Journal: ACP Title: Chemical characterization and source apportionment of submicron aerosols measured in Senegal during the 2015 SHADOW campaign Author(s): Laura-Hélèna Rivellini et al. MS No.: acp-2016-1127

The authors want to thank Reviewer #3 for his/her helpful comments. They are addressed below in blue. Changes in the manuscript are written in red.

Anonymous Referee #3

Overview:

This manuscript presented the highly-time resolved chemical characterization and source apportionment of atmospheric submicron aerosol particles (PM1) in West Africa, along with field online measurements (including an ACSM and a 7-wavelength aethalometer) and offline model analysis. The campaign was deployed under the environment affected by anthropogenic emissions (e.g., traffic, cooking, and biomass burning) and natural sources (e.g., desert dust and marine air masses), etc.. The results showed that the ten times lower average concentrations of NR-PM1 were observed here compared to the results from other megacities with persistent air pollution issues, i.e., Beijing and Paris. Sea breeze phenomena and Saharan desert dust outbreaks may lead to pollution events with high concentrations of PM10 (up to 900 µg/m3). Organic matter (OM) and sulfate could dominate the major fraction of aerosol particles when air massed could be associated to different influences, i.e., continental and sea breeze and oceanic region related. The authors also estimated the mass concentrations of particulate Fe from the Aethalometer data, for which an average contribution (4.6%) of Fe to PM1 was obtained. A new organic aerosol factor (LCOA), Local Combustion Organic Aerosol, was resolved by PMF analysis, with relatively low contribution (3%). Both regional and local photochemistry processes could contribute the formation of oxygenated organic aerosols in this area. The results seem to be interesting. The manuscript is well written and organized. I would recommend this paper could consider to be published in ACP once the following comments are addressed.

Specific comments:

1. Page 4, line 30: Should keep the same abbreviations for those species throughout the manuscript. For example, what's the different between "NO3-" and "NO3" (Page 5 and line 5), and somewhere else "SO42-" and "SO4", "Cl-", "Cl" and "Chl", etc.. If they are different for the discussion in this manuscript, please the authors give the related text to explain them.

Author's response: As suggested we have harmonized the nomenclature regarding the sum of nitrate $(NO_x, ONO_x...)$, ammonium (NH_x) , sulfate (SO_x, H_ySO_x) and chloride (Cl, HCl) related fragments. The SO_4^{2-} , NO_3^{-} and Cl⁻ ions are only used in the neutralization equation.

Changes in the manuscript:

Page 4 lines 29-31: "Non-refractory species, such as organic matter (OM), sulfate (SO₄), nitrate (NO₃), ammonium (NH₄) and non-refractory chloride (Chl), are vaporized at this temperature and then ionized by electron impact (70 eV). The abovementioned names of the different NR species correspond to the sum of all m/z fragments related to one given species in the fragmentation table (Allan et al., 2004), that is to say $H_{0\le x\le 2}S_{0\le y\le 1}O_{0\le z\le 4}$ for sulfate, $NH_{0\le x\le 2}$ for ammonium, $NO_{0\le x\le 2}$ and HNO₃ for nitrate, and $H_{0\le x\le 1}Cl$ for chloride."

2. Page 5, line 3: It was interesting to perform the chloride calibration with ammonium chloride particles. Could the authors also present the related calibration results in supporting information, as showing in Fig. S1, since your RIEChl is much higher than the default value (1.3). In addition, did the authors try to validate chloride data based on your calibration results? It's also interesting to know how it works about the chloride calibration.

Author's response: Chloride RIE calibrations (relative to nitrate) were performed using the same methodology as for ammonium nitrate and sulfate calibrations. A monodisperse aerosol at 300 nm was generated from an aqueous solution of NH_4Cl (> 99.8%, Merck) at 5×10^{-3} mol L⁻¹. The fragments at m/z 15, 16 and 17 were taken into account to determine the concentration of NH_4 whereas those at 35, 36, 37 and 38 were used for Chl.

Chl concentrations (in $\mu g m^{-3}$) were then calculated using the following equation:

Chl =
$$N_{CPC} \times S \times V_{part} \times \rho \times \frac{M(Cl^{-})}{M(NH_4Cl)}$$

where N_{CPC} is the number concentration given by the CPC in particles per cm³, S the shape factor (taken as 1), V_{part} the particle volume (in cm³) corresponding to 300 nm and assuming spherical shape, ρ the ammonium chloride density (1.53 g cm⁻³), M(X) the molar mass in g mol⁻¹. Using the ratio of the slopes obtained by plotting the sum of Chl signals vs Cl mass, and the similar plot for NH₄, combined with RIE(NH₄), allows to retrieve RIE(Chl) through the following equation:

 $RIE(Chl) = RIE(Chl/NH_4) \times RIE(NH_4/NO_3)$

with RIE(Chl/ NH₄) and RIE(NH₄/NO₃) mean values of 0.39 ± 0.04 and 5.72 ± 0.55 , respectively, we obtained RIE(Chl) = 2.26 ± 0.02 .

Comparing this value with external chloride calibrations is tricky since only non-refractory chloride can be detected by AMS/ACSM techniques, whereas most chloride ambient analyses (using ion chromatography for instance) would be dominated by (refractory) sea-salt chloride. Furthermore, NR-Chl tend to be rather low at most sites and therefore has not been a major concern in the AMS/ACSM community so far.

Changes in the manuscript: An example of chloride calibration with NH₄Cl has been added in the supplementary (Figure S1e). Page 5 line 7 now reads: "S1(a-e)".

3. Page 7, line 32: Would it be possible that the authors could give uncertainties of estimated Fe concentrations with this method for your study?

Author's response: Indeed 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 β and α (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 β (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 $\beta = -4$, 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 R1), 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 R1.

Reference	Location / Period	Wavelengths (nm)	Fraction	β
Fialho et al. (2006) ^a	Azores Islands Jul. 2001 – 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) °	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 R1. 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

Therefore applying a relatively small increase (resp. decrease) of 10% on the value of β for our dataset led to a 33% decrease (resp. 50% increase) of iron concentrations, as shown in Figure R1, but no change in the temporal behavior.



Figure R1. Scatter plot of iron concentrations (in μ g m⁻³) obtained from Fialho's deconvolution method using an AAE value of \pm 10% compared to the one from the literature and used in the manuscript.

Changes in the manuscript:

A new appendix (S2) in the Supplementary Information now includes this whole discussion. Changes in the main text have been also done page 8, line 18 with a new sentence added: "Applying the propagation for uncertainties approach on the values of K_{Fe} (10%) and the slope b (39%, calculated using a variability of 0.2 for α and β (Fialho et al., 2006)) gives an overall uncertainty of ~40% for iron concentrations. However the deconvolution algorithm is highly sensitive to the values of the Angström absorption exponents (α and β) and a more detailed discussion can be found in Appendix S2." 4. Page 8, line 19: In this paragraph, I suggest that the authors could consider to also mention some brief information about ME-2 algorithm how it works for constraining organic aerosol factors (Canonaco et al., 2013), since this will be helpful and easier for readers to quickly understand the SoFi how it works in this study.

Changes in the manuscript: Page 9 lines 4, sentence added at the end of the paragraph: "In case of mixed (known) factors, the solution can be furthermore constrained by imposing reference factor profiles (F, from the literature) as inputs. The user can apply those constraints with a certain degree of freedom defined by a scalar a-value ranging from 0 (no degree of freedom) up to 1 (totally unconstrained)."

5. Page 10, line 20: The authors should consider to explain which kind of combustion sources for the ACSM m/z 57 tracer is. When I am reading here, I immediately realized that why the authors did not perform the source apportionment of black carbon by using the Aethalometer model (Sandradewi et al., 2008). As described in Section 2.1, there are both traffic and biomass-burning emissions that would potentially contribute the ambient black carbon burden at this sampling site. So, is it possible to identify blackcarbon aerosols related to traffic and biomass-burning emissions here? This will be very helpful for the source apportionment of organic aerosol.

Author's response: m/z 57 is mostly the $C_4H_9^+$ fragment, which has been linked to combustion sources, and is one of the key fragments in HOA and COA spectra but appears as well in the BBOA one without being the main tracer (Ng et al., 2011a).

As to the second part of the comment, although biomass burning (BB) events can sometimes be observed in the region, no BB aerosols were detected during IOP-1 as mentioned in section 2.3.2. That was in fact the first condition required to apply the deconvolution method from Fialho et al. between BC from fossil fuel and Fe from mineral dust. Using this method does assume that no brown carbon (BrC) is present since the Angström absorption exponent (AAE) for BC is taken as the one from fossil fuel (AAE \sim 1).

On the other hand, the method proposed by Sandradewi et al. (2008) assumes that absorbing particles are only BC from fossil fuel or wood burning sources, and that there is no significant absorption from dust, which we know to be untrue at the M'Bour site. Therefore, as both dust and BC from wood burning absorb in the shortest wavelengths, the two models cannot be applied at the same time unless we could have constrained the time profile of each source with external tracers. In the absence of external data, a three-factor deconvolution has been tried but would still be highly hypothetical and therefore is not presented here.

Anyway, during the campaign, mineral dust was clearly present, sometimes at high concentrations, whereas sources of BrC were almost unsignificant. Therefore we chose to exclude the very few periods when BrC could be suspected to influence our measurements (1% of the data) and therefore the empirical deconvolution using Fialho's algorithm.

Changes in the manuscript:

Page 10 lines 19-20, sentence modified: "The higher concentrations can be attributed to local anthropogenic combustion processes as BC concentrations present a significant correlation (r = 0.79) with the ACSM m/z 57 tracer of all types of combustion."

Page 7 line 36 – page 8 line 1, sentence now reads: "As mentioned by Fialho et al. (2014), this method allows to estimate elemental iron concentrations only in the absence of brown carbon since an absorption Angström exponent of 1 (which correspond to fossil fuel BC) is applied. Therefore, other methods, such as the one proposed by Sandradewi et al. (2008) to deconvolve BC from fossil fuel and biomass burning, cannot be used in our conditions."

6. Page 11, line 3: Here is a little bit confusion about the ratio of Fe/PM10, since your Fe concentrations were estimated by the PM1 aethalometer, but not PM10 Fe. Is this the case? If yes, the

authors could consider to add "PM1" in front of "Fe" when you discuss this ratio in the main text of the manuscript.

Author's response: Indeed Fe was deconvolved from PM_1 absorption measurements and we agree that using the Fe/PM₁₀ ratio was confusing. We have now removed these direct comparisons and focused on the only available study for which we could derive Fe/DD_{PM1} in Dakar, Senegal, although in the absence of significant dust events. We only use the Fe/DD ratios found in the literature to emphasize the influence of the size fraction on the iron contribution to DD since most of it can be found in the clay fraction (~PM_{2.5}; Journet et al., 2014; Kandler et al., 2009), as part of Appendix S2.

Changes in the manuscript:

Page 11 lines 3-13: "From the only study in the literature focusing on iron concentrations in the submicron fraction in West Africa (Val et al., 2013), we could infer an elemental iron contribution of 7.8% to PM₁ dust, in Dakar, in the absence of dust events. Other studies focused on dust gave the iron contribution for size fractions higher than PM₁, thus no straightforward comparisons can be made with our average ratios of Fe/DD_{PM1} (20, 23, 21 and 16% for respectively IOP-1, continental, sea breeze and marine days). It can nevertheless be interesting to have in mind values retrieved within the same region as it is known that iron oxides mainly belong to the finest fraction (Journet et al., 2014; Kandler et al., 2009) and therefore the elemental iron contribution should be lower for larger sizes, which is consistent with values reported in Table S2.2."

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 - 6.1		
(Lafon et al., 2006)	Cape Verde	XRF; CBD	TSP	5.3 - 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	M'Bour 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 - 4.7		
(Lafon et al., 2006)	Banizoumbou,	XRF; CBD	10.2 μm [*] 2.5 μm [*]	5.3 5.8		
(Joshi et al., 2017)	M'Bour, Bordj (Algeria), Nefta (Tunisia)	XRD	100 µm	< 0.5		

	Table S2.2: Com	parison of iron conter	t (in %) determined in Saharan dust and soil samples
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^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

7. Page 11, lines 27-28: Why didn't the authors consider to give the contribution of chloride to total NR-PM1? I suggest the authors could also mention it.

Changes in the manuscript: The contribution of chloride (~1%) was added page 11 line 28.

8. Page 11, lines 32-34: Is there evidence to support this discussion? Otherwise, the authors should give related reference(s).

Author's response: We have now lengthened the discussion on that point, plus corrected a typo $(SO_4 and not SO_2)$.

Changes in the manuscript:

Page 11 line 30: "In our case these differences could be explained both by the semi-volatile nature of NH₄NO₃ combined with the limited use of fertilizers that prevent NH₃ emissions and ammonium nitrate formation, and more sources of non sea salt(nss)-SO₄ such as marine DMS oxidation processes. The first point can be assessed by emission inventories that provide annual NH₃ emissions (in 2010) of 53 kT in Senegal against 870 kT in France and 204 kT in the Netherlands (source EC-JRC/PBL. EDGAR version 4.2. <u>http://edgar.jrc.ec.europa.eu/</u>, 2011). nss-SO₄ comes from secondary origin and has been investigated in PM₁₀ at the Cape Verde Atmospheric Observatory (Fomba et al., 2014). This study showed increased concentrations of nss-SO₄ during dust events, linked to the oxidation of anthropogenic SO₂ transported by continental air masses. They also evidenced a seasonal variability of nss-SO₄ for marine air masses, increasing during summer, which was attributed to increased photochemistry and changes in the emission of dimethyl sulfide (DMS) due to higher biological activities in the ocean. This activity can be traced back using satellite data from AQUA/MODIS, in particular the algae concentrations along the Senegalese coast (Ocean biology processing group, 2003)."

9. Page 14, Section 3.2.1: It would be more convinced about the discussion on geographical origins, if the authors would also combine with some modeling methods, e.g., potential source contribution function (PSCF) that might be easily performed on highly-time resolved data (Petit et al., 2017). In addition, it could be also interesting to perform PSCF on organic aerosol factors.

Author's response: Indeed we have hopefully improved the discussion on geographical origins by adding a supplementary figure (Figures S5a-c) that presents: (i) back-trajectory clusters for the entire period and the different day categories (continental, sea breeze, marine); (ii) non-parametric wind regression (NWR) plots, which combine atmospheric concentrations with measured wind speed and direction for the different species and PMF factors; (iii) probability source contribution function (PSCF) maps for the variables presenting a regional origin according to the NWR plots.



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: 0.1, angle smoothing: 2, radial smoothing: 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.

Changes in the manuscript:

A new sub-section was added in the methodology section to introduce back-trajectory calculations, NWR plots and PSCF maps page 9 line 4:

"2.3.4. Geographical origins of air masses and chemical species

Air masses reaching the site were characterized through 48-hour back-trajectories (every 3 hours) retrieved from the computer version of the Hybrid Single-Particle Lagrangian Integrated Trajectory model (HYSPLIT; Draxler and Hess (1998)), for an altitude set at one half of the mixed layer depth and coupled with the GDAS (1 degree) meteorological database. Note that sea breeze phenomena, which occur at short time and spatial scales, cannot be satisfactorily reproduced by this type of model. However given the dynamics of sea breezes, only back-trajectories arriving on site at 3 pm and eventually at 6 pm during sea breeze days (< 8.2%) could not be representative of the ground dynamic observations. Therefore all the back-trajectories available for IOP-1 were kept and could be statistically grouped into clusters according to the variation of the total spatial variance, for the whole period and also by day type.

We also used pollution roses to identify local wind directions leading to high concentrations for each species or PMF factors, but also two additional tools provided by the ZeFir Igor-based package developed by Petit et al. (2017):

(i) Non-parametric regression (NWR, Henry et al. (2009)) plots, which combine smoothed surface concentrations and local wind speed and direction, to discriminate between local and more distant/regional sources;

(ii) Potential Source Contribution Function (PSCF, (Polissar et al., 2001)) maps for regional sources, which couple time series of one variable with air mass back-trajectories to redistribute the concentrations observed at the site into geographical emission parcels."

Page 14 line 28: "From back-trajectory analysis (Figure S5a) three different clusters were encountered during the whole period. The prevailing one (77% for the whole IOP-1; 91, 80 and 43% for continental, sea breeze and marine days, respectively) evidences air masses transported along the Western African coast and over Dakar. A second cluster corresponds to air masses purely originating from the ocean (19% of the total back-trajectories) and appeared as two clusters during marine days. A last cluster coming from the Saharan desert contributes only 4% of the IOP-1 air masses but reaches 9 and 10% for the continental and sea breeze days, respectively."

Page 14 line 31: "NWR plots and PSCF maps can be found in Figure S5b and S5c, respectively."

Page 14 line 34: "BC and NO₃ both exhibit local and regional influences, as suggested by their NWR plots (Figure S5b). The corresponding PSCF maps (Figure S5c) indicate regional background concentrations could come from anthropogenic emissions from Dakar (~1 million inhab. within city limits and ~3 in the metropolitan area) and possibly from maritime traffic along the Western African coast."

Page 15 line 5: "These species may also be released by anthropogenic activities in distant cities like Dakar, whose emissions may be carried toward the ocean and brought back to M'Bour by western winds. This hypothesis is also supported by back-trajectory analysis (Figure S5a)."

Page 15 line 10: "Regarding the iron pollution rose and NWR plots reported in Figure 8 and Figure S5b, maxima are measured when the site is under the influence of NE winds. The NWR plot evidences both local emissions possibly linked to traffic resuspension of DD and a regional component, that the Fe PSCF map clearly attributes to the Saharan region."

Page 16 line 34: "The HOA rose plot shows marked peaks in the directions of the two open waste burning areas and of the fish-smoking area located northeast of the site in the outskirts of M'Bour. HOA and Chl NWR plots are very similar, which suggests either common sources or a mixture of both compounds in the air masses which resulted into a correlation of 0.64 between these two variables."

Page 17 line 29: "Besides the NWR plots of Chl (local influence) and LCOA (both local and regional) rather suggest the presence of chlorinated organics. The PSCF maps identify two possible origins, one clearly from the ocean that could be related to chlorine-driven photo-oxidation processes (Hossaini et

al., 2016) and the other linked to air masses carried over Dakar where similar massive anthropogenic emissions from waste burning could be expected from Mbeubeuss, the largest dumpsite in Senegal located 25 km north-east of Dakar along the coast, which receives 250,000 tons of garbage per year from the Dakar region (Cissé, 2012)."

Page 17 line 21: "whereas LCOA pollution rose and NWR plots clearly point out toward the local combustion areas already mentioned previously"

Page 18 line 11: "OOA might not be only emitted by long distant sources, as also suggested by its NWR plot (Figure S5b)"

Page 18 line 14: "(Figures 8 and S5b)"

Page 18 line 23: "As shown by the PSCF map (Figure S5c), higher OOA concentrations are associated to air masses that moved along the coast and could transport oxidized anthropogenic species to the receptor site."

10. Page 15, lines 24-25: Should "CnH2n-1" and "CnH2n+1" be "CnH2n-1+" and "CnH2n+1+", respectively?

Changes in the manuscript: The "+" charges have been added page 15 lines 24-25.

11. Page 15, line 13: Change "Source apportionment" to "Source apportionment of OM".

Changes in the manuscript: Page 15 line 13: the title has been changed.

12. Page 15, Section 3.2.2: The biggest question I have in this manuscript is about the PMF-OA solution.

1) Page 15, lines 15-17: Please the authors could also present the results of 3 - 10 factors from the PMF-free runs in supporting information.

Changes in the manuscript: The results of 3-10 factors from the PMF unconstrained runs are now available in Supporting Information (Figure S6.1).

A sentence has been added page 15 line 21: "This factor appeared constantly above 4 factors in the unconstrained runs from 3 to 10 factors (Appendix S6, Figure S6.1) and was associated with one of the OOA for the continental, sea breeze and marine 4-factor unconstrained solutions (Figure S6.2)".







(b) 4-factor solution





(c) 5-factor solution















(f) 8-factor solution









(h) 10-factor solution



Figure S6.1. PMF unconstrained solutions from 3 to 10 factors, with (left) factor profiles and (right) corresponding daily cycles.

2) About the LCOA factor related to local open waste-burning emissions, did the authors try to compare it with any tracers? For example, please try to do some correlation analysis between LCOA with f60 (an AMS/ACSM biomass-burning tracer), f36 (as mentioned by the authors), and black-carbon aerosols from different sources, etc..

Author's response:

LCOA was compared with some tracers, as mentioned in section 3.2.2 (page 17 lines 14-16), namely Chl (r = 0.44), m/z 36 (r = 0.55) and 58 (r = 0.84).

LCOA correlation with m/z 60 remains moderate (r = 0.52), and when considering f_{36} (= mz36 / OA) and f_{60} (= mz60 / OA), correlations drop down to 0.16 and 0.25, respectively. No correlation is observed with BC (r = -0.02). We have also compared LCOA with m/z 39 (r = 0.29), which is commonly attributed to potassium ion K⁺ but can be emitted by various sources including biomass burning, industrial processes and waste incineration (Olmez et al., 1988; Riffault et al., 2015; Simoneit, 2002; Vassilev et al., 2010).

The following figure shows scatter plots related to the above-mentioned correlations between LCOA and tracers.



Figure R2. Scatter plots of LCOA vs. m/z 36, 60, BC (units are in µg m⁻³) and m/z 39 (unit Amps).

At the same time, the authors did not find any reasonable BBOA profile instead of LCOA factor. Did the authors try to compare the LCOA profile with any BBOA related profiles? What's different from them?

Author's response: Figure R3 compares our LCOA profile from the 4-factor constrained solution with two BBOA profiles from the literature (Crippa et al., 2013; Ng et al., 2011b). The LCOA factor remains atypical with higher signals at m/z 37, 56, 60, 83, 91; and lower signals at m/z 15, 27, 41, 43, 55.



Figure R3. Scatter plots of LCOA m/z profile from the 4-factor constrained solution vs. two BBOA literature profiles, with marker symbols as m/z numbers.

And did the authors find any similar such mass spectrum of LCOA during your unconstrained runs and/or constrained HOA and COA runs, respectively? I am thinking whether the LCOA factor is a kind of splitted factors due to constrained HOA and COA? Could the authors give those results from your 3-10 factor runs and make comparison with your LCOA profiles.

Author's response: The 3-10 factor unconstrained solutions are now provided in Appendix S6 Figure S6.1 (cf. reply to comment 12). The LCOA factor consistently appears <u>without constraints</u> as a stable factor (F2) from 4 factors and more as shown in Figure S6.1.

Based on the results of Fig. S6, the constrained five-factor solution seems also good. Why didn't the authors choice this one for the finally PMF-factors solution?

Author's response: First, it should be emphasized that both solutions (the 4-factor mildly constrained one and the 5-factor strongly constrained one) lead to physically realistic modelling of the observations. As for any statistical source receptor model, there is no unique solution and therefore it is the responsibility of the user (based on one's modelling expertise and knowledge of the field site) that generally guides toward one solution over the other. This feature can indeed be a weakness since the user can drive the solution toward his/her preconceived expectations. Therefore the constraints should be ideally as low as possible and always consistent with other available information. In order for our PMF solution to be comparable to other studies in the literature, we chose to present the 4 factor solution in the main text, for which more conventional model input data (that is to say only the organics matrix) were used with (i) profiles from the literature and (ii) mild constraints on the factor profiles. The 5-factor solution was obtained by using m/z 36 (HCl⁺) as an additional input for the PMF m/z matrix, and strong constraints on all the primary OA profiles (HOA, COA and LCOA all taken from unconstrained runs and not from the literature). It nevertheless gives an interesting insight into the use of non-refractory Chloride species or fragments as possible tracers of specific activities not observed so far in previous studies, as well as an estimation of the attribution of a more oxidized (and therefore more regional) OOA (MO-OOA), and one that is rather locally formed due to enhanced photochemical processes (LO-OOA) and that is why we decided to present it in the Supplementary Information as well.

Did the authors also try to constrain all BBOA, COA, and HOA factors together to check the fivefactor solution? And the authors could also try to just constrain BBOA and HOA factors to check the results. There is in factor that the BBOA factor/profile could be affected when HOA and COA factors were constrained together.

Author's response: The BBOA factor was constrained for different a-values, either alone or in combination with other primary factors (HOA/COA/LCOA) as mentioned in section 3.2.2 (page 15 line 36 to page 16 line 16) but no realistic profile or solution could be found. Page 8, lines 1-5, we also reported the average f_{60} signal (0.3%) highlighting the absence of significant BBOA at the site.

3) In addition, could the authors explain why the median mass concentrations of COA and HOA show relatively similar diurnal variations (Fig. 9), and the similarly high peaks of HOA, COA, and LCOA around 8 am? I suggest that the authors could also make correlation analysis among HOA, COA, and LCOA each other in supporting information. In addition, the authors should also consider to perform the source apportionment of black carbon as mentioned above. It will be very useful to evaluate the PMF solution by checking the relationships between HOA, COA, and LCOA with black carbon from fossil fuel combustion and biomass burning, respectively.

Author's response: Weak correlations were obtained between HOA vs. LCOA and COA vs. LCOA with respectively r =0.20 and 0.38 while HOA vs. COA present a higher correlation (r=0.77). Indeed the morning wind conditions were really stable from day-to-day for continental and sea breeze days so air masses arriving at the site around 8 am were likely loaded with the three types of POA from the different combustion sources encountered in the NE direction. We have added some pictures of the three different sites identified as possible sources for the LCOA factor in Figure 1. It can be noted also that the HOA and COA factors were hard to deconvolve because of this repetitive temporal dynamic pattern on continental days (as has already been shown for other datasets, e.g. Fröhlich et al., 2015) but they appeared without any constraints when running the PMF on sea breeze days (see Figure S6.2c, formerly Fig S4.1c) and were further used as anchors for the constrained PMF solutions. HOA was compared with BC (estimated using $\alpha = -1$ so mainly resulting from fossil fuel combustion) but we are not able to compare our factors with BC_{bb} (not retrievable using Fialho's

deconvolution, see reply to comment 5) and chose instead to use other tracers like m/z 36 or 58 for LCOA.

Changes to the manuscript: Pictures of three sites identified as contributing to the LCOA factor (Gandigal and Saly Douté open waste burning areas and a suburban fish-smoking site in M'Bour) were added to Figure 1.

Page 15 line 33: "(Figure 1 and Appendix S6, Figure S6.3)"

Page 18 line 6: "The hot temperatures and intense solar irradiation encountered in the region enhance these processes and can explain the major contribution (45%) observed for the OOA factor during IOP-1, and the predominance (\sim 3/4) of the more-oxidized fraction in the solution presented in Appendix S8."





Figure1. (top left) Dakar and M'Bour locations with city delimitations in orange and (top right) local sources located around the IRD sampling site (red star), with open waste burning areas (green circles), fish-smoking sites (blue triangles) and the M'Bour port (light blue diamond). (bottom) Photographs of (from left to right) smoldering fire in the Gandigal open waste burning area; flaming fire in the Saly Douté open waste burning area; fish-smoking location (drying stage) in the suburb of M'Bour.

4) Why did the authors select a-value = 0.6 for both HOA and COA factors (Fig. 9)? I suggest that the authors could also perform the sensitivity test of a-values (e.g., from 0 to 1, with delta a = 0.1/0.05) on HOA and COA factors for your data sets. And why did the authors apply the reference mass spectrum of COA from HR-AMS (Crippa et al., 2013) for ME-2 constraining runs, but not from the ACSMs (Fröhlich et al., 2015;Ng et al., 2011)?

Author's response: We applied different combinations of a-values based on the approach described in Elser et al. (2016); the value of 0.6 was the one offering the best solution without using too strong constraints (in order not to drive the solution to what we are expecting). We also used this approach when constraining 1, 2, 3 or 4 primary factors at a time (LCOA, HOA, COA and BBOA). There were not many differences between both the Ng et al. (2011b) and Crippa et al. (2013) COA profiles especially as we used a-values between 0.3 and 0.9. It must be noted that in the intercomparison study of Fröhlich et al. (2015) mentioned by referee #3, the COA factor could not be deconvolved by Q-ACSMs without constraints and therefore the Crippa et al. (2013) factor obtained in a previous field campaign in Paris was used as the reference profile as well.

Please check "Ng et al., 2016" in the plot?

Changes in the manuscript: Fig 9 corrected from "Ng et al., 2016" to "Ng et al., 2011".

5) Page 18, lines 3-23: It would be also interesting to discuss the different types of OOA factor, i.e., LO-OOA and MO-OOA, as showing in Fig. S6. Why didn't the authors keep both them for OOA factors in the final PMF solution? The authors would consider to try to take a look at the relationship between OOA and Fe concentrations. This might make sense to find something new.

Author's response: In the 5-factor constrained solution presented in Appendix S6 of the submitted manuscript (now Appendix S8), two different kinds of OOA were obtained: one more oxidized (MO-OOA; 76.5% of OOA) and considered from a more regional origin (mostly marine as highlighted by its NWR plot and PSCF map in Figure R4 below) and the other less oxidized (LO-OOA; 23.5% of OOA), locally emitted as per its NWR plot. Nonetheless, without using m/z 36 as input and literature profiles for constraining HOA and COA none of the solution leads to two completely distinct OOA profiles. When comparing both LO-OOA and MO-OOA with Fe and BC, only low correlations (r < 0.4) were found between the different variables, except for LO-OOA and BC (r = 0.64; n=3854) which might underline common sources for these species. Iron and OOA have completely different origins as also shown in the NWR plots and PSCF maps now presented in Figure S5 (see comment 9). If considering MO-OOA only, most of it could be rather due to the oxidation of ship emissions along the Western African coast, which would also explain the better correlation observed with NO₃ from NO_x emission processing despite the predominance of this regional oxidized factor over the local one.



for MO-OOA (left) and LO-OOA (right) obtained with the 5-factor constrained solution including m/z 36.

3.5

3.0

20

1.0

0.5

0.0

Е

LOOOA

Changes in the manuscript:

Abstract, page 2 lines 4-6: "The remaining fraction was identified as oxygenated organic aerosols (OOA), a factor that prevailed regardless of the day type (45%) and was representative of regional $(\sim 3/4)$ but also local $(\sim 1/4)$ sources due to enhanced photochemical processes."

Page 15 lines 34-36: "Since the behavior of Chl had also been suspected to come from the same sources, PMF solutions adding the m/z 36 signal in the input matrix were investigated, and a solution is presented in Appendix S8, where regional OOA accounts for ~3/4 of the OOA and local OOA ~1/4."

Page 18 line 21: "The OOA PSCF map (Figure S5c) seems to trace back its origin along the entire Western African coast, where shipping emissions could be a major source of organic aerosols."

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