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Interactive comment on "Molecular Insights into New Particle Formation in Barcelona, Spain" *by* James Brean et al.

Anonymous Referee #2

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The manuscript "Molecular Insights into New Particle Formation in Barcelona, Spain" by Brean et al. discusses the observations of summer-time new-particle formation (NPF) events in Barcelona, Spain. A wide scope of capable instrumentation was deployed, allowing for deriving a decently comprehensive picture of the mechanisms that likely facilitated observed NPF events. Consequently, premise and results of this study are certainly of interest for the ACP audience, and in principle I would like to recommend their publication. However, I have substantial concerns regarding presentation and conclusions, which I feel need to be addressed.

First off, the introduction is pleasant to read, and well structured overall (except for some technicalities, see minor/technical comments below). I also only have minor/technical comments on Section 2 (Methods). My main concern starts with the interpretation of the "burst events" in Section 3.

MAJOR COMMENTS:

1) "Burst" events and air mass histories It is well established that NPF events for which formation followed by continuous growth over many hours can be observed (here called "full event"), are observable as such at a point site because NPF takes place more or less in sync across a fairly wide area (i.e. regional-scale NPF). Therefore, I wonder if the so-called "burst events" could be due to NPF that occurs more localized? I.e., that the more localized character of the NPF is why growth beyond 10 nm is not observed (with smallest observed particles having formed closest-by, whereas the largest observed new particles would have formed farthest away within the NPF area, upwind). The time resolution of the particle sizing measurements was quite low, but an estimate of the overall growth rate of the newly-formed particles could anyway be made, and from that, plus wind back trajectories, even the size of the hypothesized local NPF area could be estimated. Related to that: The manuscript mentions at least twice that NPF events, both "full" and "burst" types, are associated with "southerly and south-westerly air masses" (e.g. L 396-399). But Fig. S6 (showing back trajectories) clearly contradicts that statement! I suspect the mistake is in the text? That suspicion is (a) because I would expect a regional-scale BVOC-HOM-driven NPF event to have air masses NOT arriving from sea+town, and rather from inland, as suggested, presumably, in Fig. S6; and (b) upon noticing that the burst event shown in more detail (e.g. Figs. 1 and 8; July 15) is indeed the only event that does actually show a southerly back trajectory in Fig. S6, which puts the trajectory mostly over the ocean, with the exception of its final path across town (and, possibly critically, over shipping, as the authors also point out) towards the measurement site.

2) Number of events and data points Line 204 states that there was only 2 "burst" events observed. Then, it would be very useful to also learn how many "full" event were observed (and how many were non-event days)? However, with only 2 samples for the burst events, how can Figs. 2 and 3 include a boxplot for conditions during those

two events? That may be down to the too sparse explanation of what data were used for these boxplots. E.g., data from which times were used in each event class (a vs b vs c)? Is the boxplot based on event-wise averages, or something else? But then again, Figs. 4+ suggest there is many more events of each type (judging from # of markers). A Fig. S6 again suggests again there's only been 5 events total!? I have some suspicions, but overall I am left rather confused. So, all that clearly should be presented more clearly, i.e. data quantity and usage in figures, resolved by event type.

3) Section 2.2: Was "sensitivity" applied to any detected compound? From the rest of the paper I conclude that it was applied to H2SO4 and HOMs, but not to ammonia and amines. Overall, some more detailed discussion of concentration quantifications based on CIMS signals would be interesting. See also next comment.

4) Ammonia and amines: Section 2.2: Are there any estimates on detection limits or sensitivity regarding ammonia and amines? (And which amines are expected to be detectable?) There is some discussion of amine detection late in Section 3.1. But it would be helpful if that more general instrumental aspects of their detection would already be at least mentioned in the Methods section. Section 3.1: Which amines were actually detected? I think that information is only provided in the caption of Fig. 3 and in Fig. S1 (implying C2H7N and C4H11N), and that should be mentioned also in the main text, and much earlier. (And is that in agreement with expectations from amine abundances and amine-specific sensitivities indicated by previous studies (if any)?) The authors do discuss relative sensitivities later in Section 3.1, implying that sensitivities to all those small bases correlate to NPF enhancement potential. That argument could be brought sooner. Figure 3, and related discussion (Section 3.1, page 9): From the beginning of the discussion of Fig. 3b, I have been wondering why are ammonia & amine signals only presented as a sum of all signals? Even if the concentrations of these compounds could not be quantified in these measurements, it still appears it would be more insightful not to lump them together. Especially given the respective differences in NPF enhancement capabilities. Also, if lumped together,

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there is the chance that differences in atmospheric abundance of ammonia vs. amines (almost certain, as also described in Section 3.1) or in instrument sensitivity to these compounds (plausible) lead to one compound (or group of compounds) controlling the lumped signal... Only very late in Section 3.1, L 241 mentions that all the bases' time series correlated quite well, thus justifying the lumping. That argument for lumping should be made more clearly and earlier. And supported by a figure or two in the Supplement. L 217: From looking at Figure 3, I am not sure I would also arrive at the conclusion that ammonia+amine concentrations were enhanced for full events. The medians are practically identical. Have the authors applied some quantitative measure of statistical significance regarding differences of the parameters presented in Figs. 2-3?

5) Figure 5 and/or related discussion Environmental conditions should be mentioned and discussed, in particular in light of the CLOUD experiments being compared to: T, RH, compound concentrations (as known), as all those will have affect formation rates. Also: given available parametrizations of NPF rates as a function of sulfuric acid, HOM (or "BioOxOrg") and amine/ammonia concentrations, are the authors able to explain observed NPF rates and infer concentrations of either involved BioOxOrg or amines? Combined with expected amine concentrations and measured VOC and HOM concentrations, some closure could be attempted. Some hand waving may be necessary, but the attempt could be quite interesting. And it could strengthen the paper, especially if it can be argued that closure ∼works out. Similarly, growth rates of new particles could be estimated (see also 1st comment) and evaluated against HOM concentrations.

6) Figure 6 and related discussion (in particular L 289-293): Could the SA dimer signal also be affected by instrument settings? It is conceivable that some instruments or settings would fragment a certain fraction of SA dimer ions (that is, at some point after their formation by NO3-ionization), and that that fraction is instrument- or tuning-specific. If so, conclusions can likely still be made anyway from comparisons between

measurements within the same campaign (provided settings remained the same), and probably even from comparisons across campaigns/longer time periods as long as the same instrument was used. But could such instrumental differences cause (part of) the discussed discrepancies between dimer signals here and results shown from other field and lab experiments? My feeling is that the SA dimer anion is stable enough that such instrumental fragmentation should not be expected, but I would ask the authors to at least point that out (i.e., if my "feeling" can be defended based on previous studies – I apologize for not remembering expected cluster stabilities vs the fragmentation potency of the APi-TOF instrument), OR recognize/discuss potential issues.

MINOR COMMENTS:

Abstract: a) I would already here mention roughly the most important measurement methods used for the study. No details, and a side sentence may be enough. Especially as there is talk about sulfuric acid monomer and dimer concentrations, I would have liked to be informed already here that those are based on NO3-CIMS measurements. b) Growth beyond 10 nm: my immediate thought already here was that limited growth could also be a sign of more local NPF (vs. regional, i.e. on a larger geographical scale), in which case the observed lower concentrations of low-volatility organics could be irrelevant (see 1st major comment). So I would already here, in a compact way, give the reasoning for claimed conclusion.

Introduction: The last paragraph (review of NPF observations in the Barcelona area) is a somewhat confusing to read. Should be restructured for clarity.

I found the usage of the term "background" not clear (end of introduction, beginning of methods, beginning of results).

L 143: The meaning of "sensitivity" here (in previous studies called also "sensitivity coefficient" or "calibration factor") remains a mystery for any reader who is not fairly intimate with operation of that CIMS instrument. So, I would at least cite some paper where that meaning is discussed, e.g. Kürten et al., 2012 (10.1021/jp212123n). Re-

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garding the "sensitivity" value used, the authors cite here a previous calibration, paper also led by UBirmingham. However, I could not find, in that paper, how that calibration was performed. Indeed that paper contains the statement (in their section 2.2) "No sensitivity calibration was performed for these measurement..." Bottom line is that I have remained wondering where the used value (3e9 cmˆ-3) derives from. (Or simply from comparison to the sulfuric acid proxy?)

L 221: It is not clear if this is a general statement regarding amine concentrations, or specific to observations (which, however, I understand could not be quantified, so I assume it's the former?)? Should be clarified.

Figure 1 is lacking all labels for the axes. At least the somewhat-less-obvious vertical axis should be labelled.

L 244: Should start new paragraph when starting discussion HOMs.

L244-245: It appears odd to discuss HOMs (Fig. 3b) with only 1 sentence, following a page of discussion of ammonia/amines! Should at least add a reference to a later section, where organics, including HOM, are being discussed.

L247-248: This last sentence of Section 3.1 is very vague. How high (or low) are those concentrations of marine compounds? (Or estimated to be?) What observations would have been considered evidence FOR an influence of oceanic emissions on NPF/growth?

Fig. 4: How steep ist that slope? That is usually interesting information, at least for comparing with other studies.

L 261: Does "losses" refer to amines? If so, I don't see how photochemical reductions of amine mixing ratios could mask an actual dependence of NPF rates on those mixing ratios. (If I caught the inference correctly.)

L 273: Suggest rephrasing to make it clear immediately that the discussion shifts from literature results to new results. And it is not clear which observations the last part of

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the sentence refers to ("on these days").

L 282-283: ambiguous what is meant by "strength of sulfuric acid clustering". It becomes clear thereafter, but if I understand correctly, "strength" is not the right word.

L 293+: Could the point raised in major comment (6) explain the flatter slope observed here vs. the Germany observations?

L 337: Getting confused here. Should it read "not largely radiation dependent" instead of "not largely temperature dependent"?

L 342: Should they be transportent FROM inland by the land breeze?

L 357, 361: Should be explained what is meant by "detailed criteria", and by "updated criteria" (i.e. what are the respective criteria).

L 367: could be informative to point out some of those formulae explicitly

L 371-372: would be instructive to be more specific regarding "large" and "smaller"

L 378-382: Something went wrong with this sentence, especially the first part. Think I get the idea, but not sure.

L 381: Please state the size range the ACSM is sensitive to

L 393: Could the mechanisms also support each other (i.e. be combined) rather than be in competition?

Fig. S6: Please include information on which kind of events are shown, and when (... see also major comments (1) and (2))

TECHNICAL COMMENTS

L 61: i.e. should be e.g.?

L 79/80: those "loss processes" haven't been mentioned yet, so would be instructive to name the most important ones (here, for < 50 nm particles)

L 81: "at these diameters" ... rather "from these diameters onward"

L 86: I believe that range should read "0.5-11" (i.e., 11 instead of 1.1)

L 86-90: two redundant consecutive sentences. combine.

L 138: if I remember correctly, the flow containing the reagent ions is not "guided into the sample flow", but rather only the ions are guided there (electrically).

L 162: redundant mentioning of "4 flows"

Fig. 3, a and b: the "+" in the exponents (tick labels) are conventionally omitted

L 371: compromise -> comprise

Figs. S6 and S7 are not referred to in the main text (not sure if that's a problem).

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