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TITLE: "Characterization of ultrafine particles and the occurrence of new particle formation events in an urban and coastal site of the Mediterranean area"

Replies to Reviewer 1

The authors wish to thank the reviewer for his/her constructive suggestions and comments. We took them into careful consideration, and we hope that the revised version of the paper is improved. Each of the comments is addressed point-by-point below.

RC1: 'Comment on acp-2022-512', Anonymous Referee #1, 27 Sep 2022 reply
The MS deals with the properties of NPF events and particle number concentrations in various size fractions at an urban background site in Lecce and at a costal location in central Mediterranean, southern Italy. It presents valuable results and conclusions and contributes to the growing knowledge on the atmospheric nucleation and consecutive particle growth phenomenon in this larger region. However, the MS could be and should be improved substantially in several ways before deciding whether it is acceptable or not for publication in the ACP. The corrections can hopefully be accomplished by a very careful and thorough revision of the present version.

Major concerns

1. **The MS is too much of the descriptive character. Lots of simple statistical results are just supplied without interpreting them or putting them into appropriate frameworks or formulating clear conclusions or messages from them. Examples could be large parts of Sect. 3.2, lines 221–228 or Table 3. Further possibilities for improved interpretations could involve e.g. explaining and better comparing the seasonality of NPF events and diurnal concentration patterns of various particle number size fractions. Further important references on urban NPF could also be added to this purpose.**
   REPLY: as suggested, the manuscript was shortened in some places, including from lines 221 to 225. Also, we added the following references: Putaud et al., 2010; Asmi et al., 2011; Kalivitis et al., 2019; Casquero-Vera et al., 2020; Kalkavouras et al., 2020. Additional comments were added to better explain the seasonality of the events and the contribution of NPF events on particle number concentrations.
   Sect. 3.2 was modified: *"A clear diurnal pattern in each mode particle number concentration was observed in every season. Fig. 4 shows the trend of each mode fraction considering separately the days of NPF events (E, solid line) and the days of non-events (NE, dashed line). The timing of measurements is expressed in solar time (UTC + 1). Nucleation, Aitken, and accumulation mode particles have very similar behavior during non-events and, except for the different concentrations, both sites show a pronounced diurnal cycle with a morning and evening peak. The two peaks are shifted by one hour between spring-summer and autumn-winter because of daylight savings time and are mainly linked to vehicular emissions, most intense during the morning and evening rush hour. In addition, the evening peaks of Aitken and accumulation mode particles in winter and autumn can be linked to domestic heating emissions, mainly biomass burning considered an important source of ultrafine particles in urban sites. In cold months the pollutants tend to accumulate during the night due to the reduced boundary layer compared to the daytime layer. These peaks are also present in LMT but are less intense due to the greater distance of the site from the urban centre. Regarding event days, in both sites together with the two peaks of rush hours, nucleation mode particles present further picks around noon, more marked in summer, spring, and winter in ECO, and spring, summer, and autumn in LMT, and less marked instead in winter and autumn in LMT and ECO respectively. Similar observations have been reported in Cusack et al. (2013), Kalivitis et al. (2019), Kalkavouras et al. 2020, Dinoi et al. (2020, 2021a), for the western Mediterranean sites where the diurnal variation in nucleation mode particles presents a clear maximum at noon under both polluted and clean conditions. The contribution of the NPF process to the number concentration is also observed in the Aitken mode particles, more noticeable in the LMT site with 30 % in autumn-winter and 41 % in spring-summer, and with 21 % only in spring-summer in the ECO site. Nucleation mode particles show an increase of 52 %, 65 %, 61 %, and 49 % in winter, spring, summer, and autumn in LMT, and of 47 %, 52 %, 55 %, and 39 % in ECO. These results highlight that the formation of new particles contributes to the overall particle population more in the warm months and more significantly in the coastal site than in the urban background site, probably because the urban site is also affected by local emission of ultrafine particles that tend to suppress the NPF process. No contribution is observed in the concentration of accumulation mode particles where especially in the first half of the day, the concentrations were higher on non-event than event days, especially at the ECO site. This could explain the*

different frequency of events that characterized the two sites in these seasons, assuming that the NPF events were favored on those days with lower particle number concentrations (Salma et al., 2017). "

2. **The SO_2 is often used in the existing interpretations (e.g. in Sect. 3.3). Despite the fact that 1) its photochemical oxidation to the key nucleating vapour of H_2SO_4 was shown to be slow, complex and of less direct influence on the NPF, and 2) the authors possess all necessary properties and variables for deriving the proximity value of H_2SO_4 (which is more directly connected to the process) either by the classical method of Petäjä et al. (ACP, 2009) without the scaling factor or by its improved estimation proposed in Dada et al. (ACP, 2020). The authors may want to amend this part, which could contribute to the improved overall quality of the final MS.**
REPLY: as suggested, we included the analysis of H_2SO_4 and discussed it.
In 2.2 Data analysis we added *"Sulfuric acid (H_2SO_4) is considered a key precursor for new particle formation, therefore its concentrations were derived by calculating the H_2SO_4 proxy (ppbWm^{-2}s-^{1}), without scaling factor, using the method presented by Petäjä et al. (2009):*

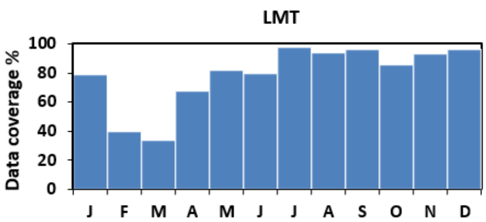
$$[H_2\ SO_4\ ]\alpha\ \frac{SO_4\ x\ SRad}{CS} \qquad (4)$$

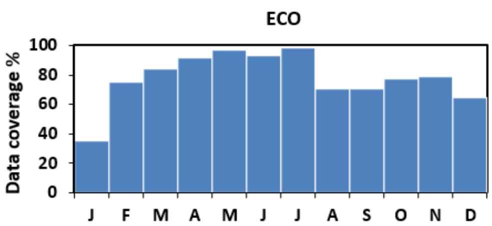
where SO2 is the sulphur dioxide concentration, SRad is the solar radiation flux, and CS the condensation sink.

In Sect. 3.3 we added "*Sulphuric acid is identified as one of the key components directly connected to NPF process (Sipil¨a et al., 2010). Because no direct measurements of it were done in this study, we investigate its role, considering the proxy of sulphuric acid (Eq.4), without a scaling factor (Petaja et al. 2009). The proxy only allows us to estimate the order of the average concentration levels of H_2SO_4 and although the results obtained are subject to uncertainties, they can still provide indications of trends (Salma et al., 2019). The average monthly values of H_2SO_4 proxy showed substantial differences between the two sites on event days (Fig 5d), 40 x10^{3} ppbWm^{-2}s (ranging from 18 x10^{3} to 61 x10^{3} ppbWm^{-2}s) at ECO and 20x10^{3} ppbWm^{-2}s (from 11 x10^{3} to 38 x10^{3} ppbWm^{-2}s) at LMT. These values are about 35% higher than non-events days in both sites. The proxy values of H_2SO_4 are larger in warm months and are substantially higher, by a factor of 2, in the urban background than in the coastal site, mainly due to the values of CS and SO_2. The conditions for the occurrence of NPF events are mainly driven by the ratio of the source and sink terms for the condensing vapors, therefore a greater availability of this gas precursor could have favored the occurrence of NPF events at ECO, although the higher values of CS, as well as the lower levels, could have limited its development at LMT."*

3. **It was shown in several publications that the size range below 10 nm is crucial for identifying and characterizing NPF events in particular in cities (e.g. Nieminen et al., ACP, 2018). The authors are asked to discuss how they avoided the limitations imposed by their relatively large measurable diameter of 10 nm in Lecce. For instance, how did this fact influence the share of the undefined days?**
REPLY: The reviewer is right, the size range below 10 nm is very important for studying the beginning of NPF and characterizing the early stages of growth. Therefore, in this case, the events in which new particles were unable to grow beyond 10 nm could not be identified. However, as widely reported in many studies in the literature, a detection limit of 10 nm in diameter does not prevent the correct identification and characterization of those events whose growth stage of newly formed particles fully falls in the studied size range.

4. **The frequency of missing days was relatively large around 22% at both sites. It is wondered how these days were distributed over the years or the measurement campaign since the NPF occurrence frequency showed a remarkable seasonal dependency, which could possibly impact the representativity of the remaining days.**
REPLY: as suggested by the reviewer, we checked how the missing days were distributed over the years. The following figures show that the lack of data is mainly in the months of February/March for LMT, and January for ECO. Therefore, we believe that the data are representative on yearly and monthly timescales for all months except those just mentioned which, due to the larger ratio of missing days, could be less representative.





5. **The reader can have the feeling at several places (e.g., in lines 154–160) that the nucleation or NPF processes and the particle growth process are not clearly distinguished. For instance, it could be clarified what the authors meant by "the temporal evolution of the events".**

   REPLY: during the NPF process, a marked increase in the number concentration of particles in the nucleating mode is observed, followed by their growth. So, with "temporal evolution of the events" we mean the temporal evolution of the particle number size distribution and the respective variation of the geometric mean diameter (Dp) of nucleation mode particles.

6. **It is not described properly how some important properties were obtained. An example could be the lines 222–224 where the CS is mentioned only very briefly. By the way, this (in a more detailed extent) should be shifted from the section Results and discussion to e.g. Sect. 2.3 since this is not their result. In this respect, it is also mentioned that the original NSF in Salma et al., ACP, 2017 was further developed, and its NSF_{GEN} and NSF_{NUCL} are more informative than the original form and should be used or at least mentioned. It is not clear (lines 225–228) how the start and end times of the growth events and more importantly, the geometric diameters Dp1 and Dp2 were derived and whether the latter were modal median diameters or something else.**

   REPLY: the CS was detailed and moved to Section 2.3.

   "The condensation sink, CS (s^{-1}), quantifies how rapidly a condensable gaseous compound condenses on available aerosol particles (Kerminen et al., 2018), and then it depends on the effective surface area of pre-existing particles. CS was calculated, using the methods available in the literature (Dal Maso et al., 2005, and references therein) considering sulphuric acid (H_2SO_4) as the condensable species:

$$CS = 2\pi D \sum_{D'_p} \beta_m(D'_{pi}) D'_{pi} \, N_i \qquad (2)$$

   where D is the diffusion coefficient for H_2SO_4, N_i is the particle number concentration with diameter D'_{pi} of the size bin i, and β_m is the transition correction factor (Fuchs et al., 1971)."

   As suggested, we mentioned NSF_{GEN} and integrated more information "*The relative increase in particle number concentration due to the NPF process was also quantified with the nucleation strength factor (NFS) proposed by Salma et al. (2016, 2017, 2019). It measures the effects of nucleation events on ultrafine particles at a site considering two factors, NSF_{NUC} that provides a measure of the concentration increment on nucleation days exclusively caused by NPF, and NSF_{GEN} gives a measure of the overall contribution of NPF over a longer time span. In this work, we considered only NSF_{NUC}, calculated following Eq. (5)…"*

   "From the coastal to urban background site, we found a decrease in the contribution of NPF events to particle number, similar to what was observed by Salma et al., (2017) between the near city background (2.3) and the city center (1.6) of Budapest over 5 years. In the study of Bousiotis et al., (2021), on 13 sites from five countries in Europe it was found that for almost all rural background sites NFS_{NUC} was greater than 2, and reached 4 in a very clean site of Finland. Nemet et al (2018) found lower values of NFS_{NUC}, 1.58, 1.54, and 2.01, in the cities of Budapest, Vienna and Prague, respectively, while in Granada urban site NFS_{NUC} was 1.05 (Casquero-Vera et al., (2021). The decrease in the contribution of NPF events to particle number, moving from a more polluted to a less polluted site, may be related to the higher contribution to particle number concentrations of other sources, i.e. traffic and heating, and the associated increased condensation sink."

   Related to growth events we integrated "*Particle growth rate (GR) was calculated from time evolution of the mean geometric diameter D_p in the size range of 10-20 nm, using Eq. (1) (Kulmala et al., 2012):*

$$GR(nm\,h^{-1}) = (D_{p2} - D_{p1})/(t_2 - t_1) \qquad (1)$$

   with Dp_1 and Dp_2 the geometric diameter at the start time t_1 and end time t_2 of the growth event. Using the maximum concentration method, we identified the time when the concentration is at the maximum in each size bin. The growth rates were obtained as the slope of the linear fit of the times with the corresponding geometric mean diameters of the particles."

7. **Figure 4 (and possibly some others as well) contains too many lines and it is difficult to follow. In addition, it should be discussed whether a local time involving the daylight-saving time (clock change in the EU) or UTC+1 or else were used as the time scale. This could be related to the shift in the positions of the diurnal peaks in different seasons.**

   REPLY: we split Figure 4 into multiple single plots.

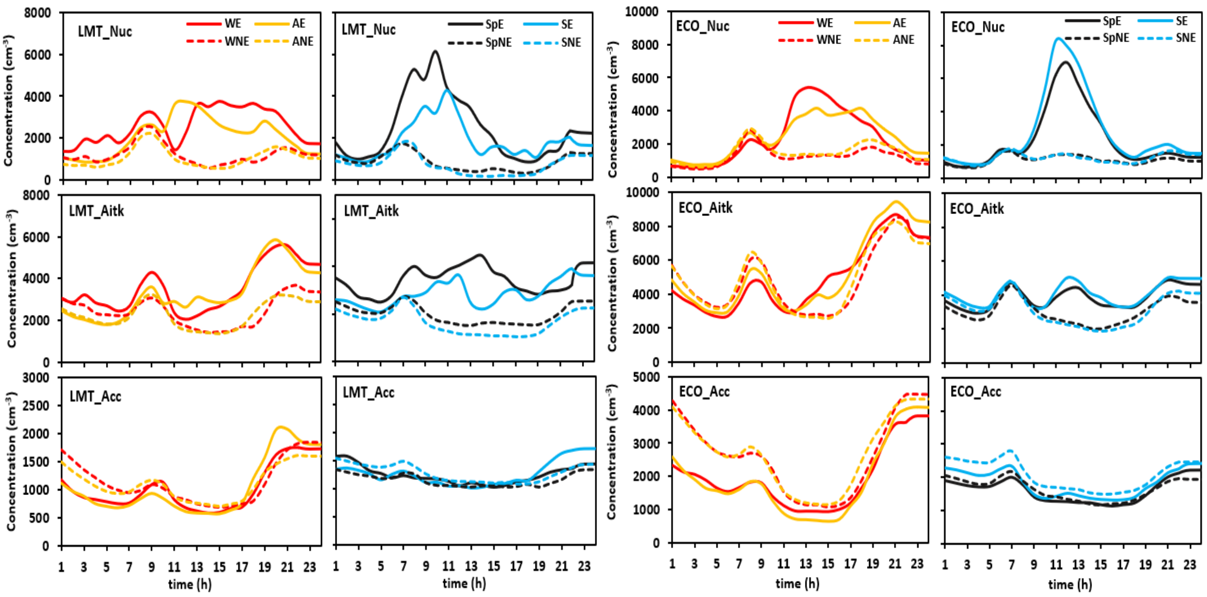


Fig. 4. Average diurnal variation in nucleation, Aitken, and accumulation mode particle number concentration (from top to bottom) over the whole period of study at LMT and ECO. Solid lines are for NPF events days (E) and dashed lines for non-events days of (NE), red for winter, grey for spring, blue for summer, and yellow for autumn.

In both observatories, all the measurements were carried out maintaining the solar time throughout the years, therefore UTC + 1. We specified in the text that *"The timing of measurements is expressed in solar time (UTC + 1)."*
Also that *"The two peaks are shifted by one hour between spring-summer and autumn-winter because of daylight savings time"*

8. **Line 239 and further: the phenomenon or process is somewhat more sophisticated. The authors perhaps want to include and discuss the NPF occurrence with respect to the ratio of sources and sinks of low-volatility vapours and not just the amount of CS alone.**
   REPLY: line 239 to 250 were removed**.** We included the comment "*The conditions for the occurrence of NPF events are mainly driven by the ratio of the source and sink terms for the condensing vapors, therefore a greater availability of this gas precursor could have favored the occurrence of NPF events at ECO, although the higher values of CS, as well as the lower levels, could have limited its development at LMT.*"

Minor comments

9. **Line 33: use either primary or emission (source).**
   REPLY: we deleted "emission"

10. **The references should be ordered chronologically and not alphabetically, e.g. lines 36–37.**
    REPLY: thanks, we ordered the references.

11. **Some abbreviations are not explained, e.g. line 101: MPSS, or Table 3 W, Sp, S and A.**
    REPLY: the abbreviation MPSS (Mobility Particle Size Spectrometer) was explained in the abstract but now we also added in line 101. At the same way, the abbreviation (winter W, spring Sp, summer S, and autumn A) was explained in the line 200 and now we also added in caption of Table 3.

12. **Line 105: is TSI Inc. really based in Rome, Italy?**
    REPLY: the reviewer is right, it is based in USA.

13. **Line 239: replace "discouraged" by not favoured or something similar.**
    REPLY: we replaced "discouraged" by not favoured.

14. **What is the advantage of using a CNR4 net radiometer which measures the energy balance between incoming short-wave and long-wave far infrared radiation versus surface-rejected short-wave and outgoing long-wave radiation to measuring global or direct solar radiations.**

REPLY: The CNR4 consists of two pyranometers which measure the solar radiation both incoming and reflected, and two pyrgeometers which measure the far Infrared radiation. From a spectral point of view, the pyranometer and pyrgeometer are complementary and together cover the full spectral range, the pyranometer from 0.3 to 3 microns, and the pyrgeometer from 4.5 to 42 microns. The advantage of using this kind of instrument is that all components are measured separately, and this allows every single parameter to be used according to specific work requirements.