Response to Referee #1's comments on "New particle growth and shrinkage observed in subtropical environments" *by* L.-H. Young et al.

Anonymous Referee #1

Received and published: 2 September 2012

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.

Response:

We are grateful to Anonymous Referee #1 for providing insightful comments and additional relevant references that helped us improve our manuscript substantially. Our point-to-point responses to the reviewer's comments are provided and highlighted in blue-colored font, as follows.

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.

Response:

We agree with the reviewer's comments that, by not taking into account the losses, the present formation rate (J_{10}) calculations indeed underestimate the atmospheric formation rates. The diffusion losses were at that time considered of minor importance and hence not taken into account in the analysis because of the following reasons. First, the J_{10} is determined by the rate change of number concentrations of 10-25 nm particles ($dN_{10\text{-}25}/dt$) and their coagulation losses (F_{coag}). The loss was 15% for 10 nm particles, whereas only 6 % for 25 nm particles. Second, at the same study sites, Young et al. (2012) have shown the temporal variability of $N_{10\text{-}25}$ in terms of relative standard deviation (i.e., standard deviation divided by the average concentration) was in the range of 59% to 195%. Given that, the overall diffusion losses of ~10% for 10-25 nm particles were relatively small. Nevertheless, we have revised the manuscript to acknowledge the potential underestimations of the presented formation rates.

Cited reference:

Young, L.-H., Wang, Y.-T., Hsu, H.-C., Lin, C.-H., Liou, Y.-J., Lai, Y.-C., Lin, Y.-H., Chang, W.-L., Chiang, H.-L. and Cheng, M.-T.: Spatiotemporal variability of submicrometer particle number size distributions in an air quality management district, Science of The Total Environment, 425, 135–145, 2012.

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?

Response:

A more detailed description of the sampling instrumentation has been provided by Young et al. (2012). We have provided more details about the measurements in the revised manuscript, as follows.

The sheath airflow (3 lpm) was dried with a silica gel canister to a RH of ~10% and then filtered through a HEPA before entering the differential mobility analyzer (DMA). The aerosol size distributions were therefore measured under dry conditions, and hygroscopic growth was not considered.

The size distributions inversion was carried out using the manufacturer-provided software

(GRIMM 5.477 Version 1.35 Build 1), which is developed and described in detail by Reischl (1991). In brief, the DMA classifies charged particles based on their electrical mobility (Z), which is related to the particle diameter (dp) and DMA parameters as follows:

$$Z = \frac{ieC(d_p)}{3\pi\eta d_p} = \frac{(Q_{sh} + Q_e)\ln(\frac{R_2}{R_1})}{4\pi VL}$$

where i is the number of charges, e is the elementary charge, C(dp) is the slip correction factor as a function of particle size dp, η is the gas viscosity, Q_{sh} is the sheath flow, Q_e is the excess flow, R_1 is the outer radius of the electrode, R_2 is the inner radius of the electrode, V is the voltage and L is the length of DMA. The classified particle number size distribution function (Fc(dp)) at a given voltage is then given by the particles' original number size distribution (F(dp)), the transfer function of the DMA (Tr(Z)) and the bipolar charge probability of the particles (α(dp, i) as follows:

$$F_c(d_p) = \frac{dN_c}{dlnd_p} = \sum_{i=1}^{\infty} F(d_p) \times T_r(Z) \times \alpha(d_p, i)$$

In the software, the DMA and CPC correction efficiencies were taken into account in the calculations, whereas the charging correction is only available for single channel measurements and therefore not applied to the size distribution (i.e., multiple channels) measurements. To minimize multiple charging from large particles, an impactor with a nozzle diameter of 0.6 mm and 50% size-cut of 1082 nm was attached to the inlet of the neutralizer and DMA.

The SMPS has been routinely sent back to the manufacturer for calibration each year. In addition, the sizing accuracy was determined before the study by classifying NaCl of known mobility sizes (50, 76, 113, 168, and 241 nm) from a monodisperse aerosol generator (TSI; Model 3475), simultaneously with another SMPS (TSI; Model 3936). The differences between the expected and the measured particle sizes were less than 3 nm.

Cited references:

Young, L.-H., Wang, Y.-T., Hsu, H.-C., Lin, C.-H., Liou, Y.-J., Lai, Y.-C., Lin, Y.-H., Chang, W.-L., Chiang, H.-L. and Cheng, M.-T.: Spatiotemporal variability of submicrometer particle number size distributions in an air quality management district, Science of The Total Environment, 425, 135–145, 2012.

Reischl, G. P.: Measurement of Ambient Aerosols by the Differential Mobility Analyzer Method: Concepts and Realization Criteria for the Size Range Between 2 and 500 nm, Aerosol Science and Technology, 14(1), 5–24, 1991.

3) Please report gas analyzer models.

Response:

The gas analyzer models are added to the revised manuscript, as follows.

At the sites, the $PM_{2.5}$ were continuously monitored by means of β-ray attenuation (Met One Instruments, Oregon, USA, Model BAM-1020), SO_2 by UV fluorescence (Ecotech, Victoria, Australia, Model 9850), NO_x by chemiluminescence (Ecotech, Victoria, Australia, Model 9841), CO by nondispersive IR (Horiba, Kyoto, Japan), and O_3 by UV absorption (Ecotech, Victoria, Australia, Model 9810).

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?

Response:

We have revised the manuscript to focus on the J_{10}, whereas the modeled J_1 are retained in the manuscript as supplementary information. In addition, we have included Korhonen et al. (2011)’s work to cautious the readers about the potential uncertainties in deriving the J_1 because of the lack of knowledge on the size dependence of particle growth rate below 10 nm as well as the possible erroneous assumptions about the initial cluster size of ~1 nm. Specifically, the decreased growth rate with decreasing particle size and the assumption of a possible too small critical cluster size of 1 nm together likely leads to an overestimation of mean nucleation rates by the PARGAN inversion method. Nevertheless, unless equipped with instruments capable of detecting ~1 nm particles, we suggest that the highly time-resolved PARGAN approach still provides useful information about the intensity of atmospheric nucleation that can be used as a reference and benchmark for future improvement studies.

Cited reference:

Korhonen, H., Sihto, S. L., Kerminen, V. M. and Lehtinen, K. E. J.: Evaluation of the accuracy of analysis tools for atmospheric new particle formation, Atmos. Chem. Phys., 11(7), 3051–3066, 2011.

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.

Response:

We have adopted the estimation method of condensable vapor concentration (C) by Kulmala et al. (2005), as follows. The results are presented in a newly organize and created Table 2 that shows the pollutant concentrations of $PM_{2.5}$, CS, SO_2, C and H_2SO_4 proxy (P).

$$C = \frac{\rho}{\Delta t D m_v}\left(\frac{d_p^2 - d_{p,0}^2}{8} + \left(\frac{2}{3\alpha} - 0.312\right)\lambda\left(d_p - d_{p,0}\right) + 0.623\lambda^2 ln\frac{2\lambda + d_p}{2\lambda + d_{p,0}}\right)$$

where ρ is the particle density (1.84 g cm^{-3}), D is the diffusion coefficient (0.104 cm^2 s^{-1}), mv is the molecular mass of the condensable vapor (1.63×10^{-22} g $molec^{-1}$), α is the mass accommodation coefficient (1), and λ is the mean free path (6.7×10^{-6} cm) at 1 atm and 298K.

As shown in Table 2 below, assuming H_2SO_4 as the condensable vapor, the derived C in this study ranged from 1.69×10^8 molec cm^{-3} – 6.59×10^8 molec cm^{-3}, with an average of $3.46\pm1.49\times10^8$ molec cm^{-3}. These levels are comparable to that estimated for polluted New Delhi, India (Kulmala et al., 2005).

Table 2. Daily air pollutants, condensable vapor (C) and H_2SO_4 proxy (P) concentrations during the NPF events.

Date (mm/dd/yy)	Site[1]	Shrink[2]	$PM_{2.5}$ (μg m^{-3})	CS (10^{-2} s^{-1})	SO_2 (ppb)	C (10^8 molec cm^{-3})	P[3] (10^7 molec cm^{-3})
3 Dec 2008	D	No	46.6	3.9	3.4	2.08	1.72
17 Dec 2008	U	No	40.4	3.2	3.3	6.59	-
3 Jan 2009	C	Yes	19.4	2.2	3.7	1.93	2.46
10 Aug 2010	U	No	17.9	2.1	3.5	4.73	5.98
11 Aug 2010	U	No	15.8	2.4	2.8	2.72	3.04
12 Aug 2010	U	Yes	18.9	2.0	2.6	3.09	4.92
13 Aug 2010	U	No	17.0	1.9	2.1	1.69	3.20
14 Aug 2010	U	No	17.0	2.2	2.3	4.59	3.55
15 Aug 2010	U	No	16.5	2.0	2.0	2.32	3.46
16 Aug 2010	U	Yes	17.0	2.2	-	5.00	-
17 Aug 2010	U	No	19.0	2.6	4.6	4.05	6.36
5 Sep 2010	D	Yes	15.5	1.7	2.1	4.51	3.94
7 Sep 2010	D	Yes	26.4	2.0	2.4	1.70	3.73
12 Sep 2010	D	No	10.1	1.6	2.9	3.38	7.79

[1] U indicates urban, C coastal and D downwind site. There were no NPF events at the mountain site.

[2] Particle shrinkage following the NPF and growth event.

[3] The H_2SO_4 proxy concentration assuming the scaling factor k of 9.9×10^{-7} m^2 W^{-1} s^{-1} reported by Petäjä et al. (2009).

Cited reference:

Kulmala, M., Petäjä, T., Mönkkönen, P., Koponen, I., Dal Maso, M., Aalto, P., Lehtinen, K. and Kerminen, V. M.: On the growth of nucleation mode particles: source rates of condensable vapor in polluted and clean environments, Atmos. Chem. Phys., 5(2), 409–

416, 2005.

Petäjä, T., Mauldin, R. L., III, Kosciuch, E., McGrath, J., Nieminen, T., Paasonen, P., Boy, M., Adamov, A., Kotiaho, T. and Kulmala, M.: Sulfuric acid and OH concentrations in a boreal forest site, Atmos. Chem. Phys., 9(19), 7435–7448, 2009.

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

Response:

We have adopted the proxy estimation method of H_2SO_4 concentration (P) by Petäjä et al. (2009), as follows. The results are presented in a newly created Table 2 (see above) that shows the pollutant concentrations of $PM_{2.5}$, CS, SO_2, C and P.

$$P = kP' = k\frac{[SO_2]UVB}{CS}$$

where k is the scaling factor and CS is the condensation sink. The SO_2 concentration has unit of molec cm^{-3}. The UVB is determined from the measured daily maximum UV index (UVI), in which 1 UVI equals to 25 mW m^{-2} (or 90 J m^{-2}).

In the present study, the P' ranged from 1.74×10^{13} (molec cm^{-3}) W m^{-2} s – 7.86×10^{13} (molec cm^{-3}) W m^{-2} s, with an average of $4.22\pm1.78\times10^{13}$ (molec cm^{-3}) W m^{-2} s. As shown in Table 2, using the k value of 9.9×10^{-7} m^2 W^{-1} s^{-1} reported by Petäjä et al. (2009), the H_2SO_4 concentration P ranged from 1.72×10^7 molec cm^{-3} – 7.79×10^7 molec cm^{-3}, with an average of $4.18\pm1.76\times10^7$ molec cm^{-3}. It is important to note that, because we have used the daily maximum UVI, these derived P values represent the upper limits. Most field observations have shown that the atmospheric H_2SO_4 concentrations during NPF are typically on the order of 10^6-10^7 molec cm^{-3} (e.g., Riipinen et al., 2007; Kuang et al., 2008; Yue et al., 2010).

Cited references:

Kuang, C., McMurry, P. H., McCormick, A. V. and Eisele, F. L.: Dependence of nucleation rates on sulfuric acid vapor concentration in diverse atmospheric locations, J. Geophys. Res., 113(D10), 2008.

Petaja, T., Mauldin, R. L., III, Kosciuch, E., McGrath, J., Nieminen, T., Paasonen, P., Boy, M., Adamov, A., Kotiaho, T. and Kulmala, M.: Sulfuric acid and OH concentrations in a boreal forest site, Atmos. Chem. Phys., 9(19), 7435–7448, 2009.

Riipinen, I., Sihto, S. L., Kulmala, M., Arnold, F., Dal Maso, M., Birmili, W., Saarnio, K., Teinilä, K., Kerminen, V. M., Laaksonen, A. and Lehtinen, K. E. J.: Connections between atmospheric sulphuric acid and new particle formation during QUEST III-IV campaigns in Heidelberg and Hyytiälä, Atmos. Chem. Phys., 7(8), 1899–1914, 2007.

Yue, D. L., Hu, M., Zhang, R. Y., Wang, Z. B., Zheng, J., Wu, Z. J., Wiedensohler, A.,

He, L. Y., Huang, X. F. and Zhu, T.: The roles of sulfuric acid in new particle formation and growth in the mega-city of Beijing, Atmos. Chem. Phys., 10(10), 4953–4960, 2010.

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?

Response:

Because of the poor statistics, as suggested by the reviewer, the classification of a small number of NPF events into subsets (Types A and B) has been removed. In effect, we have changed our focus to the differences between non-event and event days, as well as the particle shrinkage events. As a result, new boxplot figures showing the range of CS and SO_2 for non-event and event days are created to replace the original Fig. 2, which will be moved to the Appendix Figure A2 as supplementary information.

Below is the newly created Figure 2, showing the boxplots of the daily CS and SO_2 for non-event and event days. The solid and dash line inside the box is the median and mean, respectively; the whiskers mark the 10th and 90th percentile. As shown, the CS and SO_2 on event days were both typically below the 50th percentile values on non-event days. This indicates that the NPF events were favored on days with low concentrations of both pre-existing particles and SO_2. The preference for low SO_2 is somewhat counterintuitive as it is the precursor of the major nucleating vapor H_2SO_4. Further explanations are given in the original manuscript p.18622, lines 1-13.

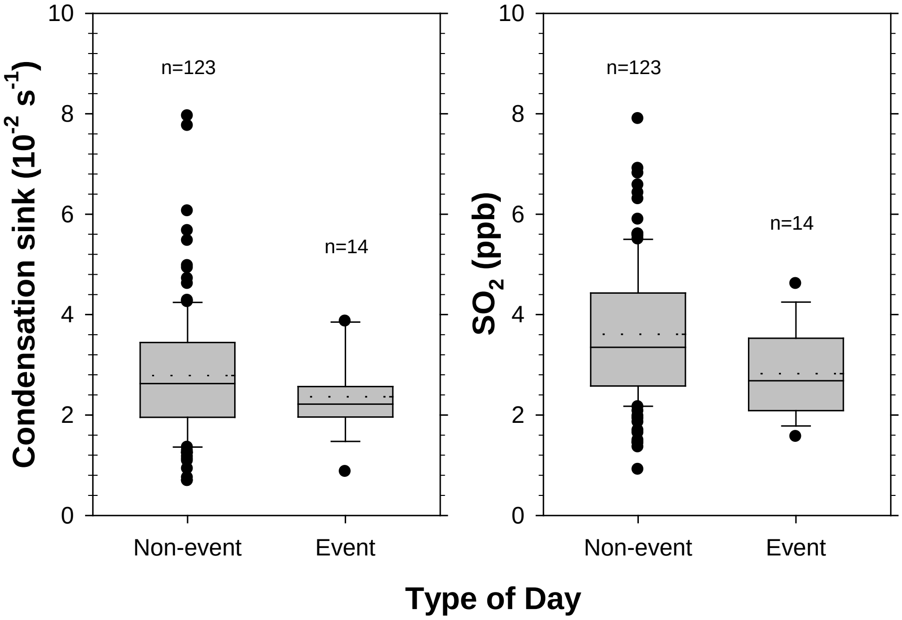

Fig. 2. Boxplots of the daily CS and SO_2 for non-event and event days. The solid and dash line inside the box is the median and mean, respectively; the whiskers mark the 10th and 90th percentile.

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.

Response:

Because of the poor statistics, as suggested by the reviewer, the classification of a small number of NPF events into subsets (Types A and B) has been removed. In effect, we have changed our focus to the differences between non-event and event days, as well as the particle shrinkage events. Please refer to our response to the General Comments #1 (p. 7).

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

Response:

The number of NPF events at each measurement location is given in Table 1 (second column; Site) and described in p.18616 lines 20-22. Specifically, there were 9 events at the urban site (denote as U), 4 events at the downwind site (D), one at the coastal site (C) and none at the mountain site (M). At the urban site during the warm period, we observed 8 consecutive NPF events as shown in the Appendix Figure A1.

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?

Response:

Table 1 reports only the daily average $PM_{2.5}$ concentrations during NPF event days. The contribution of larger particles (> 1 μm) to the CS is considered of minor importance due to (1) their negligible number concentration in comparison to ultrafine particles (< 0.1 μm) and (2) the CS is proportional to dp^a, (particle diameter)^a, with the exponent *a* in the range of 1-2 for particles in the transitional region (Kulmala et al., 2001); in other words, the major contributor to the CS is the particles with diameters between 0.1-1 μm.

Cited reference:

Kulmala, M., Maso, M., Mäkelä, J., Pirjola, L., Väkevä, M., Aalto, P., Miikkulainen, P., Hämeri, K. and O'Dowd, C. D.: On the formation, growth and composition of nucleation mode particles, Tellus B, 53(4), 479–490, 2001.

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).

Response:

We agree with the reviewer’s suggestions on the careful selection of case studies. As a result, we have revised the manuscript to include two growth events (with each representing the morning and midday NPF, respectively) and two shrinkage events (with each representing the positive and negative correlation, respectively, between the number concentration of 10-25 nm particles, $N_{10\text{-}25}$, and the particle mode diameter, D_{mode}). Although the underlying mechanisms were not clearly elucidated in the present study, we suggest that the timing at which the NPF commence is an important factor because it provides clues as to what conditions (e.g., atmospheric mixing or photochemistry) are conducive to NPF at the study sites. Similarly, the increasing (or decreasing) $N_{10\text{-}25}$ with increasing D_{mode} provides possible mechanisms (e.g., evaporation) related/leading to particle shrinkage.

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.

Response:

We have added the specific aims of the study to the last paragraph in the introduction, as follows:

Previously, Young et al. (2012) have characterized the spatiotemporal variability of particles in the size range from 10-1000 nm in various environments (urban, coastal, mountain and downwind) in subtropical Taiwan. It was found that the variability is largely driven by primary emissions of local traffic and, to as lesser extent, by secondary NPF. Unlike the primary pathway, the secondary NPF is oftentimes accompanied with intense new particle growth over extended period of time. This growth process causes the new particles to grow to larger sizes of environmental health implications. With that in mind and building upon our previous work, here we aim to characterize the aerosol kinetics and properties during NPF and growth events and, along with meteorological conditions, to identify favorable conditions leading to those events. Also presented are several notable observations of new particle shrinkage following NPF and growth.

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

Response:

We have included the methodology and instruments to measure and characterize NPF events described in the review article by Kulmala et al. (2012) and selected references therein in the revised manuscript.

Cited reference:

Kulmala, M., Petäjä, T., Nieminen, T., Sipilä, M., Manninen, H. E., Lehtipalo, K., Dal Maso, M., Aalto, P. P., Junninen, H., Paasonen, P., Riipinen, I., et al.: Measurement of the nucleation of atmospheric aerosol particles, Nat Protoc, 7(9), 1651–1667, 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.

Response:

We have included the work by Vanhanen et al. (2011) that presents a commercially available CPC that detects particles as small as ~1 nm.

Cited reference:

Vanhanen, J., Mikkilä, J., Lehtipalo, K., Sipila, M., Manninen, H. E., Siivola, E., Petaja, T. and Kulmala, M.: Particle size magnifier for nano-CN detection, Aerosol Science and Technology, 45(4), 533–542, 2011.

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

Response:

The experimental work by Zhang et al. (2009) showed no apparent growth or shrinkage of 3-30 nm H_2SO_4 particles exposed to extremely high NH_3 of ~12.2 ppm. They concluded that the role of NH_3 to nanoparticle growth is limited to the stabilization of particulate H_2SO_4. On the other hand, the reaction between alkylamines and H_2SO_4 is considered completely irreversible and thus contributes to enhanced particle growth (Zhang et al., 2012).

Cited references:

Zhang, R., Khalizov, A., Wang, L., Hu, M. and Xu, W.: Nucleation and Growth of Nanoparticles in the Atmosphere, Chem. Rev., 112(3), 1957–2011, doi:10.1021/cr2001756, 2012.

Zhang, R., Wang, L., Khalizov, A. F., Zhao, J., Zheng, J., McGraw, R. L. and Molina, L. T.: Formation of nanoparticles of blue haze enhanced by anthropogenic pollution, Proceedings of the National Academy of Sciences, 106(42), 17650–17654, 2009.

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

Response:

The first paragraph of Sect. 2.3 has been moved to Sect. 2.2 Sampling and instrumentation in the revised manuscript.

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

Response:

We have revised the manuscript to focus on the J_{10}, whereas the modeled J_1 are retained in the manuscript as supplementary information. In addition, we have included Korhonen et al. (2011)'s work to cautious the readers about the potential uncertainties in deriving the J_1 because of the lack of knowledge on the size dependence of particle growth rate below 10 nm as well as the possible erroneous assumptions about the initial cluster size of ~1 nm. Specifically, the decreased growth rate with decreasing particle size and the assumption of a too small critical cluster size of 1 nm together leads to an overestimation of mean nucleation rates by the PARGAN inversion method. Nevertheless, unless equipped with instruments capable of detecting ~1 nm particles, we argue that the highly time-resolved PARGAN approach still provides useful information about the intensity of atmospheric nucleation that can be used as a benchmark for future improvements.

Cited reference:

Korhonen, H., Sihto, S. L., Kerminen, V. M. and Lehtinen, K. E. J.: Evaluation of the accuracy of analysis tools for atmospheric new particle formation, Atmos. Chem. Phys., 11(7), 3051–3066, 2011.

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

Response:

The calculation of CS was adopted from Kulmala et al. (2001).

Cited reference:

Kulmala, M., Maso, M., Mäkelä, J., Pirjola, L., Väkevä, M., Aalto, P., Miikkulainen, P., Hämeri, K. and O'Dowd, C. D.: On the formation, growth and composition of nucleation mode particles, Tellus B, 53(4), 479–490, 2001.

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)?

Response:

The differences between the PARGAN-derived and modal-derived GR are due to the differences in the time resolution between the two methods. Specifically, the GR_{PARGAN} was determined from consecutive size distribution measurements, whereas the GR_{MOD} was averaged across the start and end of particle growth (i.e., only one GR value for each growth event). Based on highly time-resolved measurements, the PARGAN approach tends to produce variable GR values. However, we argue that results with strong variability do not necessarily mean they are incorrect; instead, it may reflect the dynamic, non-linear nature of atmospheric nucleation.

The description on p.18617, lines 5-6 is incorrect and has been revised as follows: The percentages of GR_{PARGAN} over GR_{MOD} ranged from 51% to 187%, with an average of 88±44%. It can therefore be concluded that the differences between the two GRs are within a factor of 2.

As described on p.18610 lines 23-25 and p.18611 lines 5-7 of the original manuscript, the sampling campaigns were conducted consecutively at the four study sites from October 2008 to January 2009 (cold season) and from August 2010 to October 2010 (warm season). A total of 26,075 aerosol number-size distributions were collected over 137 effective sampling days (with the data coverage of ~92.5%); among them, 43 days were at the urban site, 35 days at the coastal site, 32 days at the mountain site and 27 days at the coastal site.

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.

Response:

The description on p.18617, lines 5-6 is incorrect and has been revised as follows: The percentages of GR_{PARGAN} over GR_{MOD} ranged from 51% to 187%, with an average of 88±44%. It can therefore be concluded that the differences between the two GRs are within a factor of 2.

On a few days (e.g., 3 January 2009 and 14 August 2010), the differences between GR_{PARGAN} and GR_{MOD} were indeed large (i.e., 187% and 51%, respectively). However, the differences in most other days were between 70% and 114%. Nevertheless, the strong variability in the results by the highly time-resolved PARGAN approach does not necessarily mean the results are incorrect; instead, it may reflect the dynamic, non-linear nature of atmospheric nucleation.

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.

Response:

We agree with the reviewer's comments that, indeed, the amount of condensable vapor loss due to evaporation should be considered with respect to volume, not diameter. The volume loss of the prior condensed vapor during the shrinkage can be roughly estimated by the growth from d_1 to d_2 and the loss from d_3 to d_4 as follows:

$$Loss = \frac{d_2^3 - d_1^3}{d_3^3 - d_4^3} \times 100\%$$

On days with small d_p variability, the d_2 could equal to d_3. The results show that on the 3 January 2009 and the 7 September 2010 the volume losses were above 90%, suggesting nearly complete evaporation. On other days, the volume losses ranged from 18% to 38%. These results indicate that a notable fraction of the prior condensed vapor was likely or had become semi-volatile.

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.

Response:

We agree with the reviewer's comments that there may be other sources of 10-25 nm particles during some of the shrinkage periods. For example, on 12 August and 7 September 2010, the increasing N_{10-25} coincided with elevated SO_2, indicating possible impact of SO_2 plume. Though, the impact of traffic emissions of such strong intensity is less likely at that period of time of ~15:00 LT. The impact of traffic emissions typically occurs during rush hour periods, between 07:00-09:00 LT and 17:00-19:00 LT as indicated by the elevated NOx and CO in Figs 3-9.

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.

Response:

At the time we were interested in the impact of NPF on the levels of ultrafine particles (<100 nm), a size class of important environmental and human health implications. The impact of NPF on the nucleation mode and Aitken mode particles is summarized in Table 2 of the original manuscript and described on p.1860, lines 23-28.

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.

Response:

We agree with the reviewer's comments that strong correlation itself does not proof causality. The close timing and short time lag nevertheless suggests that the traffic emissions may have facilitated the onset of nucleation. In addition, the polluted PM-laden air during traffic rush hours supposedly would suppress NPF unless there were sufficient nucleating/condensable vapors to overcome such barrier. Therefore, we have revised the original sentence as follows:

"The start of the morning NPF event prior to 09:30 LT may have been facilitated by the traffic emission of nucleating/condensable vapors."

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

Response:

We have revised the sentence as follows:

"Furthermore, the solar intensity is also the strongest during midday hours."

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.

Response:

We agree with the reviewer's comments that the differences in the diurnal variations (Fig. 2) were mostly insignificant, except the $N_{10\text{-}100}$ during periods of NPF. The classification of a small number of NPF events into subsets (Types A and B) has also been removed. Therefore, we have changed our focus to the differences between non-event and event days. New boxplot figures showing the range of CS and SO_2 for non-event and event days are created to replace the original Fig. 2, which will be moved to the Appendix as supplementary information. Please refer to our response to General Comments #1 (p.7).

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

Response:

We have revised our manuscript to focus on the differences between non-event and event days, instead of the Type A and B. Please refer to our response to Specific Comments #15 (p.14).

Clean and polluted days were determined qualitatively according to the median daily CS value of 2.6×10^{-2} s^{-1} for the entire study period.

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

Response:

We have revised our manuscript to focus on the differences between non-event and event days, instead of the Type A and B. Please refer to our response to General Comments #1 (p.7) and Specific Comments #15 (p.14).

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

Response:

Along with the traffic indicator CO and NOx, the time lag is important to differentiate the new particles emitted by local traffics from those formed by regional NPF. This is especially true for the morning NPF events, which occurred at a time shortly after traffic hours. On the other hand, the midday NPF events are more obvious that they not directly related to traffic emissions.

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

Response:

We have calculated the sulfuric acid proxy. Please refer to our response to General Comments (Data analysis methods) #3 (p.6-7).

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

Response:

The citation has been deleted.

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

Response:

The measurement locations are given in the second column ("Site") of Tables 1 and 2. The U refers to the urban site, C as the coastal, and D as the downwind site. There were no NPF events at the mountain site.

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

Response:

In the revised manuscript, all the growth rate values are given with 2 significant figures.

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

Response:

In the revised manuscript, long paragraphs have been broken up in shorter ones to be more concise and readable.

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.

Response:

In 2009, the coal-fired power plant in Taichung City is ranked the #1 CO_2 emitting power plant (~3.6×10^7 tons per year) as well as power generation (~3.9×10^7 MWh Energy) in the world by Carbon Monitoring for Action (CARMA), a database developed by an independent and non-partisan think tank located in Washington, DC (http://carma.org/).

The annual emission of SO_2 and NOx from that power plant in 2010 was 11,564 and 19,143 tons, respectively, according to the Environmental Protection Bureau of Taichung City Government (http://www.epb.taichung.gov.tw/). We could not obtain creditable data on PM emission, hence not provided here.

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.

Response:

We thank the reviewer for the comments on the text writing and data interpretation. We have reduced both the paragraph length and the number of figures, as well as being more cautious with data interpretation.

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.

Response:

As shown in Fig. 3 during traffic rush hours between 07:00-09:00 LT, the appearance of large amount of ~20 nm particles coincided with elevated CO and NOx. This indicates that those 20 nm particles are likely primary particles from traffic exhaust. After 09:00 LT, the size distribution contour plot clearly shows a burst of ~10 nm particles followed by intense particle growth for 3.5 hrs, whereas the CO and NOx were gradually decreasing with time. This, on the other hand, indicates that those 10 nm particles are likely secondary particles from regional NPF event. After ~13:30 LT, there was another intense burst of 10-20 nm particles over a period of 2 hrs, without particle growth. As suggested by the reviewer, those particles are likely from SO_2-related regional NPF event and that they did not have enough time to grow to larger sizes.

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.

Response:

In an Eulerian framework, air masses enter and leave the air monitoring site. Measurements made at a fixed site thus only provide a snapshot of the passing air mass. If an observed NPF event was confined to a small spatial scale, the particle growth could disappear from our observations because of changes in wind direction. Such a NPF event is referred to as “short-lived” event, according to Stanier et al. (2004). On the other hand, the observed particle growth of a “regional” NPF event (i.e., large spatial scale) would more likely not be affected by changes in wind direction as long as the measurement site is still within the nucleation zone. In this study, the durations between the start of NPF and end of particle growth ranged from 1.5 hrs to 5 hrs. Therefore, the identified NPF events are all considered regional events.

We agree with the reviewer’s comments on the NPF event on the 3 December 2008. The NPF event was not suppressed by the polluted air. Instead, the measurement site was impacted by the polluted SO_2 plume due to changing wind direction.

Cited reference:

Stanier, C. O., Khlystov, A. Y. and Pandis, S. N.: Nucleation Events During the Pittsburgh Air Quality Study: Description and Relation to Key Meteorological, Gas Phase, and Aerosol Parameters, Aerosol Science and Technology, 38(sup1), 253–264, 2004.

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?

Response:

We chose to present the data based on their temporal evolution (Figs 3-9), instead of scatter plots, because of the limited number of particle shrinkage observations, limited data points during the particle shrinkage period, and the ever-changing atmospheric conditions. Bivariate scatter plot (i.e., correlation) has limitations in that it is most useful when all other variables are more or less held constant. With the same reasons we therefore thought the case-study approach is more appropriate to focus on subtle trends during the particle shrinkage events. These subtle trends may provide insights to key variables or conditions leading to particle shrinkage, with which we can build upon for future in-depth study. The outcome of this approach thus has limited statistical power and is relatively more descriptive, as suggested by the reviewer.

We did consider the other major source of N10-25, namely traffic emissions. As described in our response to the reviewer's comments on Section 3.4, we used CO and NOx as the indicator of traffic emissions, along with the information on the traffic rush-hour periods, to differentiate primary emission and secondary NPF.

As shown in Figure 1, the downwind site is located at the southern border of the study area. The prevailing northeasterly winds are conducive for the transport of air pollutants from the central Taiwan to the downwind site. As a result, the Taiwan EPA had designated it as a photochemistry site. We therefore speculate that the potentially stronger photochemical activities at the downwind site would lead to a smaller fraction of volatile species in the particulate phase. For example, Kim et al. (2011) reported that the volume fraction of volatile species in ultrafine particles (40, 50, 60 and 80 nm) heated to 100°C was 10-50% in the absence of events, while 7-30% during photochemical events.

Cited reference:

Kim, J. S., Kim, Y. J. and Park, K.: Measurements of hygroscopicity and volatility of atmospheric ultrafine particles in the rural Pearl River Delta area of China, Atmospheric Environment, doi:10.1016/j.atmosenv.2011.05.054, 2011.

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.

Response:

In our original manuscript, we may have focused too much on the organics from primary emissions (i.e., alkanes and PAHs) because they are the major contributor to the carbon content in urban fine particles (e.g., Fraser et al., 1997). In addition, high molecular weight hydrocarbons (carbon number > ~12) are known to be semi-volatile and therefore exist in both the vapor and particulate phase. Nevertheless, organics from secondary photochemical pathway are also important and very complex (Jimenez et al., 2009). Therefore, we have revised the manuscript to remove the reference to specific organic species. Also, we have revised the section title to “The role of semi-volatile species” and simply stress that the new particle growth can be a reversible process due to the involvement of semi-volatile species.

Cited references:

Fraser, M. P., Cass, G. R., Simoneit, B. R. T. and Rasmussen, R.: Air quality model evaluation data for organics. 4. C2-C36 non-aromatic hydrocarbons, Environ. Sci. Technol., 31(8), 2356–2367, 1997.

Jimenez, J. L., Canagaratna, M. R., Donahue, N. M., Prevot, A. S. H., Zhang, Q., Kroll, J. H., DeCarlo, P. F., Allan, J. D., Coe, H., Ng, N. L., Aiken, A. C., et al.: Evolution of Organic Aerosols in the Atmosphere, Science, 326(5959), 1525–1529, 2009.

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