Supporting online informations

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Content

1 Information about the measurements used

Measurements were performed in the context of air quality observations at both sites, i.e. (i) Taunus observatory (Mt. Kleiner Feldberg, Germany) and (ii) SMEAR II station (Hyytiälä, Finland). Gas phase data were recorded in 30 min intervals since the 14th of January 1997 in Germany and since the first of April 1996 in Finland. Measurements were controlled from either measurement containers (Germany) or cottages (Finland), with the later at a tower at different heights.

1.1 Taunus observatory (TO), Mt. Kleiner Feldberg, Germany (810 m a.s.l., 50°N 13' 25" N, 8° 26' 56" E)

Measurements are taken on the hill top from two containers, one for the gas phase measurements (Hessian Institute for Environment and Geology, Wiesbaden, HLUG) and one for aerosol measurements (Frankfurt University) as close as twenty meters. The hill top (about 100 m in radius) was cleared for the German Weather Service station and is surrounded by coniferous forest consisting predominantly of spruce with minor contribution of birch and pine. Forest top is approximately 20 m above soil level and the tree age somewhere around 80 years, depending on the clear cut.

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The next city thus anthropogenic pollution is Bad Homburg at a distance of about 16 km to the southwest with 52,000 inhabitants, The Frankfurt area, major traffic routes and industrialized regions are located at 25 km distance at minimum and a height difference of about 700 m. Therefore the station can be assumed as remote for Central European conditions. Further information about the details of individual measurements are available at the following official site: http://www.hlug.de/

1.2 Station for Measuring Ecosystem Atmosphere Relationships (SMEAR) II, Hyytiälä, Finland (170 m a.s.l., 61° 51'N, 24° 17' E)

The station is a cross disciplinary approach for ecosystem-atmosphere relationship studies measuring physical, chemical and biological parameters since its built up in 1996. For detailed measurement descriptions see *Hari and Kulmala* (2005) and references therein or at http://www.atm.helsinki.fi/SMEAR/
In addition to gas phase measurements aerosol parameters and fluxes of particles and gases are recorded in Finland, making the longest and most extensive dataset regarding the aspect of aerosol formation and biosphere-atmosphere relationships.

2 Correlation of temperature and ozone

In order to show the correlation of ozone with ambient temperature at the Taunus observatory (Germany) we use 11 years of data obtained from the Hessian Institute for Environment and Geology (HLUG) in Wiesbaden. The scatter plot is shown in Figure 1. Although there is some scatter along the cubic fitting, a clear dependency is apparent. However, this works only down to about -5°C below which the vegetation is at a rest and practically no biogenic activity and emission is taking place. The behavior is nearly exponential,

which nicely agrees with the temperature dependent emission of biogenic terpenes such as the monoterpenes (*Guenther et al.*, 1995).
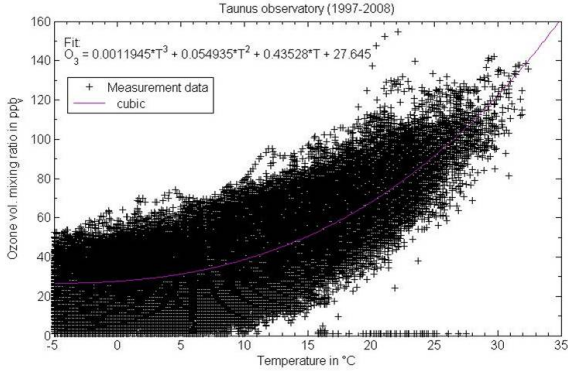
Fig. 1. Scatter plot of temperature and ozone at Taunus observatory for 11 years of data. Displayed is the cubic fitting used in the article.

The cubic fitting result applicable between 0 and 30°C is:

$$Ozone(fit) = 0.0011945 \frac{ppbv}{(°C)^3} \cdot T^3 + 0.054935 \frac{ppbv}{(°C)^2} \cdot T^2$$

$$+ 0.43528 \frac{ppbv}{°C} \cdot T + 27.645 ppbv \qquad (1)$$

3 Annual pattern of formaldehyde to organic acid ratio

Since both carbonyl compounds and acids are reacting with the nucleation precursor stabilised Criegee intermediate, their annual pattern is relevant. The predominant atmospheric carbonyl compound is formaldehyde (HCHO), which favours nucleation. On the contrary the predominant organic acid, i.e. formic acid (HCOOH) suppresses nucleation. Due to both effects, i.e. the one of HCHO and the one of HCOOH, the ratio of both is of interest.

For this, calculations of a chemical transport model (MATCH-MPIC) with included isoprene and monoterpene chemistry is used. For details the reader is referred to *Bonn et al.* (2004) as well as to *Bonn et al.* (2005) and references therein. The results of the matching grid cell for Hyytiälä at the surface is then used to calculate the ratio between nucleation supporting reactions to nucleation suppressing reactions of the stabilized Criegee intermediate (sCI):

$$ratio = \frac{10^{-14} cm^3 molecule^{-1} s^{-1}}{1.4 \times 10^{-13} cm^3 molecule^{-1} s^{-1}} \qquad (2)$$

$$\cdot \frac{([HCHO] + [pinonaldehyde])}{([HCOOH] + [CH_3COOH] + ... + [pinonicacid])}$$

$$ratio \approx \frac{1}{14} \cdot \frac{[HCHO]}{[HCOOH]} \qquad (3)$$

The results are displayed in Figure 2.

The resulting nucleation rate estimate is shown in the next figure (Fig. 3), which is in line with the article of *Bonn et al.* (2008) and with the observations of *Dal Maso et al.* (2005).

4 Change of emissions and water vapor with changing temperature

According to *Guenther et al.* (1995) the emission of monoterpenes exhibits an exponential temperature dependency:

$$E_{mono} = E_{mono,0} \cdot exp(\beta \cdot (T - 30°C)) \qquad (4)$$

with the emission factor at standard conditions $E_{mono,0}$ and the prefactor β of 0.09 K^{-1}. Thus, any change in temperature by one Kelvin compared to the normal situation results in an emission change of exp(0.09 K^{-1}·(T+1 K-30°C))/exp(0.09 K^{-1}·(T-30°C)) = exp(0.09) = 1.0942 (+9.42%), independent of temperature present at normal conditions.

This is different for water vapor, which is described by the Goff-Gratch equation (*Pruppacher and Klett*, 1997). A change by one Kelvin results in the following change in water vapor assuming an unchanged relative humidity:

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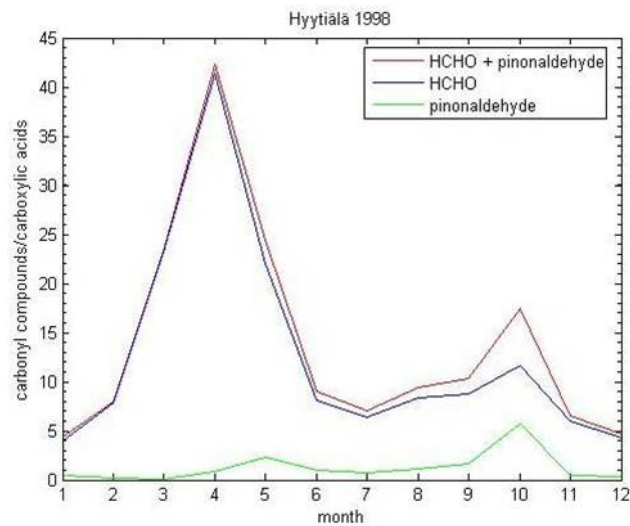
Fig. 2. Displayed is the ratio 3 including mean monthly calculated formaldehyde (HCHO), pinonaldehyde and organic acid concentrations in the grid box over Hyytiälä (Finland) for 1998 using MATCH-MPIC.
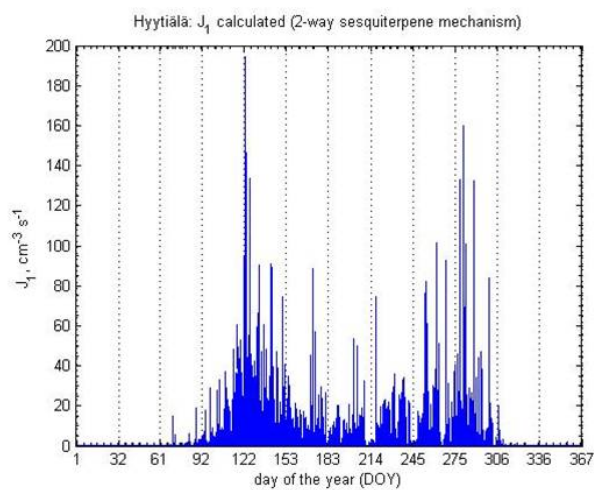
Fig. 3. Estimated nucleation parameter in accordance with *Bonn et al.* (2008).
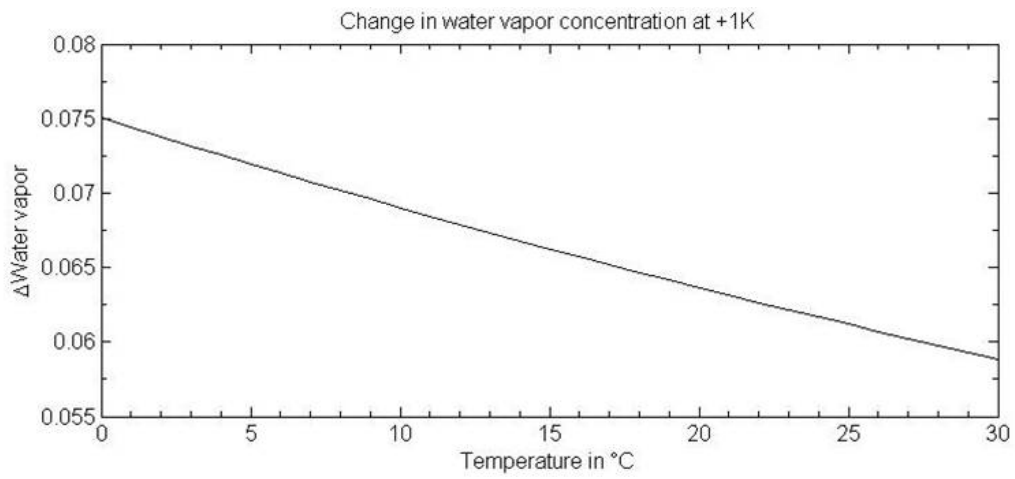
Fig. 4. Relative change in water vapor at identical relative humidity and a temperature increase of +1 K. It is highest at smallest temperatures (7.5% at 0°C) and declines towards the higher.