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Atmospheric
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Discussions

Interactive comment on "New particle growth and shrinkage observed in subtropical environments" *by* L.-H. Young et al.

Anonymous Referee #1

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The authors present analysis of approximately 7 months of atmospheric measurements of sub-micron aerosol number size distributions in Taiwan. The work concentrates on 14 new particle formation events, where particles are formed from gaseous precursors. There is also an attempt to scale the observed J10 values down to J1. Growth rates are analyzed in two different methods (modal fitting and inverse modeling approach). Five out of those 14 days, the authors also observe shrinkage of the nucleation mode particles, which seems to point toward reversible condensation. The role of semi-volatile species is speculated.

The measurements, which are not described in sufficient detail, only start from 10 nm. Inverse modeling is used to address "nucleation rate" at 1 nm. In such a non-linear system this is prone to errors as the growth rate as a function of particle size is not

known. This is not discussed in the article.

The work has promise. However, in a current form the paper is too descriptive. The experimental results are depicted in both figures and words, but scientific discussion is not well justified or even missing. The paper could be condensed substantially and more analysis is needed to substantiate the findings.

I recommend this manuscript to be published in Atmos. Chem. Phys., but only after my comments are addressed carefully.

Major comments

Conclusions suffer from poor statistics. The differences between event types and non-events need to be reassessed, whether they are significantly different. The regional formation and growth events should be separated carefully e.g. from nanoparticles from the traffic sources. How this is done, can affect the reported GR and J. Thus, reported J10 and GR values need to be checked. The nucleation rates (J1) are highly suspect as the GR cannot be assessed as a function of diameter in the size range below 10 nm. The observation of shrinkage is interesting. More effort should be paid to find out condensable vapor concentrations and needed saturation vapor pressures explaining this phenomenon.

On measurements:

1) Why was the diffusion losses not taken into account? Not taking into account 15% loss of 10 nm particles make at least the formation rate calculations underestimate the atmospheric formation rates.

2) Was the aerosol sample dried? Was the size distribution measured in dry conditions? Did you consider hygroscopic growth? How was the inversion done from voltage-concentration space to diameter – concentration space? Did you consider multiple charging? How was the SMPS calibrated?

3) Please report gas analyzer models.

Data analysis methods:

1) I recommend the authors first report J10 values only. The use of inverse modeling (PARGAN) is only as good as the measurements. If there is no knowledge on the GR (Dp) –dependency, I suspect that any model has problems reproducing the true nucleation rates. The scatter in the Fig 3-9 for J1 illustrate just that. Any small change in aerosol number size distribution will result in large variability in the estimated J1. What does J1 value 3 hours after the event start tell me?

2) To get a handle on the abundance of condensable vapors needed to explain the growth, please refer to Kulmala et al. 2001, Kulmala et al. 2005 or Kulmala et al. 2012.

3) To estimate sulfuric acid concentration, you could try a proxy, such as presented in Petäjä et al. 2009 or Mikkonen et al. 2011.

General comments:

1) 14 new particle formation events is a small number compared to 123 non-events days. Figure 2 shows typical diurnal cycles (Do you report median or mean, what are the whiskers? Standard deviation? Percentiles? Explain in figure caption.) The whiskers show, in one way or another, variability in the data. To my eyes, it seems that all cycles are nearly identical, which a notable exception being N10-100 (which should be different as you have separated the data whether you have new particles or not). What would happen, if you would randomly select 10 % of the non-event population and made the same kind of figure? Why do you report here N10-100, why not N10-25?

2) The classification between type A and B events seems quite random. Is it only based on start time of event being before or after 9 a.m.? In my opinion, it does not make sense to separate already a small data set to even smaller subsets. Or, if the separation would be required, I would do it based on whether there is shrinking or not.

3) How many of the events occurred at each measurement location? Many of the events were consecutive. What was the location?

4) There is a variable amount of PM10 mass during the event. (Table 1: 10-46.6 ug/m3). Have you considered the condensation sink provided by the larger particles? What is their contribution to the total CS?

5) I see no point of showing all the case studies. One carefully selected growth and one growth + shrinking event would suffice. This will reduce the number of event figures into two. Please make the figures larger. The time traces in the number size distribution panel is hardly visible (it might read CS and something else). Temperature does vary much in the scale between 0 and 120 (bottom panel).

Specific comments:

1) After a long introduction the aim of this paper is described only very vaguely (last paragraph in the introduction). Please explain what is the focus of this paper and what are the scientific hypotheses. No need to present any results yet.

2) For methodology and instruments to measure and characterize NPF events, see Kulmala et al. 2012.

3) Page 18607, line 15: Vanhanen et al. 2011, Aerosol Sci. Technol. presents a commercially available CPC that detects particles well below 3 nm.

4) Page 18609, line 1: How about stabilization by ammonia or amines?

5) page 18612, beginning of sect 2.3 belongs to sampling section.

6) page 18613, line 17: In my opinion, empirical nucleation rate cannot be obtained with modelling.

7) page 18615, eq 4: Was not introduced by Erupe et al. 2010.

8) page 18618, line 1: Why are GR with different methods varying so much? What is the number of days for each data set (urban, coastal etc)?

9) page 18617, line 5-6: “on average accounted for 82… “ I don’t understand. The

large differences in high GR cases do not give additional confidence to me.

10) page 18617, line7-: Comparison of shrinkage and growth rates: Based on diameter growth rates, one cannot state directly that 40-65% of the condensed vapors evaporate. You should consider changes in volume, not in diameter.

11) page 18617, line 20-: In my opinion these results indicate that there are other sources than nucleation during these cases, when N10-25 increases concurrently to shrinking, such as traffic.

12) section 3.3. Why do you report N10-100? Separation based on nucleation mode, Aitken mode and accumulation mode would be better (as you indicate also in section 2.3.

13) page 18619, line 11: Traffic peak, nucleation mode particles and mixing all happen at the same time, but it does not proof causality. In my opinion, you cannot definitely link type A events to traffic emissions of condensable vapors.

14) page 18619,line 15: . . . the strongest. . .

15) page 18619, line 20-: Small changes in the CS cycles and differences in type A and B events are interpreted too much. There is not enough statistics for such a detailed analysis.

16) page 18619, line 22: Define “clean”. A lot of PM mass still present.

17) page 18620, line 8 onwards: Small changes in SO2 in all categories. Not enough statistics.

18) page 18621, line5: Time lag is not suprising. The data was catecorized according to events or non-events.

19) page 18621, line 27: Calculate sulfuric acid proxy.

20) page 18622, line 13: Misplaced citation. Stanier did his study in the US, not in Taiwan.

21) Table 1 & 2: Add a column for the measurement location.

22) Significant figures: Based on the figures 3-9, giving GR(pargan) with 3 or 4 significant figures in Abstract is too much.

23) There is many really long paragraphs. Please consider shortening / splitting.

24) page 18610, line 18: Please specify emission rates (in terms of PM and SO2, at least). I have no idea, how large is the largest coal-fired power plant in Taiwan.

Case studies:

I will not go into the details of the text,but only state that the text is too descriptive and long-winding. The number of figures should be reduced. I only illustrate few points regarding the interpretation of the data.

Section 3.4

To me it seems that the sampling site is moving to a SO2 emission plume. This is seen in the number size distribution as an appearance of large amount of appoximately 20 nm particles. These particles have not have enough time to grow any larger. The regional event seems to be still there, but already at a larger size range.

Section 3.5

There is a change of wind direction (change of air mass). This is common in measurements at a fixed ground site. The air mass in which the regional new particle formation that was observed earlier does not anymore reach the site. The apparent change in number size distribution and particle size cannot be interpreted by a growth event. The analysis should be stopped prior the change in air mass in order to keep the data representative for the regional event.

The new particle formation was not suppressed by the pollution, again the measurement site is affected by the pollution plume.

Section 3.6

Effect of SO2, wind direction, temperature difference etc are important. Present scatter plots!

Consider also other sources of N10-25, in particularly in the urban setting. Traffic influenced sites are always more difficult to analyze for regional new particle formation events as the particle population can be changing rapidly due to intensive emissions in the vicinity of the measurement site.

Downwind case: Why would the nucleating and condensing species be different and less volatile at the downwind site?

sect 3.6.4 Candidate for evaporating vapor

This paragraph is not informative in current form, only a qualitative presentation of potential candidates. As such, it does not give much added value. The role of semi-volatile compounds may be relevant, but I not at all convinced about volatile alkanes or PAH. Highly volatile compounds would not condense to the nanoparticles in the first place (when they are small, Kelvin-effect), so they would not evaporate at a later stage. Also, all work cited deal with particle mass. New particle formation involves only a small amount of mass.

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Interactive comment on Atmos. Chem. Phys. Discuss., 12, 18605, 2012.