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Atmospheric Chemistry and Physics
Discussions

Interactive comment on "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" *by* M. Adon et al.

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Reviewer's comments on ACP manuscript acp-2013-187:

"Dry deposition of nitrogen compounds (NO2, HNO3, NH3), sulfur dioxide and ozone in West and Central African ecosystems using the inferential method" By Adon et al.

General comments

This paper reports the results of a modelling exercise aiming to estimate atmospheric

dry deposition inputs of reactive nitrogen, SO2 and O3 to semi-natural African ecosystems. The authors use long-term datasets of NH3, HNO3, NO2, SO2 and O3 measured by passive samplers (published earlier in Atmos. Chem. Phys., 10, 7467–7487, 2010), coupled to meterology and an inferential dry deposition model (Zhang et al, Atmos. Chem. Phys. 3, 2067-2082, 2003), to compute estimates of dry deposition.

There is no doubt that much research and monitoring is needed on atmospheric pollutants (and in particular reactive nitrogen) concentrations and fluxes in Africa and in the tropics generally, and to that extent a paper on long-term concentrations and fluxes is useful. There is no major flaw in this paper, which is competently written. However this manuscript fails to a large extent to address key questions related to surface/atmosphere Nr and O3 exchange, namely: the uncertainty in modelled fluxes; the comparison to measured fluxes; the gain in knowledge on exchange processes in the tropics; the improvement of parameterizations for tropical conditions in surface exchange models.

In addition, most of the data in this paper have been published in one form or another in previous papers: long-term passive sampler concentrations in Adon et al, Atmos. Chem. Phys., 10, 15 7467–7487, 2010; dry deposition in West African and in Sahelian ecosystems, based on the same methodology, concentration data and at the same sites, in Delon et al, Biogeosciences, 9, 385–402, 2012 and in Delon et al., Atmos. Chem. Phys., 10, 2691–2708, 2010, respectively. In its present shape the paper contributes little advancement over the previous papers published by the same group, or to surface/atmosphere flux modelling or process understanding in general.

The present manuscript describes in much detail the methodology for deriving model input data, but the description of modelled fluxes is rather heavy and lacks a clear synthesis, while the discussion does not assess the modelling results critically enough. Inferential models suffer notoriously large uncertainties in the best of cases (ie in regions of the world -N. America, Europe - where fluxes have often been measured, e.g. Flechard et al., Atmos. Chem. Phys., 11, 2703–2728, 2011), not to mention the situation in the tropics, for which they have hardly been parameterized. My overall impression is that savannah sites are likely to be NH3 sources at least part of the time (as suggested by consistent positive vertical gradients measured at Banizoumbou - see p11700) and that treating the surface as a permanent NH3 sink is misguided. The authors do acknowledge that savannah ecosystems do emit NH3 through grazing animals and soil turnover, but then go on, rather counter-intuitively and illogically, to treat NH3 surface exchange uni-directionnally (dry deposition), turning savannah into a net sink. At the very least they should attempt some sort of net NH3 budget accounting for soil+animal emissions and deposition on the other hand, or better, using a bi-directional model. I would certainly question the assertion made in the paper (and particularly Fig. 7) that NH3 is the dominant atmospheric N source for all these ecosystems.

The paper could be improved in several ways:

i) The results section should be streamlined; there is much material that feels repetitive and is tiresome to read

ii) While it is clear that no actual flux measurements were carried out in this study and these datasets cannot be used to derive improved parameterisations for models, still a comparison of different existing inferential models would provide an indication of the modelling uncertainties. I disagree with the proposed "uncertainty of about 30% for all the dry deposition models" as suggested on p11702; in my view the uncertainty is much larger for individual compounds, possibly up to 100-200% in some cases, especially considering that the model used here does not allow for NH3 or NOx bi-directional exchange. One thing that could be done easily, and at little cost, is to expand, for a start, the comparison to modelled fluxes in Delon et al. (2010,2012), which were based on the Wesely 1989 model. This comparison is rather laconic, only a couple of sentences on Vd on p 11702 (l3-7). Instead of the whole series of identical figures (Fig. 4, 5, 6, 8, 9) for the different chemical species, compared estimates by the two models would be more informative.

In addition, and more importantly, it would not mean much additional work to apply the NH3 bi-directional scheme by Zhang et al., JGR 115, D20310, 2010 (cited in the references), since this is based on the same overall framework (land use classes, Ra, Rb, etc) as Zhang et al 2003. The Massad et al., Atmos. Chem. Phys., 10, 10359–10386, 2010 bi-directional NH3 model could also easily be applied, again realizing that tropical flux data are under-represented in the datasets that led to the parameterizations, but still conceptually representing a step forward from the classical Rc/Vd approach, providing a range of estimates and a model ensemble-based uncertainty approach.

iii) There are, or have been, a range of published tropical flux measurements for HNO3, NO2, NH3, SO2 and O3, some of which the authors refer to in the discussion, e.g. in Thailand, Brazil, Borneo, and over various land uses, e.g. pasture, rainforest. Instead of comparing annual fluxes, the authors could assemble a summary (table or figure)of published tropical Vd mean/range values for the different ecosystem types, climates and chemical species, and then compare modelled Vd outputs using a range of models. The model/measurement comparison across sites is more straightforward using Vd than using annual mean fluxes, as Vd values are essentially fluxes normalized for concentrations. If the transfer is bi-directional, a Vtr concept (transfer velocity, positive or negative for deposition or emission) can be used, as in Trebs et al., Atmos. Chem. Phys., 6, 447–469, 2006. A targeted and comprehensive literature survey and summary of published tropical Vd/Vtr values would be really helpful to assess model performance in this African case, and certainly of great interest for the wider community.

Specific comments

p11692, l24-29: This sentence seems to imply that, in the authors mind, an inferential model necessarily means a dry deposition-only, Rc-Vd approach, and thus excludes any bi-directional, compensation point scheme. The conventional definition of an inferential model is not related to its structure or the degree of model complexity (a compensation point model can be applied inferentially), merely that the model is applied to simulate fluxes on the basis of field measured concentrations, not as part of a wider modelling scheme such as a chemical transport model (CTM). A surface exchange model is not inferential per se, only through the way it is applied when based on measured concentrations at a range of individual field sites.

P11694, l11-18: “The inferential method, i.e., an atmospheric species dry deposition flux being estimated as a product of its air concentration by modelled dry deposition velocity”: same comment as above. Inferential methods does not necessarily mean deposition velocity. Please rephrase.

P11694-5: “To give an indication of the precision of this sampling technique, the covariance of all duplicate samples over the studied period were foundto be 20 %, 9.8 %, 14.3 %, 16.6% and 10% for HNO3, NO2, NH3, SO2 and O3 respectively”. This is indeed an indication of precision, but the HNO3 case, which has interferences by at least NOx and HONO, and suffers surface interactions such as deposited aerosol nitrate evaporation, generally represents an over-estimate.

P11695, l21-26: apparent contradiction between “the shrub and tree savannas were assigned to grassland LUC (long grass)” and “for the tree and shrub savannas (Lamto, Djougou and Katibougou), we included the savanna LUC parameters of Brook et al. (1999)”: which was it?

P 11696, l3-17 and rest of the section for z0 and LAI: this whole paragraph is tough to read and confusing. A summary table (or an addendum to the existing Table 3) of the different parameterisations and the adaptations made from the Zhang et al 2003 model would be clearer. I have nothing in principle against changing/adapting parameterisations or default values for Rg, Rcut, etc, but a sensitivity study should accompany the simulations to compare with the default case of the original model.

P11697, l1: please specify whether LAI in this section is understood as single-sided, total, half of total?

P11698-699: “In addition, Vd simulations under dew or dry conditions in Zhang et al. (2003b) showed that Vd under dew conditions are not necessarily larger than under dry conditions.” This only reflects the paramerisations and assumptions made in the model about Rns; other models use different assumptions and parameterisations.

P11699, l14-15: “leads to a more precise understanding of deposition processes at the local scale.” I would dispute that assertion, to the extent that no flux measurements were carried out at these sites and surface exchange process understanding does not gain from mere concentration data at the site level. On the other hand, in conjunction with a regional CTM, a spatial network of measured concentrations can help assess (indirectly) the validity of the underlying processes and parameterisations.

P11700, l1-21: these vertical gradient measurements are certainly helpful and original, and the closest thing in this study to examining the sink-source behaviour of ecosystems, with the Banizoumbou NH3 data indicative of a consistent ground surface NH3 source.

P11701, l5-6: “Uncertainties in the estimated dry deposition fluxes result from combined uncertainties in measured gaseous concentrations and in modelled dry deposition velocities “ : please change “modelled dry deposition rates” to “modelled exchange rates” to reflect the potentially bi-directional nature of the exchange for all chemical species except O3. The Vd concept is flawed for many atmospheric pollutants as a result of non-zero surface concentrations; therefore the uncertainty in the model results of this dry deposition study also includes a model structural component (not just parameterisations for the individual resistances).

P11701, l9-10: “Uncertainties linked to the measurement of gas concentration using IDAF passive samplers have been given by the covariance of duplicates”: again I disagree; there can be systematic errors in concentrations (see earlier comment about HNO3), which are not picked up by the replicates (they all have the same bias).

P11701, l11-12: “The main uncertainty of the dry deposition velocities is mainly related to the wind forcing.” I disagree. What you probably mean is that in the Zhang et al model, Vd is most sensitive to to wind speed, but this does not necessarily reflect the main source of uncertainty of the modelled exchange velocity, which can be structural (ie use of a uni-directional model instead of a compensation point approach).

P11701, l27-28: related to the above. Bi-directional NH3 exchange “is assumed to be low for semi natural vegetation”: this is contradicted by the Banizoumbou gradient measurements.

P11702, l6: You could also add that multiple species model intercomparison show factors of 2-5 differences in exchange rates between models, depending on the chemical species (Flechard et al. ACP 2011)

P11702, l7-12: this is introduction material.

p11703, l4-5: I strongly disagree in the case of O3: there is a very large non-stomatal component to the flux, as O3 reacts readily with leaf cuticles, surface moisture, surface-deposited aerosols, soil surfaces, etc. The size of the non-stomatal O3 flux can easily be of the order of 30-50%, as demonstrated in many publications (eg. Fowler et al., Water, Air, and Soil Pollution 130: 63–74, 2001, or Stella et al., Biogeosciences, 8, 2869–2886, 2011). Thus I find that Fig.3 showing essentially identical NO2 and O3 deposition rates (Vd) in the range 1-4 mm/s is totally counter-intuitive: either Vd(NO2) is substantially over-estimated, or Vd(O3) is fairly underestimated. I believe the latter to be the case, suggesting that the non-stomatal sink (Rns) is not adequately parameterised in the model.

p11703, l8-9: "similar deposition characteristics": this is forgetting that the non-stomatal sink (eg uptake by leaf wetness) is very dependent on pH and the prevailing pollution climate, and that NH3 is alkaline while SO2 is acidic. Thus "deposition characteristics" should theoreticaly differ; eg a high atmospheric acidity load (or high total acids to NH3 ratio; see Massad et al., Atmos. Chem. Phys., 10, 10359–10386, 2010) would favour NH3 uptake, but lead to high canopy resistance for SO2 (and vice-versa).

p11706, l5-10: there seems to be a contradiction here: soil NO emissions are triggered by rainfall in the wet season, and the concomittant higher NO2 concentrations are interpreted by the model and by the authors as an increased NO2 deposition. However, the higher NO2 concentrations in the May-July period may also partly result from in-canopy NO oxidation by O3 (there is 15-20 ppb O3 at that time of year, according to Fig.9), in which case there can be a positive NO2 gradient from the canopy to the atmosphere, and thus, no net NO2 deposition. Without flux measurements it is impossible to tell the relative magnitude of all these processes, but at least the pseudo-compensation point behaviour of the NO-NO2-O3 system ought to be discussed; the model used here does not account for such bi-directional behaviour and its predictions for NO2 are highly uncertain.

p11708, section on HNO3: apart from the large uncertainties/interferences in HNO3 concentrations measured by diffusion tubes, there is a large uncertainty in the HNO3 deposition rate. This model assumes more or less perfect HNO3 uptake (Rc=0) by the surface, while recent research has shown a far more complex behaviour, which should be discussed here. The in- and above-canopy gas/particle interactions of the triad NH3/HNO3/NH4NO3 (eg Nemitz et al., 2004, Atmospheric Chemistry and Physics, 4: 989âĂŘ1005, and Twigg et al., 2011, Agricultural and Forest Meteorology, 151(12): 1488âĂŘ1503) allow for example for HNO3 evaporation and apparent canopy emission in certain circumstances (see also Trebs et al., Atmos. Chem. Phys., 6, 447–469, 2006, for tropical HNO3 flux measurements over pasture, and also for NH3, NO2, O3).

p11709, l4-5: see comment above for HNO3 flux measurements in the tropics.

p11709, l19: "due to higher NH3 Vd": please explain why Vd is higher: is this simply an LAI effect?

p11709, l26-27: "Annual mean NH3 emission fluxes by volatilization are estimated around 3.9±2.2 kgNha−1 yr−1 in the dry savannas.": then what does Figure 6A actually mean? For the net NH3 flux, should one substract the volatilisation from the dry deposition? In that case is NH3 still the largest source of atmospheric N ? (cf my earlier comment about bi-directional exchange and N/NH3 budgetting).

p11710, l7-9: presumably this is an effect of the lower Rc values in wet conditions counter-balancing the lower atmospheric concentrations ? Please explain the processes. Further on p11710, l15-17: again, what causes the differences in Vd?

p11715,l 26 to 11716, l13: it would be more telling to compare O3 deposition velocities between sites than the unusual units of kg O3/ha/yr, since O3 regimes and mean concentrations are so different across sites. It would be interesting to provide a very quick assessment of potential O3 damage to vegetation based on the modelled fluxes and what is known of O3 thresholds for the tropical ecosystems studied here.

p11716, l20-22: "In the deposition model, surface and meteorological conditions specific to IDAF sites have been adapted in order to simulate Vd representative of major African ecosystems" : I would argue that the major adaptations needed to adequately treat pollutant surface exchange in the tropics - namely: bi-directional exchange; soil emission potentials; stomatal conductance, non-stomatal resistance - have yet to be made. The adjustments made here were really marginal and not based on a study of exchange processes through flux measurements.

p11717, l22-24: "To improve this work, it is important to address the uncertainties in the determination of dry deposition velocities." . I believe that this sentence encapsulates a major conceptual problem in this paper, ie, what is actually needed is not an improvement of deposition velocities; rather, a paradigm shift is needed in modelling approaches, away from Rc-Vd concepts and towards bi-directional schemes for all species except O3. For the NH3 case, I would refer to Sutton et al, Phil. Trans. R. Soc. B 2013 368, 20130166, 2013, "Towards a climate-dependent paradigm of ammonia emission and deposition".

Technical corrections

Throughout the text the authors misuse the expression "of the same order of magnitude", when what they really mean is "of the same order", that is, the difference between two numbers A and B is less than typically 30-50%. The expression "orders of magnitude" refers to powers of 10 ratios between numbers. Please change throughout the text when appropriate. Please use ÂńÂăfind and replaceÂăÂż for each occurrence.

P11692 Flechard et al 1999 is missing from the reference list

P11696, l7: change “dew or not” to “dew or dry” ?

p11704, l18: change "involves" to "induces"

p11708, l10: "fluxes ARE very low..."

p11709, l11: change "ammoniac" to "ammonia"

p11715, l10 "interannual"

Table 1: add canopy height and LAI range

Figure 2: add Zoetele station.

Figures 4, 5, 6, 8, 9: to improve readability, please insert spacing between the adjacent column charts of the different sites (ie between the December bar of one site and the January bar of the adjacent site).

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 11689, 2013.