

# A new parametrization for ambient particle formation over coniferous forests and its potential implications for the future

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**Abstract.** Atmospheric new particle formation is a general phenomenon observed over coniferous forests. So far nucleation is either parameterised as a function of gaseous sulphuric acid concentration only, which is unable to explain the observed seasonality of nucleation events at different measurement sites, or as a function of sulphuric acid and organic molecules. Here we introduce different nucleation parameters based on the interaction of sulphuric acid and terpene oxidation products and elucidate the individual importance. They include basic trace gas and meteorological measurements such as ozone and water vapour concentrations, temperature (for terpene emission) and UV B radiation as a proxy for OH radical formation. We apply these new parameters to field studies conducted at Finnish and German measurement sites and compare these to nucleation observations on a daily and annual scale. General agreement was found, although the specific compounds responsible for the nucleation process remain speculative. This can be interpreted as follows: During cooler seasons the emission of biogenic terpenes and the OH availability limits the new particle formation while towards warmer seasons the ratio of ozone and water vapour concentration seems to dominate the general behaviour. Therefore, organics seem to support ambient nucleation besides sulphuric acid or an OH-related compound. Using these nucleation parameters to extrapolate the current conditions to prognosed future concentrations of ozone, water vapour and organic concentrations leads to a significant potential increase in the nucleation event number.

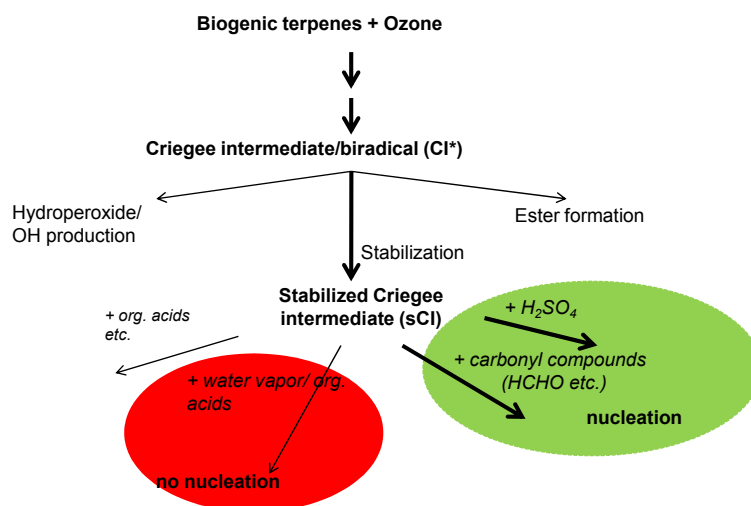
## 1 Introduction

Atmospheric new particle formation is a common phenomenon occurring nearly everywhere at the Earth's surface as well as above (Kulmala et al., 2004a). The new particles are expected to originate from a variety of different gaseous precursors such as sulphuric acid, reactive volatile organic compounds (VOCs) and iodine oxides. However the current limitation for direct chemical analysis of the tiniest aerosol particles and clusters is at around 10 nm in particle diameter. The required mass for analysis makes it necessary to use correlation methods between potential gaseous precursors and the measured number concentration of the smallest particles. A good correlation is assumed to be a necessary indicator but no proof for the reliability of a postulated nucleation mechanism, because of the similar behaviour of different gases such as OH, sulphuric acid and VOC-OH oxidation product.

Once new clusters and particles are formed they may grow to sizes, at which they will affect cloud properties and the radiation budget at the Earth's surface. The corresponding effects are some of the key uncertainties in correctly describing climate changes and are expected to be 2–14 W m<sup>-2</sup> for boreal forest sites including cloud effects (Kurtén et al., 2003; Spracklen et al., 2008). Most of these effects caused by the grown aerosols are independent of the initial nucleation process and gases involved because the growth is expected to be predominantly caused by other less volatile or soluble gases. Nevertheless, the amount of newly formed particles that can act as cloud condensation or ice nuclei depends on the nucleation mechanism in detail.



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**Fig. 1.** Schematic representation of the nuclei formation. Highlighted in red are suppressing reactions, and in blue reactions leading to nucleation.

So far ambient nucleation at coniferous forested sites have been found to depend on sulphuric acid concentration either linearly or squared (Kulmala et al., 2006; Sihto et al., 2006; Riipinen et al., 2007) and has been parameterised as follows:

$$J_{\text{act.}} = A \cdot [\text{H}_2\text{SO}_4] \quad (1)$$

$$J_{\text{kin.}} = K \cdot [\text{H}_2\text{SO}_4]^2 \quad (2)$$

The indices “act.” and “kin.” abbreviate the hypothesized mechanisms, i.e. the activation of sulphuric acid clusters by further compounds and the kinetically limited nucleation by sulphuric acid molecules. Since sulphuric acid is a gas of low volatility, thus of short atmospheric lifetime and is formed in the atmosphere from the reaction of predominantly sulphur dioxide and OH, it might serve here as a marker for any compound that is formed by reaction of OH with a precursor gas with a short atmospheric lifetime of seconds to minutes. This generalization from sulphuric acid to a broader range of compounds allows application for a different situations. However, it includes the case of sulphuric acid, since it is usually OH that drives the temporal behaviour of sulphuric acid not the moderate changes in sulphur dioxide. In this context the important OH concentration depends on radiation intensity. The correlation coefficients  $A$  and  $K$  obtained from field studies vary by orders of magnitudes between different sites and at different times throughout the year for instance for boreal forests, which cover about 15% of the global land surface. Bonn et al. (2008) explained this variation for the Finnish boreal forest site in Hyytiälä (SMEAR II; Kulmala et al., 2001; Hari and Kulmala, 2005) by a nucleation caused by reaction products of biogenic VOCs (sesquiterpenes) with ozone, which subsequently react with sulphuric acid molecules. This is in line with the observations made by

Went (1960) half a century earlier explaining the blue haze phenomenon in the United States. It also takes into account laboratory observations with respect to the suppressing effect of water vapour on terpene induced nucleation Bonn and Moortgat (2003) as well i.e. the higher the water vapour concentration (higher humidity) the less intense the nucleation. Bonn et al. (2002) explained these observations by the nucleation precursor the so-called stabilized Criegee Intermediate (sCI; Criegee, 1975), which reacts with various trace gases such as ambient water vapour, but does not form new particles in the reaction with water vapour but with other gases such as carbonyl compounds. Bonn et al. (2008) merged these laboratory findings with the observations regarding sulphuric acid (Sihto et al., 2006; Riipinen et al., 2007) leading to a postulated nucleation mechanism displayed in Fig. 1. If nucleation occurs as postulated one would expect a local minimum during the most humid period during summer, in which VOCs are emitted strongest, and two maxima during the transition periods in spring and autumn.

In this study we formulate different nucleation parameters based on the postulated nucleation mechanism of Bonn et al. (2008). By using different parameters including proxies for organic (related to organic-ozone reactions) and OH radical contributions to atmospheric particle formation either all or only some of them, we gain the possibility to investigate their individual impact on the observed seasonality and annual behaviour of these events. We define the different nucleation parameters in the following section and subsequently intercompare their behaviour with the observations of nucleation events and intensity. Finally we use this parameter to hypothesize the possible future evolution of new particle formation in and over boreal and coniferous forests.

## 2 Nucleation parameter

If nucleation is initiated by the reaction of a reactive VOC such as a terpene and ozone as it is known from Went (1960) and postulated by Bonn et al. (2008), the formation rate of the first clusters at around 1.2 nm in diameter ( $J_{1.2\text{nm}}$ ) depends on the concentration of a short-lived intermediate the so-called stabilised Criegee biradical (Criegee, 1975), sulphuric acid and carbonyl compound concentrations. As described in detail in Bonn et al. (2008) the biradical can be approximated by a steady state approach of sources and sinks. The source is the reaction of terpenes and ozone of which a certain fraction becomes stabilised (stab.fraction).

$$[\text{sCI}] = \frac{k_{\text{terpene+ozone}} \cdot [\text{O}_3] \cdot [\text{terpene}] \cdot \text{stab.fraction}}{k_{\text{sCI+H}_2\text{O}} \cdot [\text{H}_2\text{O}]} \quad (3)$$

Its major sink is the reaction with ambient water vapour. According to Bonn et al. (2008) the nucleation rate at 1.2 nm includes further sulphuric acid and carbonyl compounds (activation case only) and the corresponding reaction rate constants as well as the lifetimes of the first stage products before being activated by a sulphuric acid addition:

$$J_{1.2\text{nm,act.}} = k_{\text{aldehyde+sCI}} \cdot [\text{sCI}] \cdot [\text{aldehyde}] \cdot \tau_{\text{SOZ}} \cdot k_{\text{coll,SOZ,H}_2\text{SO}_4} \cdot [\text{H}_2\text{SO}_4] \quad (4)$$

$$J_{1.2\text{nm,kin.}} = k_{\text{H}_2\text{SO}_4+\text{sCI}} \cdot [\text{sCI}] \cdot [\text{H}_2\text{SO}_4] \cdot \tau_{\text{OS}} \cdot k_{\text{coll,OS,H}_2\text{SO}_4} \cdot [\text{H}_2\text{SO}_4] \quad (5)$$

The equations include further parameters such as the reaction rate constants of sulphuric acid ( $\text{H}_2\text{SO}_4$ ) and of aldehydes with the sCI ( $k_{\text{H}_2\text{SO}_4+\text{sCI}}$  and  $k_{\text{aldehydes+sCI}}$ ), the reaction rate of a sulphuric acid molecule with the products of aldehydes and sCIs (secondary ozonides=SOZ)  $k_{\text{coll,SOZ,H}_2\text{SO}_4}$  and of sulphuric acid and sCIs (organosulphates=OS)  $k_{\text{coll,OS,H}_2\text{SO}_4}$ . The lifetimes of SOZ and OS are given as  $\tau_{\text{SOZ}}$  and  $\tau_{\text{OS}}$ . The different reaction rate constants and lifetimes of first stage clusters to be applied are summarized in Table 1. Please see Bonn et al. (2008) for further details such as applying the collision rates as the upper value for a chemical reaction between the SOZ or OS and sulphuric acid,  $k_{\text{coll,SOZ,H}_2\text{SO}_4}$  and  $k_{\text{coll,OS,H}_2\text{SO}_4}$  respectively. Thus, when terpene, ozone, water vapour, sulphuric acid and aldehyde concentrations are known, the nucleation rate of both pathways can be calculated. The postulated formation rate of Bonn et al. (2008) either via the linear (Eq. 1) or via the squared relationship (Eq. 2) with a compound formed by OH reaction with a sufficiently short atmospheric lifetime is displayed in Eqs. 5 and 6 respectively.

Based on the two nucleation rate Eqs. 5 and 6 we define four different nucleation parameters (NP), two focussing on the organic contribution, thus named organic NP, and two including OH. Parameters, which are difficult to assess such as certain reaction rate constants and the concentration of sesquiterpenes and sulphuric acid are either omitted or a proxy approach is used. Proxies are applied for sulphuric acid and sesquiterpene concentrations. In the case of sesquiterpenes we apply the empirical temperature ( $T$ ) dependency algorithm for emissions of Guenther et al. (1995) and omit the absolute value, which is rather uncertain. Therein  $\beta$  is used as a temperature dependent coefficient varying for different terpenes:

$$\text{sesquiterpenes}^* = \exp(\beta \cdot T) \quad (6)$$

Field measurements of terpenes by Tarvainen et al. (2005) and Hakola et al. (2006) at the Finish site in Hyytiälä found mean  $\beta$ -coefficients for sesquiterpenes between 0.175 and 0.201  $\text{K}^{-1}$ . However, the exact dependency of terpene emissions in boreal environments is not well established in the case of sesquiterpenes. Because of that we use the value of 0.09  $\text{K}^{-1}$  (Guenther et al., 1995; monoterpenes) as a lower limit.

As a proxy for sulfuric acid and OH as its driving parameter we use the global UV B radiation strength. Petäjä et al. (2008) have found a linear correlation of UV B radiation and measured OH concentration. In Fig. 2 we show the correlation of UV B and global radiation with the calculated OH concentration, based on an atmospheric chemistry model (Boy et al., 2005), which displays the linear dependency as well. Both correlations make our approach expressing the OH concentration as a function of ultraviolet B radiation feasible:

$$\text{OH}^* = \text{UVB} \quad (7)$$

The most important precursor for organic derived nucleation is the stabilized Criegee Intermediate (sCI), which is therefore the core of the organic NPs. If we divide the sCI concentration by the terpene concentration, which is the one most difficult to observe for reactive hydrocarbons such as sesquiterpenes, we get the ratio of ambient sCI to terpene. This ratio effectively describes the availability of sCIs per terpene molecule present or the efficiency of terpene molecules to cause new nuclei under the present conditions.

$$\begin{aligned} \text{organic NP A} &= \frac{[\text{sCI}]}{[\text{terpene}]} \\ &= \frac{k_{\text{terpene+ozone}} \cdot [\text{O}_3] \cdot \text{stab.fraction}}{k_{\text{sCI+H}_2\text{O}} \cdot [\text{H}_2\text{O}]} \end{aligned} \quad (8)$$

**Table 1.** Reaction rate constants, stabilised fraction and lifetimes of nucleation inducing molecules considered in this study.

parameter	known or est. value	reference
reaction rate constants	in $\frac{\text{cm}^3}{\text{molec}\cdot\text{s}}$	
$k_{\text{sesqui}}^{\text{O}_3}$	$1.16 \times 10^{-14}$	Shu and Atkinson (1994)
$k_{\text{H}_2\text{O}+\text{sCI}}$	$1 \times 10^{-17}$	Bonn (2002) and ref. therein
$k_{\text{H}_2\text{SO}_4+\text{sCI}}$	$50\,000 \cdot k_{\text{H}_2\text{O}+\text{sCI}}$	Bonn et al. (2008) Kurtén et al. (2007)
$k_{\text{aldehyde}+\text{sCI}}$	$1000 \cdot k_{\text{H}_2\text{O}+\text{sCI}}$	Neeb et al. (1998) Bonn (2002)
$k_{\text{coll.},\text{SO}_2,\text{H}_2\text{SO}_4}$	coll. rate max. approach	Bonn et al. (2008)
$k_{\text{coll.},\text{OS},\text{H}_2\text{SO}_4}$	coll. rate max. approach	Bonn et al. (2008)
Yield Y of stab. Criegee intermediates		
$Y(\text{sCI}) \approx 1 - Y(\text{OH})$	0.94	Shu and Atkinson (1994)
lifetimes		
$\tau_{\text{SO}_2}$	4	Bonn et al. (2007)
$\tau_{\text{OS}}$	1/CS	Bonn et al. (2008)

The nucleation parameter *organic NP A* as given in Eq. 8 essentially depends on ozone and water vapour concentrations, which are easy to observe. Although this describes the efficiency of a terpene molecule to result in an atmospheric sCI molecule, this parameter does not include the present terpene concentration, which determines the actual concentration of sCIs as included in the nucleation rates (Eqs. 5 and 6). But it indicates *favourable* conditions for nucleation once a terpene molecule appears.

In order to include the terpene concentration according to the nucleation rate description, we include the parametrization given in Eq. 6. Thus, any different behaviour of *organic NP A* and *B* is caused by variations in terpene emission and therefore their ambient concentration:

$$\begin{aligned} \text{organic NP B} &= \text{organic NP A} \cdot \text{sesquiterpenes}^* & (9) \\ &= \text{organic NP A} \cdot \exp(\beta \cdot (T - 30^\circ\text{C})) \end{aligned}$$

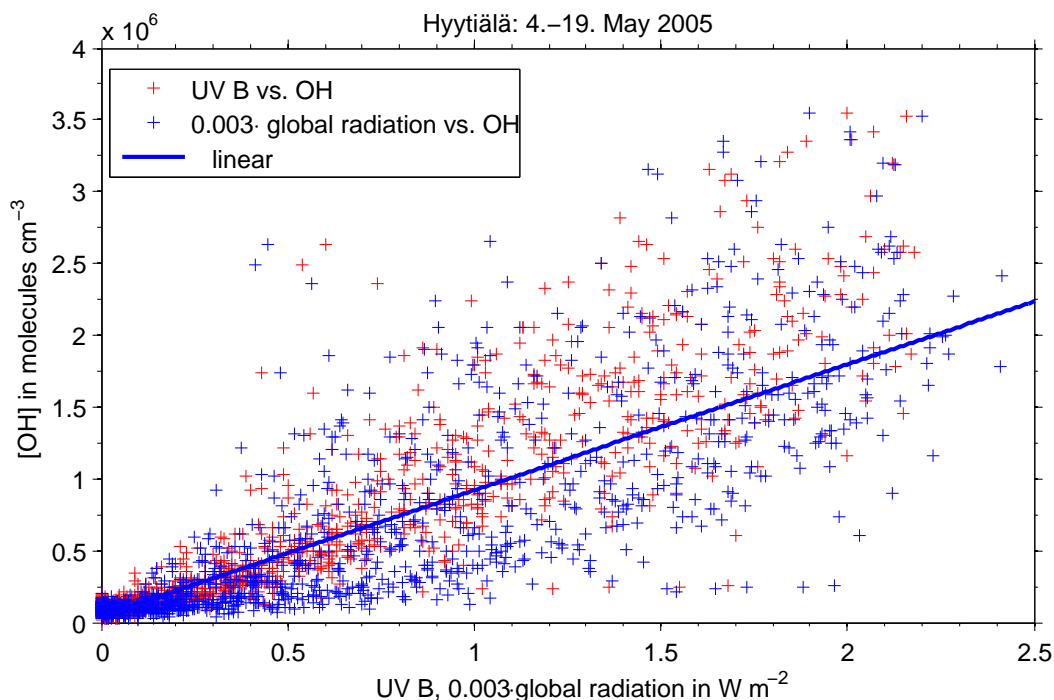
Both organic nucleation parameters are dimensionless and focus on the initial production of a nuclei only but neglect the correlation with ambient sulphuric acid or a OH-derived compound of a notably short lifetime. Because of this and the fact that numerous studies have revealed the dependence of nucleation on hydroxyl radical (OH) derived compounds, we define two further nucleation parameters *NP A* and *NP B* by multiplying the organic parameters (Eqs. 8 and 10) with if available OH concentrations or if not with the ultraviolet B radiation flux, necessary for the production of OH radicals.

$$NP A = \text{organic NP A} \cdot [\text{OH}]^* \quad (10)$$

$$NP B = \text{organic NP B} \cdot [\text{OH}]^* \quad (11)$$

In here the star \* indicates the parametrization of compounds difficult to observe directly according to Eq. 7. In situations, where even UV B measurements are not available, we use 0.003 times the global radiation (Fig. 2) as a proxy for UV B in situations, where UV B data are missing and discuss the effect. These two final nucleation parameters investigate the contribution of OH, either in combination with terpenes (water suppression dominating, *NP B*) or in situations in which the nucleation is primarily OH dependent (*NP A*). The units of both parameters *NP A* and *NP B* are either molecules  $\text{cm}^{-3}$  (using OH) or  $\text{W m}^{-2}$  (using radiation), since the dimensionless organic nucleation parameters are multiplied with either OH concentration or radiation. The emission of terpenes used in Eqs. 10 and 11 has been derived empirically by Guenther et al. (1995) and Tarvainen et al. (2005) to be exponentially dependent on temperature. This approach assumes that terpene storage is sufficiently large, i.e. not limiting and that this emission type dominates, which is a reasonable assumption especially for warmer climates.

In order to summarize, we defined four different nucleation parameters *organic NP A* and *B* and the general *NP A* and *B*. *Organic NP A* investigates the potential of the atmospheric conditions to form a notable pool of sCIs per terpene concentration, *organic NP B* addresses additionally the emission of terpenes and thus their concentration, *NP A* and *B* include



**Fig. 2.** Intercomparison of UV B and global radiation with the calculated OH concentration for the SMEAR II site in Hyytiälä, Finland in May 2005.

OH for the corresponding *organic NPs* too. A change between *organic NP A* and *B* is caused by the terpene emission, between *organic NP A* and *NP A* is due to the effect of OH on the conditions circumstances and between *organic NP B* and *NP B* displays the effect of OH on the terpene induced nucleation. A high value of any nucleation parameter is thought to identify nucleation enhancement, while low values act suppressive with respect to new particle formation. The individual value of low and high is difficult to assess because of open questions regarding the exact temperature dependency of sesquiterpene emissions, the individual structures and OH concentration values.

### 3 Intercomparison with field measurements

In order to evaluate the performance of the defined individual NPs we compare the pattern of the four parameters with particle number concentrations measured for the smallest size range at different environments: (a) SMEAR II station, Hyytiälä (Finland) (Hari and Kulmala, 2005) and (b) Taunus Observatory (Mt. Kleiner Feldberg, 812 m a.s.l., Germany). Both stations are representative sites for remote locations, with the Finnish station to be very remote and the German one facing more anthropogenic affected air masses. The instrumentation and the monitoring at the SMEAR II station in Finland was performed by the University of Helsinki

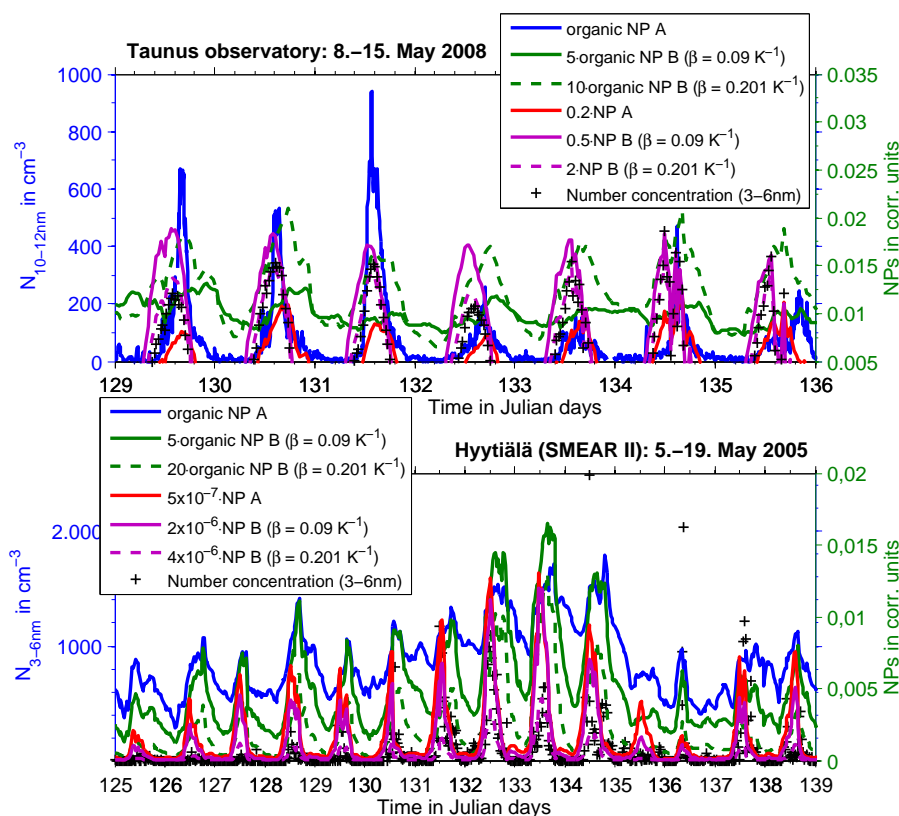
and is described elsewhere (Vesala et al., 1998; Kulmala et al., 2001; Hari and Kulmala, 2005).

At Taunus Observatory the aerosol particle size distribution is monitored by the Goethe University of Frankfurt/Main, while meteorological parameters and trace gases have been measured continuously by the Hessian Agency for Environment and Geology (HLUG, see supporting online information). Since the German aerosol measurement period is much less extensive than the Finnish one, we include the German station for short term intercomparison only and concentrate on the Finnish station for longer periods, the seasonal and the annual variation respectively.

#### 3.1 Daily intercomparison

##### 3.1.1 Taunus Observatory

Aerosol size distributions at Taunus Observatory are monitored by the Institute of Atmospheric and Environmental Sciences (Frankfurt University) since the end of February 2008, while measurements in Finland started in January 1996. Therefore, the dataset of the SMEAR II station in Hyytiälä is the most extensive one of any boreal forest site. At this site radiation data is available as global and UV B radiation data and completes the measurements of various trace gases and meteorological variables at different towers. Since neither OH values nor UV B radiation measurements are available



**Fig. 3.** Intercomparison of nucleation parameters and total number concentration of aerosols between 10 and 12 nm in diameter at the German site (top) or between 3 and 6 nm in Finland (bottom). For the Finnish site calculated OH concentrations are used (*NP A* and *NP B*), while 0.3% of the global radiation was used in Germany, since no OH values and UV B measurements are available.

for the German site, there is a need to use a parametrization of OH by the measured global radiation. From Fig. 2 performed for the Finnish station we obtain a good fit of 0.3% of the measured global radiation flux, which is gained at similar surface conditions (coniferous forest). While aerosol loadings are similar except in summer and clouds affect the individual contribution of UV B to global radiation we assumed a similar behaviour introducing a significant uncertainty. In this study we use 0.3% of global radiation instead of OH for the German station. However, the exact fraction is less important, since we compare relative changes and not absolute ones. Absolute values and thresholds can be defined once all the approximations used are checked and fixed to the best achievable values by measurements.

The Taunus Observatory is a remote site for Central Europe at an altitude of 810 m above sea level. The situation at this place differs between two extreme situations: When the wind is coming from the direction of Frankfurt (southeast), nucleation is found to be minimal. From this direction  $\text{NO}_x$  and anthropogenic hydrocarbon concentrations are increasing. Therefore pollution mainly appears from the Southeast, while nucleation is observed more often and more intense with winds from the Northwest and notably cleaner conditions.

For the German site we intercompare the NPs with the particle number concentration between 9.8 and 12 nm in mobility derived particle diameter as a proxy for the ambient nucleation rate, however slightly shifted in time due to the time needed for growth from 1.2 to 9.8 nm. The results are exemplarily shown for the second week in May 2008 (Days Of the Year DOY 129–136) in the upper graph of Fig. 3. The black crosses display the particle number concentration between 9.8 and 12 nm, while the other lines represent the individual NPs. From this it is obvious that *NP B* (purple lines) including all contributions agrees best with the pattern of the number concentration. This points to a very important contribution of both, OH and biogenic terpenes. In order to split between organic and OH contributions one can use *NP A* (OH effect mainly) and the *organic NP B*. The latter is the most important one, emphasizing the role of biogenic terpenes. In order to highlight the effect of different terpenes two *organic NP B* curves are calculated – one for mono- and one for sesquiterpenes. The results indicate that sesquiterpenes agree better with the measured particle concentrations. Nucleation always starts at rising organic *NP B* values from lowest values and is most intense at highest *organic NP B* (sesquiterpenes) values. Correlations are found independent of the time of the year, in March as well as in

July. Investigating the fit of the individual nucleation parameters (NPs), it is evident that the *organic NP A* indicates only the favourable conditions, i.e. if a nucleation event is feasible under these atmospheric conditions. The strength of the event is not captured reasonably. The multiplication of the *organic NP A* with 1% of the global radiation is not improving the situation, since the daily pattern is rather similar during the time of interest. Assuming the OH concentration to be linked linearly with the UV B radiation it can be stated that OH is a necessary parameter for the occurrence of new particles but does not seem to be the only limiting parameter at this time. The *organic NP B* improves gently the situation from 11 May (Day of the year=132) on, indicating a notable role of terpenes. Especially the dashed line with the stronger temperature dependency of the emissions ( $\beta=0.201\text{ K}^{-1}$ ) (sesquiterpenes; Hakola et al. (2006)) shows a very similar pattern, while the continuous red line with a  $\beta$  of  $0.09\text{ K}^{-1}$  (monoterpenes) agrees less. Including the radiation for *NP B* too (0.3% of global radiation), displays the best agreement. It should be mentioned that on some days with less intensive nucleation there is a time difference between the rise of the NPs and in particle number concentration. This is most likely due to the growth time from 1.2 to ten nm in diameter. As conclusion for this site and period it can be stated that larger terpenes like sesquiterpenes with a notable temperature dependent emission rate are required and OH is certainly needed as well. Which one is limiting the process might depend strongly on season and temperature.

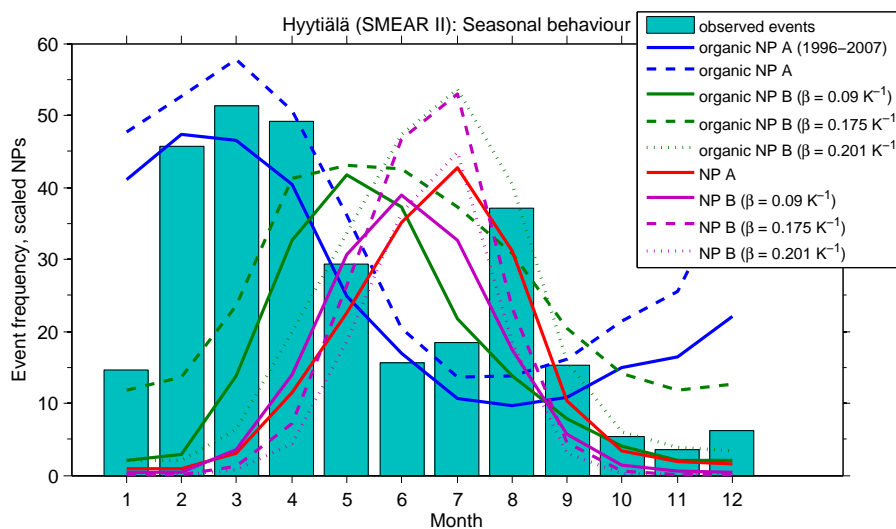
### 3.1.2 Hyytiälä

A similar but better agreement between number concentration from 3 to 6 nm in particle diameter ( $N_{3-6\text{nm}}$ ) and nucleation parameters is found for Hyytiälä in Finland. For this site both OH and UV B radiation data are available (Fig. 3, bottom graph with calculated OH values). This better agreement is also caused by the different size range considered for the comparison. For Fig. 3 (bottom) the calculated [OH] is used. Again we discuss the effect of the different NPs. In this graph the *organic NP A* shows not only a match of rise and the start of nucleation but also indicates moderately the strength of the event. Taking into account the emission of biogenic terpenes by using the *organic NP B* the situation improves except 13 May 2005 (DOY=133). Again the steeper emission factor of sesquiterpenes compared to the one of monoterpenes with respect to temperature leads to a better agreement with the number concentration between 3 and 6 nm in diameter. On the contrary to the German site graph the OH impact becomes evident when using *NP A and B*. This is especially true for *NP B*, but less in *NP A*, again highlighting the importance of both OH and terpenes. Finally the *NP B* values for sesquiterpenes with a  $\beta$  of  $0.201\text{ K}^{-1}$  (dotted line in the lower plot) shows a nearly identical pattern with the number concentration of particles between three and six nm.

From the intercomparison at both sites it can be stated that the best agreement can be observed for *NP B* with the temperature dependency of sesquiterpenes, and *organic NP B* can be used as a proxy with a slightly less agreement than *NP B* in the case OH is not available. One potential problem is the usage of UV B or global radiation instead of OH. This applies for the Taunus intercomparison in Fig. 3 (top), which indicates a less clear behaviour of particle number concentration between 10 and 12 nm and the individual NPs such as *NP B*, but might also be originated from the different size range considered for intercomparison. In order to indicate the range of uncertainty caused by using UV B instead of [OH] the reader is referred again to Fig. 2, which displays a scatter plot for OH as a function of UV B or of 0.3% of global radiation during the period shown in Fig. 3 for Hyytiälä.

### 3.2 Seasonal scale

For the seasonal behaviour we use the dataset with respect to nucleation events from 1996–2007 at Hyytiälä (partially in Dal Maso et al., 2005). This causes problems with the calculation of OH for *NP A* and *NP B*, because of missing data for OH calculation earlier than 2003. Because of that we calculated and intercompared all nucleation parameters between 2003 and 2007 and use *organic NP A* to indicate the effect of time reduction. For this parameter all necessary datasets are available. Figure 4 presents the event frequency observed at the site and the different NPs. In order to indicate the effect of using a different time frame is shown by the blue continuous and dashed lines for the *organic NP A*. The solid line refers to 2003–2007 while the dashed line includes the entire dataset. A temporal shift of the springtime maximum is obvious, which might be caused by the difference in mean monthly temperature and the increased nucleation suppressing intensity of water vapour at elevated temperatures. 2003 to 2005 were the warmest years in the dataset gained in Finland. Interestingly the springtime maximum and the summer minimum are covered best by the *organic NP A* indicating the important role of water vapour and probably draught stress of the biosphere. Including the emissions in *organic NP B* shifts the maximum period towards summer with the strongest shift in time for the strongest temperature dependency (sesquiterpenes). Taking into account OH is not improving the situation either. OH does not seem to affect the number of events much but the nucleation intensity. Therefore, the first maximum during springtime is most likely caused by high ozone and low water vapour concentrations, both strongly supporting nucleation and second by the huge storage pools of terpenes after the winter period. The second maximum in autumn (August) is not covered as good as the springtime one. Temperature and terpene emissions are still substantial, water vapour concentrations decrease, but there seems to be a further parameter not considered in the present study. This



**Fig. 4.** Seasonal variation of the *NPs* for Hyytiälä. All *NPs* have been multiplied by a constant factor in order to fit in the same range as the observed event frequency.

might partly be the condensation sink for non-volatile gases or the change in atmospheric chemistry conditions such as in the composition of carbonyl compounds needed and in the ratio of  $\text{HO}_2$  to  $\text{RO}_2$  (Bonn et al., 2005; Finlayson-Pitts and Pitts, 2000). However one should be careful applying the excellent Guenther temperature dependent emission approach for terpenes (Guenther et al., 1995) gained at notably higher temperatures to boreal environmental conditions for the season. This might cause deviations from reality.

### 3.3 Annual scale

A further important point worth consideration is the annual time scale. If any of the defined parameters is able to predict changes at daily or seasonal time scales it should be able to explain changes between different years as found at Hyytiälä (Dal Maso et al., 2005).

In order to investigate this we calculate two mean parameters, i.e. the *organic NP B* and *NP B* both for monoterpene emissions. Displayed in black colour are the observations, while red shows *NP B* including UV B radiation and green is focussed on the organic contribution via *organic NP B*. The investigated time frame for the SMEAR II site covers the years from 1997 until 2007 in Fig. 5.

Important to note here is the fact that we used UV B radiation instead of OH because of the much longer time series. Note as well that we multiplied the nucleation parameter with a constant factor to be able to use the same vertical axis as for the event frequency. Averaged over the annual scale the parameters calculated with OH and the ones calculated with UV B values behave rather similar. The pattern is reproduced by both *NP B* parameters including the OH proxy (*NP B*) and the terpene emission (both parameters), while the

other parameters (not shown) display only a slight or no tendency with a huge scattering but no significant trend. Only the *organic NP Bs* and the *NP Bs* with different temperature dependent pool emission factors ( $\beta$ ) show a moderate tendency, while *organic NP A* and *NP A* do not. This would imply that the emission of VOCs is one of the important aspects for describing event frequencies.

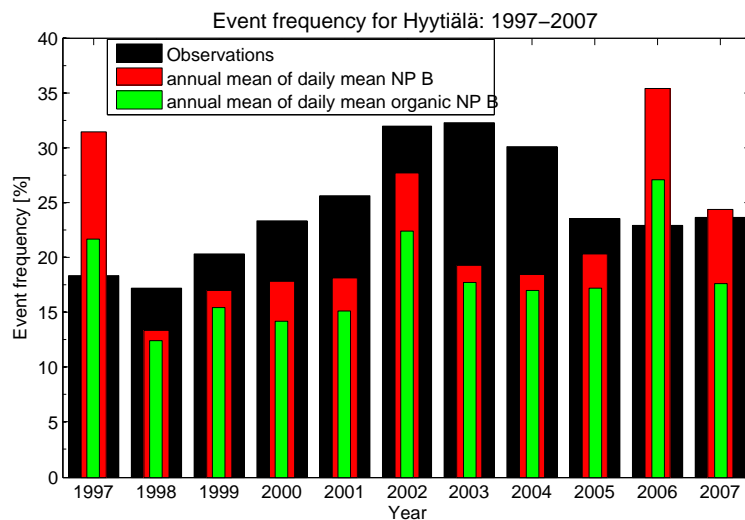
Deviations are obvious for some of the years, 1997, 2003, 2004 and 2006. This is caused by lacks of data in those years at different seasons. In 2006 the end of the end of the year with usually smaller parameter values is missing and therefore the mean value is elevated. A similar observation can be made for 1997, while during 2003 and 2004 gaps occur during summer and especially the nucleation periods, lowering the average value notably. Because of these strong effect of data gaps we skipped the year 1996, during which recording started in spring. It needs to be mentioned also that the intensity of nucleation is not investigated in this plot only the occurrence.

The good match of *NP B* is caused by an elevated temperature (terpene emission and ozone production) as well as intensive UV B radiation resulting in an intense OH formation with subsequent oxidation products to participate in the particle formation process.

## 4 Future predictions

Finally we apply the formulated *NPs* to tentatively estimate the future behaviour of nucleation event day numbers affected by climate change. Is this common phenomenon fading out or gaining in intensity?





**Fig. 5.** Annual variation of the two different *NP B* parameter, i.e. *NP B* and *organic NP B* (monoterpenes) for Hyytiälä. For this graph both parameters have been multiplied by  $10^4$  in order to fit into the same range as the observed event frequency in percent.

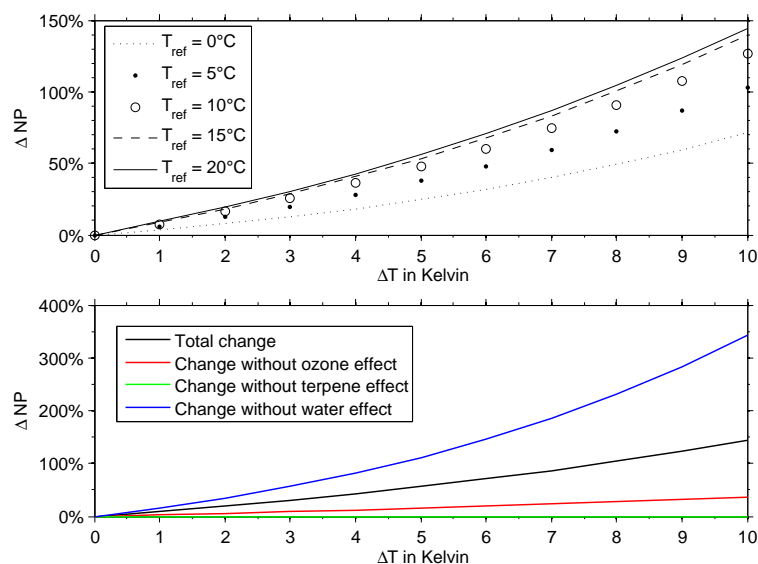
In order to estimate any future development or change in nucleation frequency or intensity one needs to know the future changes in ozone, organics, water vapour and OH or radiation. The fourth assessment report of the intergovernmental panel on climate change (IPCC report, 2007) expects a future ascent of the average surface temperature by about +3 K, with higher values towards the poles (boreal regions) and smaller towards the equator. Similarly a rise in tropospheric ozone is expected to occur as was observed by different studies such as Jaffe et al. (2003) with an increase of 1.4% per year. The exact behaviour of ozone in a changing environment depends on the  $\text{NO}_x$  and VOC emissions and the fact, if it is a  $\text{NO}_x$  or VOC limited ozone production. This varies notably over the area of interest. However, in boreal regions and coniferous forest areas there is a tendency to VOC limited ozone production, which causes the changes in VOC emission to be reflected in the change in ozone production.

For a tentative investigation of this aspect using the nucleation parameters we focus on two sites: (I) the Taunus Observatory and (II) the SMEAR II station in Hyytiälä (Southern Finland). At the Taunus Observatory ozone and relative humidity were monitored continuously by the Hessian Agency for Environment and Geology (HLUG) since 1996. This station is expected to be representative for a medium remote location of a coniferous forest in the mid-latitudes, at which the nucleation is expected to occur. From the data analysis of ozone and temperature data we find a cubic correlation with a notable scattering, since ozone production is driven by the emission of VOCs, which is predominantly a result of temperature stress on plants. This is available in the supporting online information (see supporting online information). For instance an increase of  $4.2 \text{ ppbv K}^{-1}$  is observed at  $20^\circ\text{C}$ , which represents an increase of 6%, which is about twice as

much as found for Hyytiälä conditions. At the same time water vapour volume mixing ratio rises between 6 and 7.5% per Kelvin at a similar relative humidity at warmer temperatures according to the Goff-Gratch formula (Pruppacher and Klett, 1997).

From the current knowledge about terpene emissions (Guenther et al., 1995; Tarvainen et al., 2005) it is known that the emission of the most important terpene class, i.e. the monoterpenes can be described by an exponential temperature dependency of  $\exp(\beta \cdot (T - 30^\circ\text{C}))$  with  $\beta = 0.09 \text{ K}^{-1}$ . Thus the emission increases by approximately 9–10% per Kelvin. Sesquiterpenes are proposed to have a twice as large temperature dependency (Tarvainen et al., 2005; Hakola et al., 2006). This would imply an increase by 15–20%. The UV B radiation strength is a function of latitude and time of the year and of the distance between earth and sun. The latter appears like a weak sinusoidal pattern with a 12 years cycle. But no significant changes are to be expected regarding this within the next century. Only an intensified cloud formation and extended cloud lifetime would cause a reduction. Nevertheless OH is known to decline by about 1% per year (Bousquet et al., 2005) because of increased pollutants. Because of the uncertainty of the future behaviour of OH and the expected rather stable UV B flux we omit any UV B changes in the following considerations.

This is in line with the results of the annual intercomparison, where we have shown that the nucleation parameter *NP B* is able to explain the observations made for both timescales daily and annual best. Following from the inter-comparisons *organic NP B* is the second best parameter to be used, when information on OH concentrations lack. It was pointed out that the emissions seem to be the most important aspect for the annual number. We apply the dependence of monoterpenes as a conservative estimate. Sesquiterpene



**Fig. 6.** Displayed is the calculated relative change in NP because of changes in ozone, temperature and water vapour. Top: Relative changes of NP at different reference temperatures due to a change between 0 and 10 K. Bottom: Relative changes of NP at a reference temperature of 20°C of the individual changes of different parameters.

emission is expected to have a twice as strong temperature dependency as monoterpenes. They can be taken as an upper limit with the twice as large results as for the monoterpenes. By doing so we expect the minimum relative change in the nucleation parameters as displayed in Fig. 6. In the upper graph the change in  $NP B$  is shown for different reference temperatures, thus if one compares a change by for instance 2 K at 0 or 20°C. From this plot we expect the climate warming effect on  $NP B$  – organic as well as including UV B radiation – to be a relative increase between 4 and 9% at a temperature change of +1 K. The effect is highest for the largest temperatures because of the increase of terpene emissions with increasing temperature, which is higher than the one of ozone and water vapour, which nearly cancel out. However this is highly dependent on the local increase in ozone, in terpene emissions and water vapour concentrations. These need to be understood well to make severe predictions for any site of interest.

The individual contribution of ozone, temperature and water vapour to the change in NP is investigated in the lower part of Fig. 6. Therein, the relative changes of the *organic NP B* parameter are displayed for a reference temperature of 20°C, (I) as shown in the top plot for all contributions (black), (II) omitting the change in ozone (red), (III) omitting the change in terpene emission (green) and (IV) omitting the suppressing effect of water vapour (blue). From that the statement of the role of terpenes becomes apparent. Omitting the emission change would result in an unchanged parameter as can be considered for *organic NP A* or *NP A*. Ozone is certainly important too and a possible future situation with less water (draught stress conditions) would cause the highest

effect. Since the NP represent the formation of new particles and correlate with the concentration of new aerosols, a rise in any NP would result in a higher nucleation probability and aerosol number concentration in the future.

If we consider the expected climate warming with an average of +3 K (IPCC report, 2007), which is at the lower limit for boreal regions, we obtain a rise in nucleation event number between +12% ( $T_{ref}=0^\circ NP$ ) and +30% ( $T_{ref}=20^\circ NP$ ), which is substantially. A temperature increase by +6 K would result in an increase between 32 and 71%. If sesquiterpenes participate in nucleation as indicated in section 3 the increase is expected to be even higher because of the stronger temperature dependency of the emissions. On the other hand the number of events would drop only if ozone is reduced remarkably to compensate the rise in terpene and water vapour concentration. According to the conclusions of the IPCC report (2007) this is very unlikely.

## 5 Conclusions

We have postulated four different nucleation parameters for investigation of new particle formation events and their driving forces in boreal and coniferous forest areas. These parameters use ozone and water vapour as proxies for the contribution of reactive organic trace gases and UV B radiation strength for OH production. The parametrization is found capable in explaining daily, seasonal and annual variations of observed nucleation events at different sites. Especially the parameter including OH, terpene emission and suppressing effect of water vapour, i.e. *NP B* agrees best with the

observed particle number concentrations at smallest sizes and the event frequencies observed. However, if no direct information of OH is available, the *organic NP B* can be used and behaves in a similar way. To describe the annual frequency the emission of terpenes seems to be the most important aspect, while OH is important to describe the intensity of nucleation. Using these parameters it seems very likely that nucleation events will increase in number over the entire boreal regions and several mid-latitude areas having consequences on aerosol and cloud properties. It seems a step further in understanding biosphere-atmosphere cloud climate feedback processes (Kulmala et al., 2004b) initiated by the biosphere to protect the biosphere from harm. A rise in aerosol number and thus cloud condensation nuclei will initiate cloud formation and might increase the lifetime of clouds which subsequently cools the Earth's surface (Spracklen et al., 2008). However to exactly predict the future rise and intensity of nucleation events a notably improved knowledge about terpene emissions, future ozone, carbonyl compounds and sulphuric acid is essential.

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