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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Measurement report: Long-term real-time characterisation of the submicronic aerosol and its atmospheric dynamic in a Mediterranean coastal city: Tracking the polluted events at the Marseille-Longchamp supersite" *by* Benjamin Chazeau et al.

Anonymous Referee #1

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Review

Chazeau et al. describe a 14-months measurement campaign at the urban station of Marseille-Longchamp supersite (Marseille, France) from February 2017 to April 2018. The paper focuses on the analysis of data from ToF-ACSM and aethalometer measurements. Besides, it is important to note that the station is also used by the local air quality agency providing long-term measurements of standard air quality variables

(NOx, O3, SO2; BC, PM10, and PM2.5), which are partly included in the manuscript. The discussion begins with a mass closure analysis using collocated instrumentations, following by a description of the seasonal and the diurnal profiles of the PM2.5 chemical components. Two case-study events corresponding to periods when the total PM mass exceeded the WHO recommendation of 25 μg/m3 over 24 h were considered and described in more detail (Christmas 2017 and 4 consecutive days in February 2018). Finally, the results section ends with a discussion on the influence of ship and industry emissions on the local sulfate mass concentration. Although the manuscript responds to the need for a +1 year continuous measurements at a high time-resolution to better characterize the different factors and sources influencing local air quality, the results are presented rather as a descriptive report than as an attempt to answer a well-identified scientific question or to focus on a specific topic. This lack of a central theme makes it difficult to read and to catch the link between the different sections and the sub-sections. A direct consequence is that sometimes, I had the impression that the authors have lost their focus and started to describe results that are not directly related to the measurements made at the Marseille-longchamp supersite (for example, the discussion about BC source at the Kaddouz site) or to change the subject before returning to it (for example, the seasonal variability section starts and ends on BC source estimation, with in-between results from the splitting of the ToF-ACSM nitrate signal into NO3,inorg and NO3,org) making the reading complicated. Overall, the results presented in the manuscript are worth publishing in ACP after clarification of several critical issues.

Major comments: - Although the main instrument of the manuscript is a ToF-ACSM and an aethalometer, a detailed description of the black carbon and its related sources is made in each section but the authors never seriously discuss the organics. I can imagine that the authors are preparing a paper dedicated to organic source apportionment, but it is a shame to present the different BC sources without mentioning those of organics. At least the authors can use the time series of well-known tracers (e.g. m/z 57 for HOA, m/z 60 for BBOA, m/z43, and 44 for the OOA, as well as m/z 79 for MSA?)

as well as look for a possible cooking aerosol contribution using the triangle approach from Mohr et al. (2012). This will certainly facilitate the interpretation of the results. - One of the most interesting and important points of this paper is certainly the contribution of ship emissions to the sulfate budget. This is the specificity of the sampling place which combines urban and ship emissions at the same place. Did the authors also consider the possible influence of ship emissions on the nitrate budget? It is known that ships are also an important source of NOx too. - How does the sea/land-breeze cycle affect the aerosol particle chemical composition and their diurnal profiles? At least during the summer months, the change in wind direction seems to have a pronounced diurnal variation ranging from 250 to 50 degrees (figure S11), which should correspond to the sea/land-breeze cycle. - section 2.1 Marseille Supersite: The discussion of the air quality parameters (O3, NO2, SO2, PM10, PM2.5, and BC) over the last 11 years is already a result in itself, which would be preferable to include in a dedicated section (e.g. overview of the general air quality, or trend on the air quality). Moreover, I would have preferred here more details regarding the sampling method itself in addition to the instrumental description. For example, were all the online instruments (ToF-ACSM, aethalometer, SMPS, BAM, FIDAS) connected to the same sampling line? Which type of inlet was used (PM)? What was the high of the inlet? How was the relative humidity controlled for each instrument (not only for the ToF-ACSM)? If the instruments were connected to the same inlet, how was the main flow distributed between them? Such information is mandatory when presenting a new sampling site. Additionally, how were the filters conditioned before and after being sampled? Which instruments were used for OC/EC and water-soluble ions measurements (manufacture, column, eluant, ...). - The authors should pay more attention to the homogeneity of the methodology applied to the manuscript. For example, regression fits are performed using orthogonal distance on the main text, which is appropriate for considering uncertainties on both datasets, but least squares regression is applied in the supplementary information. I also don't think all regression parameters (slope, intercept, and r^2) need 4 decimals digits. Two should be more than sufficient here. Finally, it would be nice to specify at

least once on the manuscript, "a" and "b" or to replace them with "slope" and "intercept" The same kind of comments can be made regarding wind analysis, where NWR and SWIN-2 are used. A single method will make the comparison between the results much easier and robust.

- Section 3.2.1: as mentioned above, this section is very confused and the discussion on the seasonal variability of the aerosol chemical composition is mixed with other results such as the average chemical composition over the 14-months of ToF-ACSM measurements, the average of the decade PM2.5 filter measurements, and the discussion on the aethalometer BC source estimation with no direct link to seasonal effect. Same comment for the field campaign carried out on Kaddouz site. Does it make sense to present these results here or in this paper at all? In case the authors want to keep it inside their manuscript, the sampling site must be appropriately presented in section 2, including the exact measurement period, the description of the sampling line, the list of the instruments deployed. The results must be also presented in a dedicated section and referred to in the abstract and the conclusion. Moreover, the discussion on the seasonal variation of the different aerosol compounds should be reorganized to make it consistent. For example, BC sources are discussed using the aethalometer measurements and at the end again using the UFP number concentration. The discussion will be strongly improved by combining these two parts. What about the organics? They are poorly discussed, whereas sulfate and chloride are not discussed at all. - line 438: based on which criteria the two selected case studies were selected from the 15 exceedance days? More detail will be helpful to better describe how similar were these events and discussed the factors promoting the exceedance days. Also, 2 exceeding events were selected, air mass trajectory analysis on a third one is also included. Is there any reason for that? How are the air mass trajectories for the first event? Because the 2 selected exceedance events have similar wind direction, ambient temperature, and planetary boundary layer level, it would be helpful to also discuss the wind speed during each of them or looking at the CWT profile as presented for the sulfate cases, to better understand why the first one may be considered as under

the influence of local emissions and not the second one. As the authors mentioned, the ratio BC/SO4 has some limitations which could be easily reached at the sampling according to local SO2 emissions as well as long-range transport of BC. How did the author deal with these limitations to conclude that 40 % of the exceedance days account for the local origin and 60 % for long-range transport? More explanations are strongly required. - section 3.3.2: the cluster analysis is relatively surprising here. First of all, the definition of the sea-breeze cluster is not fitting with the south-western wind sector defined line 10, and the trajectory density in Figure 11, corresponds to a land-breeze rather than a sea-breeze. Then, the discussion is focused on local processes, therefore wind direction may be more efficient for distinguishing the different wind regimes associated with such processes. What about the sea/land-breeze cycle effect as can be seen in figure S11? Is a frequency of 19 % (cluster 3) negligible? It would rather be important to compare aerosol properties (chemical composition and size distribution) during mistral and sea-breeze clusters since both are coming from the same area. -section 3.1 and Fig. 2 & S3: Is there any seasonal effect on the comparison between ToF-ACSM-BC and off-line/FIDAS/SMPS measurements? Some deviations can be seen in the comparison with SMPS and FIDAS.

Minor comments: - All acronyms must be defined before being used for the first time, even on the abstract (for example, OA and BC (line 20), UFPs (line 28), EU (line 39), LCE (line 90)). - line 13: Could you please mention the country? - line 42: 300000. - line 48: Do the authors speak about PM2.5 or PM1? - line 51: Pandolfi et al. (2020) - line 102: The dominant wind directions mentioned in the text are not visible in Figure S1. Moreover, the sea breeze wind direction is defined on the 190-270°, while in section 3.3.2, the authors named an air mass cluster “sea-breeze” having almost a pure continental origin. This is confusing. - line 134: replace lpm by L min-1 - line 138: correct lgro -line 139: Wavemetrics - line 144: How was selected the CE = 0.47? - line 167 and 170: Please check the date notation over the manuscript (with or without a 0) - line 189: How accurate is the HYSPLIT model at such a low altitude (64 m above ground level)? - line 200: How many filters were used (45 or 46)? - line 200:

Correlation coefficients are written R^2 on the main text and r^2 inside the figures. Please correct accordingly. - Line 203 acidity plot: Is there a possible seasonality effect? What happens during periods with strong deviation? For example, at the beginning of the campaign (green period) when NH4_meas strongly deviate from NH4_pred? Is there any sea-salt detected? Furthermore, it would be great to mention the different urban sources of ammonia like diesel cars. How the correlation is improved when using NO3inorg? - line 210: Please include a reference to Figure S3 when discussing the OC vs. organics. It would be also extremely interesting to compare the OC from the filter with the OC estimated from the ToF-ACSM based on the f44 signal as it can be done for the AMS (Canagaratna et al., 2015). - line 227: Please indicate the value of the selected organic density finally chosen. - line 240: Why forcing the intercept to zero here? - line 241: This conclusion can also be supported by comparing PM1 and PM2.5 from the FIDAS for the last months of the campaigns. Is this ratio constant over the 14-months? Is there any seasonal or diurnal variation on the ratio? - line 247: Is the PM1 refers here to the ACSM-BC? - line 248: Would it be simpler to always refer to the same recommendation of the WHO? Here it is 10 μg m-3, in Figure 3 it is 25 μg m-^{3}, as well as for the selection of the case studies. - line 253: Which factor was used for the conversion of the OC to OM? - line 312: Can refer to Schaap et al. (2004) for example. - line 321: Can the summer results be influenced by the low nitrate mass concentration at this time of the year? Which lowest detection limit was used here? Is there any link between the NO3,org and BCwb as the aging of wood-burning aerosol can lead to nitrogen-containing compounds? - line 384: Is it still related to BCwb? - line 393: Is there any reason why summer NO3,org is only discussed for June 2017? - line 413: How does it compare with the organics or m/z44? - line 419 – 420: Could you please detail a bit more? What does it mean “the N2(10-20 nm) number concentration, corresponding to 90% of the total number in this range”? - line 426: Does the PM1 mass concentration of the selective days also exceed the 25 μg m-3 over 24h? - line 431: Is there any explanation for the 2 outstanding years? Could it be related to specific weather conditions or local events? - line 435: This is

quite difficult to see in Figure 1. - line 455: Particle number size distribution during the selected event would be helpful. - line 470: “the aerosol chemical composition was relatively stable” - line 497: Could it be possible that the polluted air masses were rather coming from the Rhone valley than bringing Pô valley polluted air masses over the Alpes mountains? Can a trajectory analysis (CWT) help to identify the potential aerosol source area? - line 498: Why is there a new case study event? - line 519: Is there any confusion here? This section aims to discuss the summer sulfate origin and figure 8 the relation between sulfate concentration and UFP over the seasons. This should rather be done earlier on the seasonal analysis part. - line 525: Please rephrase the sentence “during summertime, the ships traffic increases by 25 % (4319 against 3263 for the 2017-2017 period)”. What are the numbers referring to? - line 530: I disagree a bit here since the SO2 concentration is continuously increasing from midnight to 9 o’clock, so much earlier than the ship traffic peak. - line 556: Is the discussion on the sulfate classification needed? It was already mentioned that sulfate is fully neutralized by ammonium. No new conclusion was drawn from this sulfate fragmetns analysis. It would be interesting here to look for example, at the time series of the 3 different sulfate species and compare the MSA results with the time series of the m/z 79. - line 559: Numbering of figures 11 and 12 should be changed. Figure 12 is discussed first. - line 574: The term long-range transport is relative here since sulfate sources look to the located relatively close to the city of Marseille.

Tables, Figures, and supplementary information: - Please used scientific notation on the axis labeling. -Figure 2-a: Did the authors investigate the deviation between ACSM-BC and SMPS when density increase? Seems that there is a deviation for density above 1.5. Could it be linked to the presence of more sea-salt or coarse particles? - Figure 6: Is there any reason why BCwb and BCff are presented in Fig 6a and not in Fig 6b? Wind speed would also be interesting here. - Figure 8: What does the number of points mean (time resolution)? Moreover, a log-scale would be helpful to better catch the number of points on each category. - Figure 9: The difference between the two red colors (arrival and departure at the South terminal) is not easy to catch. Please, provide

information for the wind speed intensity value. - Figure 10: Please include similar plots for the missing cluster 3. - Figure 12: Please include the expected limits of the triangle (location of organosulfates, MSA and ammonium sulfate). Ammonium sulfate from the 7/12 calibration is missing. -Figure S1: The central map is rather too small and it is very difficult to distinguish the different colors on the Marseille port. - Figure S3 caption: Please, correct PM1 notation. - Figure S5: please include the zero lines - It will make the reading of the supplementary information easier by including tables and figures directly in the corresponding text section. - Is figure S14c discussed?

References: -Canagaratna, M. R., Jimenez, J. L., Kroll, J. H., Chen, Q., Kessler, S. H., Massoli, P., Ruiz, L. H., Fortner, E., Williams, L. R., Wilson, K. R., Surratt, J. D., Donahue, N. M., Jayne, J. T., and Worsnop, D. R.: Elemental ratio measurements of organic compounds using aerosol mass spectrometry: characterization, improved calibration, and implications, Atmos. Chem. Phys., 15, 253-272, doi 10.5194/acp-15-253-2015, 2015. -Mohr, C., DeCarlo, P. F., Heringa, M. F., Chirico, R., Slowik, J. G., Richter, R., Reche, C., Alastuey, A., Querol, X., Seco, R., Penuelas, J., Jimenez, J. L., Crippa, M., Zimmermann, R., Baltensperger, U., and Prevot, A. S. H.: Identification and quantification of organic aerosol from cooking and other sources in Barcelona using aerosol mass spectrometer data, Atmos. Chem. Phys., 12, 1649-1665, 2012. -Schaap, M., Spindler, G., Schulz, M., Acker, K., Maenhaut, W., Berner, A., Wieprecht, W., Streit, N., Muller, K., Bruggemann, E., Chi, X., Putaud, J. P., Hitzenberger, R., Puxbaum, H., Baltensperger, U., and ten Brink, H.: Artefacts in the sampling of nitrate studied in the "INTERCOMP" campaigns of EUROTRAC-AEROSOL, Atmos. Environ., 38, 6487-6496, 10.1016/j.atmosenv.2004.08.026, 2004.

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