

# Nanoparticle Growth Mechanisms During New Particle Formation

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Atmospheric new particle formation (NPF) is a key source of ambient ultrafine particles that may contribute substantially to the global production of cloud condensation nuclei (CCN). While NPF is driven by atmospheric nucleation, its impact on CCN concentration depends strongly on atmospheric growth mechanisms since the growth rate must exceed the loss rate due to scavenging in order for the particles to reach the CCN size range. We have made chemical composition measurements of 20 nm diameter particles during NPF in urban and remote locations using the Nano Aerosol Mass Spectrometer (NAMS). These measurements provide a quantitative assessment of important growth channels. We find several common features among NPF events in different locations and different times of year, and other features that are location/time specific. These features will be discussed in the context of our most recent field campaigns in the US and Europe.

With the improved time resolution of NAMS for these measurements (Pennington et al., 2012), we are able to distinguish and quantify chemical species that are associated with nucleation vs. growth. At the onset of NPF (nucleation), we find that the composition of 20 nm particles changes even though the total aerosol mass concentration does not. These changes provide insight into the nucleation process since the chemical species that condense onto pre-existing “large” particles are likely to be similar to those that assist nucleation. In this regard, the species found to condense onto pre-existing particles during this time period include sulfuric acid, ammonia/amine and in some locations high O/C ratio carbonaceous matter. The change in nanoparticle composition coincides with an increase in the sulfuric acid gas phase concentration, which indicates the onset of NPF.

As the mode diameter increases and the aerosol mass concentration grows through the NAMS size range, other chemical species can increase relative to those involved in nucleation. While sulfuric acid condensation contributes to particle growth, it usually represents much less than half of the mass growth. The sulfur mole fraction determined by NAMS is taken as a quantitative measure of sulfate in the aerosol. (Bzdek et al., 2012) The sulfate mass fraction of growing particles (determined from NAMS measurements), along with the particle growth rate (determined from particle size measurements), can be used to back-calculate the gas phase sulfuric acid concentration. The sulfuric acid concentration calculated in this manner matches within experimental error the sulfuric acid concentration

measured with a chemical ionization mass spectrometer, confirming that sulfuric acid uptake is collision limited.

During particle growth, the sulfur and nitrogen mole fractions are highly correlated, suggesting that cationic nitrogen (ammonia, amines) is taken into the particle to neutralize the condensing sulfuric acid. In some locations, the ratio of these two elements is such that sulfate in the particles is only partially neutralized ( $N/S < 2$ ). In other locations, sulfate appears to be completely neutralized ( $N/S > 2$ ).

We define “excess” nitrogen as  $N - 2S$  where  $N$  is the nitrogen mole fraction and  $S$  is the sulfur mole fraction. We find that excess nitrogen is associated with particle *growth* but not *nucleation*. Excess nitrogen indicates that nitrate (either inorganic and/or organic) is an important growth species for NPF.

Carbonaceous matter is another important growth species. Depending on the location and time of year, the carbonaceous matter associated with particle growth can have an O/C ratio characteristic of fresh or slightly aged SOA.

Finally, we find that differences in the overall particle growth rate from one NPF event to another at a specific location and time of year are caused by variations in the growth rates of all major chemical species, not just one individual species.

## References

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