Supplementary material for manuscript:

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

L.-H. Rivellini^{1,2}*, I. Chiapello², E. Tison¹, M. Fourmentin³, A. Féron⁴, A. Diallo⁵, T. N'Diaye⁵, P. Goloub², F. Canonaco⁶, A. S. H. Prévôt⁶, and V. Riffault¹*

¹Département Sciences de l'Atmosphère et Génie de l'Environnement, IMT Lille Douai, Douai, 59508, France

²Laboratoire d'Optique Atmosphérique, Université de Lille - CNRS, Villeneuve d'Ascq, 59655, France

³Laboratoire de Physico-Chimie de l'Atmosphère, Université du Littoral Côte d'Opale, Dunkerque, 59140, France

⁴Laboratoire Interuniversitaire des Systèmes Atmosphériques, CNRS - Université Paris Est Créteil - Université Paris Diderot, Créteil, 94010, France

⁵Institut de Recherche pour le Développement, M'Bour, Senegal

⁶Laboratory of Atmospheric Chemistry, Paul Scherrer Institute, 5232 Villigen, Switzerland

^{*} Corresponding authors:

Véronique Riffault

Tel.: +33 327 712 604, Fax: +33 327 712 914, e-mail: veronique.riffault@mines-douai.fr

Laura-Hélèna Rivellini

e-mail: laura.rivellini@mines-douai.fr



Figure S1. Values of (a) RF(NO₃), (b) RIE of ammonium, and ratios to ammonium for (c) sulfate and (d) chloride obtained from calibrations performed during a previous campaign (Zhang et al., in prep.) (before Nov. 25^{th} 2014) and this study (after and including Nov. 25^{th} 2014). (e) time series of CE values corrected following Middlebrook et al. (2012) algorithm colored by ratio of NH_{4,meas}/NH_{4,pred}.



Figure S2. Averaged PM_1 chemical composition for (a) IOP-1 (n = 2952), (b) continental (n = 307), (c) sea breeze (n = 799) and (d) marine days (n = 1846). Only days with at least 50% of the total PM_1 mass concentration measurements by TEOM-FDMS were taken into account for averaging, corresponding to 11 days for continental, 21 days for sea breeze and 42 days for marine days. Unacc.: unaccounted fraction determined as the difference between the gravimetrically measured PM_1 mass concentration and the sum of chemical species from ACSM and aethalometer measurements



Figure S3. (a) Scatter plot between measured and predicted NH_4 colored by relative humidity and (b) associated rose plot, (c) $NH_{4,meas}/NH_{4,pred}$ ratios as a function of SO₄, NO₃, OM and Chl species, where OM and Chl data are colored by BC concentrations. The red ellipses highlight the data points deriving from the 1:1 ratio corresponding to aerosol neutralization.

Appendix S4. PMF analysis



Figure S4.1. 4-factor PMF unconstrained solutions with (a) factor profiles and time series for IOP-1; and factor profiles for (b) continental (Q/Qexp = 0.37), (c) sea breeze (Q/Qexp = 0.36) and (d) marine (Q/Qexp = 0.27) days with corresponding pie charts.



Figure S4.2. (top) Mass spectrum (inset: $m/z \ge 60$), daily profile and rose plot of the LCOA factor from the unconstrained 4-factor solution; (bottom) Time series and rose plots of fragments at m/z 58, 60, 83 and 91



Figure S5. Box plots of (left) the m/z 35, 36 and 60 signals and (right) of mz60/OM ratio. For each box plot, top line: 75th percentile, bottom line: 25th percentile, middle line: 50th percentile (median); top whisker: 95th percentile, bottom whisker: 5th percentile. The open circle and the cross represent the 99th percentile and maximum value, respectively.

Appendix S6. PMF 5-factor solution including organics + m/z 36 as input data

Since the behavior of Chl had also been suspected to come from the same sources, m/z signals at 35 and 36 were investigated in order to possibly implement them in the model input. However the m/z 35 signal presented an important amount of slightly negative values (- $3.0 \pm 6.2 \times 10$ -13, see Figure S5) which likely resulted from a slow vaporization of refractory chloride species both during filter and non filter measurement as previously observed (Nuaaman et al., 2015). For this reason only m/z 36 was incorporated into the model without additional normalization since the signal intensity was close to organic ones. Uncertainties were estimated as followed :

The detection limits (DL_x) for these m/z were assumed to be equal to 3 times their respective signal-to-noise ratio for filtered air. The method to determine the uncertainties has already been used to carry out source apportionment studies based on filter data (Tauler et al., 2009; Jang et al., 2013). When the mass concentrations were below the detection limit, concentrations C_x were replaced by $DL_x/2$ and the uncertainties calculated by Equation 1:

$$S_x = 0.2 \times C_x + LD/3 \tag{Eq. 1}$$

If the concentrations were above the detection limit, Equation 2 was used:

$$S_x = 0.1 \times C_x + LD/3 \tag{Eq. 2}$$

New unconstrained runs of the PMF model using the combined dataset of OM plus HCl+ signal for IOP-1 led to the almost complete (95%) attribution of the m/z 36 signal to the Local Combustion OA (LCOA), where it represented 40% of the total factor mass. Besides, in order to refine the solutions, and due to the possible specificity of local emissions, the PMF model was run with constraints on the primary factor profiles, that is to say LCOA obtained from the IOP-1 solution, and COA and HOA from the sea breeze solution, using the a-value approach with 10% freedom (a = 0.1).

References:

Jang, E., Alam, M.S., Harrison, R.M., 2013. Source apportionment of polycyclic aromatic hydrocarbons in urban air using positive matrix factorization and spatial distribution analysis. Atmospheric Environment 79, 271-285.

Tauler, R., Viana, M., Querol, X., Alastuey, A., Flight, R.M., Wentzell, P.D., Hopke, P.K., 2009. Comparison of the results obtained by four receptor modelling methods in aerosol source apportionment studies. Atmospheric Environment 43, 3989-3997.



Fig. S6. PMF constrained 5-factor solution including the m/z 36 chloride peak: (left) factor profiles of LCOA, COA, HOA (all primary factors constrained), MO-OOA, LO-OOA; (middle) corresponding daily cycles according to day types (solid lines: median; dotted lines: average); and (right) pollution rose plots colored by hour of day. (bottom) Average pie charts of the contributions to the total organic fraction for IOP-1, continental, sea breeze and marine days



Fig. S7. (a) Diurnal average profile of BC/OM ratio for continental, sea breeze and marine days and scatter plot of BC vs OM concentrations (in μ g m⁻³) for (b) IOP-1, (c) continental, (d) sea breeze and (e) marine days.