanna	Banizoumbou	13°31′ N	2°38′ E	220	Niger
	Katibougou	10°52′ N	7°33′ W	290	Mali
	Agoufou	15°3′ N	1°5′ W	300	Mali
Wet savanna	Lamto	6°13′ N	5°2′ W	105	Côte d'Ivoire
	Djougou	9°40′ N	1°55′ E	432	Benin
Forest	Zoétélé	3°15′ N	11°53′ E	720	Cameroon
	Bomassa	2°21′ N	16°19′ E	300–600	Congo

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Table 2. Definition of the dry and wet seasons in IDAF stations for the 1998–2007 period. Seasonal accumulated precipitation (mm) and annual precipitation accumulation (mm).

Station	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sept	Oct	Nov	Dec	Total
Banizoumbou	38					451				8			497
Katibougou	67					654				65			786
Agoufou	18					329				11			358
Lamto	188			979						110			1277
Djougou	55			1148						2			1205
Zoétélé	70		1508									17	1595
Bomassa	52		1481									55	1588

Dry season ☐ Wet season ▭

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Table 3. Coating solutions and chemical reactions of the HNO_3, SO_2, NO_2, NH_3, O_3 IDAF passive samplers.

Gas (Colour of the sampler)	Coating solution	Chemical reaction on the filter
HNO_3 and SO_2 (Black)	0.5 g NaOH in 50 mL methanol (pH>12)	$HNO_3(g)+OH^- \rightarrow NO_3^- + H_2O$ $2SO_2(g)+4OH^- + O_2 \rightarrow 2H_2O + 2SO_4^{2-}$
NO_2 (Grey)	0.44 g NaOH+3.95 g NaI in 50 mL methanol (pH>12)	$2NO_2(g)+3I^- \rightarrow 2NO_2^- + I_3^-$
NH_3 (White)	1.0 g citric acid in 50 mL methanol	$NH_3(g)+H^+ \rightarrow NH_4^+$
O_3 (Grey & black)	0.25 g $NONO_2$+O.25 g K_2CO_3+0.5 mL redistilled glycerol in 50 mL water	$O_3(g)+NO_2^- \rightarrow NO_3^- + O_2$

Table 4. Synthesis of L/A and L_c experimental determination.

Gaz	NO_2	NH_3	HNO_3	SO_2	O_3	Moyenne	Ecart type	%
L_c (mm)	5.2	4.5	5.3	4.6	4.3	4.8	0.5	9.6
L/A (m^{-1})	48.9	46.5	49.5	46.8	45.7	47.5	1.6	3.4

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Table 5. Mean annual concentrations (in ppb) at IDAF sites and the number of acceptable duplicates (in brackets).

	Station (period)	NO_2	HNO_3 ***	NH_3	O_3 *	SO_2 **
	West and Central African sites					
Dry Savannas	Banizoumbou (98–07)	2.4±0.4 (113)	0.5±0.2 (112)	6.3±2.0 (112)	11.9±2.3 (76)	0.6±0.2 (66)
	Katibougou (98–07)	1.9±0.3 (117)	0.4±0.1 (116)	6.6±1.0 (113)	12.6±2.2 (73)	0.6±0.2 (68)
	Agoufou (05–07)	1.8±0.4 (28)	0.5±0.1 (28)	7.4±0.8 (25)	12.2±2.6 (23)	1.0±0.2 (26)
Wet Savannas	Lamto (98–07)	1.0±0.3 (115)	0.3±0.1 (116)	4.0±1.2 (112)	10.9±1.8 (78)	0.5±0.2 (67)
	Djougou (05–07)	1.2±0.1 (30)	0.4±0.2 (30)	3.9±1.4 (27)	14.0±2.8 (29)	0.8±0.3 (29)
Forests	Zoétélé (98–07)	0.9±0.2 (112)	0.2±0.1 (113)	4.2±0.9 (103)	4.8±1.0 (73)	0.3±0.1 (65)
	Bomassa (98–06)	1.4±0.4 (83)	0.3±0.1 (81)	4.7±1.7 (76)	4.0±0.4 (45)	0.4±0.2 (44)
	Southern African sites					
Dry Savannas	Amersfoort (97–05)	2.5±1.0 (105)	0.9±0.5 (26)	1.2±0.7 (85)	27±8.3 (89)	2.8±1.1 (10)
	Louis Trichardt (95–05)	0.7±0.4 (71)	0.2±0.1 (27)	1.2±0.7 (65)	35±8.6 (72)	0.8±0.7 (70)
Coastal/Continental	Cape Point (95–05)	1.2±0.6 (114)	0.5±0.2 (29)	1.5±0.7 (120)	27±7.3 (114)	0.7±0.4 (106)

* In West and Central Africa, O_3 starts monitoring in 2001 and ** SO_2 in 2002. *** In South Africa, HNO_3 starts in 2003.

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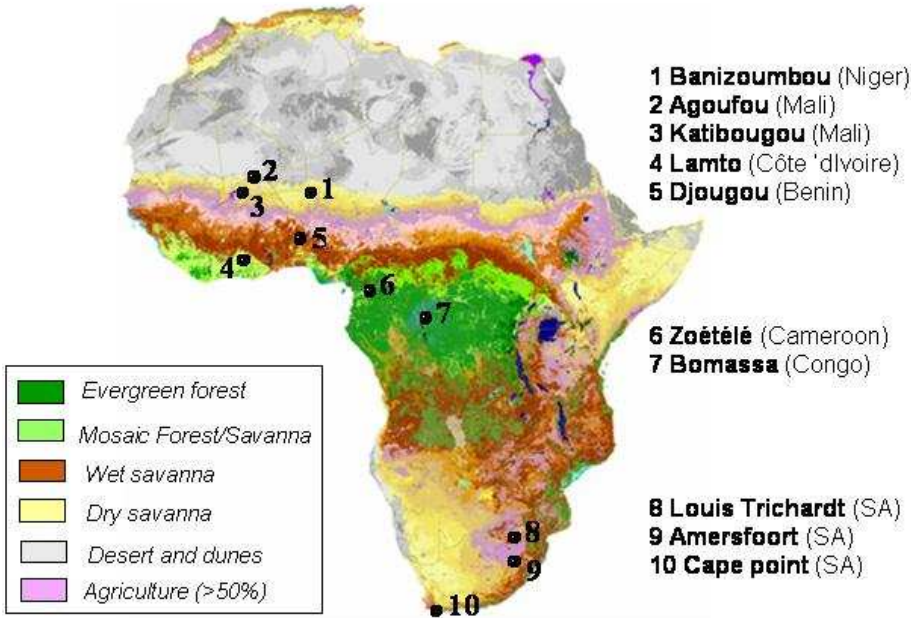

Fig. 1. Vegetation and location map of the 10 measurement stations of the IDAF network.

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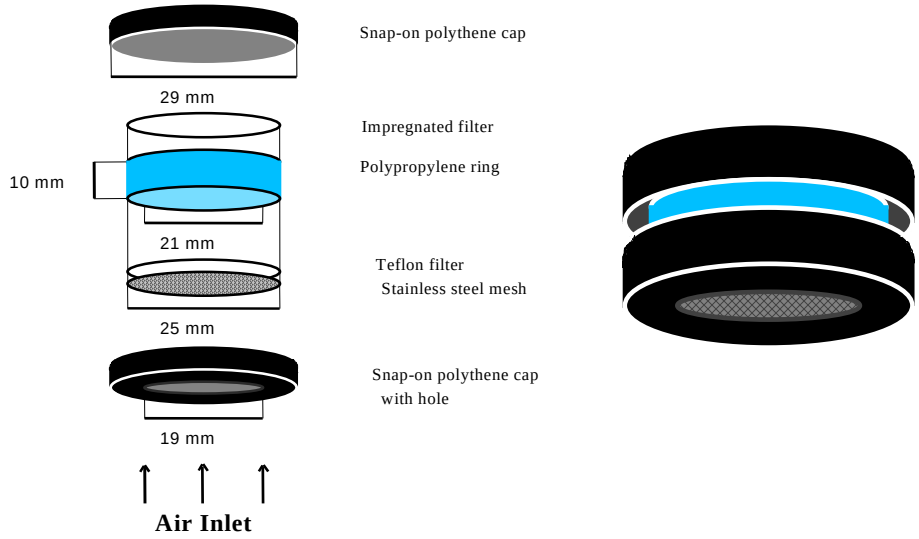

Fig. 2. Diagram of the IDAF passive diffusion sampler (adaptation from Ferm, 1991).

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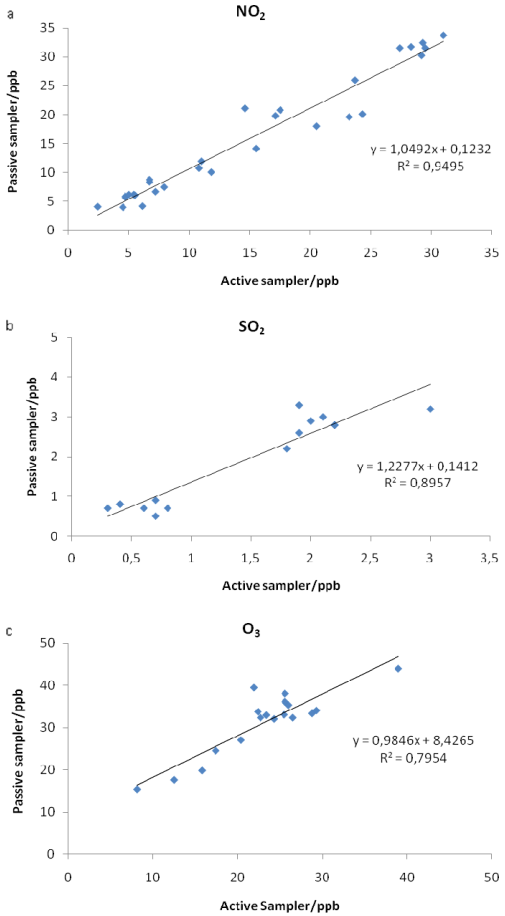

Fig. 3. Comparison of active and passive NO_2 **(a)**, SO_2 **(b)**, O_3 **(c)** measurements (ppb) at Toulouse (France) from 1998 to 2000.

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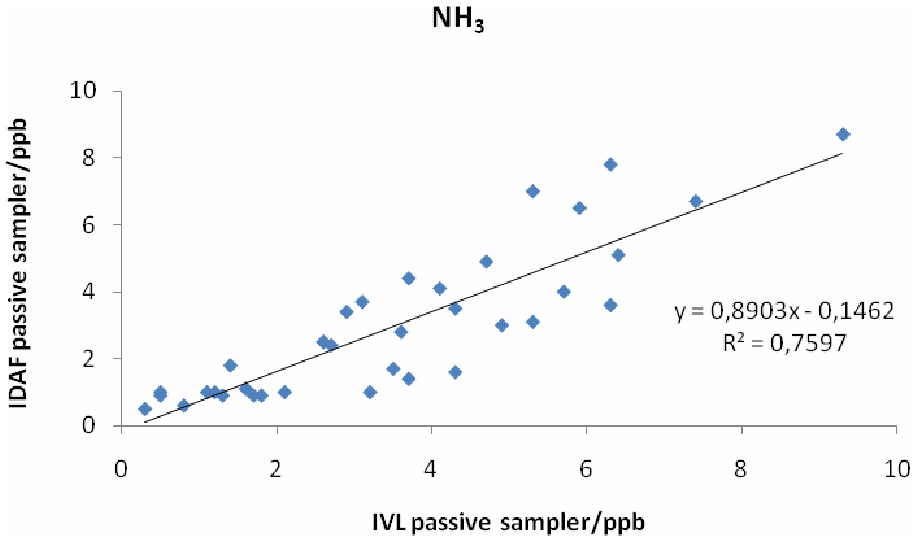

Fig. 4. Comparison of the IDAF and IVL NH_3 passive samplers (GURME project) exposed at IDAF stations from 1998 to 2000.

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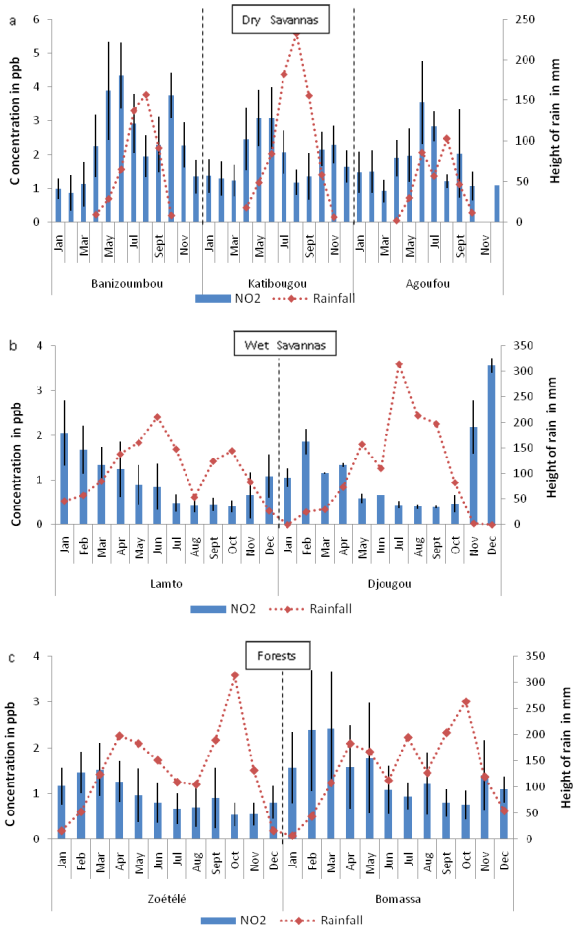

Fig. 5. Evolution of monthly NO_2 concentrations on the transect dry savannas **(a)**, wet savannas **(b)**, and forests **(c)**.

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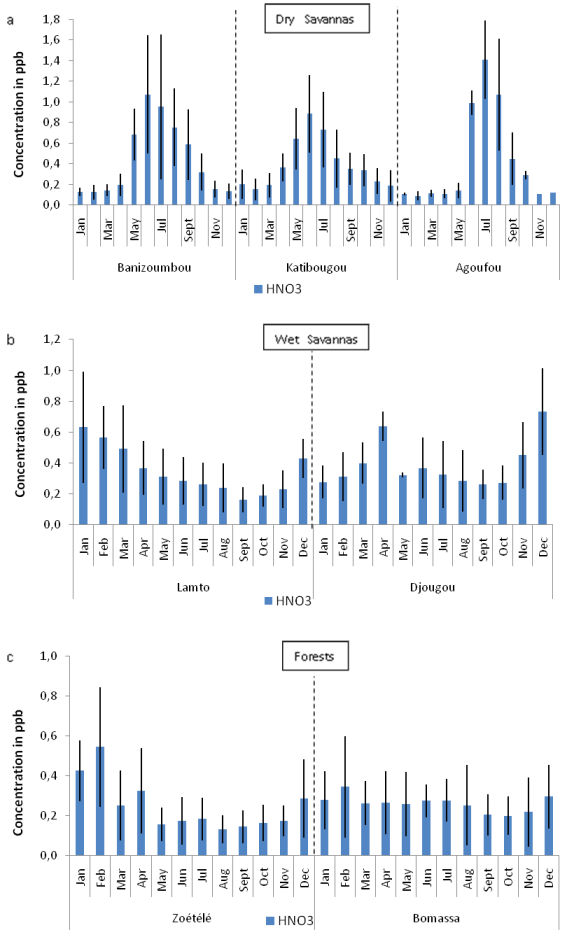

Fig. 6. Evolution of monthly HNO_3 concentrations on the transect dry savannas **(a)**, wet savannas **(b)**, and forests **(c)**.

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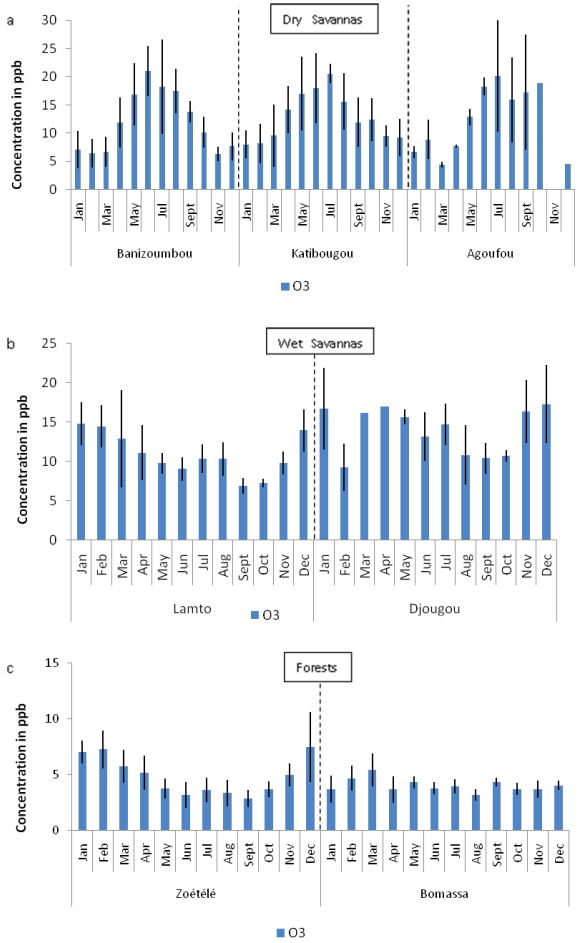

Fig. 7. Evolution of monthly O_3 concentrations on the transect dry savannas **(a)**, wet savannas **(b)**, and forests **(c)**.

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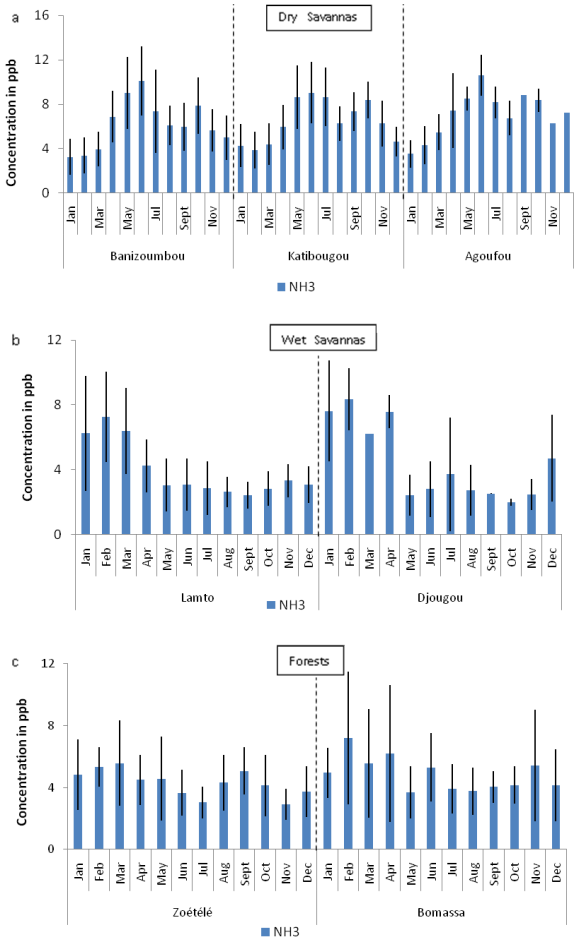

Fig. 8. Evolution of monthly NH_3 concentrations on the transect dry savannas **(a)**, wet savannas **(b)**, and forests **(c)**.

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