Conceptual study on nucleation burst evolution in the convective boundary layer ? Part IV: Comparison with previous observations

O. Hellmuth

Atmos. Chem. Phys. Discuss., 5, 11557–11581, 2005
www.atmos-chem-phys.org/acpd/5/11557/
SRef-ID: 1680-7375/acpd/2005-5-11557
European Geosciences Union

Atmospheric Chemistry and Physics Discussions

Conceptual study on nucleation burst evolution in the convective boundary layer – Part IV: Comparison with previous observations

O. Hellmuth

Modelling Department, Institute for Tropospheric Research, Permoser Str. 15, 04318 Leipzig, Germany

Received: 1 August 2005 – Accepted: 17 October 2005 – Published: 10 November 2005

Correspondence to: O. Hellmuth (olaf@tropos.de)

Abstract

In part I to III of the present paper a revised columnar high-order modelling approach to model gas-aerosol interactions in the convective boundary layer (CBL) was proposed, and simulation results of two nucleation scenarios (binary vs. ternary) on new particle formation (NPF) in the anthropogenically influenced CBL were presented. It was demonstrated that both scenarios strongly differ with respect to the amplitude and phase of the NPF burst detectable in the Prandtl layer, as well as with respect to the time-height evolution of turbulent vertical fluxes and double correlation terms of physico-chemical and aerosoldynamical variables. In the present part, an attempt is made to re-evaluate previous observations of NPF bursts in the CBL in view of the scenario simulations discussed in part III. Special attention is payed to the role of CBL turbulence in NPF burst evolution. At first, a compilation of empirical findings and hypothesis on NPF in the CBL derived from a number of field experiments, is performed. Secondly, it is demonstrated, that the binary scenario simulated in part III corresponds well to a number of NPF burst events observed in Hyytiälä (Finland) and Melpitz (Eastern Germany). Here, one of the key hypothesis on the role of turbulence in NPF is confirmed. Other NPF events, such as those observed at Hohenpeissenberg, a mountain site (Southern Germany), can not yet be conclusively explained. To note, that the results of previous box modelling studies to explain NPF events at Hohenpeissenberg are not unambiguous. Nonetheless, based on only two simulated scenarios it is demonstrated, that a columnar high-order model is a helpful tool to elucidate the genesis of NPF bursts frequently observed in the CBL. A comprehensive verification/validation study using observed high-order moments as well as further scenario simulations remain to be performed.

1. Introduction

On the bases of the binary and ternary nucleation scenario evaluated in part II and III, an attempt is made to reassign previous observational findings on NPF in the continental CBL from a "macroscopic" point of view, i.e., at scales where gas-aerosol-turbulence interactions in the boundary layer become important. Here, "microscopic" processes of nucleation, i.e., on a molecular scale, are not considered. The aim is to interprete the typically observed daytime devolution of surface-based total particle number concentration, turbulent heat flux, wind variance and temperature variance, as well as particle flux, described in the literature, by means of a columnar model.

2. Observational evidences supporting binary nucleation

2.1. General burst behaviour

One of the first comprehensive observational studies on NPF in the polluted continental boundary layer over a 1.5-year period was published by Birmili and Wiedensohler (2000, 26 March 1996 to 15 August 1997, research station Melpitz, 50 km NE of Leipzig, Germany). Significant NPF events, characterized by UCN number concentration $>10^4\,\mathrm{cm}^{-3}$ in the size range 3–11 nm, were observed on 20% of all days. On 80% of the significant events the sulfur dioxide concentration was increased by an average factor of 7. From the slightly enhanced concentration of the pre-existing particle surface area on event days it was concluded that the competition between condensation onto pre-existing particle surface area and the NPF process must have been weak (Birmili and Wiedensohler, 2000, Fig. 2). Highest statistical correlation was found between NPF events and solar radiation (Birmili and Wiedensohler, 2000, Table 2). The typical shape of a NPF event such as that observed on 7 June 1997 using two Condensation Particle Counters resembles a "banana"-form, lateron synonymously abbreviated as *"banana plot"* (Birmili and Wiedensohler, 2000, Fig. 1). The coincidence of high values of UCN number concentration, sulfur dioxide concentration and solar irradiance is a strong evidence for the key contribution of photoxidation in NPF. Furthermore, Birmili and Wiedensohler (2000, p. 3328) concluded that *"although solar radiation is the trigger for photochemical reaction, the meteorological data also indicate a stronger mixing of the boundary layer on event days, which indicates meteorological control of the new particle formation process."*

Within the Hohenpeissenberg Aerosol Formation Experiment (HAFEX) Birmili et al. (2003) evaluated a number of time series of NPF events over a 2.5-year period from April 1998 to August 2000 at Meteorological Observatory Hohenpeissenberg (47°48′ N, 11°07′ E), a rural continental mountain site in southern Germany, approximately 50 km north of the Alps, 980 m above sea level and approximately 300 m above the surrounding countryside. NPF events were detected on 18% of all days, typically during midday hours under sunny and dry conditions, whereas the number of newly formed particles was found to be significantly correlated with solar irradiance and ambient levels of sulfuric acid vapour. NPF events were oberserved to be anticorrelated with the pre-existing particle surface area, especially in the cold season associated with advection of dry and clean air from the Alps. The UCN number concentrations were generally low at night-time. During darkness, no single NPF event was observed. This supports a key role of photooxidation in NPF. On NPF event days, high UCN number concentrations occurred predominantely around noon. UCN number concentrations typically peaked around 2000–30 000 cm^{-3}, hydroxyl radical and sulfuric acid vapour showed a pronounced daytime variation peaking around noon as well with maximum concentrations between 1 and 2×10^{7} cm^{-3}.

Strong evidences for the binary NPF scenario are delivered from a number of typical particle concentration time series observed at the boreal forest measurement station for measuring forest ecosystem-atmosphere relations (SMEAR II) located in Hyytiälä, central Southern Finland, (61°51′ N, 24°17′ E): 13 March 1996 (Kulmala et al., 2004, Fig. 2), 19 September 1996 (Clement et al., 2001, Fig. 1), 14 April 1999 (Kulmala et al., 2001, Fig. 1), 19 Mai 1999 (Boy and Kulmala, 2002, Fig. 1).

The time of burst onset and the burst amplitude appearing in that time series agree well with the binary NPF type simulated in part III. According to Boy and Kulmala (2002, Table 1) the majority of observed NPF events set in ante meridiem or around noon. The NPF events were found to be strongly correlated to a photochemically produced condensable vapour. The authors empirically derived a nucleation parameter by dividing UV-A solar radiation by the water vapour concentration and temperature. On average, NPF was found to occur when the nucleation parameter exceeds a certain threshold. The present binary scenario fits well into the parameter dependency expressed by Boy's nucleation parameter.

Mechanistic arguments supporting the binary NPF type were provided by the semi-empirical modelling approach of Clement et al. (2001). Their findings clearly support the hypothesis, that NPF bursts in Hyytiälä are initiated by a vapour produced by solar radiation on a precursor. The vapour is removed by condensation on pre-existing aerosols, whereas the vapour concentration depends on the ratio of radiation intensity to the removal rate. The authors found that NPF bursts occur when the vapour concentration exceeds a certain value (Clement et al., 2001, p. 222, items (A)–(C)). Using a more complex model in the present approach, the mechanism proposed by them was demonstrated to be really able to form newly particles under typical CBL conditions.

Further hints supporting the binary scenario are provided by the NPF characterization study of Aalto et al. (2001). The authors evaluated observed particle concentrations and size distributions inside and above a boreal forest during three BIOFOR (Biogenic Aerosol Formation Over the Boreal Forest) campaigns (14 April–22 May 1998, 27 July–21 August 1998, 20 March–24 April 1999) in Hyytiälä. On average over the whole campaign, NPF events were observed during sunny days, whereas clouds were observed to efficiently suppress particle formation due to reduced photochemical activity. During all events, particle surface area and volume was lower than average. The authors derived a threshold of global radiation below which and a threshold of particle surface area concentration above which NPF was not detected. At event days enhanced concentrations of sulfur dioxide and ammonia were observed as well, whereas a key role of ammonia in nucleation was not claimed. Most often, NPF events started between 08:00 and 11:00. The overall evolution of observed NPF bursts in Hyytiäl"a is in general agreement with the binary UCN devolution depicted in Fig. 11a of part III.

2.2. Turbulence-controlled NPF

2.2.1. Hypothesis

Kulmala et al. (2001, Fig. 2) explained their NPF observations by Nilsson's NPF mixing hypothesis, i.e., according to which NPF typically follows the breakup of a nocturnal boundary layer, leading to subsequent vigorous mixing with air from residual boundary layer (Nilsson et al., 2001a). In the comprehensive NPF-CBL evolution study Nilsson et al. (2001a, Sect. 4.1, item (1)) hypothesized, that "*on days when dilution of the pre-existing aerosol number and condensation sink was observed before nucleation, this may itself be enough to trigger nucleation by decreasing the sink of precursor gases at the same time that the precursor production may be increasing due to increasing photochemical activity. Such a scenario would form favorable conditions for nucleation*". The present binary case simulation shows, that under certain circumstances NPF can easily occur in the upper part of the growing CBL followed by downward transport of newly formed particles. In such cases entrainment of free-tropospheric air does not contribute to NPF but the onset of turbulence is a pre-requisite to sample nucleation in the Prandtl layer. The binary scenario simulated here is a direct corroboration of Nilsson's first hypothesis.

The CBL turbulence scenario simulated in part II agrees well with the conditions observed on NPF days during the BIOFOR campaign at the SMEAR II measurement station. For detailed descriptions of the typical diurnal evolution of the boundary layer on NPF event days the reader is referred to Nilsson et al. (2001a, Sect. 3.1) and Buzorius et al. (2003, p. 2–3, item 14).

Nilsson et al. (2001a, pp. 449–452) reported: *"It appears that on all nucleation days during BIOFOR, the nucleation was observed 10 min to 2 h after the onset of the con-*

vection, strong turbulence and entrainment, typically in the late morning, but sometimes earlier and sometimes later.... The appearance of 3 nm particles was always observed after the onset of strong turbulence". On p. 450 the authors denoted: *"The sunlight will cause both more turbulence along with more OH production, consequently, it is very difficult to determine which has a dominating effect, or if both processes were of similar importance for the onset of nucleation.... It appears that it is more likely that the increase in turbulence in the morning controls the onset of nucleation that that the increase in photochemistry occupies this key role".* On p. 452 they wrote: *"The table indicates that by the time nucleation started, there was always a mixed layer. This implies that mixing of the near-surface air with the air from stable layer above or the residual layer had occurred".*

The present study shows, that the sampling of enhanced "burst"-like UCN concentrations near the ground is a result of interactions between CBL turbulence and photochemistry. In part III it was demonstrated, how this interactions go by. Hence, the suggestions of Nilsson et al. (2001a) regarding these processes are confirmed. In general, the simulations correspond very well to the meteorological conditions, especially the CBL turbulence observed during NPF bursts in the BIOFOR campaign and the explanations given by Nilsson et al. (2001a).

2.2.2. Connection between onset of NPF and onset of turbulence

Buzorius et al. (2003) observed a coincidence between NPF and elevated variances of temperature and vertical wind speed and turbulent heat flux. During NPF event days SODAR-based vertical wind variances at 200–300 m altitude showed slightly higher values compared to values below 100 m (Buzorius et al., 2003, Figs. 1–2). To quantify the average influence of turbulence onto NPF the authors empirically derived so-called "particle formation probabilities" as a function of the Prandtl layer heat flux, variance of vertical wind speed, and temperature standard deviation, according to which the particle formation probability increases with increasing heat flux, vertical wind variance and temperature standard deviation (Buzorius et al., 2003, Figs. 3–4). The maximal daily values of these parameters on event days were observed to occur after NPF had happened. At the onset of NPF these parameters were not different yet from those on non-event days. On event days, condensation sink is significant lower compared to other days (Buzorius et al., 2003, item 39). These observations are directly confirmed by the simulated time at which the corresponding turbulence and NPF parameters exceed their maximum in the Prandtl layer (see Figs. 7a, b of part II for turbulent heat flux and vertical wind variance; Fig. 11a in part III for the binary UCN burst).

Based on the fact, that NPF coincides with a comparatively low pre-existing aerosol surface area and condensation sink, NPF was found to be favoured by the dilution during the growth of the CBL, which is caused by recoupling between the surface layer and the nocturnal residual layer with lower aerosol concentration (Buzorius et al., 2003, p. 2–6, item 25). However, it was not obvious, that intense turbulent mixing (fully developed turbulence) is triggering the nucleation. The authors argued, that mixing in terms of moving air parcels across the inversion may enhance the nucleation rate by turbulent fluctuations as suggested by Nilsson and Kulmala (1998). According to Buzorius et al. (2003) it is more likely, that NPF is triggered by mixing of surface layer air, enriched with condensable vapours and pre-existing aerosol, with clean residual-layer air. Notwithstanding, the authors proposed the possibility that NPF occurs above the surface layer and after clean nocturnal residual layer starts mixing with surface layer, that way reducing the pre-existing aerosol surface, followed by transport of new particles to the surface. In the present study, mixing-induced diluation of pre-existing aerosol concentration does not efficiently contribute to NPF but only because pre-existing aerosol concentration was quite low in the considered scenario. However, the way that ex situ formed newly particles can be sampled at the surface due to CBL turbulence has been clearly demonstrated here.

Stratmann et al. (2003) investigated NPF events in the CBL from 27 May to 14 June 2002 during the SATURN experiment (“Strahlung, vertikaler Austausch, TURbulenz und Partikel-Neubildung”, radiation, vertical exchange, turbulence and new particle formation) at three measurements in the Leipzig region, East Germany, classified as rural, urban influenced with varying distances to the city of Leipzig (Melpitz, 51.526° N, 12.928° E, 87 m a.s.l., 42 km north-east of Leipzig; Collm, 51.3077° N, 13.0026° E, 230 m a.s.l., 40 km south-east of Leipzig; Panitzsch, 51.361° N, 12.544° E, 139 a.s.l., 10 km east of Leipzig). As far as known, the authors were the first who measured the vertical distribution of particle number concentrations and turbulence using a tethered-balloon-borne payload (ACTOS, Airship-borne Cloud Turbulence Observation System), accompanied by coinciding SODAR and LIDAR observations. The 3 June 2002 was a typical NPF event day with textbook-like CBL conditions, as seen from SODAR, LIDAR and radiosounding data as well (Stratmann et al., 2003, Figs. 7–11). That event day featured an increase in global radiation (a radiation maximum near 1000 $\mathrm{W m^{-2}}$) and temperature, and decreasing relative humidity in the course of the day, i.e., a day-time evolution, that is typical for clear-sky conditions. The sulfur dioxide concentration peaked at 08:00 UTC, half to one hour after the break-up of the nocturnal inversion layer, and at 12:00 UTC. The ammonia concentration increased fast in the early morning, afterwards decreasing during daytime. The number concentrations of particles (3–10 nm and 3–800 nm significantly increased at 07:30 UTC, both number concentrations featuring a second maximum between 10:30 and 12:00 UTC. The evolution of both followed the evolution of sulfur dioxide (Stratmann et al., 2003, Fig. 10). This behaviour strongly indicates NPF controlled by photoxidation of sulfur dioxide involving hydroxyl radical. The key feature of the observed NPF event was the pronounced increase of UCN number concentration (diameter 3–20 nm) approximately at 07:30 UTC, taking place half an hour after the break-up of the nocturnal inversion at around 07:00 UTC and coinciding with the first sulfur dioxid peak (Stratmann et al., 2003, Fig. 7, SODAR; Fig. 10d). For details of the evolution of the number size distribution the reader is referred to Stratmann et al. (2003, p. 1454). The significant size distribution changes took place in the course of the break-up of the nocturnal inversion. The ground-based observations at Melpitz revealed, that NPF occurred about 0.5 to 1 h after the break-up of the nocturnal inversion until the mixing layer had reached the CBL top in around 1000 m after a few hours (Stratmann et al., 2003, Fig. 9, LIDAR). To elucidate the role of

CBL turbulence, a number of ACTOS profiles were evaluated. The descent from 830 m to the ground level (06:31–06:53 UTC) indicated a temperature inversion between 150 and 200 m, and the water vapour density revealing strong fluctuations inside the mixed layer (Stratmann et al., 2003, Fig. 14). The vertical profile of the number concentrations $N_I(10<D_p<1500\text{nm})$, $N_{II}(5<D_p<1500\text{nm})$, and $\Delta N(5<D_p<10\text{nm})$ clearly depicted a three-layer structure: mixed layer, inversion layer, residual layer. Here, we focus on the UCN profile, represented by ΔN. In a narrow region above the inversion (between 250–300 m), no small particles could be observed. Above, ΔN increases up to values of 800 cm^{-3} between 400 and 600 m. This behaviour nearly coincides with the sulfur dioxide profile, which showed a pronounced minimum at around 220 m. The ΔN profile showed, that between 06:26 and 06:53, NPF occurred in the residual layer. The ascent from ground level to 610 m (08:43–08:48 UTC) showed the disappearance of the inversion and the near-adiabatic stratification. From the ground up to 550 m, ΔN varied between 1000 and 5000 cm^{-3}, above 550 m ΔN decreases rapidly to zero. The sulfur dioxide profile is nearly height independent. Afterwards remaining at 600 m, observed time series of ΔN showed variations of several orders of magnitude with maximum values of 4000–5000 cm^{-3}. This behaviour was related to up-drafts temporarily penetrating into the residual layer, i.e., the tethered-balloon-borne payload was sometimes inside of such an up-draft with highly increased turbulence and a significant number of UCN, and sometimes inside the residual layer where turbulence is much weaker and ΔN is close to zero (no detection of UCN). Hence, during the total sampling intervall between 08:43 and 09:05 UTC, NPF took place in the entire CBL while inside the residual layer no UCN were observed. Stratmann et al. (2003, p. 1456) summarized their observational findings as follows: (a) NPF occurred inside the residual layer before the break-up of the nocturnal inversion. (b) UCN formed in the residual layer grew up and were mixed down during the break-up process of the nocturnal inversion. (c) No NPF was observed after the break-up of the nocturnal inversion in the residual layer. (d) During and after the break-up of the nocturnal inversion NPF was observed in the mixed layer. What actually happens on 3 June 2002 was the occurrence of two different NPF events, one inside the residual layer before and the second in the mixed layer during and after the break-up of the nocturnal inversion. With respect to the second event the authors interpreted their results as a direct corroboration of the hypothesis of Nilsson et al. (2001b) about the correlation between the onset of NPF and the onset of turbulence. The present binary case simulations supports that interpretation, i.e., at least the second NPF event on 3 June 2002 agrees with the binary scenario presented in part III. Stratmann et al. (2003) suggested that the NPF event observed in the residual layer points toward hypothesis 3 in Nilsson et al. (2001b), according to which particles newly formed in the residual layer may grow into a detectable size range inside the residual layer. As shown in the ternary case scenario, the ternary nucleation might be a way to initiate NPF in the residual layer (see Figs. 4a, d and Fig. 11a of part III). However, a scenario of NPF in the residual layer remains to be simulated within a framework like this.

The most direct observational evidence supporting NPF at the CBL top followed by top-down diffusion of UCN was provided by Siebert et al. (2004). The authors evaluated ACTOS profile measurements obtained during the NPF event on 30 May 2002 of the SATURN experiment. This event day was the only one with observation of enhanced concentrations of UCN near the inversion layer, accompanied by high fluctuations of the potential temperature and water vapour density (Siebert et al., 2004, Figs. 1–2). The observed UCN at the inversion were demonstrated to be newly formed and not transported upward from the ground against their mean gradient. Simultaneously with the significantly enhanced UCN concentration near the inversion, an increase of the UCN number concentration was observed at the ground level as well (Siebert et al., 2004, Fig. 3, peak of $\sim 10\times10^{2}\,cm^{-3}$ at 07:30 UTC). To explain ground-based UCN time series by top-down diffusion Siebert et al. (2004, Figs. 3–4) applied a diffusion model based on "K-theory" to the observed UCN profile. The authors demonstrated *"that no further sources for ultrafine particles in addition to the NPF event at the inversion are needed to explain the increase of ultrafine particle number concentration at ground level."* This observation directly corroborates the hypothesis of Nilsson et al. (2001b) according to which one possible scenario of NPF is due to effective mixing near the inversion layer, followed by downward transport of UCN through the mixing layer, hence leading to enhanced particle concentration at ground level. Consequently, the NPF event on 30 May 2002 supports the binary case scenario simulated in part III of the present paper as well.

2.2.3. Observation of vertical fluxes during NPF events

During the BIOFOR NPF event on 2 April 1999 Aalto et al. (2001, Fig. 8) observed, that *"particle concentration did not increase equally at different heights. Inside the forest, the concentration was approximately half of the concentration above the forest during the strongest events"*. For the BIOFOR NPF event on 12 April 1999, Nilsson et al. (2001a, Fig. 9) depicted the surface layer turbulent aerosol number flux. They notet that *"from 09:30 to 10:00, the aerosol flux changed sign to rapidly increasing downward fluxes and reached a maximum level from noon until the evening, but with large fluctuations on a time scale of 1–2 h. The large downward flux during the nucleation event is typical for the nucleation days (87% of the cases ...), which support the concept of an elevated source, above the canopy and the surface layer, for new particles"*.

Nilsson's findings are closely related to the observations from the micrometeorological NPF characterization study for the BIOFOR campaign performed by Buzorius et al. (2001) as well. Buzorius et al. (2001, Figs. 4a, 6) observed large particle ("deposition") downward fluxes in the average diurnal course of the particle flux over the event days, indicating an elevated source, with respect to the measurement level (23 and 46 m height, approximately 10 and 33 m above the forest canopy), of particles larger than 10 nm. The authors found, that on average the turbulence intensity and the heat fluxes were significantly higher and the temperature and water content were low during the event days. Importantly to note, that based on CO_2 measurements *"no connection between the photosynthetic activity of the forest and the particle formation occurrence was observed"* (Buzorius et al., 2001, p. 399). Thus, a notably contribution of biogenic emissions of precursor gases for nucleation and/or condensation could be excluded.

Consequently, the neglection of biogenic chemistry in the present model seems not to be an objection to use it for the interpretation of the observed NPF cases. The simulated turbulent UCN flux pattern for the binary case shown in Fig. 12 of part III corresponds very well to the observed aerosol flux pattern of Nilsson et al. (2001a) and Buzorius et al. (2001).

Recently, Held et al. (2004) evaluated NPF events observed during the BEWA field campaign in the summers of 2001 and 2002 at the "Waldstein" forest ecosystem research site (50°09′ N, 11°52′ E, 776 m a.s.l.) in the "Fichtelgebirge" mountain range in NE Bavaria, Germany. Within 45 days of measurement operations during the BEWA campaign, NPF events of varying intensity were observed on 13 days (22%) (Held et al., 2004, Table 2). Next to particle size distributions, turbulent particle number fluxes were directly measured at a height of 22 m a.g.l. as well. A typical "banana-shaped" NPF event occurred on 2 August 2001, revealing the onset of NPF through gas-to-particle conversion at 08:15 CET (Held et al., 2004, Fig. 1). On average over the whole campaign, the authors could neither derived a predictive capability from observed meteorological parameters, nor find a clear correlation of NPF events and low condensation sink. It was demonstrated, that the observed sulfuric acid vapour concentrations typically explained less than 10% of the observed growth rates whereas a significant fraction of particle growth was related to condensation of organic vapours from α-pinene oxidation. Hence, in this case biogenic emissions of reactive organic compounds were suspected to play an important role in particle growth during BEWA. Typically, turbulent particle fluxes from the atmosphere to the vegetation dominate at this site, whereas strongest particle deposition fluxes were observed during NPF events. For the NPF event day 2 August 2001 it was shown, that the sudden occurrence of nucleation particles coincided with the onset of particle deposition reaching a maximum just before noon (Held et al., 2004, Fig. 3). To explain this observation the authors considered two hypotheses: (a) At first, particles smaller than the detectable size are formed within the forest stand, i.e., below the flux measuring height. Afterwards, they must have been emitted from the forest, grew up to detectable size

ACPD
5, 11557–11581, 2005

above the forest stand and deposit. (b) Emissions from the forest stand contributed to the growth of thermodynamically stable clusters (TSCs) and particles *above* the forest stand, followed by deposition. In both cases, nucleation particles are formed and after subsequent growth into the detectable range they deposit. As to note, the high deposition velocity of UCN agrees with theoretical predictions as well. While flux observations indicated net deposition of UCN and making the forest a sink of particle number, the authors pointed toward the evolution of the particle size distribution supporting NPF and growth making the forest a source of particulate matter: *"Thus the net effect of the forest stand on particle mass remains unclear in this study"* (Held et al., 2004). However, here it was demonstrated how observed deposition fluxes can be related to CBL turbulence. Nonetheless, this is only a qualitative hint supporting the binary case simulation performed here.

3. Observations not supporting the binary scenario

3.1. NPF at a rural site

Birmili et al. (2000, Fig. 1) (see Birmili et al., 2003, Fig. 5, as well) presented a typical NPF on 20 April 1998 at Hohenpeissenberg during the HAFEX field study. The daytime evolution of the particle size distribution resembles the typical "banana"-shape pattern. In connection with a synoptic high pressure ridge and subsiding air, intense solar radiation, strong temperature increase, decrease of relative humidity in the course of the day, as well as low concentration of pre-existing aerosols was observed. After the break-up of the nocturnal boundary layer inversion around 07:30 a temporary increase in sulfuric acid vapour, nitric oxide, sulfur dioxide and total particle number concentration was observed, thereafter decreasing again. Between 11:00 and 12:00, when the mixed layer was fully developed, a strong increase in UCN and total number concentration was observed. The sulfuric acid concentration reached $1.5\times10^{7}\,\mathrm{cm}^{-3}$, following the evolution of the hydroxyl radical concentration. For a two-hour time interval (10:30–

ACPD

5, 11557–11581, 2005

12:30) the authors empirically derived an apparent nucleation rate of $\sim 3\,cm^{-3}s^{-1}$ from observations, that could not be exceeded using the parameterization of the binary nucleation rate proposed by Kulmala et al. (1998). To exceed the observed nucleation rate via binary nucleation a sulfuric acid vapour concentration of $3\times10^9\,cm^{-3}$ would be required, which is a few hundreds times more sulfuric vapour than was actually observed. Assuming an ambient ammonia level of at least 20 pptv in the agricultural environment of Hohenpeissenberg, only 1 to $2\times10^7\,cm^{-3}$ sulfuric acid vapour would be necessary when applying the ternary nucleation rate of Korhonen et al. (1999). Birmili et al. (2000) concluded, that a ternary nucleation process was responsible for the NPF event observed at Hohenpeissenberg. The authors suggested, that the ammonia concentration is already so high that the noontime ammonia minimum due to turbulence-induced dilution can not be a limiting factor in NPF. However, as seen from the coincidence of the onset of the NPF burst and the maximum of sulfuric acid vapour, the appearence of the NPF burst at forenoon must be photochemically induced. In their study, the ammonia background level serves as a time-independent adjustment parameter to get the observed nucleation rate. To note, that the secondary UCN peak observed in the morning hours (Birmili et al., 2000, Figs. 1a, b) corresponds well to that appearing in the binary case shown in Fig. 11a of part III. Even if the overall UCN evolution pattern agrees with the binary case simulated in part III, the observed sulfuric acid vapour concentration was observed to be too low to explain the observed NPF burst by binary nucleation alone.

Lateron, the influence of a third component in NPF was suggested from the evaluation of the long-term HAFEX observation study performed by Birmili et al. (2003, April 1998 to August 2000). The authors considered the question: *"Can ternary homogeneous* H_2O-H_2SO_4-NH_3 *nucleation serve as a model to explain the observed particle formation events at Hohenpeissenberg?"* On average, the observed nucleation rate was explained by ternary homogeneous H_2O-H_2SO_4-NH_3 nucleation, the observed nucleation mode particle growth by co-condensation of H_2O-H_2SO_4-NH_3. The oxidation products of monoterpenes were suspected to have the capacity to contribute to the growth of UCN particles. The ternary nucleation rate was calculated on the base of in-situ measured sulfuric acid vapour, relative humidity, temperature, and an implicitely assumed ammonia mixing ratio of 100 pptv using the nucleation model of Napari et al. (2002a) and Napari et al. (2002b). The nucleation rate calculated near the ground was compared with that empirically derived from in-situ observations (Birmili et al., 2003, Fig. 12a). The experimental formation rates were found to range between 0.01 and 9 $cm^{-3}s^{-1}$ while the ternary rates were scattered across the range 10^{-9} – 10^{3} cm^{-3} s^{-1}. However, the authors concluded: *"Although no remarkable correlation between the two rates was found, the comparison in Fig. 12a leads to the conclusion that ternary nucleation is, in principle, able to generate the number of fresh nano-particles that are later observed as particles >3 nm."* To get more insight in the NPF during HAFEX, the authors investigated the NPF under thermodynamic conditions prevailing near the top of the boundary layer (TBL) as well (Birmili et al., 2003, Fig. 12b). The calculated ternary rates were found to be scattered around the experimental formation rates within a few orders of magnitude only. The ternary nucleation rate predicted near the TBL may be up to 6 orders of magnitude higher than that near the ground (Birmili et al., 2003, Fig. 13). For the calculation of the nucleation rate at the TBL sulfuric acid vapour was assumed to be well mixed across the CBL and, as before, the ammonia mixing ratio was assumed to be 100 pptv. Thus, the enhanced nucleation rate at the TBL mainly reflects the extremely strong nonlinear dependency of the ternary nucleation rate on thermodynamic parameters, i.e., temperature and relative humidity. To think in relative terms the authors noted right away: *"Despite the agreement shown, however, we advocate care in the interpretations of these results, especially in view of the assumptions made on the unknown precursor concentrations near the TBL* (Birmili et al., 2003, p. 370). *"Although a large number of precursor gases, aerosol and meteorological parameters were measured, the ultimate key factors controlling the occurrence of NPF events could not be identified"* (Birmili et al., 2003, p. 361). No indications were found, that reaction products of organic compounds would directly control the occurrence of NPF events. Apart from this, it was impossible to define a global set of threshold criteria to effectively separate event days and non-event days.

The assumption of an implicite and time-independent upper limit of the ammonia concentration of 100 pptv reduces the modelled UCN number concentration to a NPF process, that is fully controlled by the thermodynamic conditions and the evolution of sulfuric acid vapour, whereas ammonia serves only as a constant adjustment parameter, e.g., comparable to the turbulence-induced linear correction factor for the binary nucleation rate introduced by Uhrner et al. (2003, Fig. 5). As ammonia was not considered to be a limiting factor, the observation of an ammonia-enhanced nucleation does actually not support the ternary NPF scenario presented in Fig. 11a of part III. Birmili et al. (2003, p. 374) pointed out, that the understanding of the occurrence of NPF events is linked to the question, why the particle size distributions were closed at the smallest diameters. They hypothesized either NPF at the CBL top or non-linear particle growth rate below 3 nm.

Uhrner et al. (2003) paid special attention to the role of meteorological conditions for the NPF events occurring during the HAFEX field study. The authors compared measured particle number concentrations and inferred particle surface area concentrations with box-model simulations for 12 carefully selected data sets collected during the HAFEX experiment (Birmili et al., 2003). The aerosol model included a binary nucleation scheme. The calculated nucleation rates were corrected with a factor to match measured and calculated particle number concentrations. The authors concluded, that the NPF process maybe strongly influenced by mixing processes driven by thermal convection and/or wind shear. Among several other HAFEX days, Uhrner et al. (2003, Figs. 2c, g, k, o, 3b, 4) re-evaluated the NPF event on 20 April 1998. In the former study of Birmili et al. (2000, Fig. 1) this NPF event was explained by ternary NPF at an ambient ammonia mixing ratio of at least 20 pptv. To achieve agreement between measured and modelled particle number concentration, Uhrner et al. (2003) empirically increased the binary nucleation rate by a turbulence-related prefactor of 10^{13} for 20 April 1998. The prefactor was iteratively varied until the measured and simulated peak number concentration matched within ±25%. The event case 20 April 1998 was characterized by strong vertical exchange associated with turbulent eddies and plumes. The main increase in observed number concentration (>3 nm) was accompanied by a significant reduction in dew-point temperature, likely induced by entrainment of drier air from aloft in to the CBL followed by top-down diffusion. The well-mixed layer reached a height of approximately 750 m above the measurement site. Strong orographic effects onto the flow were ruled out. Uhrner et al. (2003, Fig. 5) found, that the nucleation prefactor strongly depends on the CBL stability in terms of near-surface layer temperature gradients, whereas the prefactor varies over many orders of magnitude and assumes larger values for more unstable conditions. The authors related the good agreement between observed and modelled number concentration (>3 nm) for the NPF event on 20 April 1998 and for similar event days to the influence of vertical exchange processes: *"For particle number concentration profiles where the simulated particle number concentration either rose faster than the measured increase, or where the onset of a sharp rise in particle number concentration occurred before the measured onset, the cause could be related to buoyancy-driven turbulent exchange processes. This indicates that under convective conditions the initial particle nucleation process occurs higher up in the atmosphere, where more favourable conditions occur followed by downward mixing and growth to detectable size. Therefore, a significant part of these differences and their variability is attributed to non-local formation of particles and micrometeorological processes that cause them to be transported to the ground-based measurement site. Our results suggest that buoyancy-driven turbulence and wind shear are the micrometeorological processes accounting for such transport. . . . To gain further insight into these processes, measurements of, e.g., vertical profiles of quantities characterizing turbulent transport processes up to the entrainment layer and* NH_3 *concentrations are desirable"* (Uhrner et al., 2003, p. 358).

The study of Uhrner et al. (2003) allows important conclusions to understand and to describe NPF under convective conditions. The use of a turbulence-related prefactor for the binary nucleation is at least as plausible as the assumption of an implicite time-independent ambient ammonia mixing ratio to get the observed nucleation rates.

Hence, in view of the different possibilities to interprete the exemplary HAFEX event day 20 April 1998, i.e., via ternary nucleation (Birmili et al., 2000) or via turbulence-enhanced nucleation (Uhrner et al., 2003), arguments ruling out binary nucleation should be thought in relative terms. Box models are normally not able to conclusively explain NPF events in the CBL, independently from the nucleation scheme considered therein. The connection link between aerosol dynamics and CBL turbulence to explain observed NPF events under convective conditions is a higher-dimensional approach, e.g., to explicitely consider transport and entrainment processes. Hence, the considered HAFEX day should be re-investigated using an enhanced model approach.

3.2. NPF in urban regions

Combining extensive field measurements during the Pittsburgh Air Quality Study (PAQS) in Pittsburg, Pennsylvania, with an aerosol dynamics and chemistry box model assuming ternary H_2O-H_2SO_4-NH_3 nucleation Gaydos and Stanier (2005) showed an excellent model-measurement agreement and predictive capability. During a 15 months period in situ NPF was observed on over 130 days. On 19 out of 19 days with complete data sets available in July 2001 and 25 out of 29 days in January 2002 presence or lack of nucleation could be successfully predicted by the ternary nucleation model. The gas-phase ammonia concentration used in the nucleation model was derived from total ammonia (gas + particle phase) using a thermodynamic equilibrium model. Hence, no implicite, time-independent ammonia level serving as a free parameter was assumed. Sulfuric acid vapour was demonstrated to be the major condensing species, i.e., producing particle growth that is similar to the observations. The contribution of other species such as nitrate, ammonium, and organic compounds to growth could not be quantified. Anyway, the success of considering sulfuric acid vapour as the sole condensing species and the neglection the contribution of organics indicated, that the role of organics in NPF and particle growth is probably secondary. The typical NPF event observed on 11 August 2001 featured the well-known “banana-shaped” particle size distribution, showing a pronounced traffic signal between 07:00 and 08:00 EST, followed by NPF occuring at just after 09:00 EST (Gaydos and Stanier, 2005, Fig. 1). Automobile traffic is the most important local sources of UCN, leading to enhanced concentrations during the morning rush hour between 06:00 and 09:00 EST. As demonstrated, local emissions did not affect the regional NPF events usually occurring after the morning traffic has decreased to the normal level. Hence, typically observed NPF events were dominated by the regional signal. Most of the NPF events observed in July 2001 started at about 09:00 EST, just a few hours after sunrise. NPF days tended to occur on days with below average $PM_{2.5}$ concentrations and clear skies, as well as to take place over a large geographic area. The events were observed to sometimes coincide with mixing of the stable nighttime ground-level atmosphere and support the hypothesis that vertical mixing can importantly contribute to NPF. Nevertheless, an important number of NPF events occurring during PAQS was found to not coincide with atmospheric mixing, and to occur either earlier or later than the rise in the MLH. The model was found to generally overpredict the UCN number concentration on NPF event days for both the summer and winter months (2.5 to 4.3 times in July). For one possible reason the authors referred to the neglection of the dilution connected with the daytime evolution of the MLH and demanded further investigations to elucidate the observed effect.

With respect to air quality policy, the authors demonstrated, that the NPF frequency is very sensitive against the ammonia concentration. For example, a reduction of ammonia emissions in July by 100% eliminates all NPF events, while doubling ammonia emissions results in NPF occuring on 89% of the modelled days. In January the relation is weaker, the corresponding percentage of NPF events ranging between 24% and 66%.

Anyway, from the results of the PAQS one can conclude, that at least a subset of NPF events observed in Pittsburgh fits into scheme of the binary scenario discussed in part III, especially with respect to the mixing hypothesis. In opposite to this, the high number of events explained by in situ ternary nucleation involving ammonia without contribution of turbulent mixing shows, that the scenarios presented in the present paper can not cover up the range of the real situations leading to the observed NPF events. To open the way for further investigations Gaydos and Stanier (2005) noted: *"The degree to which vertical transport is important to nucleation in the eastern United States is currently unknown and vertical transport is not included in the box model developed here."*

4. Summary and conclusion

Based on a revised columnar high-order model, two simulated nucleation scenarios were compared with a number of previous observations of NPF bursts in the CBL. The aim was to evaluate the model capability to predict the evolution of the UCN number concentration near the ground and to elucidate the mechanisms contributing to burst formation. A state-of-the-art hypothesis on the contribution of CBL turbulence to burst evolution could be directly verified. Furthermore, from a literature review a number of NPF observations could be identified whose burst pattern generally agree with the binary case scenario simulated here. Observations that do not correspond to the binary case scenario were listed too and discussed with respect to possible sources of misinterpretation. The large differences between the binary and ternary case scenario indicate, that ammonia can not only serve as a tuning parameter in nucleation modelling. Its contribution to the evolution of the NPF burst pattern is much more complicated and reflects the influence of CBL turbulence as well as the strong nonlinearity of the ternary nucleation rate. It was demonstrated, that both the binary as well as the ternary nucleation scenario can lead to the formation of NPF bursts, even though being different in amplitude and phase. Nevertheless, it should be pointed out, that the present study is a purely conceptual one. Consequently, a comprehensive model evaluation remains to be performed. Furthermore, care must be taken in generalizing the results of only two reference cases to the very large number of reported NPF events in the literature. While it seems to be possible to simulate NPF burst formation by simple box models, the present study shows, that completely different processes, not explicitely considered in such models, can strongly affect the burst evolution. It has become clear, that profile measurements of physico-chemical parameters throughout the CBL, from both in situ and remote sensing techniques, are needed to constrain the degrees of freedom of a model like the present one, e.g., for the model setup. Apart from this, enhanced scenario simulations are necessary to verify and/or falsify, respectively, the other NPF hypothesis of Nilsson et al. (2001a, Sect. 4.1, item (2)–(4)) too. Altogether, the present model was demonstrated to be a useful tool to simulate gas-aerosol-turbulence interactions in the PBL, especially to elucidate the role of CBL turbulence in the evolution of NPF bursts. Moreover, the model delivers the necessary prognostic high-order moments that are required to explicitely parameterize the influence of subgrid-scale onto the nucleation rate, such as proposed by Easter and Peters (1994), Nilsson and Kulmala (1998), and Hellmuth and Helmert (2002).

Acknowledgements. The work was realized at the IfT Modelling Department headed by E. Renner within the framework of IfT main research direction 1 "Evolution, transport, and spatiotemporal distribution of the tropospheric aerosol". Special thanks go to the following people for the use of their Fortran source codes: A. Nenes (inorganic aerosol thermodynamic equilibrium model ISORROPIA), M. Wilck (exact binary nucleation model), I. Napari (parameterization of the ternary nucleation rate), L. Zhang (parameterization of the particle dry deposition velocity). For the motivation and numerous discussions on the subject of the present paper I am very indepted to D. Mironov, E. Renner, K. Bernhardt, E. Schaller, M. Kulmala, A. A. Lushnikov, M. Boy, R. Wolke, F. Stratmann, H. Siebert, and T. Berndt as well. Sincere thanks are given to M. Kulmala and M. Boy for the opportunity to present and discuss previous results at the Department of Physics at the University of Helsinki. Many thanks go to the editor and the anonymous reviewers as well for their comments and, last but not least, to N. Otto for her strong support during the technical processing of the manuscript.

References

Aalto, P., Hämeri, K., Becker, E., Weber, R., Salm, J., Mäkelä, J. M., Hoell, C., O'Dowd, C. D., Karlsson, H., Hansson, H.-C., Väkevä, M., Koponen, I. K., Buzorius, G., and Kulmala, M.:

Physical characterization of aerosol particles during nucleation events, Tellus, 53B, 344–358, 2001. 11561, 11568

Birmili, W. and Wiedensohler, A.: New particle formation in the continental boundary layer: Meteorological and gas phase parameter influence, Geophys. Res. Lett., 27, 3325–3328, 2000. 11559, 11560

Birmili, W., Wiedensohler, A., Plass-Dülmer, C., and Berresheim, H.: Evolution of newly formed aerosol particles in the continental boundary layer: A case study including OH and H_2SO_4 measurements, Geophys. Res. Lett., 27, 2205–2208, 2000. 11570, 11571, 11573, 11575

Birmili, W., Berresheim, H., Plass-Dülmer, C., Elste, T., Gilge, S., Wiedensohler, A., and Uhrner, U.: The Hohenpeissenberg aerosol formation experiment (HAFEX): A long-term study including size-resolved aerosol, H_2SO_4, OH, and monoterpenes measurements, Atmos. Chem. Phys., 3, 361–376, 2003, SRef-ID: 1680-7324/acp/2003-3-361. 11560, 11570, 11571, 11572, 11573

Boy, M. and Kulmala, M.: Nucleation events in the continental boundary layer: Influence of physical and meteorological parameters, Atmos. Chem. Phys., 2, 1–16, 2002, SRef-ID: 1680-7324/acp/2002-2-1. 11560, 11561

Buzorius, G., Rannik, Ü., Nilsson, E. D., and Kulmala, M.: Vertical fluxes and micrometeorology during aerosol particle formation events, Tellus B, 53, 394–405, 2001. 11568, 11569

Buzorius, G., Rannik, Ü., Aalto, P., Dal Maso, M., Nilsson, E. D., Lehtinen, K. E. J., and Kulmala, M.: On particle formation prediction in continental boreal forest using micrometeorological parameters, J. Geophys. Res., 108, doi:10.1029/2002JD002850, 2003. 11562, 11563, 11564

Clement, C. F., Pirjola, L., Dal Maso, M., Mäkelä, J. M., and Kulmala, M.: Analysis of particle formation bursts observed in Finland, J. Aerosol Sci., 32, 217–236, 2001. 11560, 11561

Easter, R. C. and Peters, L. K.: Binary homogeneous nucleation: Temperature and relative humidity fluctuations, nonlinearity, and aspects of new particle production in the atmosphere, J. Appl. Meteor., 33, 775–784, 1994. 11578

Gaydos, T. M. and Stanier, C. O.: Modeling of in situ ultrafine atmospheric particle formation in the eastern United States, J. Geophys. Res., 110, doi:10.1029/2004JD004683, 2005. 11575, 11576, 11577

Held, A., Nowak, A., Birmili, W., Wiedensohler, A., Forkel, R., and Klemm, O.: Observations of particle formation and growth in a mountainous forest region in central Europe, J. Geophys. Res., 109, doi:10.1029/2004JD005346, 2004. 11569, 11570

Hellmuth, O. and Helmert, J.: Parameterization of turbulence-enhanced nucleation in large scale models: Conceptual study, in: Air Pollution Modeling and Its Application XV, edited by: Borrego, C. and Schayes, G., pp. 295–304, Kluwer Academic/Plenum Publishers, New York, 2002. 11578

Korhonen, P., Kulmala, M., Laaksonen, A., Viisanen, Y., McGraw, R., and Seinfeld, J.: Ternary nucleation of H_2SO_4, NH_3, and H_2O in the atmosphere, J. Geophys. Res., 104, 26 349–26 353, 1999. 11571

Kulmala, M., Laaksonen, A., and Pirjola, L.: Parameterizations for sulfuric acid/ water nucleation rates, J. Geophys. Res., 103, 8301–8307, 1998. 11571

Kulmala, M., Dal Maso, M., Mäkelä, J. M., 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, 53B, 479–490, 2001. 11560, 11562

Kulmala, M., Vehkamäki, H., Petäjä, T., Dal Maso, M., Lauri, A., Kerminen, V.-M., Birmili, W., and McMurry, P. H.: Formation and growth rates of ultrafine atmospheric particles: A review of observations, J. Aerosol Sci., 35, 143–176, 2004. 11560

Napari, I., Noppel, M., Vehkamäki, H., and Kulmala, M.: An improved model for ternary nucleation of sulfuric acid-ammonia-water, J. Chem. Phys., 116, 4221–4227, 2002a. 11572

Napari, I., Noppel, M., Vehkamäki, H., and Kulmala, M.: Parametrization of ternary nucleation rates for H_2SO_4-NH_3-H_2O vapors, J. Geophys. Res., 107, doi:10.1029/2002JD002132, 2002b. 11572

Nilsson, E. D. and Kulmala, M.: The potential for atmospheric mixing processes to enhance the binary nucleation rate, J. Geophys. Res., 103, 1381–1389, 1998. 11564, 11578

Nilsson, E. D., Paatero, J., and Boy, M.: Effects of air masses and synoptic weather on aerosol formation in the continental boundary layer, Tellus, 53B, 462–478, 2001a. 11562, 11563, 11568, 11569, 11578

Nilsson, E. D., Rannik, Ü., Kulmala, M., and O'Dowd, C. D.: Effects of continental boundary layer evolution, convection, turbulence and entrainment, on aerosol formation, Tellus, 53B, 441–461, 2001b. 11567

Siebert, H., Stratmann, F., and Wehner, B.: First observations of increased ultrafine particle number concentrations near the inversion of a continental planetary boundary layer and its relation to ground-based measurements, Geophys. Res. Lett., 31, doi:10.1029/2003GL019086, 2004. 11567

Stratmann, F., Siebert, H., Spindler, G., Wehner, B., Althausen, D., Heintzenberg, J., Hellmuth, O., Rinke, R., Schmieder, U., Seidel, C., Tuch, T., Uhrner, U., Wiedensohler, A., Wandinger, U., Wendisch, M., Schell, D., and Stohl, A.: New-particle formation events in a continental boundary layer: First results from the SATURN experiment, Atmos. Chem. Phys., 3, 1445–1459, 2003, SRef-ID: 1680-7324/acp/2003-3-1445. 11564, 11565, 11566, 11567

Uhrner, U., Birmili, W., Stratmann, F., Wilck, M., Ackermann, I. J., and Berresheim, H.: Particle formation at a continental background site: Comparison of model results with observations, Atmos. Chem. Phys., 3, 347–359, 2003, SRef-ID: 1680-7324/acp/2003-3-347. 11573, 11574, 11575