

General response to reviewers:

We thank both anonymous referees #1 and #2 for providing these second reports. We have implemented the new comments in the revised version of the manuscript. The line-by-line responses to the reviewers' comments (written in black) are written in blue.

REFEREE #1

The authors did an impressive job in revising their manuscript and paying close attention to the comments which were very satisfactorily addressed.

I have few minor comments:

- Line 56: don't forget the work from Ovadnevaite et al., (2014) which is covering three complete years of AMS measurements. It is certainly one of the longest AMS measurements that were done.

Thanks, the reference was added.

- Lines 235-240: The authors only consider uncertainties on the ACSM. What about the loss of the most semi-volatile organic on the filter samplers?

The high correlation obtained between OA and OC ($R^2=0.79$, Figure S3) over a rather wide range of temperatures (8°C to 26.5°C), suggests that losses from semi-volatile organic compounds do not significantly affect the sample integrity. However, this potential artefact is now specified in the text. "It is possible that the chosen sampling periods for the comparison (spring and summer 2017) bias high the OM-to-OC value partly because of the volatilization of semi-volatile species from the filters. The high correlation obtained between OA and OC in Figure S3 ($R^2=0.79$), suggests that this artefact does not significantly affect the sample integrity."

- Line 246 and 247: please, include the country of the stations

The countries are now stated in the manuscript.

- Line 328: the authors only considered biogenic VOCs source of secondary organic aerosol. What about anthropogenic SOA and/or aging of anthropogenic aerosol during summertime?

In the present work the clear correlation between f44 and the temperature found in summer supports the assumption of the dominant contribution of the biogenic precursor emissions to the secondary organic aerosol formation. While it is not possible to estimate their relative contribution compared to anthropogenic precursors in the present study, we now mention the estimation of $\approx 70-80\%$ provided by El Haddad et al. (2011, 2013): "This observation supports the conclusion that biogenic precursors strongly contribute to the secondary organic aerosol formation at this season. Previous studies based on radiocarbon measurements of PM_{2.5} in summer evaluated that $\approx 70-80\%$ of organic carbon was of non-fossil origin and was mainly attributed to biogenic secondary organic carbon (BSOC) (El Haddad et al., 2011, 2013)."

- Line 381: what about the contribution of biomass burning emission here.

Since the N_1 fraction was determined based on the BC_{FF} contribution to UFPs, only fossil fuel emissions are expected to contribute to the increased proportion of N_1 observed in winter and autumn. The predominant influence of fossil fuel emissions on the increasing particle number concentrations during these seasons is supported by the increased values in the same proportions observed at daily peaks related to the traffic rush hours (7000 cm^{-3} and 5900 cm^{-3} in the morning, and 6000 cm^{-3} and 4600 cm^{-3} in the early evening, in winter and autumn, respectively, versus 5000 cm^{-3} and 3500 cm^{-3} in the morning and 3900 and 3500 in the evening, in spring and summer). Very recently (Casquero-Vera et al. 2021), a new approach based on the Rodríguez and Cuevas (2007) method found that biomass burning contributes in winter to 2% and 6% in the 12-25 nm and 25-100 nm size range of the UFP respectively in a urban site in Mediterranean where the biomass burning contribution to BC is comparable to the one found in Marseille (23% to the total BC vs 28% in our study). This suggests that the contribution of biomass burning emissions to UFP are expected to be low.

- Line 513: I am still not fully convinced of the importance of the nitrate mass concentration coming from the Pô valley compared to the one coming from the Rhône valley. Especially regarding the semi-volatile properties of the ammonium nitrate. Did the authors see the same results for the other chemical species (e.g. organics)?

While it is not possible to rigorously assess its contribution to the levels of ammonium nitrate observed during the PM episodes with exceedance days, we believe that the Pô valley, being one of the main pollution hotspots in Europe, is a potential source that cannot be ignored. This assumption is based on the study of the HYSPLIT air mass 72h-backtrajectories and CWT maps for NO_3^- backtrajectories shown in Figure S15 and on the cold temperatures experienced when these episodes occur. We believe that cold temperatures can favour the transfer and stabilisation of nitrate in the particle phase, and thus allow its transport over long distances. Ammonium nitrate concentrations attributed to mid/long-range transport have already been observed in Europe (Bressi et al., 2014; Dall'Osto et al., 2009; Petit et al., 2015).

Similar results to those presented in Figure S15 were indeed obtained for organics, but the additional CWT analysis carried out on the NO_3^-/BC ratio (BC prevails for local influence from the city) and shown in Figure A1 better supports the long-range transport of ammonium nitrate.

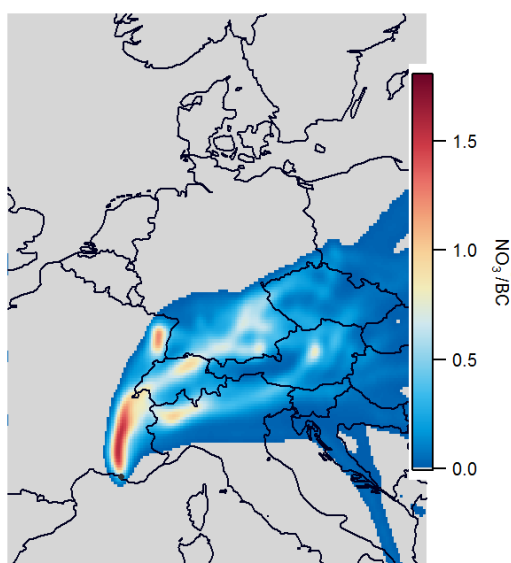


Figure A1 – CWT maps for NO₃⁻/BC during the February 2018 episode.

- Line 521: Chemical valley?

The term was corrected.

- Notation: PM1 or PM1

Corrected.

- Figure S3: some y-axis labeling is missing.

Corrected.

- Figure S12: please correct the color scale of the night-time plot.

Corrected.

references

Ovadnevaite, J., Ceburnis, D., Leinert, S., Dall'Osto, M., Canagaratna, M., O'Doherty, S., Berresheim, H., and O'Dowd, C.: Submicron NE Atlantic marine aerosol chemical composition and abundance: Seasonal trends and air mass categorization, *Journal of Geophysical Research-Atmospheres*, 119, 11850-11863, 10.1002/2013jd021330, 2014.

REFEREE #2

I thank the authors for the careful revision of the manuscript, which reads much more easily now and with a clearer message. I have just a few minor and technical comments.

Minor:

L.582: Maybe I missed it in the text, but I wonder why would cluster #1 has the highest N₂ concentration? Could it be some local contamination associated with slightly different wind direction? Also, I'd suggest adding O₃ diurnal variability in the clusters plot, which is a good proxy for photooxidation during those days.

We added the mean O₃ diurnal profiles for each cluster in Figure 12. We now refer to the ozone concentrations in the main text as following: *“The molar ratio of sulfate to total sulfur, indicative of SO₂-to-sulfate conversion grows when photochemical activity is expected to be at its highest (between 11h00 and 16h00 according to the highest concentrations of O₃ diurnal profile), from 0.3 (10h00) to 0.5 (16h00) (Figure S18).”*

About the highest N₂ concentration found in cluster 1: This is exactly the situation described by the referee, i.e. nearby coastal emissions of SO₂ and N₂ (10-20 nm) are mixed with the regional background of sulfate once the sea breeze sets in and brings the plumes of fresh emissions to the sampling site. We state this situation in the following sentences page 18 “Cluster 1 seems to be related to the regional background of sulfate as it is associated with the lowest concentration ($\approx 2\mu\text{g m}^{-3}$) and a flat diurnal

profile. Meanwhile, SO₂ and N₂ (10-20 nm) increase simultaneously as the breeze sets in to peak at 4 μg m⁻³ and 8000 cm⁻³ respectively at 10h00-12h00. The comparison of the daily profiles indicates that sulfate is fully decoupled from its precursors in this cluster and that no significant conversion of SO₂ to sulfate occurs by the time the air mass reaches the site.” and later page 19 “The NWR plots confirm the hypothesis on the potential origin of sulfate and SO₂ in the 3 clusters: in the case of cluster 1, sulfate and SO₂ are disconnected to each other...”

Fig. S23: I'd suggest to move this figure to the main text, it's quite interesting and corroborates the authors interpretation of the clusters identification based on diurnal variability and back-trajectory analysis.

We moved the Figure S23 to the main text (now Figure 14).

Technical:

Title: “atmospheric dynamics”

Corrected.

Abstract: remove sentence “These episodes contribute to an increase of 6.5% of the annual PM1 concentration.”

The sentence was removed.

L.65: add a comma between “years” and “aerosol mass spectrometer”.

Corrected.

L.351, 353 and L.355: I think there are more line skips here than originally intended.

Corrected.

L.439: add a comma between “winter” and “N2”.

Corrected.

L.468: please put the number “2” in writing.

Corrected.

Fig. 7: the axis labels are quite close, making it difficult to read it. I suggest to favor skipping line whenever possible (PBL /n (m), for example) and perhaps increase the figure height.

The axis labels were adjusted accordingly.

L.510: I'd prefer to replace "secondary" with "processed", as f44 is not a unique tracer of the former.

Corrected.

L.532: please add "fresh" before biomass burning.

Corrected.

L.620: Define concentration of which parameter (NR-PM1, PM1, PM2.5)

We now refer to the "PM₁ concentration level".

References:

Bressi, M., Sciare, J., Ghersi, V., Mihalopoulos, N., Petit, J.-E., Nicolas, J. B., Moukhtar, S., Rosso, A., Féron, A., Bonnaire, N., Poulakis, E., and Theodosi, C.: Sources and geographical origins of fine aerosols in Paris (France), *Atmos. Chem. Phys.*, 14, 8813–8839, <https://doi.org/10.5194/acp-14-8813-2014>, 2014.

Casquero-Vera, J. A., Lyamani, H., Titos, G., Minguillón, M. C., Dada, L., Alastuey, A., Querol, X., Petäjä, T., Olmo, F. J., and Alados-Arboledas, L.: Quantifying traffic, biomass burning and secondary source contributions to atmospheric particle number concentrations at urban and suburban sites, *Science of The Total Environment*, 768, 145282, <https://doi.org/10.1016/j.scitotenv.2021.145282>, 2021.

Dall'Osto, M., Harrison, R. M., Coe, H., Williams, P. I., and Allan, J. D.: Real time chemical characterization of local and regional nitrate aerosols, *Atmos. Chem. Phys.*, 12, 2009.

El Haddad, I., Marchand, N., Temime-Roussel, B., Wortham, H., Piot, C., Besombes, J.-L., Baduel, C., Voisin, D., Armengaud, A., and Jaffrezo, J.-L.: Insights into the secondary fraction of the organic aerosol in a Mediterranean urban area: Marseille, 11, 2059–2079, <https://doi.org/10.5194/acp-11-2059-2011>, 2011.

El Haddad, I., D'Anna, B., Temime-Roussel, B., Nicolas, M., Boreave, A., Favez, O., Voisin, D., Sciare, J., George, C., Jaffrezo, J.-L., Wortham, H., and Marchand, N.: Towards a better understanding of the origins, chemical composition and aging of oxygenated organic aerosols: case study of a Mediterranean industrialized environment, Marseille, 13, 7875–7894, <https://doi.org/10.5194/acp-13-7875-2013>, 2013.

Petit, J.-E., Favez, O., Sciare, J., Crenn, V., Sarda-Estève, R., Bonnaire, N., Močnik, G., Dupont, J.-C., Haefelin, M., and Leoz-Garziandia, E.: Two years of near real-time chemical composition of submicron aerosols in the region of Paris using an Aerosol Chemical Speciation Monitor (ACSM) and a multi-wavelength Aethalometer, 15, 2985–3005, <https://doi.org/10.5194/acp-15-2985-2015>, 2015.

Rodríguez, S. and Cuevas, E.: The contributions of "minimum primary emissions" and "new particle formation enhancements" to the particle number concentration in urban air, 38, 1207–1219, <https://doi.org/10.1016/j.jaerosci.2007.09.001>, 2007.