

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 2

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.

Major comments

- The manuscript is mainly descriptive, with some statistical analysis but no conclusions about the differences between both sites. I would suggest the authors to include some additional analysis to identify the factors that affect to the differences, specially on NPF events. The growth rate is not clear how it is retrieved or for which size range (see comment below), I would also suggest the authors to calculate the formation rate and include discussion about it. I expect to see some differences between both site on GR and formation rate, if there are differences, means that the vapours contributing to the formation and the growth are different at these sites. Also, I would suggest to include the analysis of H₂SO₄ instead of SO₂ (solar radiation and CS are available and could estimate the sulfuric acid from proxies as Petäjä et al. 2009, ACP).**

REPLY: we followed the suggestions of the reviewer.

The growth rate was explained better “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):

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

with D_{p1} and D_{p2} 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.”

We also calculated the formation rate and included a discussion about it and GR “The growth rate (GR) and the particle formation rate (J) were analyzed to investigate the dynamic properties of NPF events. At the ECO site the growth rate values ranged from 3 nm h⁻¹ to 14 nm h⁻¹ (average 7.5 ± 3.3 nm h⁻¹) and J from 0.6 to 8.6 cm⁻³ s⁻¹ (average 3.3 ± 3.1 cm⁻³ s⁻¹); while at LMT the GR varied from 2.5 to 10 nm h⁻¹ (average 6.1 ± 2.3 nm h⁻¹) and the J from 0.3 to 6.2 cm⁻³ s⁻¹ (average 2.4 ± 1.8 cm⁻³ s⁻¹). The values of both parameters are comparable with what was reported for NPF events in other urban and coastal sites (Hussein et al., 2020, Kalivitis et al., 2019; Salma et al 2019; Kalkavouras et al., 2020; Nieminen et al. 2018). In particular, similarities were found with some Mediterranean sites such as the coastal station of Finokalia GR~ 5 nmh⁻¹, J~ 0.9 cm⁻³ s⁻¹ (Pikridas et al., 2012), the coastal/rural/suburban station of Akrotiri, GR~6 nmh⁻¹, J~13 cm⁻³ s⁻¹ (Kopanakis et al., 2013) and the Cyprus Island, GR~ 2.8–5 nmh⁻¹, J~ 5–11.4 cm⁻³ s⁻¹ (Debevec et al., 2018). The mean values of GR and J turned out to be higher at the ECO site than at the LMT site, and they showed a clear seasonal pattern with higher values during warm months, not observed at LMT where both parameters did not show distinctive features. As reported by Nieminen et al. (2018), the production rate of nucleation particles is generally higher in urban sites than in remote/clean ones because of the greater anthropogenic activity and the greater availability of precursors. In particular, the higher values of GR and J in warm months can be attributed to the intensification of the photochemical activity and abundance of SO₂ which acts as a precursor of sulfuric acid. The formation of nucleation mode particles is known to be influenced by the chemical and physical condition of the atmosphere”

The analysis of H₂SO₄ was included and discussed “Sulphuric acid is identified as one of the key components directly connected to NPF process (Sipilä 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 scaling factor (Petaja et al. 2009). The proxy only allows us to estimate the order of the average concentration levels of H₂SO₄ 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 H₂SO₄ proxy showed substantial differences between the two sites on event days (Fig 5d), 40 x10³ ppbWm⁻²s (ranging from 18 x10³ to 61 x10³ ppbWm⁻²s) at ECO and 20x10³ ppbWm⁻²s (from 11 x10³ to 38 x10³ ppbWm⁻²s) at LMT. These values are about 35% higher than non-events days in both cases. The proxy values of H₂SO₄ 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 SO₂. These last results are in accordance with GR and J values obtained for the two sites, where the low J and GR values at LMT could be associated with the low concentrations of H₂SO₄ (or other precursors). 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.”

2. **I recommend the authors to combine sections 3.4 and 3.5, and try to answer in these sections why there is that large differences in the event frequency in these two nearby locations? What promotes the regional NPF events? There is cases when NPF events are observed at both sites?**

REPLY: we combined sections 3.4 and 3.5 and tried to explain the differences found between the two sites “In general, these results underline the importance of specific atmospheric conditions (temperature, solar radiation, RH, origin of air mass, pollutant concentrations) under which the NPF events have occurred and emphasize how the observed differences are associated with the levels of pollution found in them. The more frequent NPF events at the urban background compared to the coastal site can be ascribed to a greater abundance of condensable species, deriving from anthropogenic emissions, which favor the growth of particles increasing their chance of survival. Regarding the different seasonality of the events, while the trend at the urban site of ECO can be associated with the increased photochemical activity and the higher concentrations of different precursors during the warm months, the seasonality at the coastal site of LMT is more difficult to explain. Along with the lower availability of precursors, local conditions could play an additional role as well. These may include synoptic systems such as increased turbulence during warm months and the different atmospheric composition (related to the proximity to the sea and the effects of land-sea breezes) due to which the newly formed particles could be more effectively suppressed preventing further growth.”

As already written in MS (lines 143) “Of all events detected during the study period, 50 were observed simultaneously at both sites”.

Also, a discussion about them was in section 3.4. “We also focused on “common” NPF events considering only the air masses pathway related to these days detected during the study period. From 3-days back-trajectory analysis, emerged that the back-trajectories of common events exhibit similar characteristics in terms of origin and pathways to what already observed, but in addition, two different cases were detected, in the first the trajectory passes from ECO before reaching LMT, while in the other case, vice versa the air mass passes from LMT and then reaches ECO. Out of 50 common NPF events, 31 were in the first case and 19 in the second. Two representative examples of back-trajectories for each case are depicted in Fig. 9 and show that there is not preferential path that can characterize them, because in both cases we find trajectories that come from both Eastern and Western Europe. These events occurred almost synchronously at the two sites, with a difference in starting time not greater than 30 minutes. The factors that characterized the concomitant events of NPF (Table 4) are similar to those observed for the non-concomitant events, with values of PM_{2.5}, SO₂, CS, and H₂SO₄ proxy in LMT lower than ECO, and similar meteorological conditions. The simultaneous observation of these events indicates that the formation of new particles has a wide horizontal extension and can be seen as a large-scale phenomenon. It is probable that the air masses already contain particles that have been formed by nucleation somewhere and then transported. Or during their travel, the air masses are enriched with gaseous precursors deriving from anthropogenic emissions and/or from biogenic production such as to foster (potentially) NPF processes, even in locations far from the sources.”

3. **In the introduction the authors focus on the importance of regional NPF events, however, the manuscript lack of results and discussion on this topic. I would suggest to include more analysis on this topic, but if no further analysis, discussion, results are included about this, I would suggest to shorten that part in the introduction.**

REPLY: as suggested we shortened part of the introduction focused on the importance of regional NPF events, deleting lines 47 to 53.

Minor comments

L12 – change “occurred” by “occurring”?

REPLY: we changed “occurred” with “occurring”.

L89 – which different meteorological dynamics?

REPLY: we changed “meteorological dynamics” with “local meteorological conditions”. We referred mainly to the effect of the breezes, as written in the following sentence.

L94-95 – please rewrite this sentence

REPLY: we rewrote “*The LMT observatory is located far from the urban agglomeration and therefore is not directly affected by the emissions deriving from the main anthropogenic activities.*”

L95-97 – would move this sentence after L89 about dynamics and would add other sentence about meteorological dynamic at ECO site.

REPLY: we moved the sentence and rephrased as: “*Being on the coast, the local weather of LMT is influenced by a system of “land-see” breezes that guarantees a temperate climate and continuous ventilation throughout the year that favors an effective dilution of air pollutants.*”

L103 – move this sentence with the next paragraph, where the authors present the quality control. Are the instrument routinely calibrated or psl checked or compared with total particle concentrations? Have the instruments been intercompared before?

REPLY: we moved it. Both instruments are routinely calibrated for aerosol flow rate, sheath air flow rate, flow rate of the aerosol dryer’s, leak test, DMA high-voltage check and psl check. The instruments have never been intercompared, but they were periodically subjected to the “round-robin test”.

L109 – multiple charged instead of negatively?

REPLY: we corrected.

Section 2 – I would recommend to name this section “Measurements and methods”, then section 2.1 “Measurement sites and instrumentation” that unifies sections 2.1 and 2.2, and section 2.3 I would rename it as “Data analysis”, “methodology”, “methods”,... “Evaluation of NPF events”, I think is not the most appropriate. Include in this section the formulas for the CS that is later discussed.

REPLY: The suggestions were adopted.

L132 – the authors use frequently paragraphs of just one sentence, please avoid this.???

REPLY: thanks for the advice.

Table 1 includes Events, Undefined and Non-event days, that sum the total number of days. However, line 134 says that there is a 78% of data coverage? How can classify more days than the data coverage (~0.78*TotalNumberDays).

REPLY: we apologize for the misunderstanding. We mean that the study is based on a period of 5 years, 1826 total days. Since the measurement we collected were 1423 days at ECO and 1440 at LMT, the coverage over 1826 days is approximately 78%. We made it explicit in the MS “*Over five years of measurements, we had a data coverage of ~78 %, where the available measurement days were 1423 at ECO and 1440 at LMT.*”

L140 – “confirming what was already observed in Dinoi et al. (2021a)” I would suggest to rephrase, something like “showing similar results than those presented by a shorter measurement period presented by Dinoi et al. (2021a)”.

REPLY: as suggested we re-phrased “confirming what was already observed in Dinoi et al. (2021a)” with “showing similar results to those found in a shorter measurement period presented by Dinoi et al. (2021a)”.

L146 – where these numbers come from?

REPLY: they come from various studies carried out in the Mediterranean area. We rephrased “*The annual frequencies of NPF (9% and 25 %) are in good agreement with frequencies (10 % - 36 %) found in other studies, based on long-term measurements, carried out in the Mediterranean area (Kopanakis et al., 2013; Kalivitis et al., 2019; Hussein et al., 2020; Kalkavouras et al., 2020; Baalbaki et al., 2021).*”

L156-160 – GR is a quantity that depends on the diameter. Here the authors don’t define the diameter range where the GR is being retrieved. If the GR changes with time, probably because the diameter range change?

REPLY: we defined in the MS the diameter range (10nm-20nm) where the GR is being retrieved.

L162 – avoid the term “emission levels”, mainly because the authors are not really measuring emissions, only measuring atmospheric concentrations.

REPLY: we deleted “emission levels” and replaced it with “concentrations”.

L166 – use the correct significant numbers, the table is correct. Same in the following paragraphs.

REPLY: thanks for the suggestion

L176 – add space before ~3100

REPLY: we did it

Eq2 – use subindex for E and NE.

REPLY: we did it

L213-218 – I would add some references where this method has been previously used at different locations and compare how important NPFs are in other locations compared to those presented in this work (e.g., Bousiotis et al., 2021; Casquero-Vera et al., 2021; Thén et al., 2022). Are the values reported averages for the NPF time of for the whole day?

REPLY: we added the suggested references and compared the results “*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.*”

The values reported are averages for the whole day.

L240 – I would not say is surprising, if there is less CS, probably there is also less precursor vapors too...

REPLY: the reviewer is right. We removed the sentence and rephrased “*Therefore a greater availability of this gas precursor (H_2SO_4) 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.*”