

Nucleation in boreal forest environments: How biogenic terpenes govern the correlation of formation rates with sulphuric acid

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Abstract. Atmospheric new particle formation is a general phenomenon observed over coniferous forests. So far nucleation is described as a function of gaseous sulphuric acid concentration with two different types of correlation between particle formation rates and measured sulphuric acid concentrations. One has been found linear and one squared to H₂SO₄ known as activation and kinetic nucleation. We explain the observed “correlation coefficients” A and K by the contribution of biogenic terpenes to the process of new particle formation acting as nucleation inducing molecules in reacting with ambient ozone. One aspect of interest is the variation of the observed A and K coefficients in different environments and at different times at the very same place. According to the mechanism presented this variation is caused by variable ambient concentration of sesquiterpenes, the ambient water vapour and available carbonyl compounds. Especially the highly reactive sesquiterpenes, released as a stress response by the vegetation have strong impact on the changes in A and K.

While binary and ternary nucleation mechanisms involving sulphuric acid dominate nucleation in the upper troposphere other compounds such as terpenoids emitted by the biosphere as a stress response are believed to contribute to the new particle formation process in the meteorological boundary layer too. Here we formulate a mechanism¹, which combines the sulphuric acid related observations and smog chamber studies of biogenic terpenes. In there a reactive terpene such as a sesquiterpene reacts with ozone leading to substantial productions of a stabilized Criegee biradical (sCI). Its predominant atmospheric reaction is the one with atmospheric water vapour forming hydroxy-

hydroperoxides not nucleating. On the contrary reactions with sulphuric acid and carbonyl compounds produce unstable and reactive intermediate species that can take up more sulphuric acid molecules and start the cluster formation process. Depending on which pathway is used predominantly one can observe either a squared or a linear relationship to sulphuric acid.

This leads to a formulation of the correlation coefficients A (linear) and K (squared relationship) as follows:

$$A = k_{coll.,SO_2+H_2SO_4} \cdot k_{sCI}^{aldehyde} \cdot [sCI][aldehyde] \cdot \tau_{SO_2}$$

$$K = \frac{k_{coll.,org.sulfate+H_2SO_4} \cdot k_{sCI}^{H_2SO_4} \cdot [sCI]}{CS_{org.sulfate}}$$

Intercomparison with field measurements result in a picture as shown in Figure 1. Assuming a radical like reaction rate of sulphuric acid with secondary ozonides or organo sulphates matches observations best. However, there are a lot of open questions remaining.

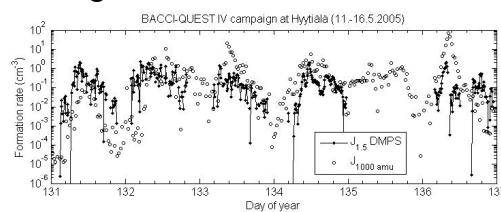


Figure 1. Intercomparison of measured formation rates at D_p = 1.5 nm at 11.-16.5.2005 and the calculated ones of the new mechanism.

References:

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