Response to Anonymous Reviewer #1:

We thank the reviewer for helpful comments. We respond below in **bold**.

Major Comment:

The finding of the strong increase in sulfate mass fraction from 5% to 30% during the onset of the nucleation events is highly interesting but it also opens some questions:

1. What time intervals were chosen for the NPF onset?

   Since this manuscript focuses on particle *growth* as opposed to *nucleation*, we define the onset of NPF as the time when the gas phase sulfuric acid (SA) concentration increases quickly. This definition is simple because it relies on a single, standard measurement (gas phase SA concentration) and functional because it coincides with a significant change in the chemical composition of 20 nm particles measured by NAMS. Other definitions, such as the onset of 1-3 nm particles or an extrapolation back in time based on the observed particle growth rate, are relevant to the study of nucleation mechanisms but less so to the study of growth mechanisms. Therefore, we have chosen the simple, functional definition. The revised manuscript will more clearly discuss what we mean by the onset of NPF.

2. Which time intervals were used to calculate the H_2SO_4 averages of Table 1?

   During NPF where particles grow quickly, ~90% of the mass of a 20 nm diameter will be gained as the particle grows from about 10 nm to 20 nm. Therefore, measuring the composition of 20 nm particles informs us of growth processes that were operative during this same time period. For this reason, the time interval for averaging the gas phase SA concentration was chosen to coincide with the time period that the mode diameter increased from 10 nm to 20 nm.

3. How did the growth rate change over time during the NPF events (during the onset and for the yellow bands when NPF particle sizes were ~20 nm)?

   Growth rates were constant over the time period for which the mode diameter increased from 10 nm to 20 nm diameter. These are the values reported in Table 1. They are relevant to this study because most of the mass of a 20 nm diameter particle is gained when the particle grows from 10 to 20 nm.

4. The limits of Eq. (2) need to be discussed. For example, one can imagine a situation where sulfuric acid is condensing while other compounds are evaporating, leading to zero net growth (or even negative net growth) and then a too low (or unphysical negative)

H_2SO_4 concentration is derived. Γ_m will typically be changing during the growth and the assumption of an average Γ_m is limited.

This is an important limit to Eq. (2). Put another way, Eq. (2) is only valid when the particles are growing quickly as in an NPF event. As such, for Eq. (2) to be applicable, the growth rate needs to be a constant, positive value during the event. Γ_m provides information on the net change in particle composition from 10-20 nm and so would provide an average value that would include condensation and evaporation of different components to or from the particles. We will expand the discussion of Eq. (2) to include these points in the revised manuscript.

5. Which Γ_m was assumed for the NPF onset time interval?

   The values of Γ_m reported in this study are for the time period when the mode diameter was within the NAMS-measured particle size range. Our intent is to use Γ_m only when referring to growth during an NPF event, i.e. when Eq. (2) applies. For other times, sulfate mass fraction can be measured but the time period over which the particles grew to 20 nm is ill-defined and Eq. (2) is not relevant. Again, we will make these concepts clear in the revised manuscript.

6. The increase of sulfate mass fraction from 5% to 30% for 20 nm particles growing by H_2SO_4/H_2O condensation by 1 (or rather 2 nm) within approximately one hour is hard to reproduce for me for H_2SO_4 concentrations during the NPF onset of $<3 \times 10^6$ cm^{-3} (18 April) and $<6 \times 10^6$ cm^{-3} (19 April). Please explain the calculation in more detail. Nieminen et al., *Atmos. Chem. Phys.*, **2010**, would yield lower growth rates for these concentrations.

   In the calculation, we assume that sulfate mass in a particle with total mass of 1 increased from 0.05 (before the increase in sulfuric acid concentration) to 0.40 (after the increase in sulfuric acid concentration) thereby increasing the total particle mass from 1 (before the increase) to 1.35 (after the increase). Since mass goes with the cube of diameter, a 1.35-fold increase in particle mass would correspond to a 1.11-fold increase in diameter:

   $$\textbf{change in diameter} = \sqrt[3]{\textbf{mass}} = \sqrt[3]{1.35} = 1.11,$$

   which corresponds to an increase in diameter from 20 nm to 22 nm. Then, we apply Eq. (2):

   $$\textbf{Growth Rate} = \frac{1}{2}[H_2SO_4]v\overline{c_1}\Gamma_m \times \frac{\rho_{sulfate}}{\rho_{particle}} = \frac{\Delta d}{\Delta t}$$

   Assuming $[H_2SO_4] = 2 \times 10^6$ molecules·cm^{-3}, $\Gamma_m = 1.35/0.40 = 3.4$, and $\Delta d = 2$ nm and then solving for Δt, we find that it requires < 3 hours for the sulfate mass fraction to increase from 0.05 to 0.30, which is consistent with the

measurement. In other words, the measured change in sulfate mass fraction keeps up with the change in gas phase sulfuric acid. We will clarify this point in the revised manuscript.

7. How can *nucleation* be explained, if during the NPF onset highly oxidized organics are not present (if they were present then they would be condensing on the 20 nm particles and contribute considerably to the particle growth of the preexisting particles as well; also low O/C ratios are observed later for the condensing SOA), and sulfuric acid + ammonia alone are not sufficient to explain the observed nucleation rates (Kirkby et al., 2011)? What can be said about amine levels in Hyytiälä in early spring? Nucleation is not the main subject of this paper but consistence/inconsistency of the results in this respect should be discussed.

   This work focuses on growth and therefore gives no direct information on nucleation. However, the observation that the N and S elemental mole fractions increase before the mode diameter grows into the NAMS size range suggests that H_2SO_4 and NH_3 are important condensable species during the approximate time period of nucleation. Highly oxidized organic species may also condense on particles during this time period, but they are very difficult or impossible to characterize because there is so much preexisting carbonaceous matter in the particles.

   We note that carbonaceous matter does play an important role in the growth of nanoparticles, as sulfate constitutes <50% of the total particle mass during these events, with the remainder composed of ammonia and carbonaceous matter. Even though the carbonaceous fraction in the particle phase decreases *relative* to sulfate during NPF, the *absolute* amount of particulate carbonaceous matter increases substantially because NPF results in a large increase in nanoparticle mass.

   Amine levels are thought to be low in Hyytiälä in the early spring (at least during this campaign) and so are thought not to contribute significantly to growth.

<u>Minor Comments:</u>

1. Page 14122, lines 15-16: Did you find other (minor) elements? Which ones were found? How high was their mole fraction at maximum?

   We did not find evidence for other (minor) elements. Most significantly, we observed no Si, which has been commonly observed in other environments where NAMS has measured nanoparticle composition (Bzdek et al.,

2013;Pennington et al., 2012;Zordan et al., 2008). We note that this does not preclude the presence of other minor elements in abundances below the NAMS detection limit.

2. Were the 8 event days all the NPF events during the measurement period?

   The eight events discussed in this manuscript are the complete set of NPF events measured by NAMS that resulted in particle growth to 20 nm or above.

3. Figure 2: It would be interesting to see how the mole fractions develop on non-event days. Is the sulfur mole fraction always increasing during the day?

   Because of the low particle concentrations, high time resolution could not be achieved on non-event days. However, in Figure 2d, we show average elemental composition on event periods and other periods (including non-event days). Non-event days had particle compositions similar to compositions measured on the mornings of event days but very different from compositions measured during event periods. These data illustrate that there is no systematic increase in sulfur mole fraction on non-event days, at least to a similar extent as observed during NPF.

   We have found in another environment that sulfur does increase during the daytime on non-event days (Bzdek et al., 2013). These measurements were made using an instrumental design that improved nanoparticle sampling efficiency relative to the setup used in Hyytiälä, thereby permitting highly time-resolved measurements on non-event days.

<u>Technical comments:</u>

1. Figure 1c: The blue and the violet colors for N and O can hardly be distinguished in a print-out. Please change the color for one of these two elements. (For consistency the color should then be changed throughout.)

   These colors were chosen to conform to the conventions used by the AMS community, which have become de facto the standard colors. They are also equivalent to colors used in other NAMS publications.

2. Figures 2 a-c should be depicted larger (especially wider) and with better time resolution.

   While we understand the reviewer’s request, Fig. 2 is already expanded as large as possible. Fig. 1 shows a detailed expansion of the most relevant time period of Fig. 2. The other days not shown in as great detail follow the same trend as Fig. 2.

References:

Bzdek, B. R., Horan, A. J., Pennington, M. R., DePalma, J. W., Zhao, J., Jen, C. N., Hanson, D., Smith, J. N., McMurry, P. H., and Johnston, M. V.: Quantitative and Time-Resolved Nanoparticle Composition Measurements During New Particle Formation, Faraday Discuss., doi: 10.1039/C1033FD00039G, 10.1039/c3fd00039g, 2013.

Pennington, M. R., Klems, J. P., Bzdek, B. R., and Johnston, M. V.: Nanoparticle chemical composition and diurnal dependence at the CalNex Los Angeles Ground Site, J. Geophys. Res.-Atmos., 117, D00V10, doi: 10.1029/2011JD017061, 2012.

Zordan, C. A., Wang, S., and Johnston, M. V.: Time-resolved chemical composition of individual nanoparticles in urban air, Environ. Sci. Technol., 42, 6631-6636, 10.1021/es800880z, 2008.