

Journal: ACP

Title: Chemical characterization and source apportionment of submicron aerosols measured in Senegal during the 2015 SHADOW campaign

Author(s): Laura-Hélène Rivellini et al.

MS No.: acp-2016-1127

---

The authors want to thank Reviewer #1 for his/her helpful comments. They are addressed below in blue. Changes in the manuscript are written in red.

### Anonymous Referee #1

Manuscript is a well-written and organized and it offers important information about the aerosols and their sources in West-Africa, Senegal. I recommend it for publishing in ACP after addressing some comments below.

1. Aerosol acidity approach (Chapter 3.1.3, equation 11?) is valid if the influence of metal ions, as well as organic acids and bases on  $\text{NH}_4^+$  concentration is negligible (Zhang et al., 2007). When the sulfate to  $\text{NH}_4^+$  ratio is high, the amount of atmospheric ammonium is not sufficient to neutralize all  $\text{SO}_4$ ,  $\text{NO}_3$  and  $\text{Cl}$  anions. In such a case at least a fraction of  $\text{NO}_3$  and  $\text{Cl}$  anions must be associated with cations other than  $\text{NH}_4^+$  and Eq. (11) is no longer valid. This should be discussed and clarified in the revised manuscript.

**Author's response:** 23% of the data are associated to a  $\text{NH}_{4,\text{meas}}/\text{NH}_{4,\text{predict}}$  ratio inferior to 0.75 and correspond to points under the 1:1 line in Figure S3a. For such points, the amount of  $\text{NH}_4$  predicted is overestimated in comparison to the amount measured on site, and considering that  $\text{NH}_4$  will preferentially react with  $\text{SO}_4$ , we agree with Reviewer #1 that other anions like  $\text{NO}_3$  and  $\text{Cl}$  are partially under chemical states other than ammonium nitrate and chloride.

Chloride species have been observed in this study as emitted by local combustion processes ( $m/z$  36,  $\text{HCl}^+$ ). Besides,  $\text{HNO}_3$  adsorption on dust as already been reported in the literature (Fairlie et al., 2010; Savoie et al., 1989) and this is consistent with ratio values inferior to 0.75 which are mainly observed while the site is under dust influence (Figure S3b).

If only  $\text{SO}_4$  is taken into account in the ion balance as described in Tiitta et al. (2014) who observed a lack of ammonium to fully neutralize the inorganic anions during the wet season, the  $\text{NH}_{4,\text{meas}}/\text{NH}_{4,\text{predict}}$  ratio increases up to 1.20 (see Figure R1 below). This clearly indicates that sulfates are fully neutralized in our case and that additional  $\text{NH}_4$  is available to neutralize at least partially other inorganic anions.

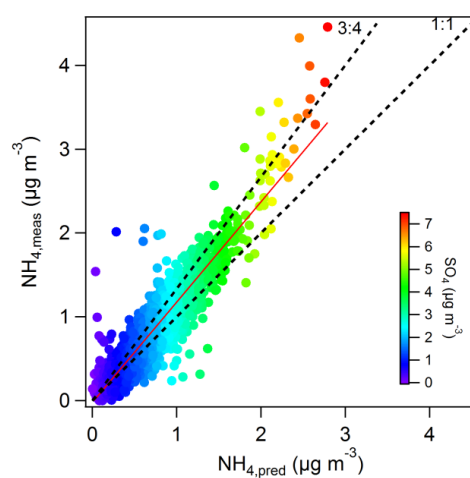


Figure R1. Scatter plot of measured-to-predicted  $\text{NH}_4$  using only  $\text{SO}_4$  in the ion balance equation. Data points are colored by sulfate concentrations.

**Changes in the manuscript:** The equation number associated with the neutralization equation has been corrected from (10) to (11), page 12 line 29.

The following paragraph has been added page 13 line 2: “On the other hand, 23% of the data are associated to a  $\text{NH}_{4,\text{meas}}/\text{NH}_{4,\text{predict}}$  ratio inferior to 0.75 and correspond to points under the 1:1 line in Figure S3a. For such points, the amount of  $\text{NH}_4$  predicted is overestimated in comparison to the amount measured on site, and considering that  $\text{NH}_4$  will preferentially react with  $\text{SO}_4$ , other anions like  $\text{NO}_3$  and  $\text{Cl}$  are partially under chemical states other than ammonium nitrate and chloride. As mentioned previously and developed in section 3.2, this can be explained by chloride species emitted by local combustion processes but also by  $\text{HNO}_3$  adsorption on dust as already reported in the literature (Fairlie et al., 2010; Savoie et al., 1989) and this is consistent with ratio values inferior to 0.75 which are mainly observed while the site is under dust influence (Figure S3b). Nevertheless these periods also correspond to low levels of inorganic species in  $\text{PM}_{1.0}$ .”

2. Recently, it has been demonstrated that some inorganic salts (e.g.  $(\text{NH}_4)_2\text{SO}_4$ ) have a positive bias on the  $\text{CO}_2^+$  signal through reaction on the aerosol mass spectrometer vaporizer (Pieber et al., 2016). This interference is highly variable between instruments and with measurement history. How big is this interference value for your ACSM and possible impacts on data analyses including PMF.

**Author’s response:** Pieber et al. (2016) have evidenced that the bias is significant when the inorganic fraction is > 50%, 3-10 times more important for ammonium nitrate than for sulfate, and also dependent on the instrument history.

The dataset has been acquired in 2015, when no calibration performed at that time took into account the impact of  $\text{CO}_2^+$  from inorganic salts on m/z 44 (using the automated procedure of the instrument). For this reason we are not able to determine the b value for this specific campaign, that would allow to estimate the magnitude of the bias and introduce an appropriate correction into the fragmentation table. Nevertheless, the maximum of possible interferences on m/z 44 (observed when  $\text{NO}_3/\text{OM}$  and  $\text{SO}_4/\text{OM}$  ratios are high) also correspond to lower  $\text{CO}_2^+$  mass concentrations (Figure R2, left). Moreover our last ammonium nitrate calibration (performed recently at a site in Northern France after 6-month sampling of air masses showing high levels of ammonium nitrate), led to an estimation of the m/z 44 vs  $\text{NO}_3$  ratio of 9% (Figure R2, right).

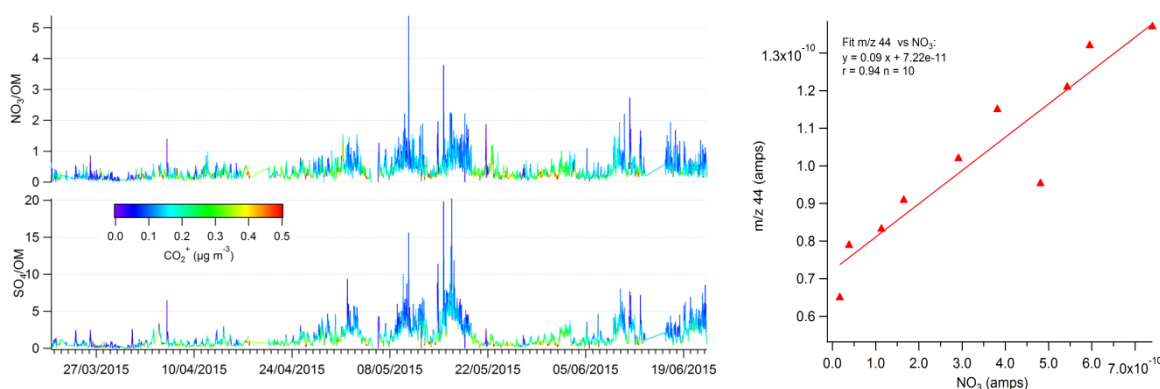


Figure R2. (left) Ratios of  $\text{NO}_3$  and  $\text{SO}_4$  over OM colored by  $\text{CO}_2^+$  signal and (right) m/z 44 vs  $\text{NO}_3$  signals (in Amps) obtained during  $\text{NH}_4\text{NO}_3$  calibration.

Based on this measurement, and considering the rather low levels of  $\text{NO}_3$  observed at M’Bour and the predominance of  $\text{SO}_4$  in the inorganic fraction, we consider this interference on m/z 44 as likely negligible.

3. How can authors explain high NO<sub>3</sub>-concentrations in air masses from South-West? The air mass history can be investigated e.g. using backtrajectories calculated with the HYbrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT).

**Author's response:** We tend to attribute these NO<sub>3</sub> concentrations from the SW wind sector (oceanic) to NO<sub>x</sub> emissions from Dakar which are transported and transformed above the ocean before reaching our sampling site. Adon et al. (2016) have observed an annual average for NO<sub>2</sub> concentrations as high as 32 ppb (60 µg m<sup>-3</sup>). This regional transport is supported by NO<sub>3</sub> NWR plot and PSCF map now added in the Supplementary Information, Figure S8.

4. What are the following steps for aerosol research in this region of the world? Are these results valuable for policy makers to guide cleanup and decision making for future industry? Please, improve discussion.

**Author's response:** We have added some additional comments in the Conclusion section regarding Reviewer #1's request.

**Changes in the manuscript:** The following paragraph has been added page 19 line 31: "As shown during this field campaign, at least half of the organic aerosols measured in the submicron fraction are from anthropogenic origins (HOA + COA + LCOA) and we were able to attribute them to specific sources. On the contrary, little is known about the oxygenated fraction – often associated to secondary organic aerosols, which constitutes the other half of OA and therefore efforts should be directed toward better characterizing SOA precursors (anthropogenic and biogenic) and their concentration levels in West Africa. Moreover, the specific LCOA source puts an emphasis on open waste burning, which is highly problematic in terms of health issues, and should be addressed through the implementation of waste disposal facilities and an effective waste collection infrastructure."

---

## References cited in this reply

Adon, M., Yoboué, V., Galy-Lacaux, C., Lioussé, C., Diop, B., Doumbia, E. H. T., Gardrat, E., Ndiaye, S. A. and Jarnot, C.: Measurements of NO<sub>2</sub>, SO<sub>2</sub>, NH<sub>3</sub>, HNO<sub>3</sub> and O<sub>3</sub> in West African urban environments, *Atmos. Environ.*, 135, 31–40, doi:10.1016/j.atmosenv.2016.03.050, 2016.

Fairlie, T. D., Jacob, D. J., Dibb, J. E., Alexander, B., Avery, M. A., van Donkelaar, A. and Zhang, L.: Impact of mineral dust on nitrate, sulfate, and ozone in transpacific Asian pollution plumes, *Atmos Chem Phys*, 10(8), 3999–4012, doi:10.5194/acp-10-3999-2010, 2010.

Savoie, D. L., Prospero, J. M. and Saltzman, E. S.: Non-sea-salt sulfate and nitrate in trade wind aerosols at Barbados: Evidence for long-range transport, *J. Geophys. Res. Atmospheres*, 94(D4), 5069–5080, doi:10.1029/JD094iD04p05069, 1989.