

On the sub-micron aerosol size distribution in a coastal-rural site at El Arenosillo Station (SW-Spain)

Sorribas et al.

Response to review by Anonymous Referee #3.

We thank the referee for comments and suggestions on the manuscript. Here we detail the response to all questions. In addition, as a consequence of responding the first Reviewer's comment, several Figures have been eliminated and replaced with a sentence or two of text. And also, new Figures and Tables have been added with the aim to: first, provide information valuable to the scientific community for regional comparisons, model initiation or testing, and second, describe the size distribution by means of air mass type and trajectory analysis. Then, the Figures and Sections have been renumbered and the text, abstract and conclusions have been accordingly modified, incorporating new results. A revised manuscript with these modifications is also available.

General comments

The paper presents two years of continuous DMPD measurements from the El Arenosillo GAW Station in Spain. The measurements seem to be carefully conducted and the calibration of the instrument has been performed at the IfT. The paper therefore presents data which is quality assured and very useful to the aerosol community. The papers contains a detailed analysis of the data, and being a GAW station I assume that the data have also been (or will be) submitted to the joint data bank.

Yes, the SMPS data will be submitted to GAWSIS.

What the paper is lacking is a coherent presentation of the data. It took several times to read the article before getting a clear picture of the message that the authors are trying to relay: a fast reader will be left confused. Thy can be fixed by moving a couple of paragraphs here and there (suggestions will follow in the detailed comments), and be carefully segregating the sections where different data are addressed. In the current form of the paper, it is sometimes difficult to understand which numbers relate to which pieces of data. In addition, the English language will need to be improved considerably. I recommend having the article proof read by a native English speaking person, or using a proof reading service. Upon correcting these issues, I can recommend the paper to be published in ACP.

The manuscript has been carefully reviewed regarding the English language. Many paragraphs have been edited to clarify the results of the study.

Detailed comments

Abstract

R.3.1- Instead of speaking about modes, here could be the size limits for “nucleation”, “Aitken” and “accumulation mode”. This would remove the mismatch with the next sentence, which mentions 4 different modes.

According to the comments of Reviewer, this suggestion has been included in the revised manuscript.

R.3.2 - There is talk about 60% of nucleation events falling under certain conditions. If I understood the paper correctly, this is valid only for events N_1 ?

Yes, this is valid only for Events N_1 . According to the comment of the Reviewer (see, R.3.23), we are going to prepare a separate paper with a longer time series to analyze in more detail the nucleation events in El Arenosillo. Then, this paragraph has been deleted of this manuscript and the analysis will be developed more carefully in the new report. In the actual study, nucleation events are presented in terms of general comments.

R.3.3 – I would no draw the conclusion “1 cm³ increase of the nucleation mode equals 0.5 cm³ decrease in accumulation mode” from the monthly averages, but from the concentration relations directly. I will come back to this later.

In order to clarify the comment of the Reviewer, it is advised to consult the R.3.12 answer.

Chapter 2.1 – Sampling station site

R.3.4. – The authors divide the air mass back trajectories into coastal marine conditions (44%), continental air masses (38%) and desert dust (18%). Could this segregation be utilized later in the chapter 3.1 Mean Levels?

Sect. 3.5 shows a classification of the airmass origin on the basic of cluster analysis to determine the influence of long-range transport aerosol sources on the particle number size distribution. The Section has been entitle ‘Size distribution in relation to air masses’. We decided to include this new analysis in a separate section, due to the relevance of the results.

R.3.5 - The authors report one longer gap in the measurements for about 2 months. Do you think having this gap increase or decreases the reported average concentrations? If so, would be the difference be notable?

Because that the evolution of the monthly mean concentration over the two-year period showed independence with the seasons, we think that the reported average concentrations could not modify considerably. But a trend in increasing the concentration for Aitken mode was also observed. But, because the reasons for this behaviour are not know with certainty, it is not possible to argue as the average concentration had changed. With regards to the trend in the concentration for Aitken mode, this paragraph has been included in the revised manuscript in Sect. 3.2:

“From the two-year period of data presented here, a trend in increasing N_{AIT} with a rate $1150 \text{ cm}^{-3} \text{ year}^{-1}$ was observed, such as the correlation line shows in Fig. 3c. This behaviour may be related to the impact of sea-land breeze patterns, when the land breeze flow is blowing from NE (called pure breeze in the following sections). Days under this regional pattern, which were more frequent in 2006 (see Sect. 3.4), evinced

an increase of N_{AIT} in comparison with those without incidence of regional circulation (see, Sect. 3.6, Table 4). But, it is desirable to take many more years of in-situ measurements, (e.g. of particle size distributions and extinction coefficients), to know the significance and more deeply the reason of this behaviour.”

R.3.6 - Rather than talking about the number of size distribution spectra per month, I would talk about data coverage in percentages. This relates to figure 3 too.

- Next sentence “The monthly number of measurements during the period of study is presented in Fig. 3, with about 3500-400 spectra per month” was modified by “The temporal coverage of data (in percentages) during the period of study was about (4-5) % of the valid size distributions per month”.
- Referee #1 suggested removing some figures. So, Figure 3 has been deleted and replaced by the previous sentence.

Chapter 3.1 Mean Levels

R.3.7 - I’m not sure if I like the comparison against data from arbitrary stations in the World. From the stations listed here, I would say Ispra is the only relevant comparison point, also located in Southern Europe. Like the earlier referees have suggested, it might be useful to check what global models suggest the concentrations are.

According to the comment of the Reviewer 2, the name of the section has been changed and the new title is ‘Mode Descriptions’. Moreover, the point of comparison has been modified and the new information reported is:

“Comparisons with other size distributions measured at similar latitudes sites has been based on previous and recent studies which used observations (Asmi et al., 2011) and results from global aerosol models (Spracklen et al., 2010) of total particle number concentration, for better understanding the diurnal, weekly and seasonal variability at different stations around the world. From measurements performed at mid-latitudes coastal locations, mean total particle number concentrations were between 1000 cm^{-3} and 2000 cm^{-3} while greater concentrations were observed at Mace Head with 3000 cm^{-3} (Spracklen et al., 2010). Given that El Arenosillo station is at mid-latitude of a coastal site, it is possible to expect that mean particle levels can be similar than in the other coastal mentioned areas. But, the influence of continental, desert dust and anthropogenic aerosol sources may increase the coastal background particle level and therefore, the mean total concentration at El Arenosillo station. Using as reference the study of Asmi et al., (2011), ($N_{AIT} + N_{ACC}$) observed at El Arenosillo Station is the second highest value measured at Central Europe; behind Ispra Station with 7188 cm^{-3} and before Cabauw and K-Pusztas Stations with 5126 cm^{-3} and 4648 cm^{-3} respectively. Referring to N_{NUC} at El Arenosillo Station, this value is higher than the particle concentration at Ispra (Rodríguez et al., 2005) and Melpitz Stations (Birmili et al., 2003). So, the total and modal particle concentration at El Arenosillo was closer to the levels in rural areas, located in Central Europe, than in the coastal rural sites of the mid-latitudes.

The following references have been included:

- Asmi et al., 2011. Number size distributions and seasonality of submicron particles in Europe 2008-2009. Atmos. Chem. Phys. Discuss., 11, 8893-8976.

- Spracklen et al., 2010. Explaining global surface aerosol number concentrations in terms of primary emissions and particle formation. *Atmos. Chem. Phys.*, 10, 4775-4793.

According to the comments of Reviewer 2, the following reference has been eliminated:

- Liu, S., Hu, M., Wu, Z., Wehner, B., Wiedensohler, A., and Cheng, Y.: Aerosol number size distribution and new particle formation at a rural/coastal site in Pearl River Delta (PRD) of China, *Atmos. Environ.*, 42, 6275-6283, 2008.

R.3.8 - Discussion and related table 1. Do the “Entire period study” statistics contain the “mixed event” occurred on 27.7-4.8.2004 or are they calculated without the mixed event?

Statistics parameters for ‘entire period study’ were evaluated considering the ‘mixed event’ except to the maximum. The objective was also to report the maximum value, without considering this punctual case. In order to avoid the confusion noted by the Reviewer and for clarify in the presentation of the results, the following sentence has been included in the legend of Table 1: “(*) The maximum of the entire period of study has been calculated regardless of the ‘mixed event’”.

Chapter 3.2 – Monthly and seasonal total and modal concentrations.

R.3.9 - I would not begin this chapter by presenting data from individual case days. Consider removing this paragraph completely, or presenting it at the end of the chapter as a sub chapter with some figure similar to Fig 10.

According to the comments of the Reviewer, this paragraph was removed completely.

R.3.10 - Talking about monthly increase or decrease of different modes deserves a more rigorous examination; were there more nucleation events or just more often? How do these data relate to the different air masses mentioned in chapter 2.1?

New information has been included in the Sect. 3.2. Some of these main results were exposed with the following sentences:

- “The Period A showed an increase of N_{NUC} and N_{AIT} with 2260 cm^{-3} and 1360 cm^{-3} and a decrease of N_{ACC} with 940 cm^{-3} . This behaviour was related to an increase of the new particle formation events (see Sect. 3.7 for details about discrimination of nucleation events). This process was promoted by a reduction of N_{ACC} due to there were fewer desert dust and continental airmasses arriving to El Arenosillo (see Sect. 3.5).”

- “The trends, over the two years of study, which were observed during some similar time period, are striking. It can be evinced for the comparison between the trends of the particle concentration during Period B (April – June 2005) and Period C (April – June 2006). This way, while in April 2005 the monthly mean N_{NUC} and N_{AIT} were 4040 cm^{-3} and 1120 cm^{-3} , in April 2006 these mean values were 2710 cm^{-3} (1.5 times lower) and 1220 cm^{-3} (1.6 times higher) respectively. It is related to the desert dust episodes, as it is shown below. In Toledano et al (2007b) on the basic of photometric measurements, April is not mentioned as a month influenced by desert dust episodes. In April 2005,

mean aerosol optical depth (AOD – 440 nm) of 0.15 and mean Ångström exponent (α) of 1.09 were reached, (AERONET Level 2.0) and in April 2006 these mean values were 0.25 and 0.76 respectively, (AERONET Level 1.5 - no data in Level 2.0 were achieved). Taking into account these mean values and those obtained by the inventory of African desert dust events over El Arenosillo (Toledano et al., 2007b), the number of observations produced by the desert aerosols is higher in April 2006 than in April 2005. It is also corroborated by the back-trajectory analysis at 500 m presented in Sect. 3.7.”

R.3.11 - Page 3823, line 12: how did you deduct that 60% of the particles in nucleation mode grew to Aitken mode? I’m no sure looking at monthly averages is the proper way to do this. If nucleation occurred, this should rather be looked at case by case. After looking at the data you wouldn’t need to say: “This behaviour may be related to new particle formation”; this claim is easy to check.

- The sentence “Also, 60% of the particles,..., with a rate of $340 \text{ cm}^{-3} \text{ month}^{-1}$ ” was deleted.

- The following sentence was included in Sect. 3.2: “This relation between modal concentrations was also observed for monthly mean N_{AIT} & N_{NUC} ($R = 0.5$, $A = 0.6$) and so, from the value of slope, the growth of about 60% of the particles from nucleation mode to Aitken mode was evinced.”

- For more detail, the Reviewer is advised to consult the R.3.10 answer with information of the Period A.

R.3.12 - The conclusion “1 cm^3 increase of the nucleation mode equals 0.5 cm^3 decrease in accumulation mode” is now here. I really don’t think such a conclusion can be drawn on basis of a timeline data. Rather just plot monthly N_{nuc} versus N_{acc} and look at the slope of dataset. This would be much more quantitative.

- Page 3823, Lines 14:26 - The sentence “If the trends of N_{NUC} and N_{ACC} during the Periods A and B are compared, it....in the nucleation mode of 1 cm^{-3} ” was modified by “The linear correlation coefficients (R) and the slope (A) between monthly mean N_{ACC} & N_{NUC} ($R = 0.7$, $A = -0.4$) were calculated. As expected, these monthly averages were statistically dependents each other. Thus, it is possible to conclude that every decrease/increase in the accumulation mode of about 0.4 cm^{-3} (slope value) was related to an increase/decrease in the nucleation mode of 1 cm^{-3} . It is also corroborated from monthly means of N_{NUC} and N_{ACC} showed previously during Periods A and B.”

- Page 3826, Lines: 18:26 - This paragraph was deleted.

R.3.13 – Consider showing the trajectory information in this chapter. I would suggest the following structure for the chapter: begin with the timeline, then present the data in light of the air masses types. After that discuss the data, and whether the air mass occurrence evolved during the measurement period. There might (or not) emerge patterns that can explain the overall trends of the data, i.e., the apparent increasing trend in the N_{ait} . I leave the decision how to further develop the chapter to the authors.

According to the suggestion of Reviewer, the revised manuscript contains the following sections: the area of study, the sampling station and the aerosol instrumentation, including its intercomparison with a GAW standard, which are described in Sect. 2. The results and discussion are given in Sect. 3, showing in Sect. 3.1, 3.2 and 3.3 a statistical analysis of the size distribution over the course of two years by means of the diurnal, seasonal and annual cycles of the total and modal concentration. In Sect. 3.4, a day's segregation by means of regional and synoptic-scale patterns was performed according to surface data of wind speed and direction. This categorization was supplemented with an identification of the different types of new particle formation episodes. Sect. 3.5 shows a classification of the air mass origin on the basis of cluster analysis to determine the influence of long-range transport aerosol sources on the particle number size distribution. In Sect. 3.6 are presented and discussed the results of the size distribution analysis according to sea-land breeze processes. And finally, in Sect. 3.7, new particle formation events are illustrated, using diverse aerosol properties and meteorological parameters.

Chapter 3.3 Diurnal evolution of the modal size ranges

R.3.14 - Perhaps the heading should be changed slightly, as the size ranges of the modes are not the ones that are changing.

The heading was modified by “Diurnal evolution of the modal concentrations”.

R.3.15 - Page 3825, line 19: “The maximum for N_{NUC} were reached at 11:00 GMT and 10:00 GMT... Then, during summer time there was a delay of 1-h...” Please consider clarifying these sentences; I'm not sure I understand what the authors are trying to tell.

This sentence “Then, during summer time there was a delay of 1h between the maximum of N_{NUC} and N_{AIT}” has been deleted of the revised manuscript. According to the comment of the Reviewer (see, R.3.23), we are going to prepare a separate paper with a longer time series to analyze in more detail the nucleation events in El Arenosillo. The behaviour explained in this paragraph is related to the particle growth and we have preferred to incorporate this information, together with a more detailed analysis, in the new article.

R.3.16 – Paragraph beginning on page 3825, line 23: except for the last sentence, I would move this paragraph somewhere in the nucleation event chapter. The paragraph breaks the flow of the current chapter somewhat.

As was shown in the previous answer, we are going to prepare a separate paper with a longer time series to analyze in more detail the nucleation events. So, this comment will be included in the new article and now, it was deleted of the revised manuscript.

R.3.17 – The authors discuss an evening maximum observed in the nucleation and Aitken mode during summer evening/night. How do the DMPS plots look like? Are there additional nucleation events in the evening?

In Birmili et al., (2003), three examples of new particle formation with different maximum concentrations around noon are shown in Fig. 1. The SMPS plots, for the evening maximum, looks like similar than the event with the lower maximum value. Our information is not enough to know if this behaviour is caused by events of nucleation or by the growth of particle with diameters below 14 nm (first diameter measured by our SMPS). Then, the following sentence have been included in the revised manuscript: “Future analysis will be focused on investigating the reason of this behaviour, and determining the relationships between meteorological parameters with vertical resolution, gases measurements and aerosol data in the (3-14) nm size range.”

Birmili, W., Berresheim, H., Dülmer, C.P., Elste, T., Gilge, S., Wiedensohler, A., and Uhrner, U.: The Hohenpeissenberg Aerosol Formation Experiment (HAFEX): a Long-term Study Including Size-resolved Aerosol, H₂SO₄, OH, and Monoterpenes Measurements, *Atmos. Chem. Phys.*, 3, 361-376, 2003.

R3.18 - The authors discuss the height of the boundary layer to be the reason behind lower night time concentrations during winter. This might not be the reason, colder temperature should lead to a shallower boundary layer, opposite to what the authors suggest.

- Page 3826, Line 13 - The sentence “... it could be due to an increase of the atmospheric mixing and then the dilution processes with respect to spring and summer times” was modified by “It could be due to meteorological scenarios which produce situations of atmospheric stagnation during the warm months, characterized by the lack of renewal of the air masses. In these episodes, the particle transport to rural areas takes place through a regional atmospheric circulation (as e.g. breeze phenomenon) and its effect over rural areas is to increase the particle and gases concentration (Gangoiti et al., 2002; Querol et al., 2008; Adame et al., 2010b).”

- These references have been included:

Gangoiti, G., Alonso, L., Navazo, M., Albizuri, A., Perez-Landa, G., Matabuena, M., Valdenebro, V., Maruri, M., García, J.A., Millán, M.M. 2002. Regional transport of pollutants over the Bay of Biscay. Analysis of an ozone episode under a blocking anticyclone in west-central Europe. *Atmospheric Environment*, 36, 1349-1361.

Adame, J.A., Bolívar, J.P., De la Morena, B.A. 2010. Surface ozone measurements in the southwest of the Iberian Peninsula (Huelva, Spain). *Environ. Sci. Pollut. Res.*, 17, 355-368.

R3.19 - Paragraph beginning on page 3826, line 18: This paragraph feels again out of place. Consider moving parts of it in other chapters. It's interesting how the different timescales affect the correlations, this conclusion should appear somewhere in the manuscript. The authors may think where would be the best place for this.

According to the comment of the Reviewer, the paragraph has been deleted of the Sect. 3.3, and included in Sect. 3.1 and 3.2.

Chapter 3.4. Study of representative episodes.

R.3.20 – It may be more relevant to have this chapter as a sub-chapter in the Method. I leave this choice to the authors.

Finally, due to new incorporated results in the revised manuscript, the order that we found most suitable for sections is the previously mentioned in R.3.13.

R.3.21 - How do the air-mass types correspond to the episodes with re-circulation?

Page 3833, Lines 1:5 – The sentence “Some factors that has to be taken into account are ... , which have a size within the ultrafine range” was modified by “Recall, that the synoptic – scale pattern is also important to understand the particle number concentrations during PB and N-PB days. The clustering classification introduced in Sect. 3.5, was also applied during PB and N-PB days. It showed that 68% of PB days were influenced by continental and desert-dust airmasses (clusters 1, 4 and 7) and this may explain that the hourly concentrations for accumulation mode are higher than for N-PB days (see, the daily evolution of N_{ACC} showed in Fig. 10d.2). In addition, the Mode 3 observed in the fitted median size distribution (Table 4) should be associated with these continental and desert dust aerosols. In contrast, maritime westerly flows (clusters 2 and 5) had an occurrence frequency of about 50% for N-PB days, and it may also increase the particle levels for ultrafine size range, see also Table 4, as much by the marine particle transport processes as by the new particle formation (see, next section).”

R.3.22 - I have some troubles going through this chapter due to structure of the chapter. I would suggest making a clear division of the figures between events N1 and N2. Especially in Figure 10 there should be clear indication which figure corresponds to N1, which to N2. There is even a figure (10d) corresponding to a N-PB days. Maybe this should be a separate figure not to be mixed in the nucleation event analysis?

- From suggestions made by the Reviewer in R.3.9 and R.3.23, the individual cases have been deleted in the revised manuscript. We only include the specific case of 15 September 2004, which was shown in Figure 10d (now Figure 11) as an example of an episode caused by the sea-land breeze which can have an influence on health.

- The Section 3.7 (Entitled: New particles formation events (N_1 and N_2) in the revised manuscript, there is a separate section for each type of events, in order to make a clear division between both.

R.3.23 - Instead of case studies, it may be worthwhile to give average numbers for formation and growth rates; however, given the frequency of nucleation events, a separate paper with a longer time series might be opted as a follow-up study.

According to the comment of the Reviewer (see, R.3.23), we are going to prepare a separate paper with a longer time series to analyze in more detail the nucleation events in El Arenosillo. Moreover, the following sentences have been included in Sect. 3.7.

- Figures 12a.1 and 12b.1 show mean diurnal evolution of the particle number size distribution, N_{NUC} and S_T , as well as the wind direction for the 48 days (see Fig. 5) identified as Event N_1 .

- These nucleation events were characterized by a mean particle formation rate of $0.74 \text{ cm}^{-3} \text{ s}^{-1}$, a mean growth rate of 1.96 nm h^{-1} and a mean total duration of 9.25 h (starting at 10:55 GMT, ending at 20:10 GMT). These properties were calculated basing on the principles and methods inferred by Birmili et al., (2003) and on the mean size distribution (Fig. 12a.1).

R.3.24 – Figure 12 feels a bit out of place this chapter again – do the authors want to present correlation of the whole measurements period here, or is the focus only in nucleation events?. The discussion in the text is mostly about N1 events (red dots in the figure). Maybe the black dots could be left out – at least there should be commented if differences are seen between red and black dots. Make clear in the figure caption 12 that these are related to N1 events, also explanation for marker colors is missing.

- The following sentence has been included in the legend of Figure 12 (now Figure 13): “...meteorological parameters at El Arenosillo station during the PB days and those with the wind blowing from the NE direction during all day (black) and during the days with Event N₁ (red).”

- The values of mean total and modal surface concentration were wrong. The correct data have been included in the text and in Figure 12 (now Figure 13) of the revised manuscript.

- We want to present a correlation focus only in the nucleation events but we want also to show that Events N₁ were associated with low or medium daily mean values of S_{ACC}, N_{ACC} and V_T. Therefore we also show the days without event.

- The following sentence has been included in the revised manuscript: “Higher values of ΔT represent of better atmospheric mixing, and while in El Arenosillo the lower values of daily mean ΔT were about 6 °C, it was evinced that the Events N₁ were only produced with daily mean ΔT above 10 °C (see Fig. 13e).”

- The following sentence has been included in the revised manuscript: “So, e.g., when the daily mean S_{ACC} was higher than $320 \mu\text{m}^2 \text{ cm}^{-3}$, Event N₁ was no observed.”

R.3.25 – Figure 14 and the corresponding discussion: There seems to be a considerable increase of the nucleation mode in both pure-breeze and non-pure breeze days during mid-day. What makes these days so different that they are not considered to be nucleation event days?

The difference is that during a nucleation event, first there is an increase of concentration for nucleation mode and later for Aitken and accumulation size ranges. But, during sea-land breeze days, the maximum concentration is simultaneous for nucleation, Aitken and accumulation modes. Therefore, these episodes are mainly originated by the contribution of primary aerosols, while nucleation events are by the contribution of secondary aerosols.