



Supplement of

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

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S1. Deconvolution method uncertainties and comparison with literature data

The uncertainties on estimated Fe concentrations can be calculated by applying the propagation for uncertainties on the values of K_{Fe} (10%) and the slope b (39%, calculated using a variability of 0.2 for the two Angström absorption exponents (AAE), and (Fialho et al., 2006)), which gives an overall uncertainty of ~40%. However this method is highly sensitive to even small variations of α (BC) and (DD), with values quite well known for BC from fossil fuel ranging from 0.8 to 1.1 (Hansen, 2005; Zotter et al., 2017 and references therein) but not so much for dust. In the manuscript, we chose to use = -4, according to Fialho et al. (2006) values determined at the Azores Islands for samples influenced by Saharan dust events. But other values can be found in the literature (Table S2.1), ranging from -1.6 to -6.5 and largely influenced by the wavelength range as well as dust origins and size fractions since the iron content differ depending on emission sources and particle size (Journet et al., 2014). Even during the SAMUM campaign (May to June 2006 in Morocco), a wide range of AAE values have been reported from -1.6 up to -5.1 for ground-based measurements in the same size fraction, as shown in Table S1. Applying a relatively small increase (resp. decrease) of 10% on the value of for our dataset led to a 33% decrease (resp. 50% increase) of iron concentrations, as shown in Figure S2, but no change in the temporal behavior.

Table S2.2 summarizes the iron content determined in Saharan samples, which shows that the relative contribution of iron determined in this work is in the same order of magnitude but still significantly higher. However iron oxides can be found mostly (for $\sim 2/3$) in the clay fraction ($\sim PM_{2.5}$) and $\sim 1/3$ in the silt (coarse) fraction (Journet et al., 2014; Kandler et al., 2009), which is consistent with increased ratios in the submicron fraction compared to larger ones. It is also worth noting that Val et al. (2013) measured the iron content in the ultrafine and fine fractions (corresponding to PM₁) of particles collected in Dakar, and measured a ratio in the upper range of those already reported in the literature, even in the absence of dust event.

The approach used here leads to an estimate of the absolute concentrations of iron, although with high uncertainties given all the necessary assumptions and the empirical algorithm used to deconvolve BC and Fe from absorption measurements. However the temporal profiles, non-parametric wind regression (NWR) plots and potential source contribution function (PSCF) maps (now provided in Figures S5b and S5c, respectively) are all consistent with the expected behavior of such a desert dust tracer and show that it can be useful in determining the contribution of dust to absorption measurements. There is nonetheless quite some room

for improvement, in particular for a better estimation of the AAE value for dust similar to the efforts carried out to determine the AAE values for BC from fossil fuel and wood burning (Zotter et al., 2017). We strongly believe the lack of information for submicron particles in terms of chemical composition of refractory species and optical properties should be better addressed, but is beyond the scope of this work.

S2. 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 S9) 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:

$$S = 0.2 \times C + LD/3$$
 (Eq. 1)

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

$$S = 0.1 \times C + LD/3$$
 (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).

Reference	Location / Period	Wavelengths (nm)	Fraction	
Fialho et al. (2006) ^a	Azores Islands Jul. 2001 ó Jun. 2005	370-950	-	-4
Müller et al. (2009) ^a	Tinfou, Morocco (SAMUM) Summer 2006	467/660	PM_{10}	-2.25 to -5.13
Petzold et al. (2009) ^b	South-East Morocco (SAMUM) Summer 2006	467/660	PM _{2.5}	-2 to -6.5
Schladitz et al. (2009) ^a	Tinfou, Morocco (SAMUM) Summer 2006	537/637	PM_{10}	-1.6 to -4.73
Linke et al.(2006) ^c	Morocco Egypt	266/532	$\sim PM_4$	-4.2 -5.3
(Caponi et al., 2017) ^c	Morocco Lybia Algeria Mali	375-850 375-532 375-850 375-532	PM _{2.5} (PM _{10.6})	-2.6 -4.1 (-3.2) -2.8 (-2.5) -3.4

Table S1. Mineral dust AAE values reported from field campaigns around the Saharan region.

^a In situ ground-based measurements; ^b Airborne measurements through dust plumes; ^c Laboratory experiments with resuspended soil samples

Reference	Location	Method ^a	Size fraction	%Fe ^b
]	Dust samples		
(Lafon et al., 2004)	Banizoumbou (Niger)	XRF; CBD	TSP	6.3; 7.8
(Lafon et al., 2006)	Banizoumbou,	XRF; CBD	TSP	4.3 ó 6.1
(Lafon et al., 2006)	Cape Verde	XRF; CBD	TSP	5.3 ó 6.0
(Formenti et al., 2008)	Banizoumbou	CBD	40 µm	5.8
(Val et al., 2013)	Dakar (Senegal)	ICP-MS	1 µm	7.8
This work	MøBour	cf. text	1 µm	23 (continental) 21 (sea breeze) 16 (marine)
		Soil samples		
(Moreno et al., 2006)	Saharan region (9 samples)	ICP-AES/ ICP-MS	TSP	2.0 ó 4.7
(Lafon et al., 2006)	Banizoumbou,	XRF; CBD	10.2 μm 2.5 μm	5.3 5.8
(Joshi et al., 2017)	MøBour, Bordj (Algeria), Nefta (Tunisia)	XRD	100 µm	< 0.5

Table S2: Comparison of iron content (in %) determined in Saharan dust and soil samples

^a XRF: X-ray Fluorescence (XRF) Spectrometry for elemental analysis; CBD: chemical method based on citratebicarbonate-dithionite (CBD) reagent for quantification of iron oxides adapted from soil analysis (Mehra and Jackson, 1960)

^b Percentages of iron relative to the mass of all oxides, classically taking into account Na₂O, MgO, Al₂O₃, SiO₂, K₂O, CaO, TiO₂ and Fe₂O₃.

Soil samples resuspended using wind tunnel and collected with a 13-stage impactor



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 (before Nov. 25^{th} 2014; Zhang et al., in prep.) and this study (Nov. 25^{th} 2014 and beyond). (e) Chl and NH₄ calibration curves performed on January 22^{nd} , 2015. (f) Time series of CE values corrected following Middlebrook et al. (2012) algorithm colored by the NH_{4,meas}/NH_{4,pred} ratio.



Figure S2. Box plots of (a) Fe, (b) BC concentrations and (c) Fe/(Fe+Unacc.) ratio for continental, sea breeze and marine days. (d) Scatter plot of iron concentrations (in μ g m-3) obtained from Fialhoøs deconvolution method using an AAE value of \pm 10% compared to the one from the literature and used in the manuscript.



Figure S3. 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 S4. (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.



Figure S5. (a) 48-hour back trajectory clusters for (from left to right) IOP-1, continental, sea breeze and marine days. (b) NWR plots (input parameters: angular and radial resolution of 0.1, angle smoothing of 2 and radial smoothing of 1; upper limit of the color scale: 75th percentile) for PMF factors and NR-PM₁, BC and Fe species and corresponding (c) PSCF maps for species showing regional influence (threshold: 75th percentile) during IOP-1.

(a) 3-factor solution





(b) 4-factor solution





















(f) 8-factor solution





(g) 9-factor solution





(h) 10-factor solution



Figure S6. PMF unconstrained solutions from 3 to 10 factors, with (left) factors profiles and (right) corresponding daily cycles.



Figure S7. 4-factor PMF unconstrained solutions with (a) factor profiles, pie chart and time series for IOP-1; and factor profiles and pie charts for (b) continental (Q/Qexp = 0.37), (c) sea breeze (Q/Qexp = 0.36) and (d) marine (Q/Qexp = 0.27) days.



Figure S8. (top) Mass spectrum (inset: $m/z \times 60$), 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 S9. Box plots of (left) the m/z 35, 36 and 60 signals and (right) of the m/z 60/OM (f_{60}) 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.



Figure S10. 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



Figure S11. (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.

References

Caponi, L., Formenti, P., Massabó, D., Di Biagio, C., Cazaunau, M., Pangui, E., Chevaillier, S., Landrot, G., Andreae, M. O., Kandler, K., Piketh, S., Saeed, T., Seibert, D., Williams, E., Balkanski, Y., Prati, P. and Doussin, J.-F.: Spectral- and size-resolved mass absorption efficiency of mineral dust aerosols in the shortwave: a simulation chamber study, Atmos Chem Phys Discuss, 2017, 1639, doi:10.5194/acp-2017-5, 2017.

Fialho, P., Freitas, M. C., Barata, F., Vieira, B., Hansen, A. D. A. and Honrath, R. E.: The Aethalometer calibration and determination of iron concentration in dust aerosols, J. Aerosol Sci., 37(11), 149761506, doi:10.1016/j.jaerosci.2006.03.002, 2006.

Formenti, P., Rajot, J. L., Desboeufs, K., Caquineau, S., Chevaillier, S., Nava, S., Gaudichet, A., Journet, E., Triquet, S., Alfaro, S., Chiari, M., Haywood, J., Coe, H. and Highwood, E.: Regional variability of the composition of mineral dust from western Africa: Results from the AMMA SOP0/DABEX and DODO field campaigns, J. Geophys. Res. Atmospheres, 113(D23), D00C13, doi:10.1029/2008JD009903, 2008.

Hansen, A. D. A.: Aethalometer Operations Manual, Magee scientifique, Berkeley, CA, USA., 2005.

Joshi, N., Romanias, M. N., Riffault, V. and Thevenet, F.: Investigating water adsorption onto natural mineral dust particles: Linking DRIFTS experiments and BET theory, Aeolian Res., 27, 35645, doi:10.1016/j.aeolia.2017.06.001, 2017.

Journet, E., Balkanski, Y. and Harrison, S. P.: A new data set of soil mineralogy for dustcycle modeling, Atmos Chem Phys, 14(8), 380163816, doi:10.5194/acp-14-3801-2014, 2014.

Kandler, K., SchÜTz, L., Deutscher, C., Ebert, M., Hofmann, H., JÄCkel, S., Jaenicke, R., Knippertz, P., Lieke, K., Massling, A., Petzold, A., Schladitz, A., Weinzierl, B., Wiedensohler, A., Zorn, S. and Weinbruch, S.: Size distribution, mass concentration, chemical and mineralogical composition and derived optical parameters of the boundary layer aerosol at Tinfou, Morocco, during SAMUM 2006, Tellus B, 61(1), 32650, doi:10.1111/j.1600-0889.2008.00385.x, 2009.

Lafon, S., Rajot, J.-L., Alfaro, S. C. and Gaudichet, A.: Quantification of iron oxides in desert aerosol, Atmos. Environ., 38(8), 121161218, doi:10.1016/j.atmosenv.2003.11.006, 2004.

Lafon, S., Sokolik, I. N., Rajot, J. L., Caquineau, S. and Gaudichet, A.: Characterization of iron oxides in mineral dust aerosols: Implications for light absorption, J. Geophys. Res. Atmospheres, 111(D21), D21207, doi:10.1029/2005JD007016, 2006.

Linke, C., Möhler, O., Veres, A., Mohácsi, Á., Bozóki, Z., Szabó, G. and Schnaiter, M.: Optical properties and mineralogical composition of different Saharan mineral dust samples: a laboratory study, Atmos Chem Phys, 6(11), 331563323, doi:10.5194/acp-6-3315-2006, 2006.

Moreno, T., Querol, X., Castillo, S., Alastuey, A., Cuevas, E., Herrmann, L., Mounkaila, M., Elvira, J. and Gibbons, W.: Geochemical variations in aeolian mineral particles from the

SaharaóSahel Dust Corridor, Chemosphere, 65(2), 261ó270, doi:10.1016/j.chemosphere.2006.02.052, 2006.

Müller, T., Schladitz, A., Massling, A., Kaaden, N., Kandler, K. and Wiedensohler, A.: Spectral absorption coefficients and imaginary parts of refractive indices of Saharan dust during SAMUM-1, Tellus B, 61(1), 79695, doi:10.1111/j.1600-0889.2008.00399.x, 2009.

Petzold, A., Rasp, K., Weinzierl, B., Esselborn, M., Hamburger, T., Dörnbrack, A., Kandler, K., Schütz, L., Knippertz, P., Fiebig, M. and Virkkula, A.: Saharan dust absorption and refractive index from aircraft-based observations during SAMUM 2006, Tellus B, 61(1), 1186 130, doi:10.1111/j.1600-0889.2008.00383.x, 2009.

Schladitz, A., Müller, T., Kaaden, N., Massling, A., Kandler, K., Ebert, M., Weinbruch, S., Deutscher, C. and Wiedensohler, A.: In situ measurements of optical properties at Tinfou (Morocco) during the Saharan Mineral Dust Experiment SAMUM 2006, Tellus B, 61(1), 646 78, doi:10.1111/j.1600-0889.2008.00397.x, 2009.

Val, S., Liousse, C., Doumbia, E. H. T., Galy-Lacaux, C., Cachier, H., Marchand, N., Badel, A., Gardrat, E., Sylvestre, A. and Baeza-Squiban, A.: Physico-chemical characterization of African urban aerosols (Bamako in Mali and Dakar in Senegal) and their toxic effects in human bronchial epithelial cells: description of a worrying situation, Part Fibre Toxicol, 10(10), 2013.

Zotter, P., Herich, H., Gysel, M., El-Haddad, I., Zhang, Y., Mo nik, G., Hüglin, C., Baltensperger, U., Szidat, S. and Prévôt, A. S. H.: Evaluation of the absorption Ångström exponents for traffic and wood burning in the Aethalometer-based source apportionment using radiocarbon measurements of ambient aerosol, Atmos Chem Phys, 17(6), 422964249, doi:10.5194/acp-17-4229-2017, 2017.