Atmos. Chem. Phys. Discuss., 15, C9076–C9086, 2015
www.atmos-chem-phys-discuss.net/15/C9076/2015/

Atmospheric Chemistry and Physics Discussions
Open Access

Interactive comment on "Evolution of gaseous precursors and meteorological parameters during new particle formation events in the Central European boundary layer" *by* J. Größ et al.

J. Größ et al.

birmili@tropos.de

Received and published: 9 November 2015

Response to Anonymous Referee #2

GENERAL COMMENTS. The paper analyses a new and unique data-set: aerosol particle number size distributions (PNSD) measured by Neutral cluster and Air Ion Spectrometer (NAIS) in the diameter range 2-20 nm for 2008-2011 at the research station Melpitz. Data are statistically analyzed by a new method, a convolution of measured PNSDs, and PNSDs observed during strong New Particle Formation (NPF) events. Results are very interesting, clearly presented, concise and well-structured (particu-

larly, the figure 4), and do represent a substantial contribution to the understanding of the NPF. I recommend publication in ACP, taking due account of the following issues.

SPECIFIC COMMENTS. To help the reader to understand results, my suggestion is to better explain the physical meaning of the convolution integral used here. (Is it similar to a cross-correlation between PNSDs and the selected 27 NPF events?)

Reply: We agree that the current explanation and motivation of the CI method is rather short. We will consequently add the following text to the manuscript: “The motivation of the convolution integral is to enable automatic detection and classification of the NPF events. The CI function represents a simple time series where NPF events can be detected as peaks in that series. The height of the peaks in the CI function is sensitive towards both, the number concentration of new particles ($N_{[2;20]}$) occurring during an event and the time duration of an event. Besides an automatic detection of the time window when NPF occurred, it is possible to objectively rank the detected NPF events according to the height of the detected peaks. The computation of the convolution integral also avoids some aspects that make the classification of NPF events problematic: 1) Due to the finite width of the $f(t)$ function, the CI function includes a smoothing of the original time series, which averages out possible experimental noise or very short-lived peak concentrations. This might help make the detection of NPF events more representative in that it captures the more significant events. 2) Experimental data might, in reality, include different time resolutions, short gaps of data, etc. The CI method will even our such deficiencies in that it yields a standardised CI function, on a regular time grid, which can be compared, for example, among different sites.”

I also suggest to explain: (i) how results rely on the manual selection of the 27 NPF events, (ii) how the CI thresholds were selected (Table 2), ...

Reply: 27 NPF events were selected to provide a “realistic” initialisation to the CI method. Of all properties of the function $f(t)$, its width (relative to the time scale) is probably the most salient property. (The width of $f(t)$ is visible as the red curve in

Fig. A2). Of all peaks in the original time series $g(t)$ ($N_{[2;20]}$), those peaks that have a similar width like $f(t)$ will obtain a maximum response in the CI function in relation to their peak area. (This is a consequence of Equation 3). The width of $f(t)$ is thus more important than its height because the height will come to effect in a multiplicative manner for all NPF events while the width gains numerical relevance for such NPF events whose peak width in $g(t)$ is the same or bigger than the width of $f(t)$. It is therefore clear that the CI integral method favours, in its ranking, events of such characteristics. For this reason, we selected the 27 most outstanding events (from visual inspection) with respect to both, $N_{[2;20]}$ and also the continuous evolution of a new nucleation mode for a long duration as much as possible. We thought that these events are the ones that this analysis should ideally be looking for, although we would not aim at excluding other patterns of NPF events by default. As a matter of fact, the CI method will classify any day of observations on a continuous scale of CI ranging between values close to 0 and Max(CI). We are aware that the CI integral method might provide different results if, for instance, only very short-duration events would be chosen. Such a choice would push NPF events with higher peak $N_{[2;20]}$ concentrations (even if only short-lived) higher in the ranking. We will include this text in the revised version of the manuscript.

(iii) reasons for the different average time of peak N2-20 for the three classes (Table 2).

Reply: Among the time differences to be taken from Table 2, the difference between Class I and II is of major concern. (Class III exhibits only very low peaks in $N_{[2;20]}$ compared to the rest so that their time of peak concentrations is subject to considerable uncertainties.) Class I events take place, on average, 52 min earlier than Class II events. We observed two prime differences between those event classes: 1) temperature rises faster on the mornings of Class I events (see Fig. 1 attached to this author comment). 2) SO2 increases faster on the mornings of Class I events (see Fig. 2 attached to this author comment). Observation 1) will have implications for the development of vertical atmospheric mixing due to convection in that elevated layers will be mixed in sooner on Class I days compared to Class II days. Observation 2) points to the efficient downward mixing of SO2 plumes that are aloft. In some recent research we found experimental suggestions for the presence of SO2-enriched plumes above Melpitz, where particle nucleation might take place some time before NPF is detected on the ground (Platis et al., 2015). That work suggests that certain NPF events apparently start in a layer some few hundred meters aloft, to be measured near the ground only after considerable delay. Returning to your original question, two factors might cause Class I events to occur earlier than Class II events: a) more rapid transport of elevated layers (often SO2-enriched), where nucleation can take place before it might be observed on the ground and b) the presence of higher SO2 concentrations, allowing H2SO4 concentrations less time to reach a threshold where significant nucleation could take place. We agree that these hypotheses are largely speculative, but propose to include some of them in the final version of the manuscript.

To reinforce findings, it would be worth to discuss how dependant results are on the observation site (Melpitz), or conversely how they can be considered as general findings. For instance, a large dependence of NPF events on solar radiation and [SO2] was found: can this be considered a general finding or a result specific of the Melpitz station (due to local availability of [OH], relative humidity, H2SO4 parameterization)? Also, both the condensational sink (as a factor inhibiting NPF events) and [NH3] (as a precursor of particle nucleation) were found to have a subordinate role: is that a general finding or a finding due to the low road traffic emissions and available agricultural emissions, respectively, at the Melpitz station?

Reply: We agree that this aspect has been somewhat of a shortcoming in our present work. To answer your question, we compared our work more specifically with a number of previous studies. Those former studies can roughly ordered into the following groups:

1) Fundamental study on the influence of solar radiation

Boy and Kulmala (2001) show strong correlations between NPF events and solar radiation at the Boreal forest research site Hyytiälä (SMEAR-II) in Finland. The preferred band of solar radiation was UV-A, while the study also found an anti-correlation with water vapour. The statements about solar radiation and water vapour coincide with this work.

2) Studies suggesting a critical influence os SO2 and/or H2SO4

Jeong et al. (2006), report for two sites in Canada and the northern U.S., that "SO2 and UV-B were highly correlated with particle concentration, suggesting a high association of photochemical processes with these local [NPF] events." Stanier et al. (2004) report nucleation events during the Pittsburgh Air Quality Study concluding that "local nucleation events were usually associated with elevated SO2 concentrations". Zhang et al. (2004), from the same campaign, report that sulfate appeared to be the major species involved in the early growth of nucleation mode particles while organic particle growth to set on only later. Woo et al. (2001) report a similar, strong correlation between NPF events in Atlanta, U.S., and anthropogenic SO2 as a precursor.

Dunn et al. (2004) report, for observations in Mexico City, that "concentrations of particles with diameter greater than 10 nm increased an order of magnitude, and concentrations of sub-10 nm diameter particles increased at least two orders of magnitude over concentrations just before the event or on a day without nucleation. Large increases in SO2 concentrations and northerly winds also coincide with these events."

For the prototype of a Chinese megacity in a temperate climate with high rates of anthropogenic particulate and gaseous emissions, Beijing, the influence of SO2 and H2SO4 as a precursor for NPF could also be confirmed (Yue et al., 2010). Statistically, however, the highest nucleation mode concentrations due to photochemical production can be found in clean air masses where CS is low (Wehner et al., 2008).

Vakkari et al. (2011) report, for a site in the South African savannah, that "the occurrence of new particle formation and growth was strongly dependent on sulphuric acid", with SO2 as a precursor, and that "the contribution of sulphuric acid to the growth

ACPD
15, C9076–C9086, 2015

immediately after nucleation was significant."

3) Comparative studies (including Melpitz data)

Manninen et al. (2010) compared observations similar to this work (NAIS measurements) at 12 observation sites across Europe. Among these sites, Melpitz exhibited the highest fraction of NPF days for the observation period (57 %). Manninen et al. (2010) confirmed that at Melpitz, NPF events showed little sensitivity to CS, while at other background sites (Hyytiälä, Cabauw, Hohenpeissenberg, Finokalia) there was a clear trend towards lower CS on NPF event days.

Jaatinen et al. (2009) compared NPF event statistics and correlations for the sites Hyytiälä (Finland), Melpitz (Germany) and San Pietro Capofiume (Italy). They conclude that "Nucleation was found to occur frequently at all stations, however seasonal differences were observed for every station. [...] In Hyytiälä the formation and growth of the particles was characterized by low pre-existing condensation sink and most likely high biogenic VOC concentrations associated with the growth season, and in Melpitz and San Pietro Capofiume by the high level of pollution arriving from the nearby industrial and agricultural sources."

Our impression is that the correlation between NPF and solar radiation has been confirmed in a few statistically relevant studies, as has been the connection of NPF events and anthropogenic SO2 plumes. On the issue of CS, the conclusions in the various works are in less agreement. In clean areas where SO2 levels are low, CS seems to play a factor favourable for NPF while in areas with moderate SO2 levels, the influence of CS steps back behind the dominating influence os solar radiation and SO2. In areas with extremely high CS and general pollution levels, the occurrence of NPF events might be even limited by that high CS. So far, we found no study analysing the role of ammonia on a longer statistical basis. In this respect, we consider our study as a novelty.

Our impression is that in Melpitz, NPF occurs rather frequently, with the majority of NPF

ACPD

15, C9076–C9086, 2015

events being under the influences of anthropogenic SO2 plumes as a main precursor for H2SO4 and subsequent nucleation. Here, Melpitz compares best, perhaps, with the San Pietro Capofiume site in the Italian Po Valley, and the various North American sites. NPF at Melpitz clearly behaves in a different fashion from continental background sites such as SMEAR-II in Finland, mountain sites, coastal sites, and heavily polluted locations such as Chinese megacities.

We will formulate the statements in this section into a new part of text in the Discussions section of the manuscript.

TECHNICAL CORRECTIONS: - Caption fig.4: is "time series" correct?

Answer: Thank you, the expression should read "diurnal cycles".

- pag. 21 line 3: there is an "and" missing after "solar radiation", and pag.24 line 1: there is an "and" missing between "radiation" and "[OH]".

Answer: Thank you, this was corrected.

- Figure 4: I would better explain the panel f of [NH3].

Answer: Figure 4f only shows an idealised cycle of [NH3] (in contrast to Fig. A3, where real [NH3] are plotted.

- Title: I suggest some modification to clearly reflect the contents of the paper.

Reply: We consider this. One option might be “Atmospheric new particle formation at the research station Melpitz, Germany: Connection with gaseous precursors and meteorological parameters”.

Wolfram Birmili, on behalf of all co-authors.

References

Boy, M. and Kulmala, M.: Nucleation events in the continental boundary layer: Influence of physical and meteorological parameters, Atmos. Chem. Phys., 2, 1-16, doi:10.5194/acp-2-1-2002, 2002.

Dunn, M. J., J.-L. Jiménez, D. Baumgardner, T. Castro, P. H. McMurry, and J. N. Smith (2004), Measurements of Mexico City nanoparticle size distributions: Observations of new particle formation and growth, Geophys. Res. Lett., 31, L10102, doi:10.1029/2004GL019483.

Jeong, C.-H., Evans, G.-J., Hopke P.K., Chalupa, D.J., and Utell, M.: Influence of atmospheric dispersion and new particle formation events on ambient particle number concentration in Rochester, United States, and Toronto, Canada, Journal of the Air Waste Management Association, 56(4), 431–443, doi:10.1080/10473289.2006.10464519, 2006.

Manninen, H. E., Nieminen, T., Asmi, E., Gagne, S., Häkkinen, S. et al.: EUCAARI ion spectrometer measurements at 12 European sites – analysis of new particle formation events, Atmos. Chem. Phys., 10, 7907-7927, doi:10.5194/acp-10-7907-2010, 2010.

Jaatinen, A., Hamed, A., Joutsensaari, J., Mikkonen, S., Birmili, W., Wehner, B., Spindler, G., Wiedensohler, A., Decesari, S., Mircea, M., Facchini, M. C., Junninen, H., Kulmala, M., Lehtinen, K. E. J. & Laaksonen, A.: A comparison of new particle formation events in the boundary layer at three different sites in Europe. Boreal Env. Res. 14: 481–498, 2009.

Platis, A., Altstädter, B., Wehner, B., Wildmann, N., Lampert, A., Hermann, M., Birmili, W., and Bange, J.: An observational case study on the influence of atmospheric boundary-layer dynamics on new particle formation. Boundary Layer Meteorology. Online version September 19, 2015. http://dx.doi.org/10.1007/s10546-015-0084-y

Stanier, C. O., Khlystov, A. Y., and Pandis, S. N.: Ambient aerosol size distributions and number concentrations measured during the Pittsburgh Air Quality Study (PAQS). Atmospheric Environment, 38(20), 3275-3284, 2004.

Wehner, B., Birmili, W., Ditas, F., Wu, Z., Hu, M., Liu, X., Mao, J., Sugimoto, N., and

Wiedensohler, A.: Relationships between submicrometer particulate air pollution and air mass history in Beijing, China, 2004–2006, Atmos. Chem. Phys., 8, 6155-6168, doi:10.5194/acp-8-6155-2008, 2008.

Woo, K. S., D. R. Chen, D. Y. H. Pui, and P. H. McMurry: Measurement of Atlanta aerosol size distributions: Observations of ultrafine particle events, Aerosol Sci. Technol., 34(1), 75-87, 2001.

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, 4953-4960, doi:10.5194/acp-10-4953-2010, 2010.

Zhang, Q. I., Stanier, C. O., Canagaratna, M. R., Jayne, J. T., Worsnop, D. R., Pandis, S. N., Jimenez, J. L.: Insights into the chemistry of new particle formation and growth events in Pittsburgh based on aerosol mass spectrometry. Environmental Science & Technology, 38(18), 4797-4809, 2004.

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 2305, 2015.

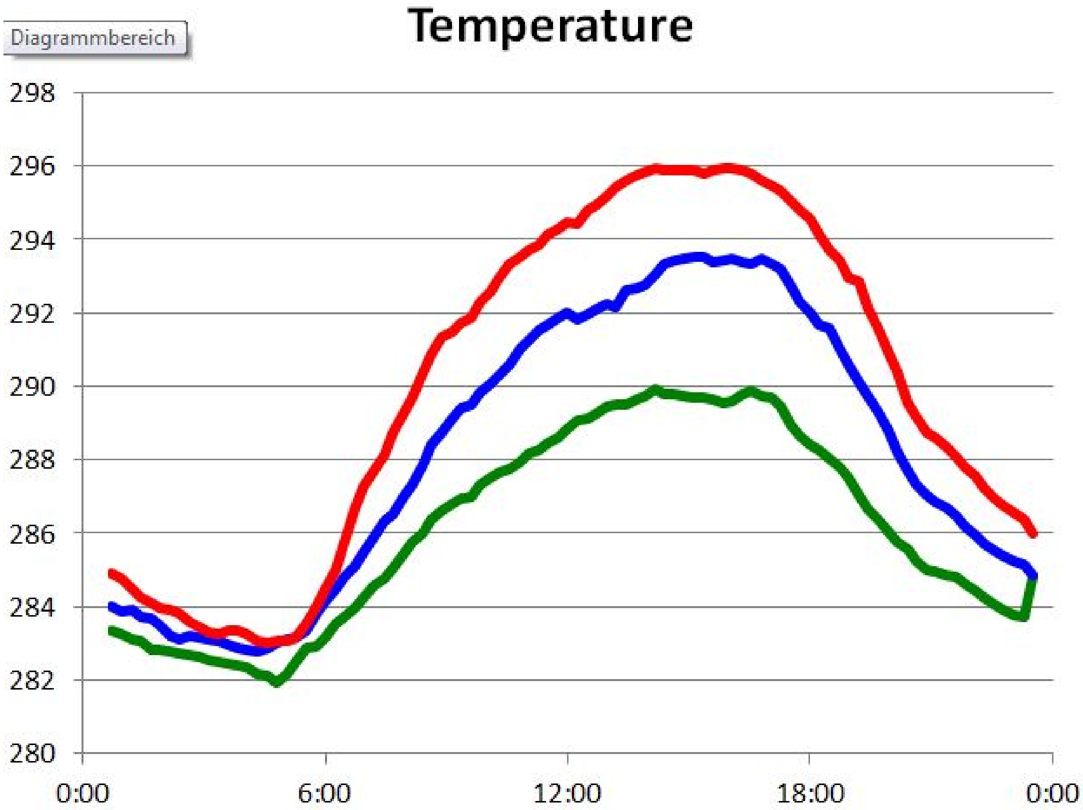

Fig. 1. Mean diurnal cycle of ambient temperature (in K) at Melpitz, whithout shift on the time axis.

ACPD
15, C9076–C9086, 2015

Interactive Comment

ACPD

15, C9076–C9086, 2015

Interactive Comment

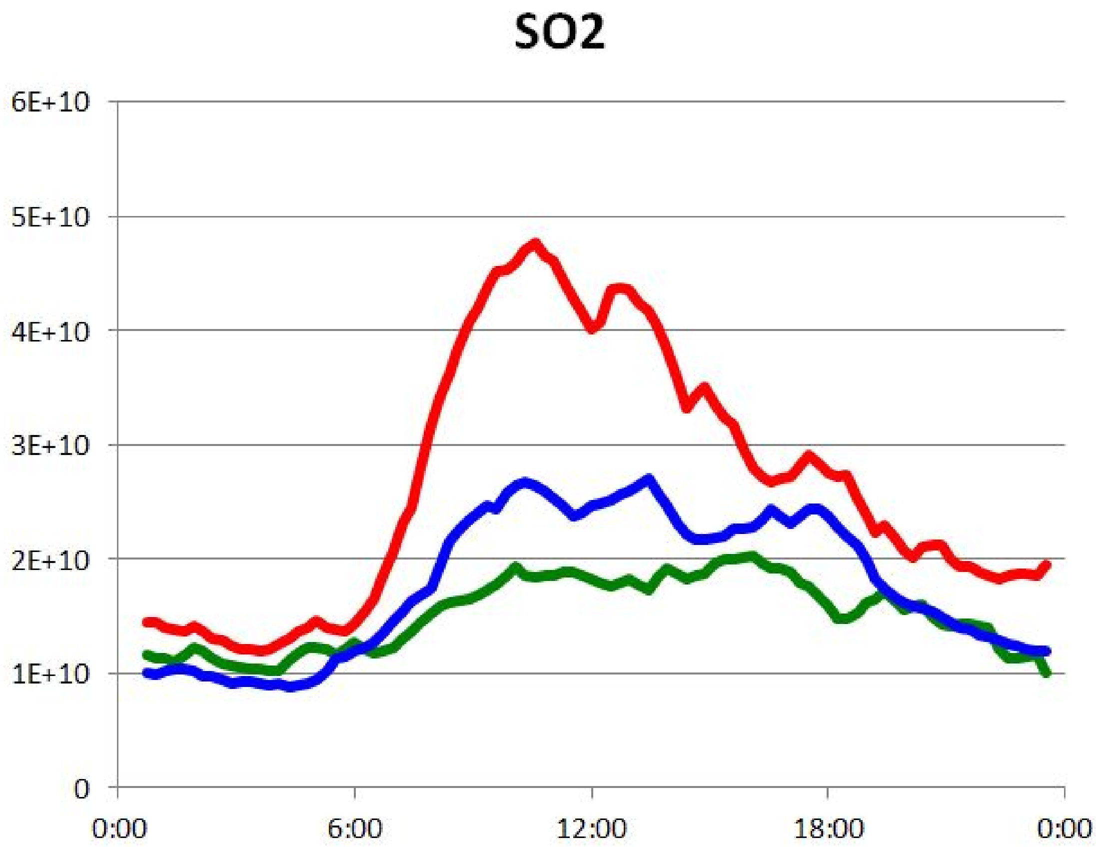

Fig. 2. Mean diurnal cycle of ambient SO2 (in molec./cm3) at Melpitz, whithout shift on the time axis.