Atmos. Chem. Phys., 13, 11351–11374, 2013
www.atmos-chem-phys.net/13/11351/2013/
doi:10.5194/acp-13-11351-2013

Atmospheric Chemistry and Physics Open Access

Dry deposition of nitrogen compounds (NO_2, HNO_3, NH_3), sulfur dioxide and ozone in west and central African ecosystems using the inferential method

M. Adon[1,2], C. Galy-Lacaux[1], C. Delon[1], V. Yoboue[2], F. Solmon[1,3], and A. T. Kaptue Tchuente[4]

[1]Laboratoire d'Aérologie, UMR5560, CNRS/UPS, Toulouse, France
[2]Laboratoire de Physique de l'Atmosphère, Université Félix Houphouët-Boigny de Cocody, Abidjan, Côte d'Ivoire
[3]International Centre for Theoretical Physics, Trieste, Italy
[4]Geographic Information Science Center of Excellence, South Dakota State University, Brookings, USA

Correspondence to: M. Adon (adonatma@yahoo.fr) and C. Galy-Lacaux (lacc@aero.obs-mip.fr)

Received: 12 March 2013 – Published in Atmos. Chem. Phys. Discuss.: 2 May 2013
Revised: 1 October 2013 – Accepted: 12 October 2013 – Published: 22 November 2013

Abstract. This work is part of the IDAF program (IGAC-DEBITS-AFRICA) and is based on the long-term monitoring of gas concentrations (1998–2007) established at seven remote sites representative of major African ecosystems. Dry deposition fluxes were estimated by the inferential method using on the one hand surface measurements of gas concentrations (NO_2, HNO_3, NH_3, SO_2 and O_3) and on the other hand modeled exchange rates. Dry deposition velocities (V_d) were calculated using the big-leaf model of Zhang et al. (2003b). The bidirectional approach is used for NH_3 surface–atmosphere exchange (Zhang et al., 2010). Surface and meteorological conditions specific to IDAF sites have been used in the models of deposition. The seasonal and annual mean variations of gaseous dry deposition fluxes (NO_2, HNO_3, NH_3, O_3 and SO_2) are analyzed.

Along the latitudinal transect of ecosystems, the annual mean dry deposition fluxes of nitrogen compounds range from -0.4 to $-0.8\,kg\,N\,ha^{-1}\,yr^{-1}$ for NO_2, from -0.7 to $-1.0\,kg\,N\,ha^{-1}\,yr^{-1}$ for HNO_3 and from -0.7 to $-8.3\,kg\,N\,ha^{-1}\,yr^{-1}$ for NH_3 over the study period (1998–2007). The total nitrogen dry deposition flux (NO_2+HNO_3+NH_3) is more important in forests ($-10\,kg\,N\,ha^{-1}\,yr^{-1}$) than in wet and dry savannas (-1.6 to $-3.9\,kg\,N\,ha^{-1}\,yr^{-1}$). The annual mean dry deposition fluxes of ozone range between -11 and $-19\,kg\,ha^{-1}\,yr^{-1}$ in dry and wet savannas, and -11 and $-13\,kg\,ha^{-1}\,yr^{-1}$ in forests. Lowest O_3 dry deposition fluxes in forests are correlated to low measured O_3 concentrations, lower by a factor of 2–3, compared to other ecosystems. Along the ecosystem transect, the annual mean of SO_2 dry deposition fluxes presents low values and a small variability (-0.5 to $-1\,kg\,S\,ha^{-1}\,yr^{-1}$). No specific trend in the interannual variability of these gaseous dry deposition fluxes is observed over the study period.

1 Introduction

Deposition of chemical species onto the Earth's surface plays an essential role in controlling the concentration of gases and aerosols in the troposphere. The study of deposition thus allows for tracing the temporal and spatial evolution of atmospheric chemistry and is a pertinent indicator for evaluating natural and anthropogenic influences. The deposition of atmospheric nitrogen (N) species constitutes a major nutrient input to the biosphere. On a long-term scale, the increase of N inputs into terrestrial or aquatic ecosystems leads to important environmental consequences such as a loss of biodiversity, eutrophication, acidification of seminatural ecosystems, leaching of nitrate into groundwater and increased carbon storage (Vitousek et al., 1997; Rodhe et al., 2002; Bobbink et al., 1998; Bouwman et al., 2002b; Liu et al., 2013). N deposition on the terrestrial surface thus impacts both atmospheric chemistry and ecosystem dynamics. Ammonia (NH_3), nitrogen dioxide (NO_2) and nitric acid (HNO_3) are the most important contributors to N dry deposition (Trebs et al., 2006).

Sulfur dioxide (SO_2) is one of the important species considering the acid deposition issues, and it is also the precursor of sulfate. Dry deposition estimation of SO_2 is essential to assess ecological impact research, crop growing and air quality research (Tsai et al., 2010). Tropospheric ozone (O_3) is known to harm human health, damage vegetation and lead to deterioration of materials. The dry deposition of O_3 is one of the most important sinks in the boundary layer ozone budget (Rummel et al., 2007).

Monitoring networks have been established around the world to measure wet and dry deposition. 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). The DEBITS network collects data from 25 stations that are distributed within the tropical belt in Africa, Asia and South America, and results are presented in the new IGAC structure or DEBITS II (Pienaar et al., 2005; Bates et al., 2006; http://debits.sedoo.fr). For tropical Africa, the IDAF (IGAC/DEBITS/AFRICA) project started in 1994 and was implemented in partnership with INSU (Institut National des Sciences de l'Univers, in France) and the CNRS (Centre National de la Recherche Scientifique, in France) as part of the Environmental Research Observatory (ORE, in France) networks.

The main objectives of IDAF are to measure wet and dry deposition fluxes and to identify the relative contribution of natural and anthropogenic sources, as well as the factors regulating these fluxes. IDAF activity is based on high-quality measurements of atmospheric chemical data (gaseous, precipitation and aerosol chemical compositions) on the basis of multiyear monitoring (http://idaf.sedoo.fr). Within the framework of IDAF, several studies of precipitation chemical composition representative of great African ecosystems have been recently published (Galy-Lacaux and Modi, 1998; Galy-Lacaux et al., 2001, 2009; Al-Ourabi and Lacaux, 2002; Lacaux et al., 1993, 2003; Sigha et al., 2003; Yoboue et al., 2005; Mphepya et al., 2004; 2006; Laouali et al., 2012).

To complement these studies, it is appropriate to study and quantify dry deposition fluxes. Direct methods (eddy correlation, chamber method) and indirect methods (inferential method, gradient method) are available to determine dry deposition fluxes (Seinfeld and Pandis, 2006). The DEBITS committee in charge of deposition studies in IGAC has decided to use indirect dry deposition fluxes determination in tropical sites because of difficulties in operating sophisticated direct methods of flux measurements in remote sites (Wolff et al., 2010; Sutton et al., 2007). In this study, dry deposition fluxes are estimated using the inferential method, which is a combination of gaseous concentration measurements and modeling of deposition velocities according to the resistance analogy (Wesely, 1989; Zhang et al., 2003b; and references therein). Bidirectional exchange of NH_3 and NO_2 have been frequently observed over different canopies (Dorsey et al., 2004; Trebs et al., 2006; Walker et al., 2006; Wichink Kruit et al., 2007). There has been some effort in the development of bidirectional exchange models (e.g., Sutton et al., 1998; Flechard et al., 1999; Trebs et al., 2006; Massad et al., 2010; Zhang et al., 2010, Wichink Kruit et al., 2012; Bash et al., 2013; Hamaoui-Laguel et al., 2012); however, the application of these models remains difficult over the different canopies of African ecosystems owing to the lack of necessary input parameters. Nevertheless, the two-layer bidirectional model of Zhang et al. (2010) is applied in this study to estimate NH_3 surface–atmosphere exchange fluxes.

In a recent paper, Adon et al. (2010) presented the long-term monitoring of ambient gaseous concentrations within the IDAF program. Our study presented an original database of 10 yr of measurements (1998–2007) of five important atmospheric gases (NO_2, HNO_3, NH_3, O_3, SO_2) obtained within the IDAF African network at seven sites in west and central Africa.

In the present paper, realistic dry deposition velocities according to the sites and the species involved are calculated in order to estimate dry deposition fluxes. The big-leaf model of Zhang et al. (2003b) is used to simulate dry deposition velocities representative of major African ecosystems. The results are compared to previous estimates from the literature. For NH_3 net fluxes, the bidirectional model of Zhang et al. (2010) is used. Then, we present an estimate on a long-term basis (10 yr) of dry deposition fluxes of gases (NO_2, HNO_3, NH_3, O_3 and SO_2) at the scale of major African ecosystems. The monthly, seasonal and annual mean variations of gaseous dry deposition fluxes are analyzed.

2 Sites description and methodology

2.1 Presentation of measurement sites

Figure 1 presents the location of the seven IDAF measurement stations displayed on the map of African biomes adapted from the land cover product of Mayaux et al. (2004). The IDAF sites of west and central Africa are located to represent a transect of ecosystems, i.e., dry savannas (Agoufou, Banizoumbou, Katibougou), wet savannas (Djougou, Lamto) and equatorial forests (Zoetele, Bomassa). The geographical, ecological and climatic characteristics of the study sites are presented in Table 1. Dry savannas are characterized by a long dry season from October to May and a short wet season from June to September. The mean wet season extends from April to October in wet savannas and from March to November in forests; other months are the dry season. A detailed description of IDAF monitoring stations can be found in Adon et al. (2010).

Monitoring of gases at Banizoumbou, Katibougou, Lamto, Zoetele and Bomassa began in 1998. NO_2, NH_3 and HNO_3

Table 1. Geographic, ecologic and climatic characteristics of the western and central Africa IDAF sites. WS: wet season; DS: dry season.

Ecosystem	station	Location Latitude Longitude	Land cover classes (GLC 2000 Africa)	Climate	Country (region)
Dry savannas	Agoufou	15°20′ N, 01°29′ W	Open grassland with sparse shrub	Sahelian WS: June–September DS: October–May	Mali (Mopti)
	Banizoumbou	13°31′ N, 02°38′ E	Open grassland with sparse shrub	Sahelian WS: June–September DS: October–May	Niger (Dosso)
	Katibougou	12°56′ N, 07°32′ W	Deciduous shrubland with sparse trees	Sudano-Sahelian WS: June–September DS: October–May	Mali (Koulikoro)
Wet savannas	Djougou	09°39′ N, 01°44′ E	Deciduous open woodland	Sudano-Guinean WS: April-October DS: November–March	Benin (Atakora)
	Lamto	06°13′ N, 05°02′ W	Mosaic forest/savanna	Guinean WS: April–October DS: November–March	Côte d'Ivoire (V-Baoule)
Forests	Zoetele	03°15′ N, 11°53′ E	Closed evergreen lowland forest	Equatorial WS: March–November DS: December–February	Cameroon (Sud, Dja-et-Lobo)
	Bomassa	02°12′ N, 16°20′ E	Closed evergreen lowland forest	Equatorial WS: March–November DS: December–February	Congo (Sangha)

have been monitored since 1998, while measurement of O_3 started in 2001 and that of SO_2 in 2002. As part of the Long-term Observation Period of the AMMA (African Monsoon Multidisciplinary Analysis) program, the Djougou and Agoufou sites started operating in 2005. All measurements are still continuing at all the IDAF sites.

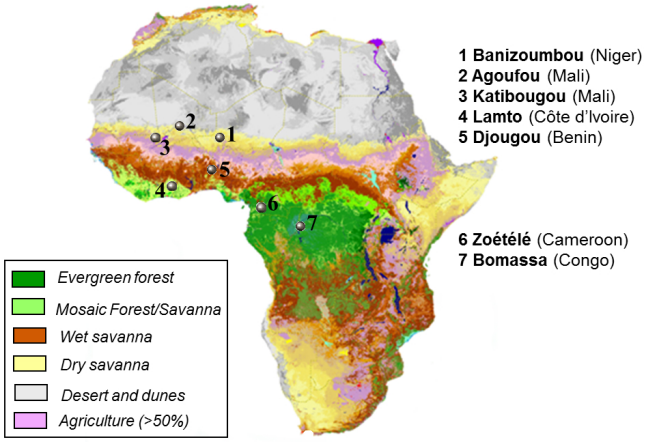

Fig. 1. Vegetation and location map of the seven measurement stations of the IDAF network. Only the seven IDAF stations of west and central Africa included in the present study are represented.

2.2 Dry deposition estimate

The inferential method, which combines measured air concentrations and modeled exchange rates, was employed in this study to estimate the dry deposition fluxes of different gaseous species. The inferential technique has been widely used in other studies for different types of ecosystems (Shen et al., 2009; Pineda and Venegas, 2009; Jin et al., 2006; Zhang et al., 2005, 2009; Delon et al., 2010, 2012; and Pan et al., 2012). This approach is more suited when routine monitoring data are available but the values of the derived fluxes are clearly dependent on the validity of the dry deposition velocity calculation.

2.2.1 Atmospheric concentration measurements

Atmospheric concentrations of NO_2, HNO_3, NH_3, O_3 and SO_2 are measured by passive samplers on a monthly basis as part of the IDAF network. Passive sampling observations at the west and central African sites have been performed over a 10 yr period from 1998 to 2007. The sampling procedure and chemical analysis of samples, as well as

Table 2. Mean annual concentrations (in ppb) at IDAF sites over the study period (1998–2007) (adapted from Adon et al., 2010).

Concentration (ppb)	Station (period)	NO_2	HNO_3	NH_3	O_3^*	SO_2^{**}
Dry Savannas	Agoufou (05–09)	1.8 ± 0.4	0.5 ± 0.1	7.3 ± 0.8	11.4 ± 2.2	0.8 ± 0.3
	Banizoumbou 98–07)	2.4 ± 0.4	0.5 ± 0.2	6.3 ± 2.0	11.9 ± 2.3	0.6 ± 0.2
	Katibougou (98–07)	1.9 ± 0.3	0.4 ± 0.1	6.6 ± 1.0	12.6 ± 2.2	0.6 ± 0.2
Wet Savannas	Djougou (05–09)	1.2 ± 0.1	0.4 ± 0.2	3.7 ± 1.1	13.6 ± 2.1	0.8 ± 0.3
	Lamto (98–07)	1.0 ± 0.3	0.3 ± 0.1	4.0 ± 1.2	10.9 ± 1.8	0.5 ± 0.2
Forests	Zoetele (98–07)	0.9 ± 0.2	0.2 ± 0.1	4.2 ± 0.9	4.8 ± 1.0	0.3 ± 0.1
	Bomassa (98–06)	1.4 ± 0.4	0.3 ± 0.1	4.7 ± 1.7	4.0 ± 0.4	0.4 ± 0.2

* O_3 starts monitoring in 2001 and ** SO_2 in 2002.

Table 3. Adaptation of land-use categories (LUC) used in the big-leaf model to IDAF sites for the calculation of canopy resistances (R_{ac}, R_{cut}, R_{st}) in V_d and range of LAI and Z_0 (roughness length).

Sites (type of ecosystem)	Land-use cover (LUC) (resistances)	Min.–max. LAI ($m^2\ m^{-2}$)	Z_0 (m)
Agoufou, Banizoumbou (grassland)	Short grass and forbs (R_{ac}, R_{cut}, R_{st}, R_g^*)[a]	0.2–1	0.02–0.06
Katibougou (shrubland)	Long grass (R_{ac}, R_{cut}, R_g^*)[a] and broadleaf shrubs with perennial ground cover (R_{st})[b]	0.5–2	0.13–0.16
Djougou, Lamto (tree savanna)	Long grass (R_{ac}, R_{cut}, R_g)[a] and broadleaf trees with ground cover or savanna (R_{st})[b]	0.5–2 (Djougou) 2–4 (Lamto)	0.13–0.2
Zoetele, Bomassa (forest)	Tropical broadleaf trees (R_{ac}, R_{cut}, R_{st}, R_g)[a]	4–6 (mean 5)	2.5[a]

[a] Zhang et al. (2003b), [b] Brook et al. (1999)
* $R_g = 400\ s\ m^{-1}$ for Agoufou and Banizoumbou and $R_g = 300\ s\ m^{-1}$ for Katibougou; for the other sites, values suggested by Zhang et al. (2003b) were used.

the validation method according to international standards, have been widely detailed in Adon et al. (2010). To give an indication of the precision of this sampling technique, the covariance of all duplicate samples over the studied period were found to be 20, 9.8, 14.3, 16.6 and 10 % for HNO_3, NO_2, NH_3, SO_2 and O_3, respectively. Furthermore, Adon et al. (2010) presented the evolution of NO_2, HNO_3, NH_3, O_3 and SO_2 concentrations along the period 1998–2007 for each station. Table 2 presents a synthesis of the mean annual gas concentrations for the IDAF sites of west and central Africa (Adon et al., 2010).

2.2.2 Modeling of the dry deposition velocity for each IDAF site

Dry deposition velocities (V_d) were calculated using the big-leaf dry deposition model of Zhang et al. (2003b). The main parameterizations of the resistances in the model are briefly presented in Appendix A. The main input parameters of this updated deposition model are physiological (parameters of land-use categories), biophysical (LAI) and meteorological data.

In general, parameters of inferential models have been largely derived from European and North American studies and may not necessarily be adequate for African (or tropical) climate, vegetation and soil conditions (Fowler et al., 2009). Based on ecological and climatic characteristic of African ecosystems, we tried to adapt the parameters of land-use categories (LUC) described in Zhang et al. (2003b) to IDAF-specific sites for the calculation of canopy resistances, i.e., cuticle resistance (R_{cut}), stomatal resistance (R_{st}), in-canopy aerodynamic resistance (R_{ac}) and soil resistance in the big-leaf model (Table 3). Note that the types of LUC described in Zhang et al. (2003b) have one vegetation layer, while the savannas (shrub, tree or woody) have two vegetation layers. As a first approximation, the shrub and tree savannas (Lamto, Djougou and Katibougou) were assigned to grassland LUC (long grass), which is the dominant vegetation type in these areas. However, for the calculation of

the stomatal resistance, we used the savanna parameters described in Brook et al. (1999). These parameters are r_{smin} (minimal stomatal resistance), b_{rs} (empirical light response coefficient), b_{vpd} (water-vapor-pressure-deficit constant), Ψ (leaf water potential), T_{min}, T_{max} and T_{opt} (minimum and maximum temperatures at which stomatal closure occurs and optimum temperature for maximum stomatal opening).

For the soil resistance (R_g), values suggested by Zhang et al. (2003b) were used for IDAF sites excepted in the Sahelian domain. Considering the semiarid climate of the Sahel, close to the Sahara (desert) and the steppe vegetation, we assumed some values based on published measurement in the literature (Wesely et al., 1989; Brook et al., 1999; Ganzeveld and Lelieved, 1995) (Table 3).

Roughness length (Z_0) is needed for calculating friction velocity, which subsequently affects aerodynamic, quasi-laminar and non-stomatal resistances (Zhang et al., 2003b). We have used Z_0 values already simulated at the savanna sites in the framework of a previous study performed with the SVAT (Soil Vegetation Atmosphere Transfer) model ISBA (Interactions between Soil, Biosphere and Atmosphere – Noilhan and Mahfouf, 1996; Noilhan et al., 1989) and explained in Delon et al. (2010) (Table 3).

LAI is an important parameter for calculating canopy resistances. For the IDAF sites, LAI was obtained from MODIS (MODerate Resolution Imaging Spectroradiometer) satellite data for the period 2000–2007. The MODIS LAI is the ratio of one-sided green foliage area per unit horizontal ground area in broadleaf canopies, or the projected needleleaf area per unit ground area in conifer canopies, and is given in $m^2\,m^{-2}$ (Myneni, 1999). To that end, we used the 1 km MODIS LAI values that are processed over an 8-day period (Yang et al., 2006). The MODIS LAI product has already been validated with field measurements on many sites over the western African region (Fensholt et al., 2004; Samain et al., 2008). The mean seasonal variations of the monthly LAI during the period 2000–2007 for IDAF sites are shown in Fig. 2 and the range values are displayed in Table 3. The MODIS LAI of IDAF specific sites are well comparable to the ones of the corresponding land covers of the ECOCLIMAP database (Kaptue et al., 2010). For our simulation of dry deposition velocity, we used the monthly LAI averaged over 8 yr (2000–2007) for savanna sites and a constant value of $5\,m^2\,m^{-2}$ for tropical forest sites. We note that Zhang et al. (2003b) and Brook et al. (1999) have used a constant LAI of 6 and $4.5\,m^2\,m^{-2}$, respectively, to simulate dry deposition velocity for tropical forests.

Meteorological data required for the simulation are wind speed and temperature at a reference height in the surface layer, surface temperature, solar irradiance at the surface, precipitation, surface pressure, relative humidity and cloud cover fraction. With the exception of cloud cover fraction, meteorological conditions are provided by the forcing developed in the frame of ALMIP (AMMA Land Surface Model Intercomparison Project) from satellite data, described in

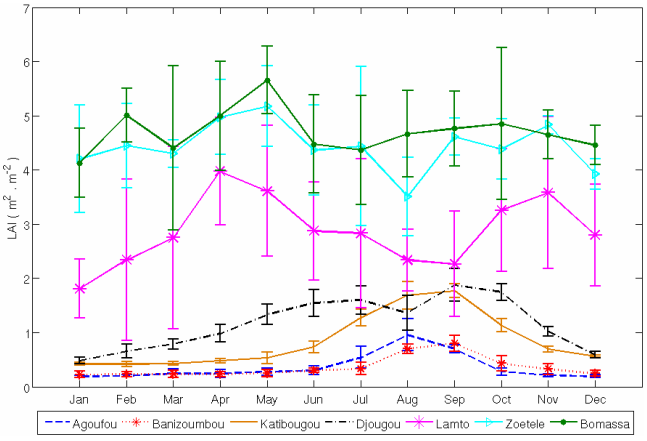

Fig. 2. Monthly variation of MODIS LAI averaged over the period 2000–2007 for IDAF sites. Vertical bars depict the standard deviation over the study period.

Boone et al. (2009). The spatial resolution of this forcing is $0.5° \times 0.5°$ with a 3 h temporal resolution. For the simulation of dry deposition velocity, we used a database of 6 yr from 2002 to 2007. Validations of surface temperature and moisture have been performed within the ALMIP project (Boone et al., 2009; De Rosnay et al., 2009). However, the forcing in ALMIP is available at 10 m, whereas the concentrations of gases are measured at around 2 m for the savanna sites and 3 m for the forested ecosystems within IDAF network. As a first approximation, a logarithmic decrease of the wind forcing from 10 to 2 m, depending on the rugosity of the site, has been applied to calculate deposition velocities at 2 m for the savanna sites, as described in Delon et al. (2010, 2012). This approach to reduce the wind from 10 m to the height of 2 m is based on the constant flux assumption (Baldocchi, 1988; Zhang et al., 2009). However for the forested ecosystems, the constant flux assumption cannot be applied below the canopy due to extra sink terms; hence another approximation is done and described below in Sect. 2.2.4.

Surface wetness controls non-stomatal resistances for soluble trace gases. The big-leaf model of Zhang et al. (2003b) predicts surface wetness semimechanistically and distinguishes dew from rain based on precipitation data for rain and on nighttime cloud cover and friction velocity for dew formation (Janssen and Romer, 1991; Brook et al., 1999). In this study, as the cloud cover information was missing, we performed sensitivity tests for the presence of dew by using the constant relative humidity (RH) threshold method for estimating dew condensation (Sentelhas et al., 2008). Various RH thresholds have been used as proxies to determine canopy wetness over forests and grasslands (Tsai et al., 2010; Wichink Kruit et al., 2008, 2010; Flechard et al., 2011). Thus, we have performed sensitivity tests using a threshold of 90 % for forest, 81 % for wet savanna and 71 % for dry savanna to test the presence of dew. Results showed that the variation

of monthly V_d is negligible when it is assumed that dew has occurred; for example the RMSE (root-mean-squared error) of V_d (SO_2) is 2, 1 and 4 % for dry savanna, wet savanna and forest, respectively (Adon, 2011). Therefore, in this study, we do not take into account the assumption of the occurrence of dew.

Previous studies of nitrogen budget in wet and dry savanna ecosystems have proposed an estimate of N compounds deposition velocities (Delon et al., 2010, 2012). In those studies, V_d were calculated according to the Wesely (1989) resistance analogy in the SVAT big-leaf model ISBA, with modifications of the cuticle and ground resistances adapted from Zhang et al. (2003b). The results were obtained at the regional scale at 0.5° resolution for the period 2002–2007, and focused on the reactive nitrogen compounds budget (with estimates of emission and deposition (dry + wet) fluxes). The present study is focused on dry deposition only, and integrates all the parameterizations developed by Zhang et al. (2003b), which gives a different but consistent and coherent estimate of V_d at the local scale, and for more species (same N compounds + O_3 and SO_2). Indeed, we investigate each specific vegetal cover representative of each IDAF measurement sites in this study. Differences between the two approaches are mainly due to the different resolutions of models and to the degree of details involved in the estimation of input parameters such as the ones detailed in the above paragraph. The previous studies of Delon et al. (2010, 2012) give a point of comparison for N compounds' V_d calculated in the present work, as very few studies are available for African ecosystems. Furthermore, as explicated below, the NH_3 bidirectional exchange is applied in the present study, which was not the case in the previous studies of Delon et al. (2010, 2012).

We present in this paper the calculation, over the period 2002–2007, of monthly means (from 3-hourly values) deposition velocities for O_3, SO_2, NO_2, HNO_3 and NH_3 for the IDAF sites.

2.2.3 NH_3 bidirectional exchange and canopy compensation point

The NH_3 net fluxes were calculated using the bidirectional air–surface exchange model of Zhang et al. (2010), which is a modification from the original big-leaf model of Zhang et al. (2003b). The main parameterization of this new bidirectional exchange model and the method of calculation of the NH_3 net fluxes in this study are briefly presented in Appendix B.

In this modified model, the main input parameters are stomatal (Γ_{st}) and ground (Γ_g) emission potentials, leading to stomatal and soil compensation points, respectively, and thus the canopy compensation point (X_{cp}) (Eq. B3). For each of the LUCs, Zhang et al. (2010) derived representative input values based on literature data.

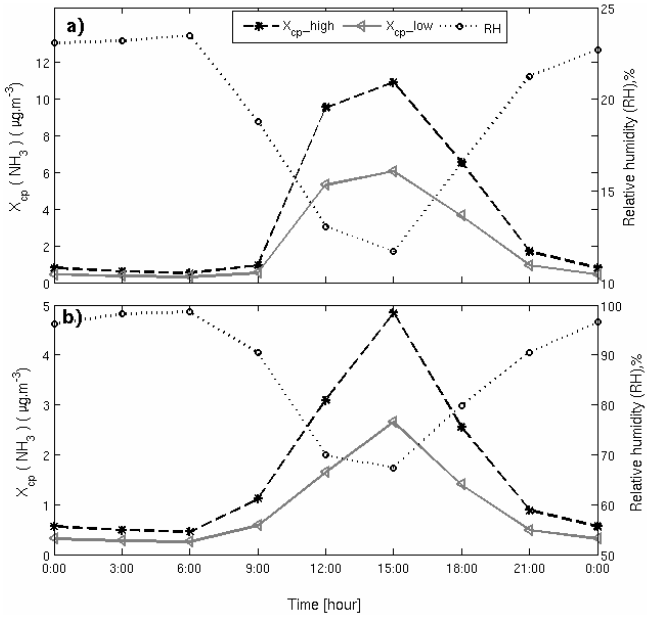

Fig. 3. Mean diurnal variation of the simulated lower (low flux) and upper (high flux) NH_3 canopy compensation point X_{cp} (NH_3) associated with the variation of the relative humidity (RH) at a Sahelian site (**(a)** Banizoumbou) and a Guinean savanna site (**(b)** Lamto) in the dry season (January, 2006).

In our simulation and for the seminatural forested ecosystem, we used the median values of Γ_{st} (300) and Γ_g (20) suggested for tropical forest LUC. The daytime canopy compensation point values of NH_3 were less than $2\,\mu g\,m^{-3}$, as predicted by Zhang et al. (2010).

For the savannas sites, a sensitivity test showed that the median values suggested for the long grass or short grass and forbs LUC, considered as fertilized, ($\Gamma_g = 2000$) would give too high daytime values of X_{cp} (50–300 $\mu g\,m^{-3}$ at Banizoumbou) in the dry season due to very high ground surface temperatures in the afternoon (38–50 °C). However, the African savannas remain either slightly or not fertilized (Bouwman and van der Hoek, 1997; Mosier et al., 1998). Delon et al. (2010) estimated the mean total nitrogen input from animal manure for the Sahelian sites from 11 to $23\,kg\,N\,ha^{-1}\,yr^{-1}$, lower when compared to fertilized vegetation input in temperate ecosystems (Loubet et al., 2002; Massad et al., 2010). Due to the lack of data for typical tropical savanna sites, we chose a range of lower-end values reported for grass or unfertilized ecosystems in the literature. Thus, we have chosen values of 100 (low scenario) and 200 (high scenario) for Γ_{st} (Spindler et al., 2001; Horvath et al., 2005; Trebs et al., 2006; Personne et al., 2009) and values of 200 (low scenario) and 360 (high scenario) for Γ_g (Massad et al., 2010; Zhang et al., 2010).

Figure 3 presents the mean diurnal variation of X_{cp} (NH_3) for a Sahelian site (Banizoumbou) and a wet Guinean savanna site (Lamto) in the dry season (January 2006). In our

simulation, the maximum ground surface temperature was fixed at 40 °C to avoid too high values of X_{cp} for the "high scenario" in dry savannas. Although low values of Γ_{st} and Γ_g were used to run the model, the estimated X_{cp} (NH_3) values are within a reasonable range of values determined for grassland in other studies (Langford et al., 1992; Hesterberg et al., 1996; Spindler et al., 2001; Loubet et al., 2002; Trebs et al., 2006; Zhang et al., 2010). This is due to high surface temperatures mainly at Sahelian sites. Note that the X_{cp} diurnal values of the Sudano-Guinean site of Djougou are comparable to those of Sahelian sites (result not shown). During the wet season, the X_{cp} diurnal values are lower due to lower surface temperatures: 0.1–1 $\mu g\,m^{-3}$ during nighttime and 0.3–5 $\mu g\,m^{-3}$ during daytime for the savanna sites.

For the NH_3 net fluxes, we used the two scenarios (lower and upper estimates) presented above compared to the "dry deposition only" scenario ($X_{cp} = 0$).

2.2.4 Corrections for within-canopy concentration data for forests

The inferential method requires atmospheric concentrations and turbulence intensity above the canopy to predict rates of dry deposition over the forest. In the IDAF network, gas concentrations are measured at about 3 m in forests. Moreover, there are very few published within-canopy vertical gas concentration profiles (HNO_3, NH_3) in the literature for forest (Flechard et al., 2011). Thus, we have carried out a pilot experiment by measuring simultaneously gas concentrations at 10 and 3 m (or 2 m) from the ground in the forested ecosystem of Zoetele (and in the wet savanna of Lamto and dry savanna of Banizoumbou) over the period of September 2010 to December 2011.

For the forested ecosystem, NO_2, HNO_3 and SO_2 monthly concentrations measured simultaneously at 10 and 3 m show no significant trend and are on the same order. Over this period, mean annual concentrations – at 3 and 10 m, respectively – are 0.81 and 0.80 ppb for NO_2, 0.2 and 0.3 ppb for HNO_3, and 1.8 and 1.6 ppb for SO_2. However for NH_3 and O_3, monthly concentrations measured at 10 m are higher and the mean ratio was 1.5 for NH_3 and 1.3 for O_3 (mean annual concentration are 3.6 and 6.1 ppb for NH_3 and 5.4 and 7.0 ppb for O_3 at 3 and 10 m, respectively). This observation is consistent with the approximation made in Flechard et al. (2011) showing that NH_3 concentrations measured in clearings and below canopy are consistently smaller than above treetops; they thus applied a constant correction factor of 1.3 for NH_3 concentrations measured below trees. We note that in the dry savanna of Banizoumbou, NH_3 concentrations measured at 2 m (annual mean 8.1 ppb) are higher than at 10 m (6.3 ppb), indicative of NH_3 sources in the ground and in the leaf litter in grasslands (Nemitz et al., 2009). For O_3, our observations are consistent with ozone vertical profile concentrations that decrease towards the ground, as observed by Krzyzanowski (2004) by measuring ozone concentrations at different heights in a forest canopy. Contrary to our observation for HNO_3 and SO_2, Hicks (2006) observed a ratio of 1.34 and 1.26, respectively, between concentrations measured above the treetops and within the canopy of forests.

In a first approximation, for forested sites of IDAF (Zoetele and Bomassa), we thus applied a constant correction factor of 1.5 for NH_3 and 1.3 for O_3 concentrations measured at 3 m in order to calculate the dry deposition flux at 10 m. For the other gases (NO_2, HNO_3 and SO_2) no correction was applied. The dry deposition fluxes of HNO_3 and SO_2 using the forest-clearing concentrations may be underestimated as discussed by Hicks (2006). In addition, the mean covariance of samplers exposed simultaneously at 3 and 10 m were found to be 13, 25.5 and 21 % for NO_2, HNO_3 and SO_2 respectively, and these values are comparable of the mean reproducibility of IDAF passive samplers calculated from 1998 to 2007 (9.8, 20 and 16.6 % for NO_2, HNO_3 and SO_2, respectively). Thus, the small difference in measured concentrations between the two heights (3 and 10 m) for NO_2, HNO_3 and SO_2 could be included in the global uncertainty for the passive sampler method.

2.3 Uncertainties in dry deposition fluxes estimates

Uncertainties in the estimated dry deposition fluxes result from combined uncertainties in measured gaseous concentrations and in modeled exchange rates. In this section, rather than quantifying the total uncertainty of the inferential method in the study, we focus on addressing the uncertainties for each contribution of the dry deposition estimates. Part of uncertainties linked to the measurement of gas concentration using IDAF passive samplers have been given by the covariance of duplicates (reproducibility), between 10 and 20 % according to the species (Adon et al., 2010). Other parts are related to the measurement techniques of passive samplers. One of the uncertainties of the dry deposition velocities is related to the wind forcing. The difference between the wind in the forcing and the wind measured in situ is between 5 and 35 % depending on the site. A mean rate of 20 to 30 % depending on the site is applied for the wind speed uncertainty, leading to an uncertainty rate for the dry deposition velocity between 10 and 20 % for all sites. Others uncertainties are related to the representation of the soil type in the model indirectly dependent on the roughness length and the soil resistances (Zhang et al., 2003b) as well as the choice of plant physical parameters.

In this study, concentrations are measured with passive samplers and are monthly integrated. Dry deposition velocities are simulated 3-hourly and then monthly averaged. As we use monthly means for concentrations and deposition velocities, the covariance between the two may induce an additional uncertainty (the missing covariance term), especially for species having strong diurnal variations, in the range of $\sim$ 20 % (Matt and Meyers, 1993; Zhang et al., 2005).

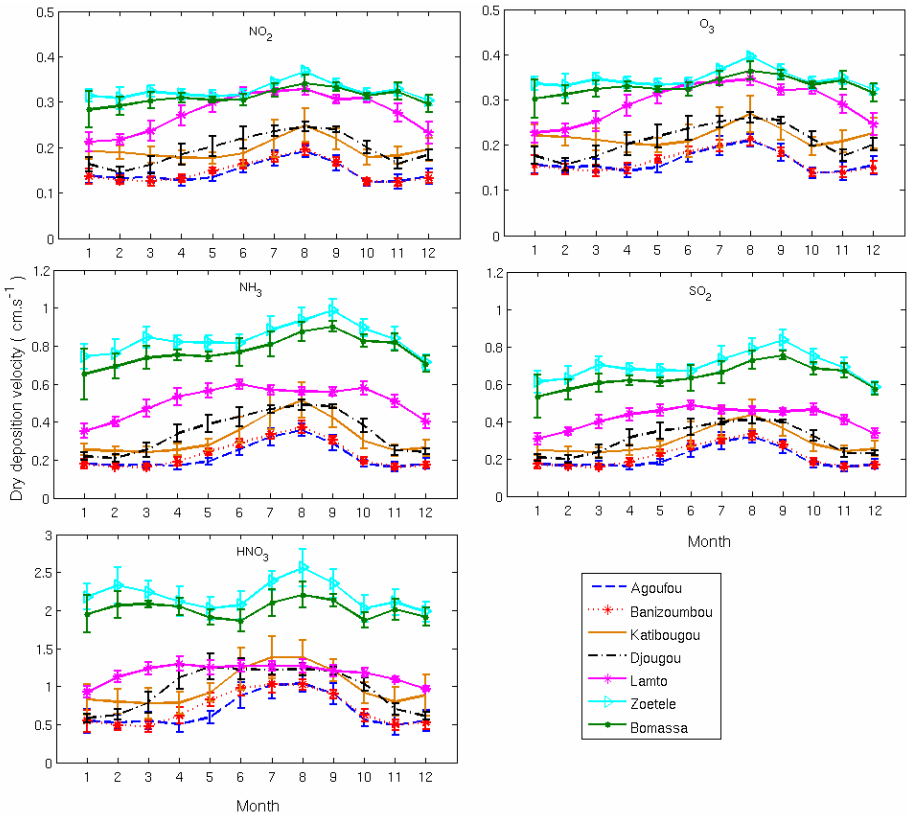

Fig. 4. Monthly variation of dry deposition velocity (V_d) of NO_2, NH_3, HNO_3, O_3 and SO_2 averaged over the period 2002–2007 for IDAF sites. Vertical bars depict standard deviation over the study period.

For the NH_3 bidirectional exchange, in addition of the uncertainties related to the model itself (Zhang et al., 2010), the ground emission potential remains the most uncertain in our simulations due to the lack of detailed investigations although flux measurements have often shown significant emission from soils and leaf litter (Sutton et al., 2013; Flechard et al., 2010). The unidirectional approach (Zhang et al., 2003b) used for the other gases could induce other sources of uncertainty.

Additional uncertainties are associated with different parameterizations of dry deposition used in deposition models. The physical, biological and chemical exchange mechanisms involved in deposition processes are too complex to be explicitly and completely modeled, and as such parameterizations tend to be empirical in the models (Flechard et al., 2011; Schwede et al., 2011). Moreover, multiple species model intercomparison show factor of 2–5 differences in exchange rates between models depending on the chemical species (Flechard et al., 2011).

3 Results and discussion

3.1 Dry deposition velocities

Monthly means (from 3-hourly values) of deposition velocities for O_3, SO_2, NO_2, HNO_3 and NH_3 have been calculated for the period 2002–2007 in order to reproduce the seasonal cycle of the deposition processes at each site (Fig. 4). We note a fairly clear distinction between the different ecosystems and climatic domains. The monthly V_d values of each gas increase from the semiarid savannas (Agoufou, Banizoumbou) to the equatorial forested ecosystems (Zoetele, Bomassa) indicating that the dry deposition velocity increases with the vegetation density. As a first approximation, along the African ecosystem transect, the V_d gradient thus follows the climatic gradient. In fact, there exists a marked latitudinal gradient over the west and central African zone. Areas with the highest rainfall have the greatest volume of biomass or primary productivity; as a consequence, surface deposition (cuticle) and stomatal uptake become important, and the canopy resistance (R_c) is the main factor determining the deposition rate in vegetative zones (Tsai et al., 2010).

The monthly variation of NO_2 V_d follows the same pattern as O_3 but with slightly smaller values. In fact, in this model of deposition, the NO_2 V_d is parameterized similar to

the one of O_3 due to similar behavior for a variety of conditions and the importance of their stomatal uptake (Zhang et al., 2002a). However, some studies pointed out the importance of the non-stomatal deposition fluxes in the case of O_3 (Fowler et al., 2001; Stella et al., 2011). NH_3 V_d is similar to SO_2 but slightly higher due to its higher molecular diffusivity. NH_3 and SO_2 are reasonably soluble gases in pure water and are effectively removed at higher rates under moist conditions (Erisman et al., 1993a, b; Erisman and Wyers, 1993). Even if the chemical characteristics of NH_3 are not the same as SO_2, the NH_3 V_d is parameterized similar to SO_2 in this deposition model (Zhang et al., 2002a, 2003b). HNO_3 presents the highest V_d among all the chemical species in this study because of its high solubility and reactivity. Note that in the big-leaf model of Zhang et al. (2003b), SO_2 and O_3 are used as base species to scale the dry deposition rate for other chemical species. The monthly means of dry deposition velocities range from 0.16 to 0.84 cm s^{-1} for SO_2, from 0.14 to 0.40 cm s^{-1} for O_3, from 0.16 to 0.99 cm s^{-1} for NH_3, from 0.13 to 0.37 cm s^{-1} for NO_2 and from 0.48 to 2.56 cm s^{-1} for HNO_3 on the transect dry savannas–wet savannas–forests. In addition, V_d are higher in the wet season for each ecosystem, especially in dry savannas, where the dry season is well marked. It is considered that higher deposition velocities in the wet season are mainly caused by non-stomatal uptake of wet canopies (Matsuda et al., 2006; Tsai et al., 2010). The interannual variability of V_d for the 7 yr period (2002–2007) is low and range from 3 to 12 % for NH_3 and SO_2, from 2 to 11 % for NO_2 and O_3, and from 2 to 17 % for HNO_3 on the transect of ecosystems. These variations could be attributed to the spatio-temporal variations of meteorological data.

The comparison between our modeled V_d and previous studies is shown in Table 4. The V_d of O_3 and SO_2 lie well within the range of values determined for other tropical forests (Matsuda et al., 2006, Rummel et al., 2007; Tsai et al., 2010) and grasslands (Takahashi et al., 2001; Sorimachi et al., 2003). The modeled V_d of NO_2 and NH_3 are within a reasonable range compared to reference values (Zhang et al., 2005, 2009; Trebs et al., 2006; Kirkman et al., 2002; Delon et al., 2010; Endo et al., 2011). The modeled V_d of HNO_3 on forest and grass were the lowest values of those reported by Endo et al. (2011), Huebert and Robert (1985) and others studies (e.g., Hanson and Lindberg, 1991; Duyzer and Fowler, 1994; Zhang et al., 2002a) mainly due to lower wind velocities in African ecosystems.

3.2 Dry deposition fluxes

Monthly dry deposition fluxes of NO_2, NH_3, HNO_3, SO_2 and O_3 were estimated using the inferential method at west and central African sites of the IDAF network over the study period (1998–2007). By using the monthly V_d from each year and the monthly 6 yr average V_d (2002–2007) for the years that do not have V_d data, the monthly deposition fluxes have been calculated for each year and then averaged over the study period in order to estimate the mean range values of gaseous deposition fluxes representative of African ecosystems.

3.2.1 Nitrogen compounds (NO_2, HNO_3, NH_3)

Table 5 presents a synthesis of the mean seasonal and annual exchange fluxes of nitrogen compounds (NO_2, HNO_3, NH_3) for all the IDAF sites.

Nitrogen dioxide (NO_2)

Figure 5 presents the monthly evolution of NO_2 dry deposition flux (NO_2_dd) estimated at the dry savannas of Niger and Mali (Fig. 5a: Banizoumbou, Agoufou, Katibougou), at the wet savannas of Côte d'Ivoire and Benin (Fig. 5b: Lamto, Djougou) and at the evergreen equatorial forests of Cameroon and Congo (Fig. 5c: Zoetele, Bomassa). Vertical bars indicate the standard deviation calculated over the study period (1998–2007). Average monthly evolution of NO_2 concentrations over the same study period is superimposed on the monthly dry deposition fluxes. The axes of fluxes are inverted for all figures. We note a good correlation between gas concentrations and dry deposition fluxes on the transect dry savannas–wet savannas–forests.

In the dry savannas, maximum flux values are observed in May/June as for concentration values (Fig. 5a). In general, higher deposition fluxes in the wet season are due to both higher measured NO_2 concentrations and its higher dry deposition velocity calculated in this season. In the Sahelian sites (Agoufou, Banizoumbou), seasonally averaged dry deposition fluxes are 2 times higher in the wet season than in the dry season (Table 5). Annual average dry deposition fluxes of NO_2 are around -0.4 to -0.7 kg N ha^{-1} yr^{-1} in the dry savannas. These values calculated in these pastoral areas are in the lower range of deposition fluxes calculated for a tropical pasture site in Brazil (Rondonia) (annual NO_2 deposition flux: -0.76 to -2.4 kg N ha^{-1} yr^{-1}), which is considerably higher, mainly due to higher NO_2 mixing ratios observed (Trebs et al., 2006).

In the wet savannas, higher deposition flux values are obtained in the dry season with maximum fluxes in December at Djougou and January at Lamto, such as NO_2 concentrations (Fig. 5b). Biomass burning is the most important source of NO_x ($NO+NO_2$) during the dry season in the wet savannas, where the vegetation density is more important than in the dry savannas. Galanter et al. (2000) showed that more than 75 % of the NO_x at the surface near equatorial Africa is the result of biomass burning that occurs from December to February. In the dry season, deposition flux values are 1.5 times higher at Lamto and around 3 times higher at Djougou than in the wet season (Table 5) due to higher NO_2 concentrations. Annual average dry deposition fluxes of NO_2 are on the same order (-0.4 kg N ha^{-1} yr^{-1}) for the two wet savanna sites (Table 5).

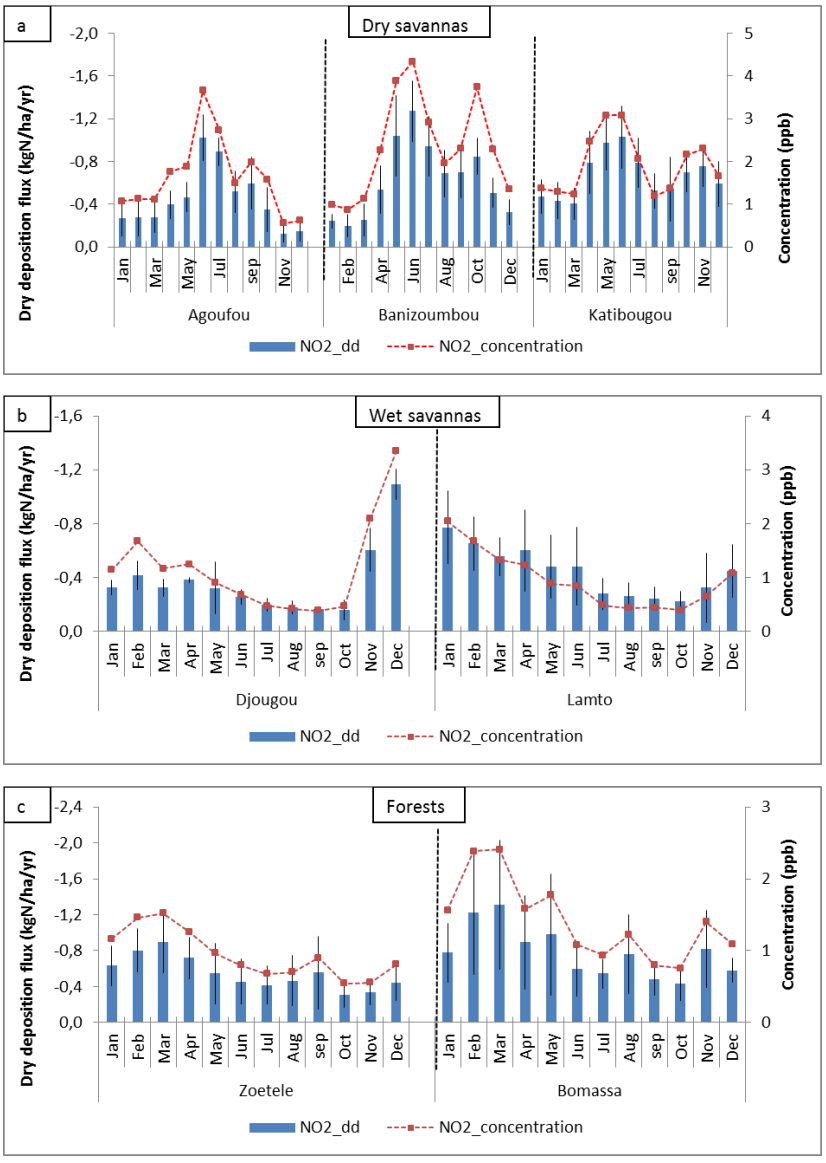

Fig. 5. Evolution of monthly dry deposition fluxes of NO_2 (NO_2_dd) in kg N ha^{-1} yr^{-1} (1998–2007) on the transect dry savannas **(a)**, wet savannas **(b)** and forests **(c)** associated with evolution of NO_2 concentrations (ppb).

In forests, higher deposition fluxes are observed in February and March, i.e., at the end of the dry season and at the beginning of the wet season (Fig. 5c). Seasonal average fluxes are on the same order between the two seasons (Table 5). NO_2 concentration measurements tend to show that the biomass burning source during the dry season is equivalent to soil emissions buffered by canopy uptake in forests during the wet season (Adon et al., 2010). Annual average dry deposition fluxes of NO_2 in forests (-0.5 to -0.8 kg N ha^{-1} yr^{-1}) are on the same order as in dry savannas (Table 5) due to higher V_d values in forests and higher concentrations measured in dry savannas (Table 2). These values are well within the range of measurements derived by Hanson et al. (1989), who showed that N deposition from NO_2 was between -0.008 and -1.9 kg N ha^{-1} yr^{-1} for natural forests. They are also comparable to NO_2 deposition fluxes estimated by Zhang et al. (2005) that range from -0.1 to -1.5 kg N ha^{-1} yr^{-1} at seven eastern Canadian rural sites for a 1 yr period.

Note that the NO_2 deposition fluxes estimated in this study could be overestimated since the photochemical reaction of NO, NO_2 and O_3 and the NO_2 compensation point approach are not included in the deposition model. In fact, soil emission of NO that reacts rapidly with O_3 to produce NO_2 can greatly diminish the magnitude of the downward NO_2 flux and sometimes cause it to be directed upward (Bakwin et

Table 4. Comparison of dry deposition velocities ($cm\,s^{-1}$) for ozone, sulfur and nitrogen compounds between this study and previous studies.

Ecosystems		Previous studies			This study*	
V_d ($cm\,s^{-1}$)	Conditions (season, time of day)	Method	Range or mean	Reference		Sites (condition if different)
V_d (O_3)						
Forest (Thailand)	Dry, daytime	GM	0.37–0.39	Matsuda et al. (2006)	0.54–0.61	Zoetele
	Dry, nighttime		0.12–0.13		0.14–0.18	
	Wet, daytime		0.62–0.65		0.62–0.70	
	Wet, nighttime		0.25–0.27		0.15–0.21	
Forest (Amazonia)	Dry, daytime	EC	0.5	Rummel et al. (2007)		
	Dry, nighttime		0.6			
	Wet, daytime		1.1			
	Wet, nighttime		0.5			
Forest (Congo/RCA)	Dry, morning	EC	1.5	Cros et al. (2000)		
Grass (FNS site) (Brazil)	Dry, daytime (median)	IM	0.6	Rummel et al. (2007)	0.30–0.38	Lamto
	Wet, daytime		0.7		0.46–0.64	
Savanna (Congo/RCA)	Dry, morning	EC	0.4	Cros et al. (2000)		
V_d (SO_2)						
Forest (Thailand)	Dry, daytime	GM	0.10–0.31	Matsuda et al. (2006)	0.61–0.67	Zoetele
	Dry, nighttime		0.08–0.11		0.42–0.59	
	Wet, daytime		0.95–1.39		0.72–0.84	
	Wet, nighttime		0.26–0.42		0.55–0.71	
Forest (Taiwan)	Dry (canopy), daytime	GM	0.44	Tsai et al. (2010)		
	Dry (canopy), nighttime		0.19			
	Wet (canopy), daytime		0.83			
	Wet (canopy), nighttime		0.47			
Forest (Japan)	Yearly average	IM	0.88	Takahashi et al. (2001)	0.69	Zoetele
Short grass (northern China)	Summer (day)	GM	0.2	Sorimachi et al. (2003)	0.10–0.20	Dry season (day)
	Winter		0.4		0.20–0.45	Wet season (Banizoumbou)
V_d (NO_2)						
Forests, grass (Canada)	Summer, monthly	IM	0.3–0.4	Zhang et al. (2005)	0.12–0.37	Forests and savannas
	Monthly average		0.06–0.29	Zhang et al. (2009)		
Grass (FNS site) (Brazil)	Daytime (median)	IM	0.4	Kirkman et al. (2002)	0.28–0.38	Dry, daytime
	Nighttime		0.3		0.13–0.14	Dry, nighttime
	Dry–wet transition				0.44–0.62	Wet, daytime
					0.14–0.22	Wet, nighttime (Lamto)
Grass (bare soil) (Lamto)		CM	0.13–0.29	Serça (1995)	0.14–0.62	Lamto
Sahelian sites	Monthly average	IM	0.1–0.33	Delon et al. (2010)	0.12–0.25	Dry savannas
Grass, heathland	Monthly average	GM	0.1–0.4	Erisman et al. (1994)	0.12–0.33	Savannas
	Hourly	EC	0.1–0.35	Coe and Gallager (1992)	0.1–0.62	(dry and wet)
V_d (NH_3)						
Forests, grass (Canada)	Monthly average	IM	0.2–0.6	Zhang et al. (2009)	0.71–0.99	Forests
					0.16–0.60	Savannas
Forests, grass (Japan)	Yearly average	IM	0.5–0.9	Endo et al. (2011)	0.77–0.84	Forests
			0.2–0.6		0.22–0.51	Savannas
Grass (Netherlands)	Yearly average	GM	0.8	Erisman et al. (1994)	0.22–0.51	Savannas
Grass (FNS site)	Dry, wet, hourly average	IM	0.5–1.5	Trebs et al. (2006)	0.1–1.0	Savannas
Sahelian sites	Monthly average	IM	0.11–0.39	Delon et al. (2010)	0.16–0.51	Dry savannas
V_d (HNO_3)						
Forests, grass (Canada)	Monthly average	IM	0.61–2.11	Zhang et al. (2009)	1.86–2.39	Forests
					0.48–1.39	Savannas
Forests, grass (Japan)	Yearly average	IM	1.2–11.7	Endo et al. (2011)	2.0–2.2	Forests
			0.3–3.2		0.68–1.17	Savannas
Grass (pasture) (Illinois)	Hourly average (daytime) June	GM	1.0–4.7 (2.5)	Huebert and Robert (1985)	0.4–1.85	Savannas
Sahelian sites	Monthly average	IM	0.34–0.61	Delon et al. (2010)	0.48–1.39	Dry savannas

* In this study, monthly and yearly V_d are mean values averaged over the study period (1998–2007). Hourly (daytime, nighttime) V_d are diurnal values averaged over a month (January for dry season and August for wet season) of 2006.
GM: gradient method; EC: eddy correlation method; IM: inferential method; CM: chamber method

Table 5. Mean seasonal and annual dry deposition fluxes and standard deviation (F_{dry}) of NO_2 and HNO_3 as well as NH_3 net bidirectional fluxes (F_t, from high to low scenario estimates) at IDAF sites of west and central Africa over the period 1998–2007. Annual NH_3 dry deposition fluxes are added for comparison. Fluxes are expressed in kg N ha^{-1} yr^{-1}.

Fluxes (kg N ha^{-1} yr^{-1})		NO_2 F_{dry}			HNO_3 F_{dry}			NH_3 Net Flux (F_t) F_t_high to F_t_low scenarios			NH_3 F_{dry} only
Season		Dry	Wet	Annual	Dry	Wet	Annual	Dry	Wet	Annual	Annual
Dry savannas	Agoufou*	-0.3 ± 0.1	-0.8 ± 0.2	-0.4 ± 0.1	-0.1 ± 0.1	-1.8 ± 0.9	-0.7 ± 0.3	-0.1 to -1.0	-1.9 to -3.0	-0.7 to -1.6	-2.9 ± 0.4
	Banizoumbou	-0.4 ± 0.2	-0.9 ± 0.3	-0.6 ± 0.1	-0.2 ± 0.1	-1.4 ± 0.4	-0.7 ± 0.3	$+0.3$ to -0.6	-2.0 to -3.0	-0.7 to -1.6	-2.7 ± 0.9
	Katibougou	-0.6 ± 0.2	-0.8 ± 0.2	-0.7 ± 0.1	-0.4 ± 0.1	-1.3 ± 0.5	-0.8 ± 0.2	$+0.3$ to -1.0	-3.6 to -4.6	-1.4 to -2.5	-3.9 ± 0.6
Wet savannas	Djougou*	-0.6 ± 0.3	-0.2 ± 0.1	-0.4 ± 0.1	-0.5 ± 0.2	-0.8 ± 0.2	-0.7 ± 0.2	$+0.1$ to -0.8	-1.0 to -1.6	-0.5 to -1.3	-2.2 ± 0.7
	Lamto	-0.6 ± 0.2	-0.4 ± 0.2	-0.4 ± 0.1	-0.9 ± 0.3	-0.6 ± 0.2	-0.7 ± 0.1	-2.4 to -3.1	-1.5 to -2.3	-1.9 to -2.6	-3.5 ± 1.0
Forests	Zoetele	-0.6 ± 0.2	-0.5 ± 0.1	-0.5 ± 0.1	-1.6 ± 0.6	-0.8 ± 0.2	-1.0 ± 0.3	-7.5 ± 1.8	-8.5 ± 1.4	-8.2 ± 2.2	-9.7 ± 2.2
	Bomassa	-0.9 ± 0.3	-0.8 ± 0.2	-0.8 ± 0.2	-1.1 ± 0.2	-0.9 ± 0.2	-1.0 ± 0.3	-8.1 ± 2.7	-8.3 ± 2.4	-8.3 ± 3.3	-10.0 ± 3.3

* Deposition flux values of Agoufou and Djougou are averaged over the period 2005–2009.

al., 1992; Coe and Gallagher, 1992; Gao et al., 1996). Previous studies reported NO_2 compensation point concentrations ranging from 0.05 to 3 ppb depending on tree species and environmental conditions (Sparks et al., 2001; Raivonen et al., 2009; Breuninger et al., 2013, and references therein). However, the existence of such a compensation point is questionable (Lerdau et al., 2000; Chaparro-Suarez et al., 2011).

Nitric acid (HNO_3)

Monthly evolution of HNO_3 dry deposition fluxes is similar to that of HNO_3 concentrations on the transect of ecosystems (Fig. 6a, b, c). In the dry savannas, HNO_3 dry deposition fluxes are very low in the dry season, especially at Agoufou and Banizoumbou, and much (4–12 times more) higher in the wet season due to both higher HNO_3 concentrations and dry deposition velocities in this season for the three sites. Seasonal average fluxes range from -0.1 kg N ha^{-1} yr^{-1} in the dry season to -1.8 kg N ha^{-1} yr^{-1} in the wet season (Table 5). In the wet savannas, the difference in deposition fluxes between the two seasons is low with higher values in the dry season at Lamto (-0.9 kg N ha^{-1} yr^{-1}) and in the wet season at Djougou (-0.8 kg N ha^{-1} yr^{-1}). The deposition fluxes are less important in the dry season at Djougou due to smaller HNO_3 V_d in this season. In forests, seasonal average deposition fluxes of HNO_3 are on the same order between the two seasons (-1 kg N ha^{-1} yr^{-1}) at Bomassa and higher (-1.6 kg N ha^{-1} yr^{-1}) in the dry season of Zoetele due to higher values of HNO_3 concentrations. Annual mean dry deposition fluxes of HNO_3 are around -0.7 kg N ha^{-1} yr^{-1} in the dry and wet savannas and -1.0 kg N ha^{-1} yr^{-1} in forests (Table 5). Annual mean HNO_3 deposition fluxes show a low variability according to the ecosystems, with seasonal differences especially pronounced in the dry savannas. Although HNO_3 concentrations (0.3–0.5 ppb) were lower than NO_2 (0.9–2.4 ppb) on the African ecosystems transect (Table 2), HNO_3 dry deposition fluxes were typically as important as NO_2 dry deposition fluxes owing to higher V_d values for HNO_3.

Ammonia (NH_3) bidirectional fluxes

Figure 7 presents the monthly evolution of estimated low and high surface–atmosphere exchange fluxes of NH_3 on the transect of ecosystems. For the forests, only one scenario has been estimated (Sect. 2.2.3). Bidirectional NH_3 flux scenarios complemented by a "deposition only" scenario (X_{cp} (NH_3) = 0) are presented in Table 5.

In the dry savannas, seasonal mean fluxes of NH_3 range from a deposition of -1.0 kg N ha^{-1} yr^{-1} to an emission of $+0.3$ kg N ha^{-1} yr^{-1} in the dry season and a deposition of -1.9 to -4.6 kg N ha^{-1} yr^{-1} in the wet season (Table 5). The NH_3 net emission fluxes observed in the dry season for our higher scenario estimate are due to higher X_{cp} (NH_3) in this season (Fig. 7a, Fig. 3). This is consistent with observations made in some seminatural ecosystems where air concentrations are low under very dry condition or at high temperatures (Langford and Fehsenfeld, 1992; Erisman et al., 1994; Sutton et al., 1995; Flechard and Fowler, 1998). In the wet season, NH_3 dry deposition fluxes are more important due to higher measured NH_3 concentrations and higher NH_3 V_d simulated during the short vegetative period. Dry savannas are generally pastoral areas; the main sources include bacterial decomposition of urea in animal excreta, which is very active in the wet season with the hydrolysis of urea, and emissions from natural soils (Schlesinger and Hartley, 1992; Bouwman et al., 1997, 2002a). Because of the short lifetime of NH_3 (1–5 days or less), low source height and relatively high V_d, a substantial fraction (20–40 %) would likely deposit near its source (Aneja et al., 2001).

In the wet savannas, seasonal average net fluxes of NH_3 range from -3.1 kg N ha^{-1} yr^{-1} (deposition) to $+0.1$ kg N ha^{-1} yr^{-1} (emission) (Table 5). In the Guinean savanna of Lamto, the estimated NH_3 deposition fluxes are more important at the beginning of the dry season (January–March) where concentrations are higher (Fig. 7b). However, in the Sudano-Guinean site of Djougou, lower NH_3 deposition fluxes were estimated in the dry season, although higher measured NH_3 concentrations. This is mainly due to higher simulated X_{cp} (NH_3) in the dry season that led to net

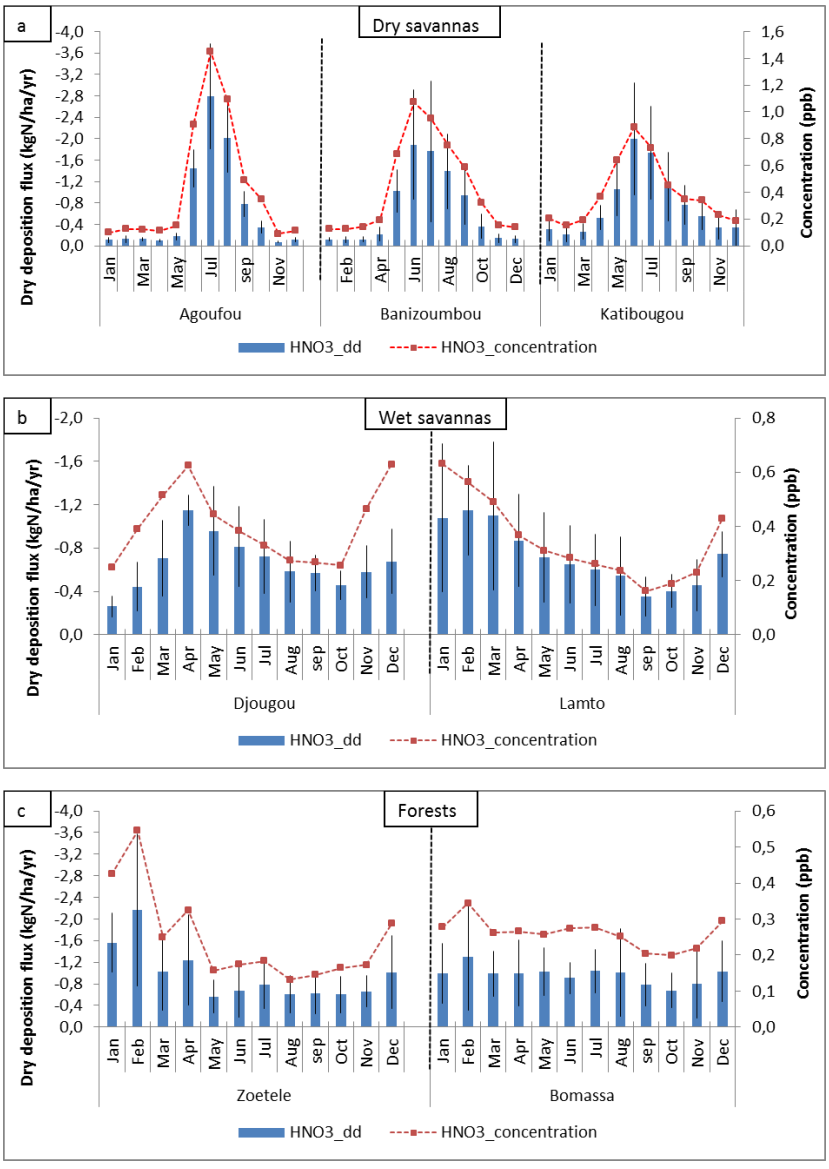

Fig. 6. Evolution of monthly dry deposition fluxes of HNO_3 (HNO_3_dd) in kg N ha^{-1} yr^{-1} (1998–2007) on the transect dry savannas **(a)**, wet savannas **(b)** and forests **(c)** associated with evolution of HNO_3 concentrations (ppb).

emission fluxes, like in the dry savannas. Generally, higher concentrations of NH_3 in the dry season are due to savanna fires, which are a significant source of ammonia in tropical regions (Lobert et al., 1990; Delmas et al., 1995). For the forested ecosystems, only dry deposition occurs due to low compensation point and no significant difference between wet and dry seasons (Fig. 7c). Seasonal NH_3 dry deposition fluxes are around -8 kg N ha^{-1} yr^{-1} in the dry and wet seasons (Table 5).

Over the study period, annual average dry deposition fluxes of NH_3 range from -1.6 to -2.5 kg N ha^{-1} yr^{-1} in the dry savannas and from -1.3 to -2.6 kg N ha^{-1} yr^{-1} in the wet savannas for our lower scenario estimate, and reduced by 26 to 62 % in the case of our higher scenario (Table 5). In the forests, the mean annual NH_3 net fluxes are around -8 kg N ha^{-1} yr^{-1}. If NH_3 were assumed to be deposited only (i.e., no bidirectional exchange, X_{cp} (NH_3) = 0), then the mean annual dry deposition fluxes would be more important and would range from -2.2 to -3.9 kg N ha^{-1} yr^{-1} in dry and wet savannas and would be around -10 kg N ha^{-1} yr^{-1} in forests (Table 5).

These estimates of nitrogen dry deposition from NO_2, HNO_3 and NH_3 on the transect of African ecosystems has allowed us to make a partial assessment of the total quantity of nitrogen deposited in gaseous form.

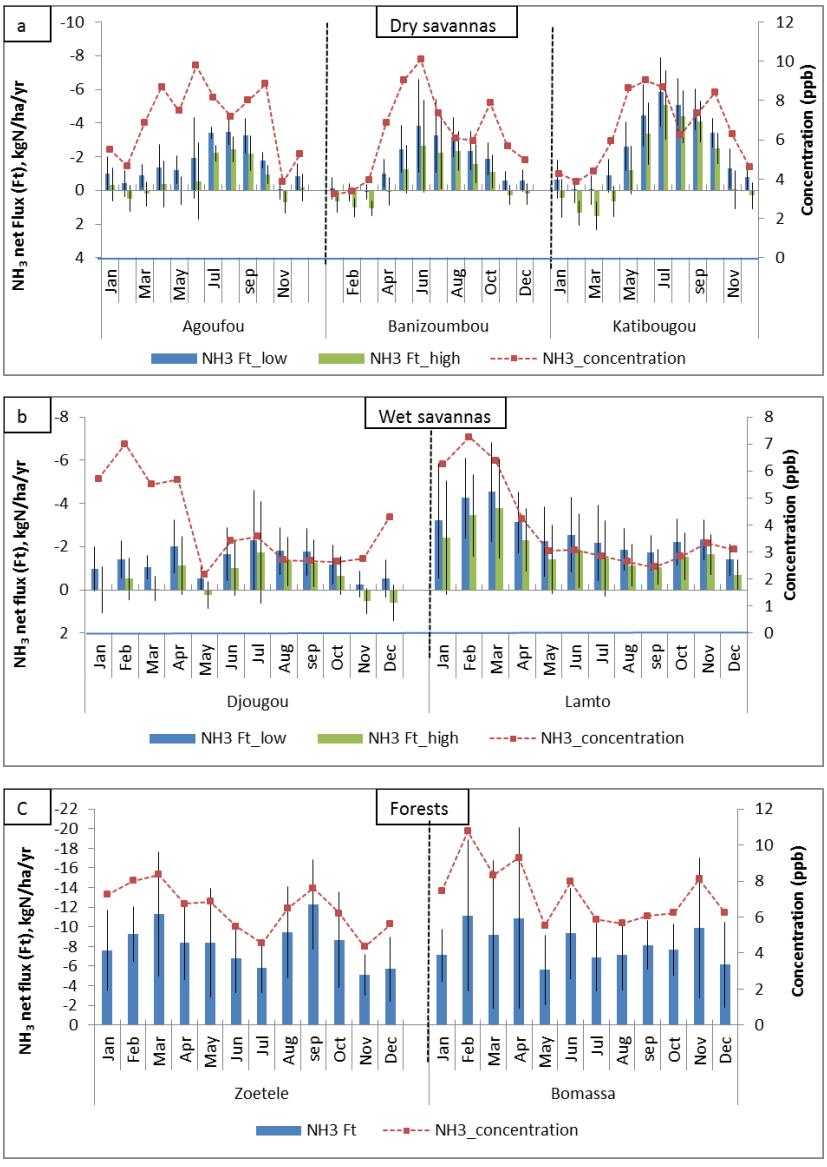

Fig. 7. Evolution of monthly bidirectional fluxes of NH_3 in kg N ha^{-1} yr^{-1} (1998–2007) on the transect dry savannas **(a)**, wet savannas **(b)** and forests **(c)** associated with evolution of NH_3 concentrations (ppb). For the savannas, lower (Ft_low) and higher (Ft_high) scenarios of NH_3 net fluxes were estimated.

Total nitrogen dry deposition fluxes from NO_2, HNO_3 and NH_3

Using the two bidirectional NH_3 exchange scenarios, the annual total N (NO_2+HNO_3+NH_3) dry depositions fluxes are estimated to range from -1.8 to -3.9 kg N ha^{-1} yr^{-1} in dry savannas and from -1.6 to -3.8 kg N ha^{-1} yr^{-1} in wet savannas and are estimated to be around -10 kg N ha^{-1} yr^{-1} in forests. On the transect, annual total N dry deposition is more important in forests due to higher NH_3 deposition fluxes, and is on the same order in wet savannas and dry savannas. In savannas, N dry deposition is more important at Katibougou for the Sahelian sites and at Lamto for the wet savanna sites due to its higher vegetation density than the other sites in the same climatic domain. Higher NH_3 V_d are related to important non-stomatal uptake of wet canopies, which lead to higher NH_3 deposition fluxes. Our annual N dry deposition estimates for the savanna sites are well comparable with those estimated at a tropical pasture site (-1.57 to -3.68 kg N ha^{-1} yr^{-1}) by Trebs et al. (2006), although they considered more species (NO_2, HNO_3, NH_3, HONO and aerosols (NO_3^-, NH_4^+)). In our study, particulate dry deposition (NO_3^-, NH_4^+) is not taken into account in this partial assessment due to very low concentrations measured at IDAF sites (Delon et al., 2010).

If NH_3 were considered to be deposited only (no bidirectional exchange), the annual total N dry deposition would range from -4.0 to $-5.3\,kg\,N\,ha^{-1}\,yr^{-1}$ in dry savannas, from -3.2 to $-4.6\,kg\,N\,ha^{-1}\,yr^{-1}$ in wet savannas and from -11.2 to $-11.7\,kg\,N\,ha^{-1}\,yr^{-1}$ in forests.

Over the study period (1998–2007), the interannual variability of the dry deposition fluxes ranged from 23 to 63 % for NH_3 (low scenario), from 13 to 30 % for NO_2 and from 21 to 43 % for HNO_3 on the transect dry savannas–wet savannas–forests. No specific trend in the variability is observed, as already concluded in the study of Delon et al. (2012). The interannual variability is largely attributable to the variability of gaseous concentrations due to the potential variation of the intensity of atmospheric sources and the variability of meteorological data.

To give the relative contribution of dry to total deposition fluxes, we calculated total nitrogen wet deposition fluxes from the IDAF database (http://idaf.sedoo.fr) for the same study period (1998–2007) for each site (Adon, 2011). The wet deposition flux has been calculated as the product of the ammonium and nitrate concentrations in rain (annual volume-weighted mean VWM) by the annual rainfall (Galy-Lacaux and Modi, 1998; Galy-Lacaux et al., 2009, and references therein). The total N wet (NO_3^-+NH_4^+) deposition fluxes estimated range from -1.6 to $-3.2\,kg\,N\,ha^{-1}\,yr^{-1}$ in dry savannas, from -3.5 to $-5.2\,kg\,N\,ha^{-1}\,yr^{-1}$ in wet savannas and are around $-4.6\,kg\,N\,ha^{-1}\,yr^{-1}$ in forests. These values are well comparable with those reported by previous studies (Yoboue et al., 2005; Sigha et al., 2003; Laouali et al., 2012) but not exactly in the same period. Using the bidirectional scenarios, the total N (dry + wet) deposition fluxes were estimated to range from -3.4 to $-7.1\,kg\,N\,ha^{-1}\,yr^{-1}$ in dry savannas, from -5.1 to $-9.0\,kg\,N\,ha^{-1}\,yr^{-1}$ in wet savannas and be around $-14.4\,kg\,N\,ha^{-1}\,yr^{-1}$ in forests. We estimate that dry deposition process in gaseous form contributes 31–68 % of the total N deposition fluxes over African ecosystems.

3.2.2 Sulfur dioxide (SO_2)

The monthly evolution of SO_2 dry deposition flux (SO_2_dd) on the transect of ecosystems is generally comparable to SO_2 concentrations over the period 2002–2007 following the same gradient (Fig. 8a–c). We note that the standard deviation of monthly mean fluxes is important. In fact, monthly SO_2 concentrations measured at IDAF sites are low and vary considerably from one year to another for the same month.

If we consider the season, average SO_2 dry deposition fluxes range in the wet season from -0.8 to $-1.0\,kg\,S\,ha^{-1}\,yr^{-1}$ in dry and wet savannas and from -0.7 to $-1.1\,kg\,S\,ha^{-1}\,yr^{-1}$ in forests, and in the dry season from -0.3 to $-0.5\,kg\,S\,ha^{-1}\,yr^{-1}$ in dry savannas and from -0.8 to $-0.9\,kg\,S\,ha^{-1}\,yr^{-1}$ in wet savannas and forests. Adon et al. (2010) observed the same order of SO_2 concentrations in dry and wet seasons in each ecosystem with higher values in the wet season for dry savannas. This suggests a contribution of soil emission, biosphere and biomass burning sources (Van Breemen, 1982, 1993; Macdonald et al., 2004; Bates et al., 1992; Arndt et al., 1997). The sulfur content of vegetation is lower compared to carbon and nitrogen elements and SO_2 emissions factors for combustion processes are lower than those for carbonaceous or nitrogen species (Lacaux et al., 1995). The 6 yr mean annual dry deposition fluxes of SO_2 are $-0.7 \pm 0.3\,kg\,S\,ha^{-1}\,yr^{-1}$ at Agoufou, $-0.5 \pm 0.2\,kg\,S\,ha^{-1}\,yr^{-1}$ at Banizoumbou and $-0.7 \pm 0.3\,kg\,S\,ha^{-1}\,yr^{-1}$ at Katibougou in dry savannas; $-0.9 \pm 0.2\,kg\,S\,ha^{-1}\,yr^{-1}$ at Djougou and $-0.8 \pm 0.4\,kg\,S\,ha^{-1}\,yr^{-1}$ at Lamto in wet savannas; and $-0.8 \pm 0.3\,kg\,S\,ha^{-1}\,yr^{-1}$ at Zoetele; and $-1.0 \pm 0.5\,kg\,S\,ha^{-1}\,yr^{-1}$ at Bomassa in forests. Along the ecosystem transect, the annual mean of SO_2 dry deposition fluxes presents low values and a small variability (-0.5 to $-1\,kg\,S\,ha^{-1}\,yr^{-1}$). The interannual variability over the 6 yr period is between 25 and 49 % for all the sites and no specific trend is observed.

In general, dry deposition fluxes of SO_2 estimated at African ecosystems are lower compared to other tropical ecosystems (Takahashi et al., 2002; Sorimachi et al., 2003) although the V_d modeled are on the same order (Table 4). This is due to low measured concentrations (on the order of 1–2 ppb). Indeed, the remote measurement sites of the IDAF network have not yet been impacted on by anthropogenic activities or industrial emissions.

3.2.3 Ozone (O_3)

The monthly evolution of O_3 dry deposition fluxes (O_3_dd) is similar to that of O_3 concentrations on the transect of ecosystems over the period 2001–2007, as in the case of NO_2 (Fig. 9a–c). In the semiarid savannas, the seasonal cycle is clear with maximum O_3 deposition fluxes in the heart of the wet season due to higher values of both O_3 concentrations and V_d. In fact, high ozone concentrations during the wet season are the result of active photochemical production of O_3 in the boundary layer associated with high NO_x concentrations (Stewart et al., 2008). In the Sahelian region, the ozone production in the wet season is mainly related to natural biogenic precursor sources (Adon et al., 2010). The seasonal average deposition fluxes are -6.4 ± 4.1 and $-21.0 \pm 3.2\,kg\,ha^{-1}\,yr^{-1}$ at Agoufou, -7.2 ± 2.0 and $-20.4 \pm 3.6\,kg\,ha^{-1}\,yr^{-1}$ at Banizoumbou and -13.0 ± 2.5 and $-23.0 \pm 4.1\,kg\,ha^{-1}\,yr^{-1}$ at Katibougou, in dry and wet seasons, respectively. In the wet savannas, the seasonal average O_3 deposition fluxes are on the same order with values of -20.3 ± 1.5 and $-18.6 \pm 3.3\,kg\,ha^{-1}\,yr^{-1}$ at Lamto, and -16.0 ± 3.6 and $-17.6 \pm 3.8\,kg\,ha^{-1}\,yr^{-1}$ at Djougou, in dry and wet seasons, respectively. The difference between the seasonal ozone deposition fluxes is reduced with higher values of V_d in the wet season and higher O_3 concentrations in the dry season as a consequence of strong regional biomass burning activities. For forested ecosystems,

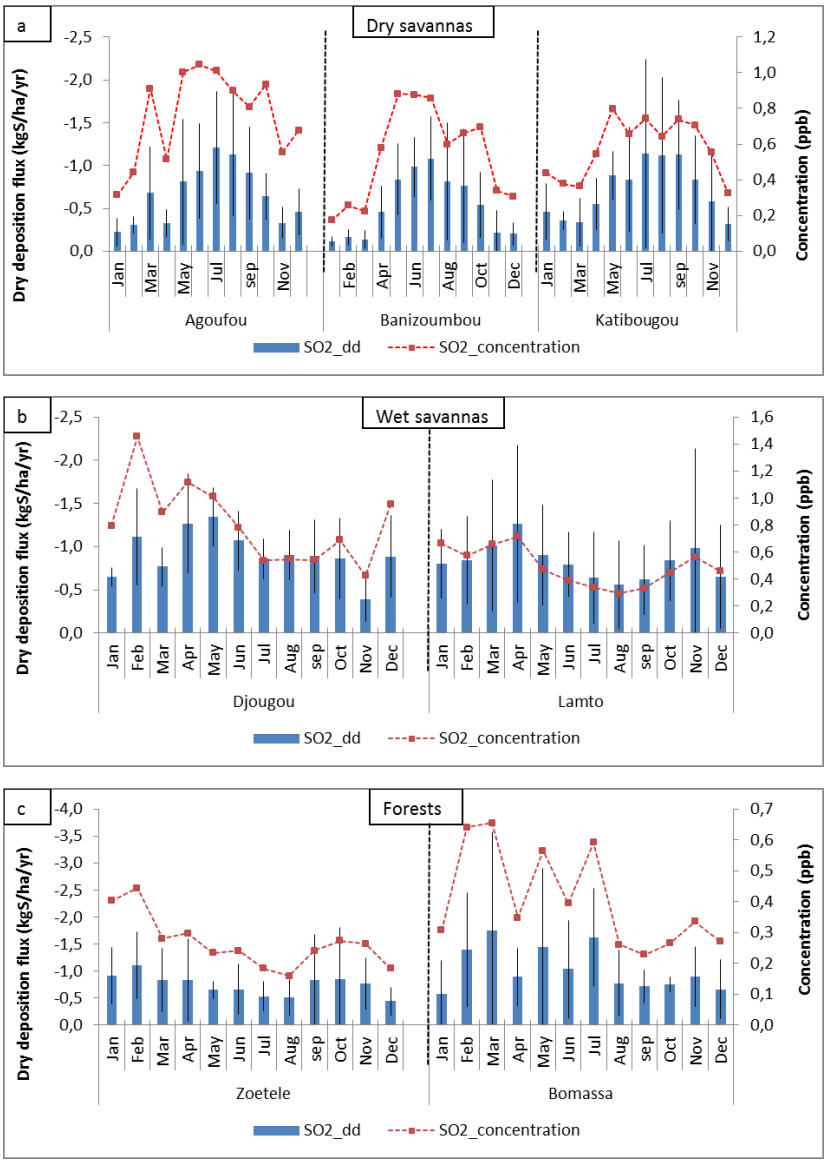

Fig. 8. Evolution of monthly dry deposition fluxes of SO_2 (SO_2_dd) in kg S ha^{-1} yr^{-1} (2002–2007) on the transect dry savannas **(a)**, wet savannas **(b)** and forests **(c)** associated with evolution of SO_2 concentrations (ppb).

the mean seasonal deposition fluxes of O_3 are -18.8 ± 0.3 and -11.3 ± 0.9 kg ha^{-1} yr^{-1} at Zoetele and -10.1 ± 1.1 and -10.8 ± 0.8 kg ha^{-1} yr^{-1} at Bomassa, in dry and wet seasons, respectively. We note that these seasonal values are on the same order between the two seasons at Bomassa but they are higher in the dry season at Zoetele due to higher O_3 concentrations measured in this season.

The 7 yr mean annual dry deposition fluxes of O_3 range from -11 to -19 kg ha^{-1} yr^{-1} in dry and wet savannas (-11.2 ± 3.3 kg ha^{-1} yr^{-1} at Agoufou, -12.7 ± 2.4 kg ha^{-1} yr^{-1} at Banizoumbou and -17.2 ± 2.7 kg ha^{-1} yr^{-1} at Katibougou, -16.9 ± 3.2 kg ha^{-1} yr^{-1} at Djougou and -19.3 ± 3.4 kg ha^{-1} yr^{-1} at Lamto) and from -11 to -13 kg ha^{-1} yr^{-1} in forests (-13.2 ± 2.9 kg ha^{-1} yr^{-1} at Zoetele and -10.6 ± 0.7 kg ha^{-1} yr^{-1} at Bomassa). The unadjusted estimates of O_3 dry deposition fluxes in forests (if the correction factor was not applied for O_3 concentrations (see Sect. 2.2.3), the O_3 deposition fluxes would range from -8 to -10 kg ha^{-1} yr^{-1}. The interannual variability of O_3 deposition fluxes is between 7 and 25 % over the period 2001–2007 for all sites. This variability is mainly related to the spatio-temporal evolution of ozone concentrations that depends on various processes (precursor emissions, biogenic and anthropogenic sources) (Adon et al., 2010). In savannas, the values of annual O_3 deposition fluxes are lower at Agoufou and Banizoumbou due to the low vegetation cover

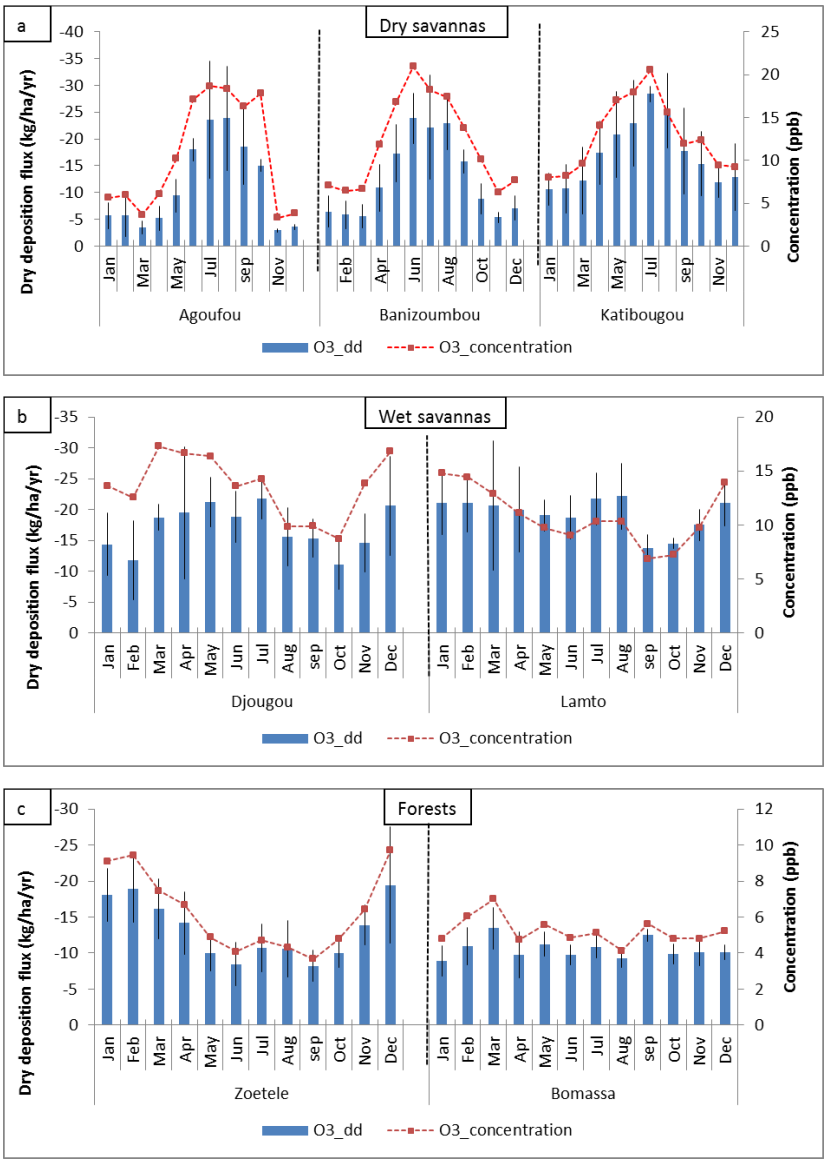

Fig. 9. Evolution of monthly dry deposition fluxes of O_3 (O_3_dd) in kg ha^{-1} yr^{-1} (2001–2007) on the transect dry savannas **(a)**, wet savannas **(b)** and forests **(c)** associated with evolution of O_3 concentrations (ppb).

of the Sahelian zone (thus, low V_d). The low values of O_3 dry deposition in forests are correlated to low values of O_3 concentrations that were 2 to 3 times lower than those measured in the other ecosystems (Table 2). Several studies have shown that tropical forests appear to be major O_3 sinks, through 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).

Few observational studies of O_3 deposition fluxes for a long-term period are available over tropical areas, although several studies concerning the diurnal evolution have been conducted in the rainforests (Cros et al., 1992, 2000; Andreae et al., 1992; Rummel et al., 2007; Matsuda et al., 2005). The modeled O_3 V_d in our study are within the range of values determined in other tropical ecosystems (Table 4). In general, the O_3 deposition fluxes estimated in African forests are lower compared to other tropical forests (Mikkelsen et al., 2004; Zeller and Nikolov, 2000); this is due to lower concentrations measured.

4 Conclusions

In this study, we estimated dry deposition fluxes of nitrogen compounds (NO_2, HNO_3, NH_3), sulfur dioxide (SO_2)

and ozone (O_3) in major African ecosystems, represented by IDAF sites.

NO_2, HNO_3, SO_2 and O_3 were considered to be net deposited, while surface–atmosphere exchange of NH_3 is considered to be bidirectional for all ecosystems. Monthly dry deposition fluxes have been estimated by the inferential technique, using air concentrations measured monthly by passive samplers for a long-term period (1998–2007) and modeled exchange rates. Surface and meteorological conditions specific to IDAF sites have been used in the deposition models. Along the transect of ecosystems, simulation results show that V_d increases with the vegetation density. Thus, the lower values of V_d for all gases have been obtained in the dry savannas and the higher values in the forests. For each ecosystem, the seasonal and annual mean variations of gaseous dry deposition fluxes have been analyzed. Dry deposition fluxes are more important in the wet season for all the gases in the dry savannas due to higher values of both concentrations and V_d in this season. For the wet savannas and forested ecosystems, seasonal dry deposition fluxes are generally on the same order between the dry and wet seasons for all the gases except for NO_2 in the wet savannas, and for HNO_3 and O_3 at the Zoetele forested site, where flux values are higher in the dry season due to much higher concentrations.

Along the latitudinal transect of ecosystems, the annual mean dry deposition fluxes of nitrogen compounds range from -0.4 to $-0.8\,\mathrm{kg\,N\,ha^{-1}\,yr^{-1}}$ for NO_2, from -0.7 to $-1.0\,\mathrm{kg\,N\,ha^{-1}\,yr^{-1}}$ for HNO_3, and from -0.7 to $-8.3\,\mathrm{kg\,N\,ha^{-1}\,yr^{-1}}$ for NH_3 over the study period (1998–2007). The total nitrogen dry deposition flux (NO_2+HNO_3+NH_3) is more important in forests ($\sim -10\,\mathrm{kg\,N\,ha^{-1}\,yr^{-1}}$) than in wet and dry savannas (-1.6 to $-3.9\,\mathrm{kg\,N\,ha^{-1}\,yr^{-1}}$). If NH_3 was considered to be deposited only to the ecosystems, the annual total N dry deposition would range from -3.2 to $-5.3\,\mathrm{kg\,N\,ha^{-1}\,yr^{-1}}$ in dry and wet savannas, and from -11.2 to $-11.7\,\mathrm{kg\,N\,ha^{-1}\,yr^{-1}}$ in forests. Along the ecosystem transect, the annual mean of SO_2 dry deposition fluxes presents low values and a small variability (-0.5 to $-1\,\mathrm{kg\,S\,ha^{-1}\,yr^{-1}}$). For ozone, the annual mean dry deposition fluxes range from -11 to $-19\,\mathrm{kg\,ha^{-1}\,yr^{-1}}$ in dry and wet savannas and from -11 to $-13\,\mathrm{kg\,ha^{-1}\,yr^{-1}}$ in forests. The lower O_3 dry deposition fluxes in forests are due to low measured O_3 concentrations despite higher V_d. Over the study period, the interannual variability of gaseous dry deposition fluxes showed no specific trend. Over African ecosystems, our study assumed that gaseous dry deposition contributes to 31–68 % of the total (dry + wet) N deposition fluxes.

This study allowed for estimates of the mean range of gaseous dry deposition fluxes representative of major tropical African ecosystems in west and central Africa. This is one of the major scientific objectives of the IDAF program. It is based on original and unique data from remote and seldom-explored regions. To improve this work, it is important to not only address the uncertainties in the determination of dry deposition velocities but also use the bidirectional approach for other gases such as NO_2; more investigation on the ground emission potential in the case of NH_3 surface–atmosphere exchange is needed. Within the IDAF network, we suggest to perform an experimental determination of dry deposition fluxes by other methods (e.g., gradient method, eddy correlation) on the measurement sites to be compared with fluxes estimated by the inferential method. Furthermore, we plan to use the model RegCM4 (regional climatic model) (Giorgi et al., 2012; Shalaby et al., 2012) to simulate the regional trends of gaseous dry deposition fluxes and to compare these results to long-term IDAF observations. This work will allow for providing a high-resolution map of dry deposition at regional scales of the African ecosystems useful for impact studies.

Appendix A

The dry deposition flux (F_{dry}) can be expressed as a function of a dry deposition velocity (V_d) and an atmospheric concentration (X_a):

$$F_{dry} = -V_d \cdot X_a. \tag{A1}$$

The V_d is obtained from the sum of three resistances in series as follows:

$$V_d = (R_a + R_b + R_c)^{-1}, \tag{A2}$$

where R_a is the aerodynamic resistance to transfer of a species as a result of atmospheric turbulence in the surface layer between a height Z and the surface, characterized by Z_0 (roughness length). It is computed from the following equation (Padro et al., 1991):

$$R_a = \frac{1}{k u_*}\left[0.74 \ln(Z/Z_0) - \Psi_H(Z/L)\right], \tag{A3}$$

where Ψ_H is the integrated stability function for heat and k is the von Karman constant (0.4). L is a stability parameter (Monin–Obukhov length) and can be computed jointly with u_* (friction velocity) from the basic surface layer equations, requiring only the temperatures at two different heights and the wind at one height. The conditions of application of Eq. (A3) are discussed in Padro et al. (1991). Under very stable conditions, the Richardson number is constrained to an upper limit value of 0.21. In our simulation, after a statistical analysis, the friction velocity is constrained to a lower limit value of $0.1\,\mathrm{m\,s^{-1}}$ for savanna sites and $0.2\,\mathrm{m\,s^{-1}}$ for forest sites.

R_b is the quasi-laminar sublayer resistance above the canopy and it is computed from the following equation (Padro and Edwards, 1991):

$$R_b = \frac{2}{k u_*}\left(\nu / D_j\right)^{2/3}, \tag{A4}$$

where ν is the kinematic viscosity of air and D_j is the molecular diffusivity of a species j in air.

R_c is the surface or canopy resistance, and characterizes the surface affinity for pollutant uptake. A large part of the uncertainty of the inferential method might be attributed to the parameterization of R_c. Zhang et al. (2003b) proposed a revised parameterization of R_c by including non-stomatal resistance (R_{ns}) parameterizations based on study results over five different vegetation types in North America (i.e., Zhang et al., 2002b, 2003a):

$$\frac{1}{R_c} = \frac{1 - w_{st}}{R_{st} + R_m} + \frac{1}{R_{ns},} \quad \text{(A5)}$$

$$\frac{1}{R_{ns}} = \frac{1}{R_{cut}} + \frac{1}{R_{ac} + R_g}, \quad \text{(A6)}$$

where the sub-resistances R_{st}, R_m, R_{cut}, R_{ac} and R_g are respectively stomatal, mesophyll, cuticle, in-canopy aerodynamic and soil resistances. w_{st} is the fraction of stomatal blocking under wet conditions. One of the improvements to the model of Zhang et al. (2003b) includes more realistic treatment of cuticle resistance, which is parameterized as functions of leaf wetness (dry vs. wet; dew vs. rain), relative humidity, leaf area index (LAI), friction velocity and land-use-specific reference values. R_{ac} is also a function of the LAI, the friction velocity and the land-use specific reference value. Note that R_g and R_{cut} are calculated for SO_2 and O_3 and then scaled for other gases. R_{st} is calculated using a sun-lit/shade stomatal resistance sub-model (Zhang et al., 2002a). Thus, in this improved parameterization, R_c depends on the type of canopy, the chemical species and the meteorological conditions. It is important to note that R_c of HNO_3 is calculated in this model and constrained to a lower limit value of $10\,s\,m^{-1}$, although previous studies showed that dry deposition of HNO_3 is mostly controlled by aerodynamic resistances (Zhang et al., 2002a, and references therein). The parameterizations of all these sub-resistances, the land-use categories (LUC) and all related parameters as well as more details can be found in Zhang et al. (2003b).

Appendix B

The net bidirectional flux at a reference height above the canopy can be expressed as

$$F_t = \frac{(X_a - X_c)}{R_a + R_b}, \quad \text{(B1)}$$

where X_a and X_c are the ambient concentrations at the reference height and at the canopy top, respectively. In the model, X_c itself is expressed as a function of X_a (Zhang et al., 2010). The formulas of resistances are the same as in the original big-leaf model (Zhang et al., 2003b).

Zhang et al. (2010) demonstrated that the differences in the fluxes (ΔF) between the new bidirectional model (F_t) and the only dry deposition big-leaf model (F_{dry}, Zhang et al., 2003b) can be estimated from the following equation:

$$\Delta F = F_t - F_{dry} = X_{cp} \cdot V_d \quad \text{(B2)}$$

with X_{cp} the canopy compensation point and V_d the deposition velocity calculated from the original big-leaf model.

X_{cp} can be estimated from Eq. (B3):

$$X_{cp} = \left[\frac{x_{st}}{R_{st}} + \frac{x_g}{R_a + R_g}\right]\left[\frac{1}{R_{st}} + \frac{1}{R_{ac} + R_g} + \frac{1}{R_{cut}}\right]^{-1}, \quad \text{(B3)}$$

where x_{st} and x_g are stomatal and soil compensation points, respectively. x_{st} is a function of stomatal emission potential (Γ_{st}) and the temperature of the leaf stomata, and then x_g is a function of the ground emission potential (Γ_g) and the temperature of the ground surface. The compensation point increases exponentially with increasing temperature (Zhang et al., 2010).

In this study, as we use monthly measurement concentrations for a long period, we infer the NH_3 net fluxes (F_t) from the following equation:

$$F_t = \Delta F + F_{dry} = -V_d(X_a - X_{cp}), \quad \text{(B4)}$$

where $\Delta F (> 0)$ is calculated monthly (from 3-hourly values) directly in the bidirectional model (Eq. B2) and F_{dry} (< 0) calculated monthly by Eq. (A1).

The canopy compensation point (X_{cp}) is the atmospheric NH_3 concentration for which the fluxes between the surface and the atmosphere change directions from emission ($F_t > 0$) to deposition ($F_t < 0$) (or vice versa).

More details on the parameterizations of this new bidirectional model can be found in Zhang et al. (2010).

Acknowledgements. This work is part of the IDAF (IGAC/DEBITS/AFRICA) project, and was funded by the INSU/CNRS "Institut National des Sciences de l'Univers/Centre National de Recherche Scientifique" in France and the API "African Monsoon Multidisciplinary Analyses" (AMMA in 2005).

Edited by: A. B. Guenther

The publication of this article is financed by CNRS-INSU.

References

Adon, M.: Etude des concentrations de gaz atmosphérique et estimation des flux de dépôt sec à l'échelle des principaux écosystèmes africains, PhD, Université Paul Sabatier-Toulouse III, France, 2011.

Adon, M., Galy-Lacaux, C., Yoboué, V., Delon, C., Lacaux, J. P., Castera, P., Gardrat, E., Pienaar, J., Al Ourabi, H., Laouali, D., Diop, B., Sigha-Nkamdjou, L., Akpo, A., Tathy, J. P., Lavenu, F., and Mougin, E.: Long term measurements of sulfur dioxide, nitrogen dioxide, ammonia, nitric acid and ozone in Africa using passive samplers, Atmos. Chem. Phys., 10, 7467–7487, doi:10.5194/acp-10-7467-2010, 2010.

Al-ourabi, H. and Lacaux, J. P.: Dry and wet deposition for nitrogen and sulphur at seven IDAF stations in Tropical Africa. International Global Atmospheric Chemistry (IGAC), Symposium, Crete, Greece, 18–25 September, 2002.

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.

Aneja, V. P., Roelle, P. A., Murray, G. C., Southerland, J., Erisman, J. W., Fowler, D., Asman, W. A. H., and Patni, N.: Atmospheric nitrogen compounds II: emissions, transport, transformation, deposition and assessment, Atmos. Environ., 35, 1903–1911, 2001.

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.

Bakwin, P. S., Wofsy, S. C., and Fan, S.-M.: Measurement of NO_x and NO_y concentrations and fluxes over Arctic tundra, J. Geophys. Res., 97, 16545–16557, 1992.

Baldocchi, D. D.: A multi-layer model for estimating sulfur dioxide deposition to a deciduous oak forest canopy, Atmos. Environ., 22, 869–884, 1988.

Bash, J. O., Cooter, E. J., Dennis, R. L., Walker, J. T., and Pleim, J. E.: Evaluation of a regional air-quality model with bidirectional NH_3 exchange coupled to an agroecosystem model, Biogeosciences, 10, 1635–1645, doi:10.5194/bg-10-1635-2013, 2013.

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.

Bobbink, R., Hornung, M., and Roelofs, J. G. M.: The effects of air-borne nitrogen pollutants on species diversity in natural and semi-natural European vegetation, J. Ecol., 86, 717–738, 1998.

Boone, A., De Rosnay, P., Balsamo, G., Beljaars, A., Chopin, F., Decharme, B., Delire, C., Ducharne, A., Gascoin, S., Grippa, M., Guichard, F., Gusev, Y., Harris, P., Jarlan, L., Kergoat, L., Mougin, E., Nasonova, O., Norgaard, A., Orgeval, T., Ottl, C., Poccard-Leclerq, I., Polcher, J., Sandholt, I., Saux-Picart, S., Taylor, C., and Xue, Y.: The AMMA Land Surface Model Intercomparison Project (ALMIP), B. Am. Meteor. Soc., 12, 1865–1880, doi:10.1175/2009BAMS2786.1, 2009.

Bouwman, A. F. and Van Der Hoek, K. W.: Scenarios of animal waste production and fertilizer use and associated ammonia emission for the developping countries, Atmos. Environ., 31, 4095–4102, 1997.

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, 1024, doi:10.1029/2000GB001389, 2002a.

Bouwman, A. F., Van Vuuren, D. P., Derwent, R. G., and Posch, M.: A global analysis of acidification and eutrophication of terrestrial ecosystems, Water Air Soil Pollut., 141, 349–382, doi:10.1023/A:1021398008726, 2002b.

Breuninger, C., Kesselmeier, J., and Meixner, F. X.: Field investigations of nitrogen dioxide (NO_2) exchange between plants and the atmosphere, Atmos. Chem, Phys., 13, 773–790, doi:10.5194/acp-13-773-2013, 2013.

Brook, J., Zhang, L., Franco, D., and Padro, J.: Description and evaluation of a model of deposition velocities for routine estimates of air pollutant dry deposition over North America, Part I: Model development, Atmos. Environ., 33, 5037–5052, 1999.

Chaparro-Suarez, I. G., Meixner, F. X., and Kesselmeier, J.: Nitrogen dioxide (NO_2) uptake by vegetation controlled by atmospheric concentrations and plant stomatal aperture, Atmos. Environ., 45, 5742–5750, doi:10.1016/j.atmosenv.2011.07.021, 2011.

Coe, H. and Gallagher, M.W.: Measurements of dry deposition of NO_2 to a Dutch heathland using the eddy correlation technique, Q. J. Roy. Meteor. Soc., 118, 767–786, 1992.

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 ozone between 0 and 400 meters in and above the African equatorial Forest, J. Geophys. Res., 97, 12877–12887, 1992.

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.

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, doi:10.5194/acp-8-2351-2008, 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., 10, 2691–2708, doi:10.5194/acp-10-2691-2010, 2010.

Delon, C., Galy-Lacaux, C., Adon, M., Liousse, C., Serça, D., Diop, B., and Akpo, A.: Nitrogen compounds emission and deposition in West African ecosystems: comparison between wet and dry savanna, Biogeosciences, 9, 385–402, doi:10.5194/bg-9-385-2012, 2012.

De Rosnay P., Drusch, M., Boone, A., Balsamo, G., Decharme, B., Harris, P., Kerr, Y., Pellarin, T., Polcher, J., and Wigneron, J.-P.: AMMA Land Surface Model Intercomparison Experiment coupled to the Community Microwave Emission Model: ALMIP-MEM, J. of Geophys. Res., 114, D05108, doi:10.1029/2008JD010724, 2009.

Dorsey, J. R., Duyzer, J. H., Gallagher, M. W., Coe, H., Pilegaard, K., Weststrate, J. H., Jensen, N. O., and Walton, S.: Oxidized nitrogen and ozone interaction with forests. I: Experimental observations and analysis of exchange with Douglas fir, Q. J. Roy. Meteorol. Soc., 130, 1941–1955, doi:10.1256/qj.03.124, 2004.

Duyzer, J. and Fowler, D.: Modelling land atmosphere exchange of gaseous oxides of nitrogen in Europe, Tellus B, 46, 353–372, doi:10.1034/j.1600-0889.1994.t01-3-00002.x, 1994.

Endo, T., Yagoh, H., Sato, K., Matsuda, K., Hayashi, K., Noguchi, I., and Sawada, K.: Regional characteristic of dry deposition of sulfur and nitrogen compounds at EANET sites in Japan from 2003 to 2008, Atmos. Environ., 45, 1259–1267, 2011.

Erisman, J. W. and Wyers, G. P.: Continuous measurements of surface exchange of SO_2 and NH_3: implications for their possible interaction in the deposition process, Atmos. Environ., 27, 1937–1949, 1993.

Erisman, J. W., Verluis, A. H., Verplanke, T. A. J. W., de Haan, D., Anink, D., van Elzakker, B. G., Mennen, M. G., and van Aalst, R. M.: Monitoring the dry deposition of SO_2 in the Netherlands: results for grassland and heather vegetation, Atmos. Environ., 27A, 1153–1161, 1993a.

Erisman, J. W., Mennen, M. G., Hogenkamp, J., Kemkers, E., Goedhart, D., van Pul, A., Boermans, J., Duyzer, J., and Wyers, P.: Dry deposition measurements of SO_2 over the Speulder forest, estimation of a surface resistance parametrization, in: Air Pollution Report, edited by: Angeletti, G., Pio, C., and Slanina, J., CEC, Brussels, Belgium, 1993b.

Erisman, J. W., van Elzakker, B. G., Mennen, M. G., Hogenkamp, J., Zwart, E., van den Beld, L., Römer, F. G., Bobbink, R., Heil, G., Raessen, M., Duyzer, J. H., Verhage, H., Wyers, G. P., Otjes, R. P., and Mols, J. J.: The Elspeetsche Veld experiment on surface exchange of trace gases: Summary of results, Atmos. Environ., 28, 487–496, 1994.

Fensholt, R., Sandholt, I., and Rasmussen, M. S.: Evaluation of MODIS LAI, fAPAR and the relation between fAPAR and NDVI in a semi-arid environment using in situ-measurements, Remote Sens. Environ., 91, 490–507, 2004.

Flechard, C. R. and Fowler, D.: Atmospheric ammonia at a moorland site. II: Long-term surface-atmosphere micrometeorological flux measurements, Q. J. Roy. Meteor. Soc., 124, 759–791, 1998.

Flechard, C. R., Fowler, D., Sutton, M. A., and Cape, J. N.: A dynamic chemical model of bi-directional ammonia exchange between semi-natural vegetation and the atmosphere, Q. J. Roy. Meteor. Soc., 125, 2611–2641, 1999.

Flechard, C. R., Spirig, C., Neftel, A., and Ammann, C.: The annual ammonia budget of fertilised cut grassland – Part 2: Seasonal variations and compensation point modeling, Biogeosciences, 7, 537–556, doi:10.5194/bg-7-537-2010, 2010.

Flechard, C. R., Nemitz, E., Smith, R. I., Fowler, D., Vermeulen, A. T., Bleeker, A., Erisman, J. W., Simpson, D., Zhang, L., Tang, Y. S., and Sutton, M. A.: Dry deposition of reactive nitrogen to European ecosystems: a comparison of inferential models across the NitroEurope network, Atmos. Chem. Phys., 11, 2703–2728, doi:10.5194/acp-11-2703-2011, 2011.

Fowler, D., Flechard, C., Cape, J. N., Storeton-West, R. L., and Coyle, M.: Measurements of ozone deposition to vegetation quantifying the flux, the stomatal and non-stomatal components, Water Air Soil Pollut., 130, 63–74, 2001.

Fowler, D., Pilegaard, K., Sutton, M. A., Ambus, P., Raivonen, M., Duyzer, J., Simpson, D., Fagerli, H., Schjoerring, J. K., Neftel, A., Burkhardt, J., Daemmgen, U., Neiyrink, J., Personne, E., Wichink-Kruit, R., Butterbach-Bahl, K., Flechard, C., Tuovinen, J. P., Coyle, M., Gerosa, G., Loubet, B., Altimir, N., Gruenhage, L., Ammann, C., Cieslik, S., Paoletti, E., Mikkelsen, T. N., Ro-Poulsen, H., Cellier, P., Cape, J. N., Horvath, L., Loreto, F., Niinemets, U., Palmer, P. I., Rinne, J., Misztal, P., Nemitz, E., Nilsson, D., Pryor, S., Gallagher, M. W., Vesala, T., Skiba, U., Brüeggemann, N., Zechmeister-Boltenstern, S., Williams, J., O'Dowd, C., Facchini, M. C., de Leeuw, G., Flossman, A., Chaumerliac, N., and Erisman, J. W.: Atmospheric composition change: ecosystems and atmosphere exchange, Atmos. Environ., 43, 5192–5263, 2009.

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, doi:10.5194/acp-9-1579-2009, 2009.

Ganzeveld, L. and Lelieveld, J: Dry deposition parameterization in a chemistry general circulation model and its influence on the distribution of reactive trace gases, J. Geophys. Res., 100, 20999–21012, 1995.

Gao, W., Wesely, M. L., Cook, D. R., and Martin, T. J.: Eddy correlation measurements of NO, NO_2, and O_3 fluxes, Proceedings of an International Specialty Conference, Measurement of Toxic and Related Air Pollutants, Air Waste Management Association, Pittsburgh, PA, 146–150, 1996.

Giorgi, F., Coppola, E., Solmon, F., Mariotti, L., Sylla, M. B., Bi, X., Elguindi, N., Diro, G. T., Nair, V., Giuliani, G., Turuncoglu, U. U., Cozzini, S., Guttler, I., O'Brien, T. A., Tawfik, A. B., Shalaby, A., Zakey, A. S., Steiner, A. L., Stordal, F., Sloan, L. C., and Brankovic, C.: RegCM4: Model description and preliminary tests over multiple CORDEX domains, Clim. Res., 52, 7–29, doi:10.3354/cr01018, 2012.

Hamaoui-Laguel, L., Meleux, F., Beekmann, M., Bessagnet, B., Génermont, S., Cellier, P., and Létinois, L.: Improving ammonia emissions in air quality modelling for France, Atmos. Environ., doi:10.1016/j.atmosenv.2012.08.002, in press, 2012.

Hanson, P. J. and Lindberg, S. E: Dry deposition of reactive nitrogen compounds: a review of leaf, canopy and non-foliar measurements, Atmos. Environ., 25A, 1615–1634, 1991.

Hanson, P. J., Rott, K., Taylor Jr., G. E., Gunderson, C. A., Lindberg, S. E., and Ross-Todd, B. M.: NO_2 deposition to elements representative of a forest landscape, Atmos. Environ., 23, 1783–1794, 1989.

Hesterberg, R., Blatter, A., Fahrni, M., Rosset, M., Neftel, A., Eugster, W., and Wanner, H.: Deposition of nitrogen-containing compounds to an extensively mangaged grassland in central Switzerland, Environ. Pollut., 91, 21–34, 1996.

Hicks, B. B.: Dry deposition to forests – On the use of data from clearing, Agr. Forest Meteorol., 136, 214–221, 2006.

Huebert, B. J. and Robert, C. H.: The dry deposition of nitric acid to grass, J. Geophys. Res., 90, 2085–2090, 1985.

Horvath, L., Asztalos, M., Fuhrer, E., Meszaros, R., and Weidinger, T.: Measurement of ammonia exchange over grassland in the Hungarian Great Plain, Agr. Forest Meteorol., 130, 282–298, 2005.

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.

Janssen, L. H. J. M. and Romer, F. G.: The frequency and duration of dew occurrence over a year, Tellus, 43B, 408–419, 1991.

Jin, L., Shao, M., Zeng, L., Zhao, D., and Tang, D.: Estimation of dry deposition fluxes of major inorganic species by canopy throughfall approach, Chinese Sci. Bull., 51, 1818–1823, 2006.

Johansson, C., Rodhe, H., and Sanhueza, E.: Emission of NO in tropical savanna and a cloud forest during the dry season, J. Geophys. Res., 93, 7180–7192, 1988.

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.

Kaptue, T. A. T., Roujean, J.-L., and Faroux, S.: ECOCLIMAP-II: an ecosystem classification and land surface parameter database of Western Africa at 1 km resolution for the Africa Monsoon Multidisciplinary Analysis (AMMA) project, Remote Sens. Environ., 114, 961–976, 2010.

Kirkman, G. A., Gut, A., Ammann, C., Gatti, L. V., Cordova, A. M., Moura, M. A. L., Andreae, M. O., and Meixner, F. X.: Surface exchange of nitric oxide, nitrogen dioxide, and ozone at a pasture in Rondonia, Brazil, J. Geophys. Res., 107, 8083, doi:10.1029/2001JD000523, 2002.

Krzyzamowki, J.: Ozone variation with height in a forest canopy – results from a passive sampling field campaign, Atmos. Environ., 38, 5957–5962, 2004.

Lacaux, J. P., Cachier, H., and Delmas, R.: Biomass burning in Africa: An overview of its impact on atmospheric chemistry, in: Fire in the Environment: The Ecological, Atmospheric and Climatic Importance of Vegetation Fires, edited by: Crutzen, P. J. and Goldammer, J. G., 159–191, Environmental Science Research Report 13, John Wiley, New York, 1993.

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 Issue Nr. 2, 2003.

Langford, A. O. and Fehsenfeld, F.C.: Natural vegetation as a source or sink for atmopsheric ammonia: a case study, Science, 255, 581–583, 1992.

Langford, A. O., Fehsenfeld, F. C., Zachariassen, J., and Schimel, D. S.: Gaseous ammonia fluxes and background concentrations in terrestrial ecosystems of the United states, Global Biogeochem. Cy., 6, 459–483, 1992.

Laouali, D., Galy-Lacaux, C., Diop, B., Delon, C., Orange, D., Lacaux, J. P., Akpo, A., Lavenu, F., Gardrat, E., and Castera, P.: Long term monitoring of precipitation chemical composition and wet deposition over three Sahelian savannas, Atmos. Environ., 50, 314–327, 2012.

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., Bourles, B., Flamant, C., Marticorena, B., Peugeot, C., Gaye, A., Haywood, J., Mougin, E., Polcher, J., Redelsperger, J.-L., and Thorncroft, C. D.: The AMMA field campaigns: Multiscale and multidisciplinary observations in the West African region, B. Am Meteorol. Soc., 88, in press, 2007.

Lerdau, M. T., Munger, L. J., and Jacob, D. J.: Atmospheric chemistry – the NO_2 flux conundrum, Science, 289, 2291–2293, doi:10.1126/science.289.5488.2291, 2000.

Liu, X., Zhang, Y., Han, W., Tang, A., Shen, J., Cui, Z., Vitousek, P., Erisman, J. W., Goulding, K., Christie, P., Fangmeier, A., and Zhang, F.: Enhanced nitrogen deposition over China, Nature, 494, 459, doi:10.1038/nature11917, 2013.

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.

Loubet, B., Milford, C., Hill, P. W., Tang, Y. S., Cellier, P., and Sutton, M. A.: Seasonal variability of apoplastic NH_4^+ and pH in an intensively managed grassland, Plant Soil, 238, 97–110, 2002.

Macdonald, B. C. T., Denmead, O. T., Ian White, I., Michael, D., 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, 336–342, 2007.

Massad, R. S., Nemitz, E., and. Sutton, M. A.: Review and parameterization of bi-directional ammonia exchange between vegetation and the atmosphere, Atmos. Chem. Phys., 10, 10359–10386, doi:10.5194/acp-10-10359-2010, 2010.

Matsuda, K., Watanabe, I., Wingpud, V., Theramonkol, P., Khummongkol, P., Wangwongwatana, S., and Totsuka, T.: Ozone dry deposition above a tropical forest in the dry season in northern Thailand, Atmos. Environ., 39, 2571–2577, 2005.

Matsuda, K., Watanabe, I., Wingpud, V., Theramongkol, P., and Ohizumi, T.: Deposition velocity of O_3 and SO_2 in the dry and wet season above a tropical forest in northern Thailand, Atmos. Environ., 40, 7557–7564, 2006.

Matt, D. R. and Meyers, T. P.: On the use of the inferential technique to estimate dry deposition of SO_2, Atmos. Environ., 27, 493–501, 1993.

Mayaux, P., Bartholome, E., Fritz, S., and Belward, A.: A new land cover map of Africa for the year 2000, J. Biogeogr., 31, 861–877, 2004.

Mikkelsen, T. N., Ro-Poulsen, H., Hovmand, M. F., Jensen, N. O., Pilegaard, K., and Egelov, A. H.: Five-year measurements of ozone fluxes to Danish Norway spruce canopy, Atmos. Environ., 38, 2361–2371, 2004.

Mosier, A., Kroeze, C., Nevison, C., Oenema, O., Seitzinger, S., and van Cleemput, O.: Closing the global N_2O budget: nitrous oxide emissions through the agricultural nitrogen cycle, Nutr. Cy. Agroecosys., 52, 225–248, 1998.

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.

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.

Myneni, R. B., Knyazikhin, Y., Zhang, Y., Tian, Y., Wang, Y., Lostch, A., Privette, J. L., Morisette, J. T., Running, S. W., Nemani, R., Glassy, J., and Votava, P.: MODIS leaf area index (LAI) and fraction of photosynthetically active radiation absorbed by vegetation (fPAR) product, Algorithm Theoretical Basis Document, Boston University, Boston, USA, 126 pp., 1999.

Nemitz, E., Loubet, B., Lehmann, B. E., Cellier, P., Neftel, A., Jones, S. K., Hensen, A., Ihly, B., Tarakanov, S. V., and Sutton, M. A.: Turbulence characteristics in grassland canopies and implications for tracer transport, Biogeosciences, 6, 1519–1537, doi:10.5194/bg-6-1519-2009, 2009.

Pan, Y. P., Wang, Y. S., Tang, G. Q., and Wu, D.: Wet and dry deposition of atmospheric nitrogen at ten sites in Northern China, Atmos. Chem. Phys., 12, 6515–6535, doi:10.5194/acp-12-6515-2012, 2012.

Personne, E., Loubet, B., Herrmann, B., Mattsson, M., Schjoerring, J. K., Nemitz, E., Sutton, M. A., and Cellier, P.: SURFATM-NH3: a model combining the surface energy balance and bi-directional exchanges of ammonia applied at the field scale, Biogeosciences, 6, 1371–1388, doi:10.5194/bg-6-1371-2009, 2009.

Pienaar, J. J.: Proposal of a new IGAC II task: DEBITS II (Deposition of Biogeochemically Important Trace Species), available at: www.igacproject.org/DEBITS, 2005.

Pineda Rojas, A. L. and Venegas, L. E.: Atmospheric deposition of nitrogen emitted in the Metropolitan Area of Buenos Aires to coastal waters of de la Plata River, Atmos. Environ., 43, 1339–1348, 2009.

Raivonen, M., Vesala, T., Pirjola, L., Altimir, N., Keronen, P., Kulmala, M., and Hari, P.: Compensation point of NO_x exchange: net result of NO_x consumption and production, Agr. Forest. Meteorol., 149, 1073–1081, doi:10.1016/j.agrformet.2009.01.003, 2009.

Rodhe, H., Dentener, F., and Schulz, M.: The global distribution of acidifying wet deposition, Environ. Sci. Technol., 36, 4382–4388, 2002.

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, doi:10.5194/acp-7-5415-2007, 2007.

Samain, O., Kergoat, L., Hiernaux, P., Guichard, F., Mougin, E., Timouk, F., and Lavenu, F.: Analysis of the in situ and MODIS albedo variability at multiple timescales in the Sahel, J. Geophys. Res., 113, D14119, doi:10.1029/2007JD009174, 2008.

Schwede, D., Zhang, L., Vet, R., and Lear, G.: An intercomparison of the deposition model used in the CASTNET and CAPMoN networks, Atmos. Environ., 45, 1337–1346, 2011.

Seinfeld, J. and Pandis, S.: Atmospheric Chemistry and Physics: From Air Pollution to Climate Change, John Wiley and Sons, 2nd Edition, 1203 pp., 2006.

Sentelhas, P. C., Marta, A. D., Orlandini, S., Santos, E. A., Gillespie, T. J., and Gleason, M. L. : Suitability of relative humidity as an estimator of leaf wetness duration, Agr. Forest Meteorol., 148, 392–400, 2008.

Serça, D.: Echanges biosphère-atmosphère de composés de l'azote en milieu tropical, Ph.D. thesis, Université Paul Sabatier-Toulouse III, France, 1995.

Shalaby, A., Zakey, A. S., Tawfik, A. B., Solmon, F., Giorgi, F., Stordal, F., Sillman, S., Zaveri, R. A., and Steiner, A. L.: Implementation and evaluation of online gas-phase chemistry within a regional climate model (RegCM-CHEM4), Geosci. Model Dev., 5, 741–760, doi:10.5194/gmd-5-741-2012, 2012.

Shen J. L., Tang, A. H., Liu, X. J., Fangmeier, A., Goulding, K. T. W., and Zhang, F. S.: High concentrations and dry deposition of reactive nitrogen species at two sites in the North China Plain, Environ. Pollut., 157, 3106–3113, 2009.

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.

Sorimachi, A., Sakamoto, K., Ishihara, H., Fukuyama, T., Utiyama, M., Liu, H., Wang, W., Tang, D., Dong, X., and Quan, H.: Measurements of sulfur dioxide and ozone dry deposition over short vegetation in northern China – a preliminary study, Atmos. Environ., 37, 3157–3166, 2003.

Sparks, J. P., Monson, R. K., Sparks, K. L., and Lerdau, M.: Leaf uptake of nitrogen dioxide (NO_2) in a tropical wet forest: implications for tropospheric chemistry, Oecologia, 127, 214–221, 2001.

Spindler, G., Teichmann, U., and Sutton, M. A.: Ammonia dry deposition over grassland – micrometeorological flux-gradient measurements and bidirectional flux calculations using an inferential model, Q. J. Roy. Meteor. Soc., 127, 795–814, 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, doi:10.5194/acp-8-2285-2008, 2008.

Stella, P., Personne, E., Loubet, B., Lamaud, E., Ceschia, E., Beziat, P., Bonnefond, J. M., Irvine, M., Keravec, P., Mascher, N., and Cellier, P.: Predicting and portioning ozone fluxes to maize crops from sowing to harvest: the surfatm-O_3 model, Biogeosciences, 8, 2869–2886, doi:10.5194/bg-8-2869-2011, 2011.

Sutton, M. A., Fowler, D., Burkhardt, J. K., and Milford, C.: Vegetation atmosphere exchange of ammonia: Canopy cycling and the impacts of elevated nitrogen inputs, Water Soil Air Pollut., 85, 2057–2063, 1995.

Sutton, M. A., Burkhardt, J. K., Guerin, D., Nemitz, E., and Fowler, D.: Development of resistance models to describe measurements of bi-directional ammonia surface-atmosphere exchange, Atmos. Environ., 32, 473–480, 1998.

Sutton, M. A., Nemitz, E., Erisman, J. W., Beier, C., Butterbach Bahl, K., Cellier, P., de Vries, W., Cotrufo, F., Skiba, U., DiMarco, C., Jones, S., Laville, P., Soussana, J. F., Loubet, B., Twigg, M., Famulari, D., Whitehead, J., Gallagher, M. W., Neftel, A., Flechard, C. R., Herrmann, B., Calanca, P. L., Schjoerring, J. K., Daemmgen, U., Horvath, L., Tang, Y. S., Emmett, B. A., Tietema, A., Penuelas, J., Kesik, M., Brueggemann, N., Pilegaard, K., Vesala, T., Campbell, C. L., Olesen, J. E., Dragosits,

U., Theobald, M. R., Levy, P., Mobbs, D. C., Milne, R., Viovy, N., Vuichard, N., Smith, J. U., Smith, P., Bergamaschi, P., Fowler, D., and Reis, S.: Challenges in quantifying biosphere atmosphere exchange of nitrogen species, Environ. Pollut., 150, 125–139, 2007.

Sutton, M. A., Reis, S., Riddick, S., Dragosits, U., Nemitz, E., Theobald, M. R., Tang, S., Braban, C. F., Vieno, M., Dore, A. J., Mitchell, R. F., Wanless, S., Daunt, F., Fowler, D., Blackall, T., Milford, C., Flechard, C., Loubet, B., Massad, R. S., Cellier, P., Clarisse, L., van Damme, M., Ngadi, N., Clerbaux, C., Skjøth, C., Geels, C., Hertel, O., Wichink Kruit, R. J., Pinder, R. W., Bash, J. O., Walker, J. D., Simpson, D., Horvath, L., Misselbrook, T., Bleeker, A., Dentener, F., and de Vries, W.: Towards a climate-dependent paradigm of ammonia emission and deposition, Phil. Trans. R. Soc. B, 368, 20130166, doi:10.1098/rstb.2013.0166, 2013.

Takahashi, A., Sato, K., Wakamatsu, T., and Fujita, S.: Atmospheric deposition of acidifying components to a Japanese cedar forest, Water Air Soil Pollut., 130, 559–564, 2001.

Takahashi, A., Sato, K., Wakamatsu, T., Fujita, S., and Yoshikawa, K.: Estimation of dry deposition of sulfur to a forest using an inferential method. Influence of canopy wetness on SO_2 dry deposition, Journal of Japan Society for Atmospheric Environment, 37, 192–205, 2002.

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, doi:10.5194/acp-6-447-2006, 2006.

Tsai, J. L., Chen, C. L., Tsuang, B. J., Kuo, P. H., Tseng, K. H., Hsu, T.F., Sheu, B. H., Liu, C. P., and Hsueh, M. T.: Observation of SO_2 dry deposition velocity at a high elevation flux tower over an evergreen broadleaf forest in Central Taiwan, Atmos. Environ., 44, 1011–1019, 2010.

van Breemen, N.: Acid Sulfate Weathering, Soil Science Society of America, Madison, Wisconsin, 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.

Vitousek, P. M., Aber, J. D., Howarth, R. W., Likens, G. E., Matson, P. A., Schindler, D. W., Schlesinger, W. H., and Tilman, D. G.: Human alteration of the global nitrogen cycle: sources and consequences, Ecol. Appl., 7, 737–750, 1997.

Walker, J. T., Robarge, W. P., Wu, Y., and Meyers, T. P.: Measurement of bi-directional ammonia fluxes over soybean using the modified Bowen-ratio technique, Agr. Forest Meteorol., 138, 54–68, doi:10.1016/j.agrformet.2006.03.011, 2006.

Wesely, M. L.: Parameterization of surface resistances to gaseous dry deposition in regional-scale numerical models, Atmos. Environ., 23, 1293–1304, 1989.

Wesely, M. L. and Hicks, B. B.: A review of the current status of knowledge in dry deposition, Atmos. Environ., 34, 2261–2282, 2000.

Wichink Kruit, R. J., van Pul, W. A. J., Otjes, R. P., Hofschreuder, P., Jacobs, A. F. G, and Holtslag, A. A. M.: Ammonia fluxes and derived canopy compensation points over non-fertilized agricultural grassland in The Netherlands using the new gradient ammonia-High accuracy-Monitor (GRAHAM), Atmos. Environ., 41, 1275–1287, doi:10.1016/j.atmosenv.2006.09.039, 2007.

Wichink Kruit, R. J., Jacobs, A. F. G., and Holtslag, A. A. M.: Measurements and estimates of leaf wetness over agricultural grassland for dry deposition modeling of trace gases, Atmos. Environ., 42, 5304–5316, 2008.

Wichink Kruit, R. J., van Pul, W. A. J., Sauter, F. J., van den Broek, M., Nemitz, E., Sutton, M. A., Krol, M., and Holtslag, A. A. M.: Modelling the surface-atmosphere exchange of ammonia, Atmos. Environ., 44, 945–957, 2010.

Wichink Kruit, R. J., Schaap, M., Sauter, F. J., van Zanten, M. C., and van Pul, W. A. J.: Modeling the distribution of ammonia across Europe including bi-directional surface-atmosphere exchange, Biogeosciences, 9, 5261–5277, doi:10.5194/bg-9-5261-2012, 2012.

Wolff, V., Trebs, I., Foken, T., and Meixner, F. X.: Exchange of reactive nitrogen compounds: concentrations and fluxes of total ammonium and total nitrate above a spruce canopy, Biogeosciences, 7, 1729–1744, doi:10.5194/bg-7-1729-2010, 2010.

Yang, W., Shabanov, N., V., Huang, D., Wang, W., Dickinson, E. R., Nemani, R. R., Knyazikhin, Y., and Myneni, R. B.: Analysis of leaf area index products from combination of MODIS Terra and Aqua data, Remote Sens. Environ., 104, 297–312, 2006.

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.

Zeller, K. F. and Nikolov, N. T.: Quantifying simultaneous fluxes of ozone, carbon dioxide and water vapor above a subalpine forest ecosystem, Environ. Pollut., 107, 1–20, 2000.

Zhang, L., Moran, M., Makar, P., Brook, J., and Gong, S.: Modelling Gaseous Dry Deposition in AURAMS A Unified Regional Air-quality Modelling System, Atmos. Environ., 36, 537–560, 2002a.

Zhang, L., Brook, J., and Vet, R.: On Ozone dry deposition with emphasis on non-stomatal uptake and wet canopies, Atmos. Environ., 36, 4787–4799, 2002b.

Zhang, L., Brook, J., and Vet, R.: Evaluation of a non-stomatal resistance parameterization for SO_2 dry deposition, Atmos. Environ., 37, 2941–2947, 2003a.

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, doi:10.5194/acp-3-2067-2003, 2003b.

Zhang, L., Brook, J. R., Vet, R., Wiebe, A., Mihele, C., Shaw, M., OBrien, J. M., and Iqbal, S.: Estimation of contributions of NO_2 and PAN to total atmospheric deposition of oxidized nitrogen across Eastern Canada, Atmos. Environ., 39, 7030–7043, 2005.

Zhang, L., Vet, R., OBrien, J. M., Mihele, C., Liang, Z., and Wiebe, A.: Dry deposition of individual nitrogen species at eight Canadian rural sites, J. Geophys. Res., 114, D02301, doi:10.1029/2008JD010640, 2009.

Zhang, L., Wright, P. L., and Asman, W. A. H.: Bi-directional air surface exchange of atmospheric ammonia – A review of measurements and a development of a big-leaf model for applications in regional-scale air-quality models, J. Geophys. Res., 115, D20310, doi:10.1029/2009JD013589, 2010.