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Atmospheric
Chemistry
and Physics
Discussions

Interactive comment on "Long term measurements of sulfur dioxide, nitrogen dioxide, ammonia, nitric acid and ozone in Africa using passive samplers" by M. Adon et al.

Response to reviewer's comments First of all, we would like to thank the two reviewers for their comments. The two reviewers propose a list of small changes dealing with edition, English style, errors in the text. Moreover, a number of precision on the experimental method including the validation and the measurements uncertainties are required. We have revised our paper taking into account all reviewer's comments. Here are the modifications on the paper in respect with the different remarks.

Anonymous Referee #1

Page 4421: The references Ferm et al. (2005) and Ferm and Rodhe (1997) are both cited to give examples in the literature of HNO_3, SO_2, NO_2, and NH_3 measurements in tropical or subtropical areas (and not only nitric acid). These references are cited in this section of the paper to mention the use of the passive sampling technique with tests and validations performed for different gases and over different regions of the word. On page 4428, we cite other references (Gupta et al., 2003; Tidblad et al., 2007; Ferm et al., 2005) to give specifically comparison of HNO_3 concentrations measured in IDAF African sites and other regions of the word.

Page 4422: section 3 results

We have written that the results show that monthly HNO_3 evolution is highly comparable to NO_2 monthly evolution, and thus follow the same gradient. As the reviewer said, we are aware that using passive samplers, it exists a potential interference between Nitric acid and NO_2. In the analytical process of the nitric acid passive sampler, we can have an idea of this interference. First, concerning the trapping of these two gases, i.e, NO_2 and HNO_3 :

* The presence of sodium hydroxide (NaOH) in the impregnation solution (see Table 3) aims to maintain a strongly basic pH (pH> 12) and thus limits the oxidation of nitrite ion NO_2^- to nitrate ion NO_3^-.

* In addition, we know that NaOH molecules react with atmospheric CO_2 to form water molecules that favour (or further) NO_2 retention on the filter. Then, the choice of this basic solution allows simultaneous to capture on Whatman filter other acid gases such as HNO_3.

Secondly, concerning the analysis of these two samplers in ionic chromatography:

* Nitrate ions NO_3^- were detected in IC for the NO_2 filters analysis with very low values of ppb. We only use nitrite NO_2^- ions results to estimate the concentrations of gaseous NO_2.

* In the case of HNO_3 filters, nitrite ions (NO_2^-) were not detected or at least, they are below the detection limit. So, in our opinion, the concentrations of HNO_3 do not suffer of too much interference from NO_2 or we assume that this interference is negligible.

* To give an order of magnitude of the ratio between nitrite (NO_2^-) and nitrate (NO_3^-) ions detected in IC for NO_2 filters, Table 1 indicates results for the Lamto site: IC results in µg/L, concentration in air (ppbv) and the ratio in %. This ratio is estimated around 6% (ppbv air).

Table1

NO2 sampler	Concentration(µg/L)			Concentration(ppbv)		
	NO2_NO2$^-$	NO2_NO3$^-$	Ratio (%)	NO2_NO2$^-$	NO2_NO3$^-$	Ratio (%)
La0107	372	51	13,78	2,41	0,22	8,94
La0107	365	41	11,15	2,36	0,15	6,46
La0207	378	46	12,19	2,47	0,19	7,54
La0207	332	37	11,17	2,15	0,13	6,15
La0307	310	29	9,42	1,98	0,08	4,25
La0307	310	28	9,01	1,98	0,08	3,88
La0407	199	27	13,37	1,13	0,06	5,63
La0407	252	33	13,21	1,47	0,10	6,85
Mean	**314,7**	**36,5**	**11,7**	**2,0**	**0,1**	**6,2**

Section 2.4.1 Determination of the L/A parameter

Most of the validation work of the IDAF passive sampler have been done during two PhD studies : Al-Ourabi Hammoud in 2002 at University Paul-Sabatier (France) and Dhammapala (1996) at the Potchefstroom University (South Africa). We have added these two references in the paper:

*Dhammapala R**.,:** Use of passive samplers for the sampling of atmospheric pollutants**.** M.Sc. thesis, Potchefstroom University for CHE**,** South Africa, 1996.

*Al-Ourabi, H.: Etude expérimentale de gaz azotés, du dioxide de soufre et de l'ozone à l'échelle des écosystèmes de l'Afrique tropicale: Application à l'estimation des dépôts secs gazeux dans le cadre du réseau IDAF, PhD, Univerité Paul Sabatier-Toulouse III, 2002.

To give more details about the determination of the laminar boundary layer (Lc):

In the paper, we have summarized the experimental determination of Lc (page 4419) giving the principle. We don't think that it is necessary to add in our text all the following equations but to answer to the reviewer; here is the description of the method:

For a sampler mounted "normally" (ie, with the impregnated filter normally mounted at the bottom of the sampler), the diffusion distance of the gas inside the sampler corresponds to the thickness of the laminar boundary layer and in this case to the length of the ring, which is translated mathematically by:

$(L / A)_1 = (La / Aa + Lf / Lg + Af / Ag + Lc / At)$ and $C_1 = [(L / A)_1 . X_1] / (tD)$

For a sampler mounted with the impregnated filter directly at the inlet (of the sampler), the diffusion distance of the sampler is equal to the thickness of the laminar boundary layer (in this case the ring is remove). We obtain:

$(L / A)_2 = (0 + Lf / Lg + Af / Ag + Lc / At)$ and $C_2 = [(L / A)_2 . X_2] / (tD)$

In theory, as both samplers are simultaneously exposed, we measure the same gas concentration thus: $C_1 = C_2$

After all development, we get:

$$Lc = A_t\left[\frac{(La/Aa).X_1}{X_2 - X_1} - (Lf/Af + Lg/Ag)\right]$$

$$L/A = (La/Aa).\left[1 + \frac{X_1}{X_2 - X_1}\right]$$

Where X_1 is the number of gas molecules trapped on the filter when it is mounted normally (mol) and X_2 the number of gas molecules trapped on the filter mounted against the grid (mol). A total of two hundred samplers have been exposed, about 50 for each color and gases. The synthesis of all the results is presented in table 4 of our paper. We add in the text the number of samplers (N) used in the experience and we remove the percentage given for the uncertainty (also removed in the text). The standard deviation gives already an idea of the uncertainty on the L/A value.

Concerning the experimental conditions. The experience was performed in the field on the instrumented terrace of Laboratory of Aerology in Toulouse at low wind speed. This is consistent with the wind speed measured at the IDAF sites which are generally low: around 1 m/s at 2 m height. The wind is an important factor; it can lead molecular diffusion from a laminar regime to a turbulent regime and overestimate the results by dramatically increasing the amounts of collected molecules. A sufficient number of experiments allowed us to eliminate some outliers and thus overcome problems related to experimental conditions. To apply the Fick's first law, diffusion of the gas through turbulence, convection and rotation in the sampler must be negligible. This is achieved by the use of a membrane filter and metal mesh placed at the entrance of the sampler. Moreover, samplers open side are placed down in a hooded sampler holder.

Page 4418 : detection limits For each set of measurements, we prepare two months of passive samplers to be sent on each site. It represents 4 samplers for each gas (3 samplers for O_3, NH_3, NO_2 and one sampler for both HNO_3 and SO_2) and a total of 16 passive samplers for the 4 gases (duplicate for 2 months). For the 7 sites of the network, 28 samplers are sent for one gas. At the same time, 7 blanks samplers for each gas are prepared (total 28 blanks samplers). On this total, 8 blanks are kept in the lab and 20 blanks are sent on 5 different sites. We consider that the field blanks are valid for each set of measurements. All the field blanks are analyzed with the same delay than exposed samplers. In this paper, detection limits of each trace gas are the average of 23 series of measurements (1998-2007).

Page 4420:

Ozone ratio There is a mistake on figure 3 of the paper. Axes have been reversed by error. We have done the correction in the revised version of the paper. The mean ratio of concentrations (passive sampler/active sampler) is now 0.7 for ozone.

Interference (NO_2, O_3) We assume that the coating solution used in the IDAF passive samplers have been specifically chosen, to chemisorb targeted species into another stable species in which other pollutants do not interfere. We have decided to add one sentence in our paper p4416 line 21 to cite key references in the choice of these coating solution (test of efficiency…): WMO, 1997; Ferm, 1991, Ferm and Svanberg, 1998, Dhammapala, 1996, Ourabi, 2002; Ferm and Rodhe, 1997).
We remind here that the work presented in this paper is part of the international DEBITS program. DEBITS has adopted the pioneer work of Ferm to develop the DEBITS gas passive sampler and has followed the methodology described in the WMO TD n°829.

Page 4421: Correlation of NH_3 between IDAF and IVL passive samplers According the reviewer comment, we have modified our text with this new sentence: Figure 4 details the NH_3 results and the correlation (R^2=0.76) shows an indicative measurement with 24 % accuracy between the two samplers.

Page 4423 maximum of NO_2 In the Sahelian region, ammonium and nitrate ions are accumulated in soils from grazing, manure application and decomposition of crop residues. NO biogenic emissions are caused by microbes in the soil that are water-stressed and remain dormant in dry periods. The microbes are activated by the first rains of the season and metabolise accumulated nitrogen (as ammonium and nitrate ions) in the soil leading to NO as one of the by-products, which is then emitted into the atmosphere. Although emissions from soils are in the form of NO, once in the atmosphere NO is rapidly converted to NO_2 by reaction with ozone. So, the maximum of NO_2 is consistent with the emission of inorganic nitrogen that accumulated in soils.

Misprints have been taken into account as follow:
Page 4411 : Realistic dry deposition velocity according to the site and the species needs to be determined
Page 4418 -MΩ changed by MΩ .cm (ultra pure water resistivity)
- cation detection changed by ammonium detection (all other being anions)
Page 4435 cm-^{1} changed by cm.s^{-1}
Page 4436 : the sulphur content of vegetation
Page 4449 Table 1 Côte d'Ivoire changed by Cote d'Ivoire (but we keep the French name of the country)**,** Zoétélé changed by Zoetele (in table 1 and table 5).

Response to the Anonymous Referee #2

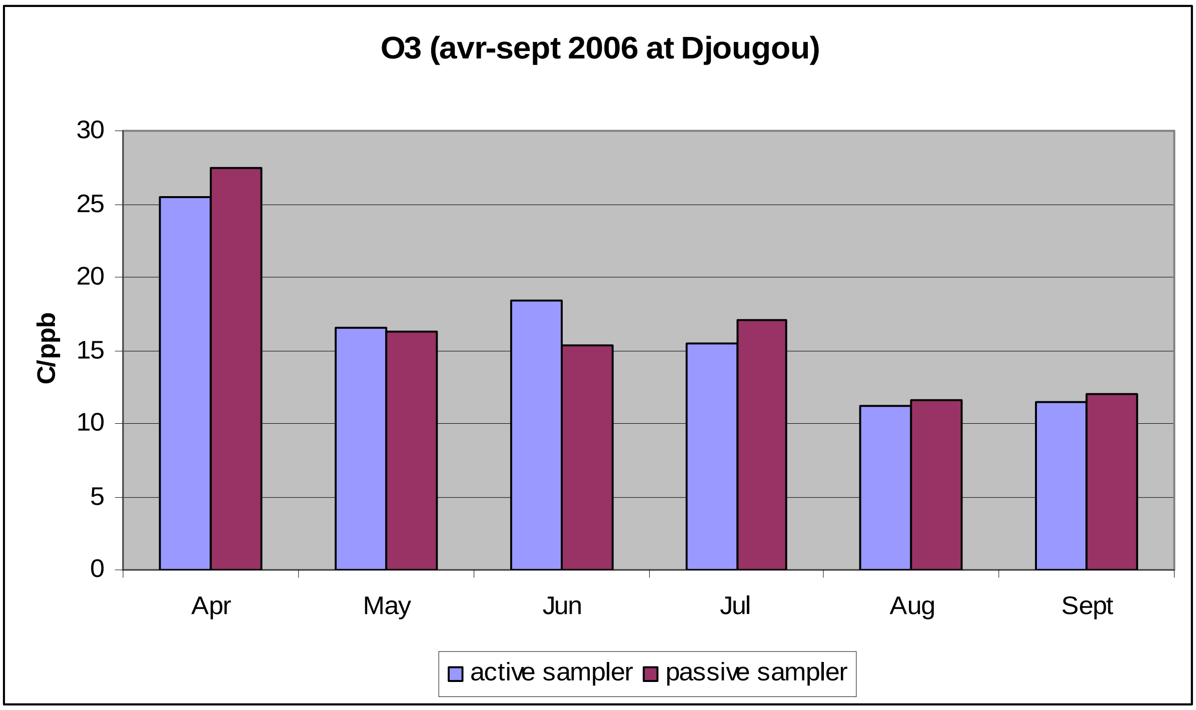
Comments on passive samplers technique

Humidity and sampling efficiency

The reviewer suggests that a comparison with active measurements of ozone should give some information. First, we have to say that O_3 measurements are scarce on the African continent. To our knowledge, we have tried to mention in the ozone section page 4429 all the references specific to natural African sites comparable to the present IDAF studied sites. We cite the work of Cros (1997) in the equatorial forest of Congo where ozone concentrations (with an active analyzer) compare quite well with mean IDAF passive samplers concentrations (<5ppb).
Moreover, to give another element of answer to the reviewer, we have done the comparison of mean monthly ozone concentrations measured with an active analyzer during the AMMA experiment (Serça et al., 2007). IDAF passive samplers and active analyzer measurements have been compared for the wet season from April to September 2006 for the site of Djougou (wet savanna of Benin) (see Figure 1). We observe that ozone monthly mean concentrations (ppb) are comparable with a mean variation around 5.6%.

Second International AMMA Conference, Karlsruhe, Germany, November 26-30 2007, EOP ground-based measurements at the Nangatchori (Benin) AMMA site: a seasonal overview, D. Serça, F. Lohou, B. Pospischal, L. Blarel, H. Cachier, B. Campistron, P. Castera, S. Crewell, S. Galle, C. Galy-Lacaux, P. Goloub C. Liousse, E. Gardrat, M. Gosset, F. Goutail, M. Mallet, A. Mariscal, J. Pelon, A. Poirson, V. Pont, J. Sciare, and D. Tanré

Figure 1



Stability and microbial activity We have no elements to discuss about nitrogen degradation trapped on filters. We can only said that samples are stored before and after sampling in a refrigerated place (4°C) to minimize bacterial decomposition or other reactions. We assume that the order of magnitude of measured gases concentrations are correct (with given uncertainties) according the results interpretation in agreement with major atmospheric processes (example: soil NOx emission pulse at the beginning of the rainy season…).
Stainless steel mesh It could be possible that the contact of gaseous ammonia and nitric acid ratios are unstable when enclosed in stainless steel walls. The use of stainless steel mesh, during the sampling, is important to protect the membrane from mechanical damage. After exposition, the samplers are stored in a fridge then the filters are removed from the samplers and analyzed to minimize any instability or oxidation of NH_3, HNO_3. Experiments by Ferm and Svanberg (1998) showed that covering the sampler inlet region with a fine mesh (stainless steel mesh) can also minimize the errors of concentrations overestimation for high-dose samplers. We added in our text this reference:
Ferm, M., and Svanberg, P.-A.: Cost-effective techniques for urban and background measurements of SO_2 and NO_2, Atmos. Environ., 32, 1377-1381, 1998.

Table 3, coating solution The coating solution is $NaNO_2$ (Sodium nitrite) and not NONO2.

Question about Interference A comment on interferences is provided in the reviewer 1 response, please refer to the comment noted page 4422 , 4420.

Saturation: The highest concentration that can be measured depends on the amount of sorbent on the impregnated filter. This is typically estimated by the stoichiometric amount of the impregnation reduced by a safety factor (typically of 2) (Ferm and Rodhe, 1997: Carmichael et al., 2003). During one month sampling at rural sites (IDAF), we assume that we do not reach the upper limit. In the POLCA program initiated in 2009, we have done passive samplers measurements in urban site (Bamako and Dakar) to estimate the maximum concentrations that can be determined before sampler saturation.

Correlation of NH_3 between IDAF and IVL passive samplers
Please, see the response to the first reviewer (page 4421)

Wind velocity
Please, see response to reviewer 1 (experimental conditions)
The wind velocity could be critical but in tropical Africa ecosystems, wind speed is generally low.

Sampling height
For all the network sites the sampling height is between 1.5 m and 2 m for the savannas. In the forested ecosystems , the sampling height is about 3m. We specify the height in the revised paper.

MEGATEC continuous analyzer(s)
For the comparison of gases measured by the two methods, the active analyzers used are:

- NO_2 : Model 42C-TL (Trace Level) , chemiluminescence
- SO_2 : MEGATEC 43i , pulsed UV fluorescence
- O_3 : MEGATEC 49i , UV photometry

As asked, the physico-chemical principle cited here are now included in the revised paper.

Lc factor: see response to reviewer I (Section 2.4.1 Determination of the L/A parameter)
It could be possible that the Lc factor overestimates results but we think that the sampling of NO_2, SO_2 and O_3 by IDAF passive samplers are not overestimated. To answer to reviewer 2 on this point, we have also to mention an error on the axes of Figures 3 that should be reversed. Correction is done in the revised paper version.

Moreover, the section (2.4.2) presents the comparison of gases concentrations (NO_2, SO_2 and O_3) measured with IDAF passive samplers and with active analyzers. Correlations are acceptable (R2= 0.95; 0.9; 0.8 respectively). The ratios (passive sampler/active sampler) equal to 0.9; 0.8; 0.7 for NO_2, SO_2, O_3 , respectively, show that concentrations measured with active analyzers are slightly higher than those measured with IDAF samplers. Although the concentrations of NH_3 measured with IDAF samplers are higher than those measured with IVL Swedish samplers.

Another part: HNO_3 and NH_3
The reviewer mentions certainly the equilibrium between HNO_3 and NH_3 to form ammonium nitrate. It is important to note that in the passive sampler technique, the adsorption of particles is minimized using a Teflon filter at the inlet. Moreover, the overestimation of NH_3 concentrations is well known after particulate contamination and decomposition on the filter that traps ammonia. To avoid this positive artefact, a special procedure is applied to the white NH_3 passive sampler. Just after the end of the exposure, we remove the inlet part of the sampler: the cap, the steel mesh and the Teflon filter to be immediately replaced by a closed cap. It avoids the filter contamination by ammonium particles before the analysis.
This procedure has not been described in our paper and is very specific to NH_3 sampler. We decided to add few lines in section 2.3.1 to explain it.

We would like also to cite the recent paper published in ACP by Delon et al 2010 (cited in this paper) that presents a first estimation of the nitrogen atmospheric budget. This work used IDAF gases HNO_3, NO_2 and NH_3 concentrations performed in the Sahelian sites. In the following, the budget is calculated first for oxygenated N compounds (NOx for emissions, NO_2, HNO_3 and NO_3^- for deposition) at the monthly and annual scale for the year 2006, and second for NHx products (NH_3, NH_4^+) at the annual time scales. Not all the nitrogen gaseous compounds are taken into account in this budget, but the main species are represented and a nitrogen compounds budget is calculated at the 3 IDAF stations, and scaled up to the Sahelian regional scale. In this work we mention that the exchange of NH_3 appears to behave as if a compensation point exists: NH_3 is both emitted and deposited. The direction of the net flux will depend on the strength of the volatilization process and environmental conditions. The NH_3 compensation point has been widely studied for temperate climate vegetation (Sutton et al. (2007).

Particulate N dry deposition (pNH_4^+ and pNO_3^-) is also not taken into account in this budget. But we have informations to say that particle concentrations have been measured in Banizoumbou and Katibougou, and are very low: $pNH_4^+ = 0.31 \pm 0.02$ ppb and $pNO_3^- = 0.16 \pm 0.03$ ppb in Banizoumbou, $pNH_4^+ = 0.17 \pm 0.06$ ppb and $pNO_3^- = 0.23 \pm 0.06$ ppb in Katibougou. The comparison of these concentrations with NH_3 concentrations in both sites (2.9 to 10.4 ppb in Banizoumbou, 1.8 to 6.9 ppb in Katibougou, and 3.5 to 10.5 ppb in Agoufou) leads to the conclusion that particulate deposition is negligible. As far as the authors know, no other particulate dry deposition measurements have been made in the remote regions of Sahel. Finally it is important to keep in mind the uncertainty given for the NH_3 sampler : 14.3%.

Additional points:

Page 4409/line=29 : IDAF site web: http://medias.obs-mip.fr/idaf/

Page 4414/10: Gourma is a region of Mali

Page 4414/25 and following Zoétélé changed by Zoetele

Page 4416/5 L, A, t, and D are added in the explanation in the paper

Page 4416/16: The reference Al-Ourabi, 2002 is added P4419 section 2.4.1 and in table 3

Page 4416/17 whatman changed by Whatman

Page 4421/15 Rondon reference have been removed (no link with passive sampler).

Page 4426/26 : Trischardt changed by Trichardt

Page 4427/28 : shown changed by deduced

Page 4428/16 : We are interested using these corrosion studies in this paper because there give unique informations of background nitric acid concentrations levels.

Page 4429/25: katibougou changed by Katibougou.

Page 4431/20 : Within IDAF framework, we measure trace gases of French Guayana but we not published the measurement yet (personal communication)

Page 4438/25: We have decided to keep 'however….' In the last paragraph of the paper. The aim here is to present future studies linked to this paper that presents remote sites gases concentrations in Africa. We want to emphasize the interest to study both remote and urban sites on the same continent.

Page 4447/32 : Williams et al. (1992) is now placed in the correct alphabetic order.

Page 4448/2 : Zhang wrote two papers in 2003 and the first is
Zhang, L, Brook, J., and Vet, R.: Evaluation of a non-stomatal resistance parameterization for SO_2 dry deposition, Atmos. Environ., 37, 2941-2947, 2003. So we decided to reference b the second Zhang paper.

We sincerely hope that you will consider our responses and modifications of the paper as acceptable. With many thanks, Regards

Marcellin Adon and Corinne Galy-Lacaux