The role of relative humidity in continental new particle formation

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[1] Relative humidity (RH) has been observed to be anticorrelated with continental new particle formation. Several reasons have been proposed for this rather surprising finding, but no firm conclusions have been drawn so far. Here we study several of the proposed reasons: Enhanced coagulational scavenging of sub-3 nm clusters at high RH, diminished solar radiation at high RH leading to diminished gas phase oxidation chemistry, and increased condensation sink (CS) of condensable gases due to hygroscopic growth of the preexisting particles. Our theoretical calculations indicate that the increase of coagulational scavenging plays a relatively small role in the inhibition of nucleation at high RH. On the other hand, field data show that the maximum observed gas phase sulphuric acid concentrations are limited to RHs below 60%. The field data also indicate that this is likely due to low OH concentrations at high RH. This finding is also supported by aerosol dynamics model simulations. The model was used to find out whether this is mainly due to decreased source (solar radiation) or increased sink (CS) terms at the elevated RH. The simulation results show that the decreased source term at high RH limits H_2SO_4 levels in the air, and therefore high new particle formation rates (above ~1 cm^{-3} s^{-1}) rarely occur above 80% RH.

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1. Introduction

[2] It has been observed at different continental locations that new particle formation (NPF) takes place preferentially at low relative humidities (RH) [e.g., *Birmili and Wiedensohler*, 2000; *Woo et al.*, 2001; *Boy and Kulmala*, 2002; *Alam et al.*, 2003; *Birmili et al.*, 2003; *Stanier et al.*, 2004; *Hyvönen et al.*, 2005; *Mikkonen et al.*, 2006; *Hamed et al.*, 2007; *Laaksonen et al.*, 2008; *Jaatinen et al.*, 2009; *Vaattovaara et al.*, 2009]. Furthermore, observations show that during NPF events, there is an anticorrelation between RH and formation rate [*Sihto et al.*, 2006] or between RH and the number concentration [*Weber et al.*, 1997; *Jeong et al.*, 2004] of freshly formed particles. These findings are somewhat surprising as the main species responsible for atmospheric nucleation and early particle growth is thought to be sulphuric acid (H_2SO_4) which is known to conucleate very efficiently with water vapor so that, in laboratory experiments, nucleation rates increase with RH at fixed sulfuric acid concentration and no background aerosol. Of course, some other species such as ammonia and organics might also be involved in atmospheric NPF. Also, a number of observations have been made on NPF in the vicinity of clouds [e.g., *Hegg et al.*, 1990; *Clarke et al.*, 1998; *Keil et al.*, 2001], where the RH is very high, usually over 90%.

[3] A number of reasons have been suggested as to why high RH could possibly suppress NPF. Preexisting aerosol particles take up water vapor as RH increases, which causes both the condensation and the coagulation sinks to increase. An increased condensation sink (CS) means a larger loss term for condensable vapors such as H_2SO_4 which might contribute to the anticorrelation between the NPF rate and RH and, in extreme cases, even inhibit nucleation. An increased coagulation sink (CoagS) causes increased coagulational scavenging of freshly formed nuclei onto the preexisting particles before the nuclei have grown large enough to be detected by aerosol instruments. This could cause an apparent anticorrelation between the NPF rate and RH; however, the anticorrelation remains even after accounting mathematically for the effect of (RH-dependent) CoagS on nucleation rate [see *Sihto et al.*, 2006]. On the other hand, increased CoagS might "mask" nucleation events in some cases by removing virtually all nuclei before they are detected.

[4] Another possible reason for the observed negative correlations between RH and NPF is that solar radiation, which

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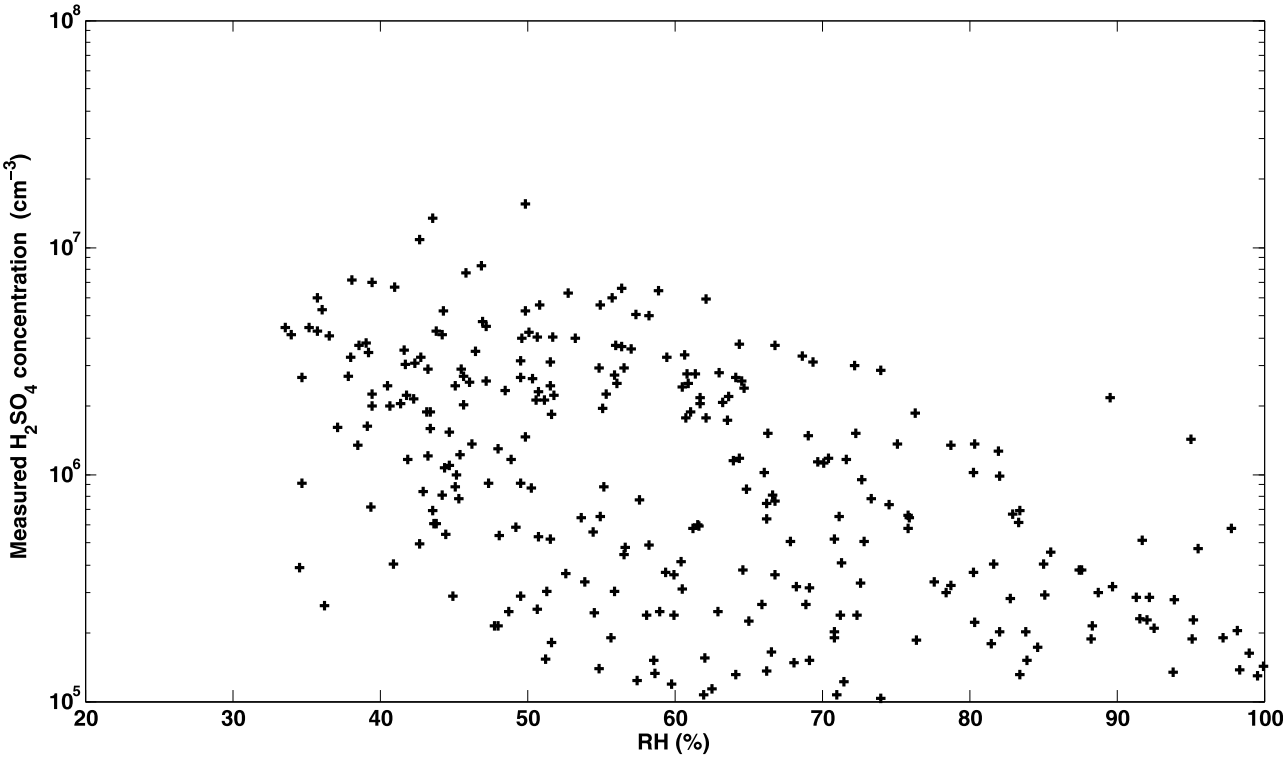

Figure 1. RH (%) versus H_2SO_4 concentrations (cm^{-3}) observed during the 2003 QUEST field campaign in Hyytiälä, Finland. Data points represent 1 h averages from 0600 to 1800 LT.

drives the photochemistry leading to formation of H_2SO_4 and condensable organics, is often less intense at high RH, either because of cloudiness or for the simple reason that diurnal RH behavior is often such that there is a minimum at around noon when NPF events are frequently observed. Still other reasons have been presented [e.g., *Hyvönen et al.*, 2005; *Bonn et al.*, 2002; *Bonn and Moortgat*, 2003], that suggest that low volatility ozonolysis products of monoterpenes and sesquiterpenes, whose formation is known to be suppressed by water vapor, might be involved in atmospheric nucleation and subsequent growth. Note however, that in this case it is not the RH but the absolute humidity which would cause the anticorrelation with NPF. Although absolute humidity has also been noted to anticorrelate with NPF [e.g., *Boy and Kulmala*, 2002; *Komppula et al.*, 2003; *Lyubovtseva et al.*, 2005; *Hamed et al.*, 2007], we will in this paper mostly focus on the role of RH.

[5] The aim of this study is to find out whether increased CS, increased CoagS, or decreased radiation suppresses NPF in humid conditions. In order to achieve this goal, we examine the above suggested possibilities in more detail, using analysis of field measurements, theoretical calculations, and aerosol dynamics model simulations.

2. Analysis of Field Measurements From QUEST 2003 Campaign

2.1. Brief Description of Measurements and Collected Data

[6] Particle size distributions have been measured continuously at the Station for Measuring Ecosystem-Atmosphere Relations (SMEAR) at the Hyytiälä forestry station (SMEAR II; 61°51′N, 24°17′E; 170 m above sea level), southern Finland since January 1996 [*Hari and Kulmala*, 2005]. The measurements are carried out using a twin Differential Mobility Particle Sizer (DMPS) system; the first DMPS measures particle size distributions between 3 and 20 nm and the second one between 15 and 600 nm. One measurement cycle lasts for 10 min (more detail is given by *Aalto et al.* [2001]). In addition to particle size distribution measurements, several gas and meteorological parameters are measured at the SMEAR II station (e.g., SO_2, NO, NO_2, NO_x, CO, CO_2, H_2O, O_3, temperature, relative humidity, wind direction, wind speed, global radiation, precipitation, and atmospheric pressure).

[7] The Quantification of Aerosol Nucleation in the European Boundary Layer (QUEST) field campaign at the SMEAR II station took place from 18 March to 9 April 2003 [*Sihto et al.*, 2006]. The QUEST 2003 data set is unique in the sense that during the campaign a large number of events were observed (from a total of 23 measurement days, 20 were NPF days that we have used in our study). During this spring campaign, the gas phase sulphuric acid concentration was measured by a chemical ionization mass spectrometer (CIMS) [*Hanke et al.*, 2002]. The time resolution of the spectrometer was less than 1 s, but the data was averaged over 60 s in order to reduce statistical error and sampling noise. The sulphuric acid detection limit was 1×10^5 cm^{-3} and the relative measurement uncertainty 30%. In our analysis of NPF days we make use of the particle size distribution data together with RH, absolute humidity, UV radiation, and SO_2 concentrations from this campaign period. As nucleation mostly takes place during

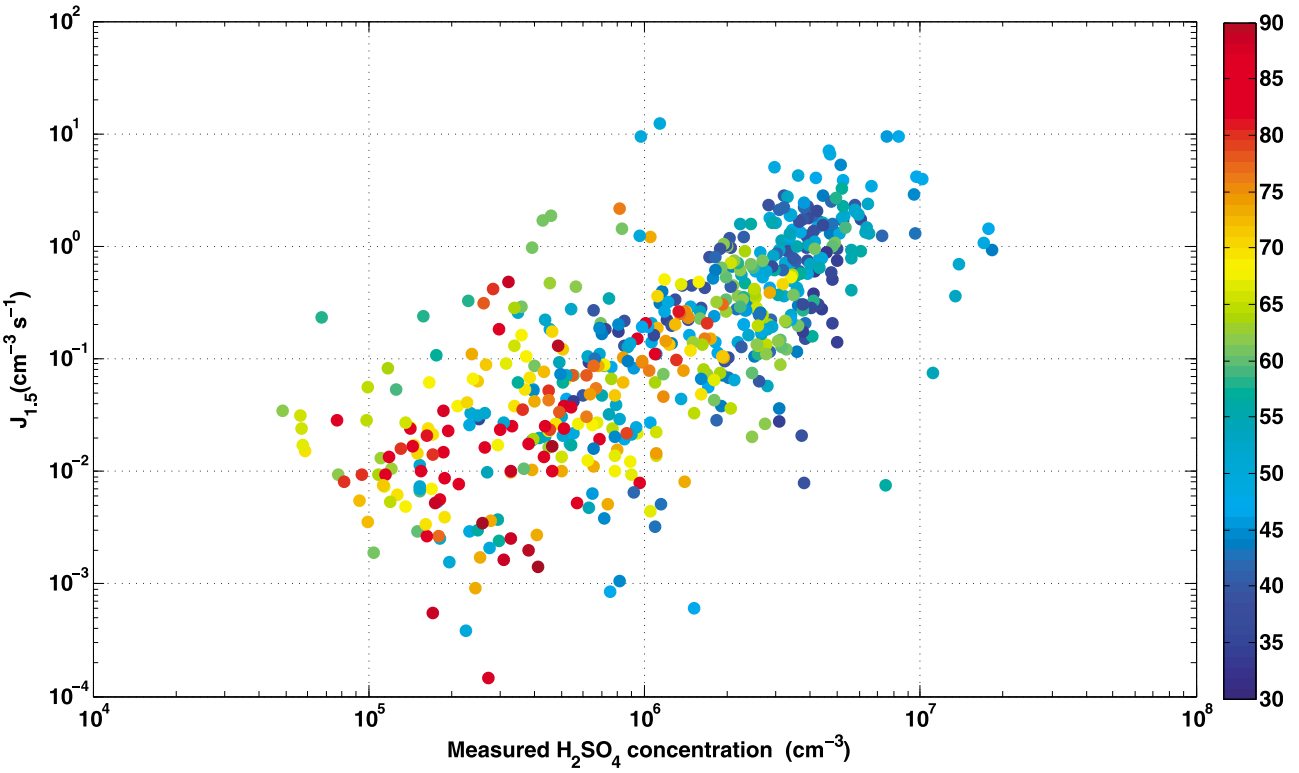

Figure 2. Nucleation rate at 1.5 nm ($J_{1.5}$) versus [H_2SO_4] measured during the 2003 QUEST campaign in Hyytiälä, Finland. Color coding indicates relative humidity (RH) expressed as percent. Data points represent 10 min averages from 0600 to 1800 LT.

daylight hours, we limit our analysis to 0600–1800 local time (LT).

[8] The nucleation rate of critical clusters of 1.5 nm in diameter ($J_{1.5}$) is a central quantity in this analysis. The $J_{1.5}$ rate was extrapolated from the formation rate of 3 nm particles, J_3, which is obtained from measured particle size distributions. Particularly, we apply the method presented by *Lehtinen et al.* [2007] (see equation (1)). The growth rate (GR in nm h^{-1}) is estimated by incorporating the probability that a particle would grow from 1 to 3 nm by vapor condensation before being scavenged by the preexisting aerosol. Time delay *dt* in equation (1) is estimated for each NPF day as the delay between the rise in sulfuric acid concentrations and particle number concentration for particles between 3 and 6 nm (N_{3-6}). The NPF event is assumed to begin when [H_2SO_4] begins to rise sharply, and N_{3-6} particle concentrations begin to increase as well. In this study, time delay values between rise of [H_2SO_4] and N_{3-6} varied between 20 min and 1.5 h for different NPF days. For more detailed information about the calculation of nucleation rates, see, for example, *Kerminen and Kulmala* [2002], *Sihto et al.* [2006], and *Lehtinen et al.* [2007].

2.2. Effect of Relative Humidity on H_2SO_4 Concentrations and Nucleation Rates ($J_{1.5}$)

[9] We will first look at how the measured sulphuric acid concentrations behave at different relative humidities. Sulphuric acid is currently thought to be the most likely nucleation precursor candidate as well as to contribute to the growth of newly formed particles [*Weber et al.*, 1999; *Kulmala*, 2003; *Kulmala et al.*, 2004a; *Sipilä et al.*, 2010]. Therefore variations in its concentration as a function of RH should directly affect both nucleation (taking place at ~1–1.5 nm) and NPF (at ~3 nm) rates. Measurements during the 2003 QUEST field campaign show a clear RH dependence of the gas phase H_2SO_4 concentrations with decreasing values at RH above ~60% (Figure 1). Figure 1 shows that the decrease of the maximum concentrations is about an order of magnitude or even more between 60 and 90% RH. The RH effect is also seen in the calculated nucleation rates. Figure 2 shows a scatterplot of $J_{1.5}$ calculated from the measured aerosol size distributions versus measured [H_2SO_4]. The data points are color-coded according to RH. As Figure 2 shows, at high RH (>80%) the H_2SO_4 concentrations are below 3×10^6 cm^{-3} and the nucleation rates are mostly below 2 cm^{-3} s^{-1}.

[10] Taken together Figures 1 and 2 strongly suggest that the suppression of nucleation at humid conditions is linked to either the formation or the loss rate of sulphuric acid. We will investigate both of these possibilities below.

2.3. Effect of RH on SO_2 and OH Concentrations

[11] High RH can, in principle, affect the atmospheric concentrations of both SO_2 and OH. At high RH the amount of liquid water available in the atmosphere (associated either with hygroscopic aerosol particles or clouds) increases, which could lead to more efficient aqueous phase conversion of SO_2 to sulfate, and thus to decreased gas phase SO_2 concentrations. However, measurements of SO_2 during the QUEST 2003 campaign do not support any significant RH dependence (Figure 3a). In Figure 3a we highlight (diamonds)

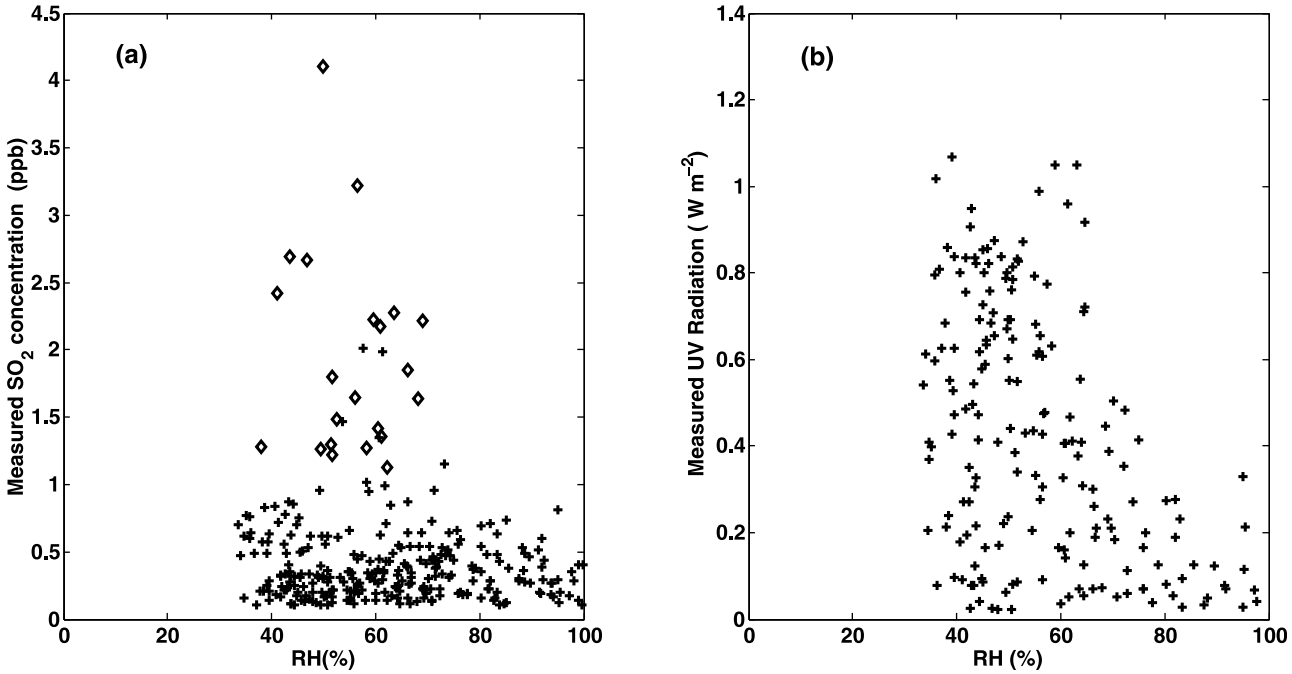

Figure 3. RH (%) versus (a) SO_2 concentrations (ppb) (the high SO_2 concentrations on 1 and 2 April 2003 are indicated by diamonds) and (b) UV radiation in W m^{-2} observed during the 2003 QUEST campaign in Hyytiälä, Finland. Data points represent 1 h averages from 0600 to 1800 LT.

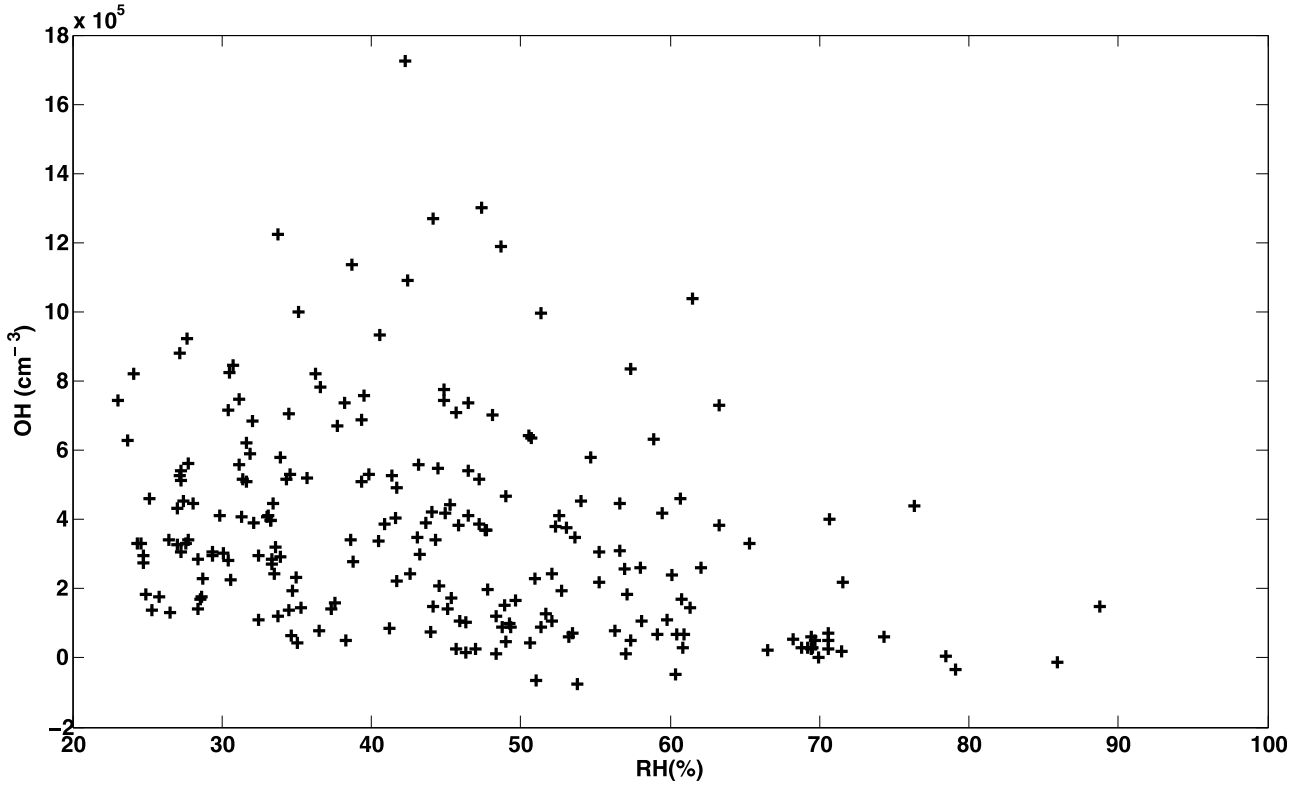

Figure 4. RH (%) versus OH concentrations in cm^{-3} units observed during a 2007 field campaign in Hyytiälä, Finland. Data points represent 1 h averages from 0600 to 1800 LT.

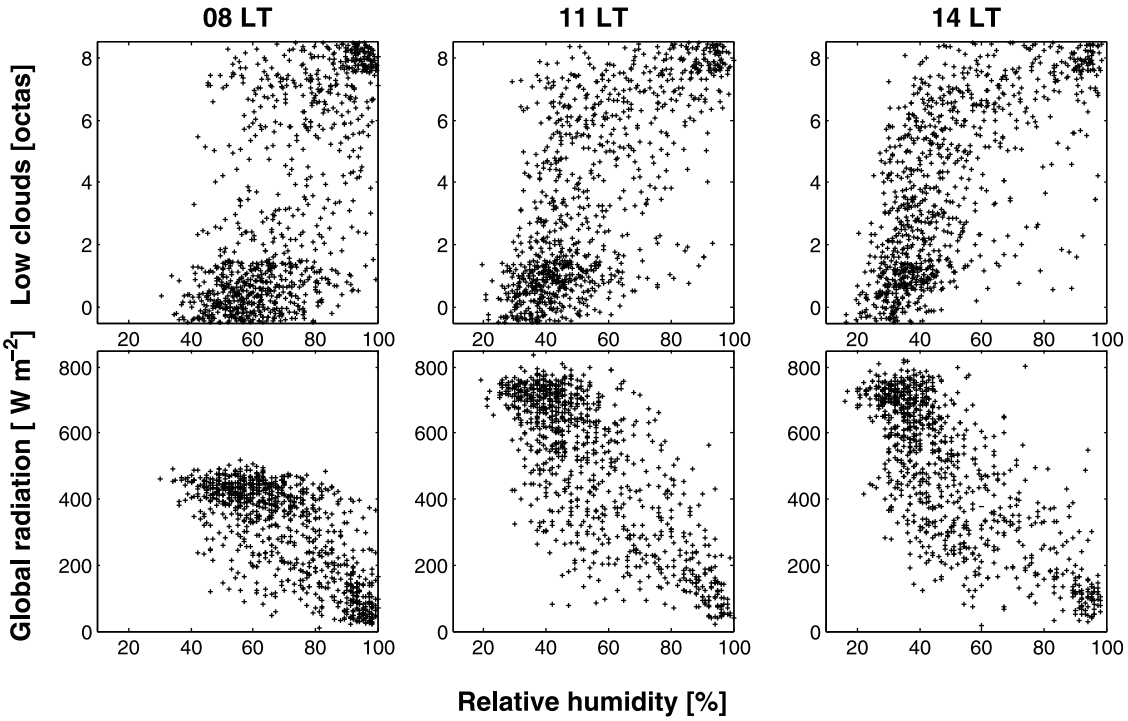

Figure 5. A 30 year data set (1970–2000) of (top) low-level cloudiness (octa units, where an octa is a cloudiness fraction given as a score of 1–8 (e.g., 3 octas indicates three eighths cloudiness)) and (bottom) global radiation (W/m^2) versus relative humidity (%) at the Finnish Meteorological Institute's observatory in Jokioinen (60°49′N, 23°30′E), southern Finland. The data shown are for (left) 0800, (middle) 1100, and (right) 1400 LT.

measurements from two days (1 and 2 April) in which polluted air impacted this remote site. These points are considered outliers, since the preponderance of SO_2 concentrations in the 40–70% RH range fall below 0.5 ppb (the average and median SO_2 concentration over this range of RH are 0.5 and 0.3 ppb, respectively). A similar analysis of longer, multiyear data sets (not shown) from Hyytiälä, Finland and San Pietro Capofiume, Italy support the observations shown in Figure 3a that SO_2 concentrations are not correlated with RH.

[12] Recent studies have suggested that the tropospheric OH radical concentration is strongly correlated with the intensity of solar UV radiation despite the complex OH chemistry in the atmosphere [*Rohrer and Berresheim*, 2006; *Petäjä et al.*, 2009]. Since direct measurements of OH concentrations were not made during QUEST, we use the measurements of UV as a proxy for OH. The highest UV radiation values during this campaign are limited to RH values of ~60% and, at higher humidities, the maximum values decrease steeply (Figure 3b). This trend is very similar to that of the measured H_2SO_4 concentrations (Figure 1) giving indications that the sulfuric acid concentration at high humidities is controlled by the reduced OH concentrations. One additional piece of evidence supports the hypothesis that reductions in sulphuric acid may be related to reduced OH levels comes from the recent European Integrated project on Aerosol Cloud Climate and Air Quality Interactions (EUCAARI) campaign [*Petäjä et al.*, 2009], during which OH concentration measurements were made. Figure 4 shows a plot of [OH] versus RH from that campaign. Qualitatively, the OH levels during the 2007 campaign display the same trends as sulfuric acid (Figure 1) and UV (Figure 3b). Thus a picture emerges from the consistent measurements made at Hyytiälä, that OH levels may play a key role in the observed dependence of new particle formation on RH.

[13] There are two reasons for the RH dependence of OH concentrations that act simultaneously. First, solar radiation is attenuated on cloudy and hazy days. This is seen in a climatological data set from the Jokioinen observatory (~100 km from Hyytiälä station) which shows that the low-level cloud cover correlates with the ground level RH (Figure 5, top). Thus as a result of cloudiness, global solar radiation anticorrelates with RH and global radiation reaching the ground level is reduced at RH greater than ~60% (Figure 5, bottom). On the other hand, it is well known from the over 10 years of measurements from Hyytiälä that NPF does not occur on cloudy days with low radiation [*Boy and Kulmala*, 2002; *Dal Maso et al.*, 2005].

[14] Second, RH and solar radiation typically show clear diurnal cycles that are opposite in phase. In the morning, as sunlight warms the ground layer, RH often starts to decrease, and will increase again at noon and toward sunset. Hence, there is an anticorrelation between RH and solar radiation. On annual time scales this anticorrelation may be smeared as the daily peak intensity of the radiation varies strongly from midwinter to midsummer, but on monthly time scales it should be detectable. On NPF days (which are in general rather sunny) the opposite diurnal cycles of RH and radiation is the most likely explanation for their anticorrelation, although cloudiness may play a minor role.

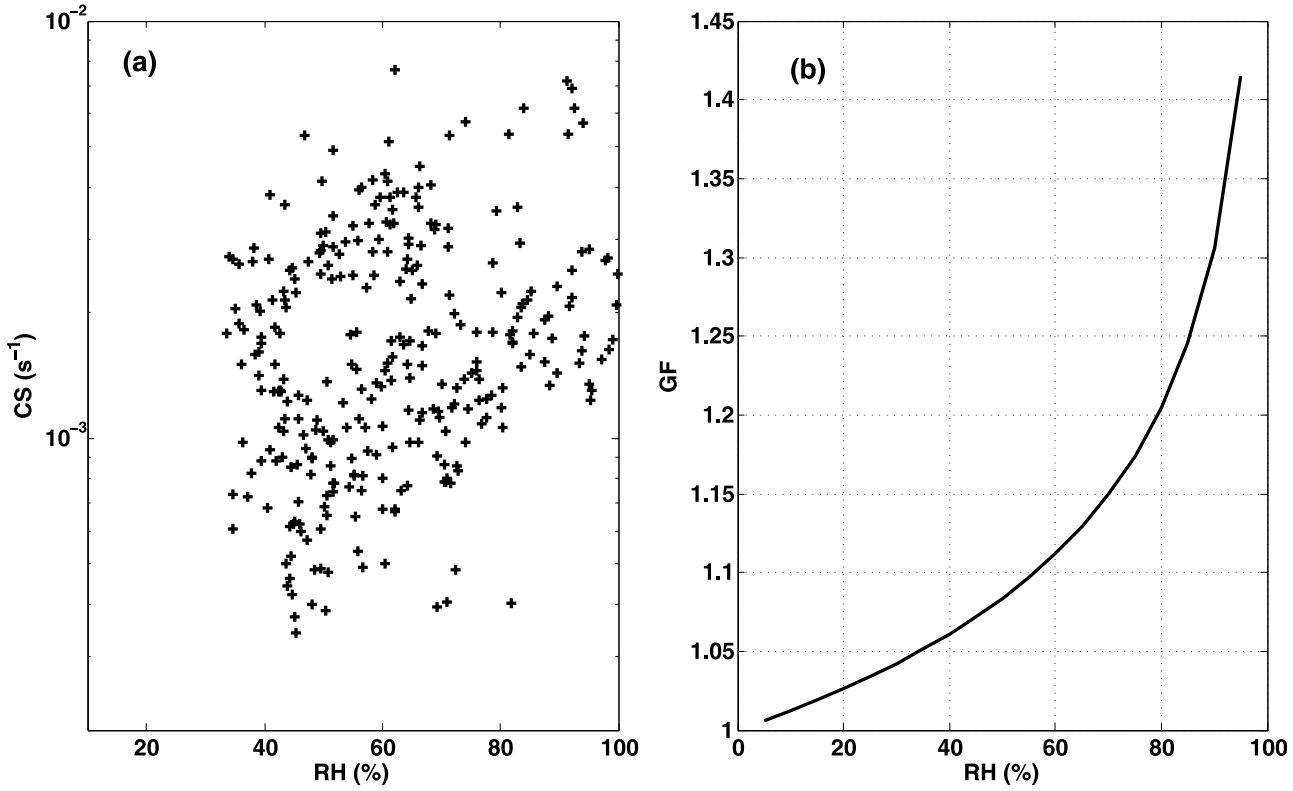

Figure 6. (a) RH (%) versus condensation sink (CS, s^{-1}) estimated during the 2003 QUEST field campaign in Hyytiälä, Finland. (b) The hygroscopic growth factor (GF) of dry 100 nm particles as a function of RH using *Laakso et al.*'s [2004] formula.

[15] It is also noteworthy that the OH concentration is very likely to affect the formation rate of low volatility and semivolatile organic compounds from plant emitted VOCs. Thus lower OH at high RH may affect the observed nucleation rates also via reduced new particle growth rates due to the lower concentrations of condensable organic materials.

2.4. Effect of RH on Condensation Sink

[16] The size of aerosol particles, and thus the sink for condensable vapors, grows very efficiently as a function of RH. Figure 6 shows the estimated condensation sink (CS) values as a function of RH measured during the 2003 QUEST campaign (note that the CS values have been calculated from dry size distributions using the method described by *Pirjola et al.* [1998] and by applying an RH correction using *Laakso et al.*'s [2004] parameterization); between 30 and 90% RH, the value of CS increases roughly by a factor of 3.

2.5. Effect of Other Atmospheric Variables

[17] *Boy and Kulmala* [2002] found that on NPF event days, the water vapor concentration (absolute humidity) is generally lower than on nonevent days of the corresponding month. One reason why high absolute humidity could affect NPF events is that water vapor inhibits certain reactions in the ozonolysis of VOCs and thus prevents the formation of condensable organics to some extent. We therefore made a plot similar to that shown in Figure 2, but color scaled according to absolute rather than relative humidity (Figure 7). It can be seen that, unlike RH, the high and low absolute humidity values are rather evenly spread within the data set, and thus reveals no absolute humidity effect on the NPF.

3. Theoretical Analysis of the Effect of Coagulation Sink (CoagS)

[18] The effect of an increased coagulation sink on NPF rates at high humidities is difficult to evaluate directly from field measurements. Therefore, we investigate its role theoretically, and make calculations based on observed variables affecting coagulational scavenging of freshly formed nuclei. In this section we focus on considering the possibility that the increase of CoagS at increased RH causes masking of NPF events (i.e., nucleation occurs at 1.5 nm, but because of the increased sink, such a large fraction of the freshly formed particles is scavenged by coagulation before reaching 3 nm that the event cannot be observed).

3.1. Background

[19] Atmospheric NPF is usually observed with instruments capable of detecting particles larger than about 3 nm in diameter (although in very recent instruments the detection limit has been lowered to ~2 nm [see *Kulmala et al.*, 2007; *Iida et al.*, 2009]). Therefore, the actual freshly nucleated particles, with diameters closer to 1 nm [*McMurry and Friedlander*, 1979; *Kulmala*, 2003] are not directly observed. The current view of atmospheric NPF is as follows: (1) Sulphuric acid and/or some other sulphur species,

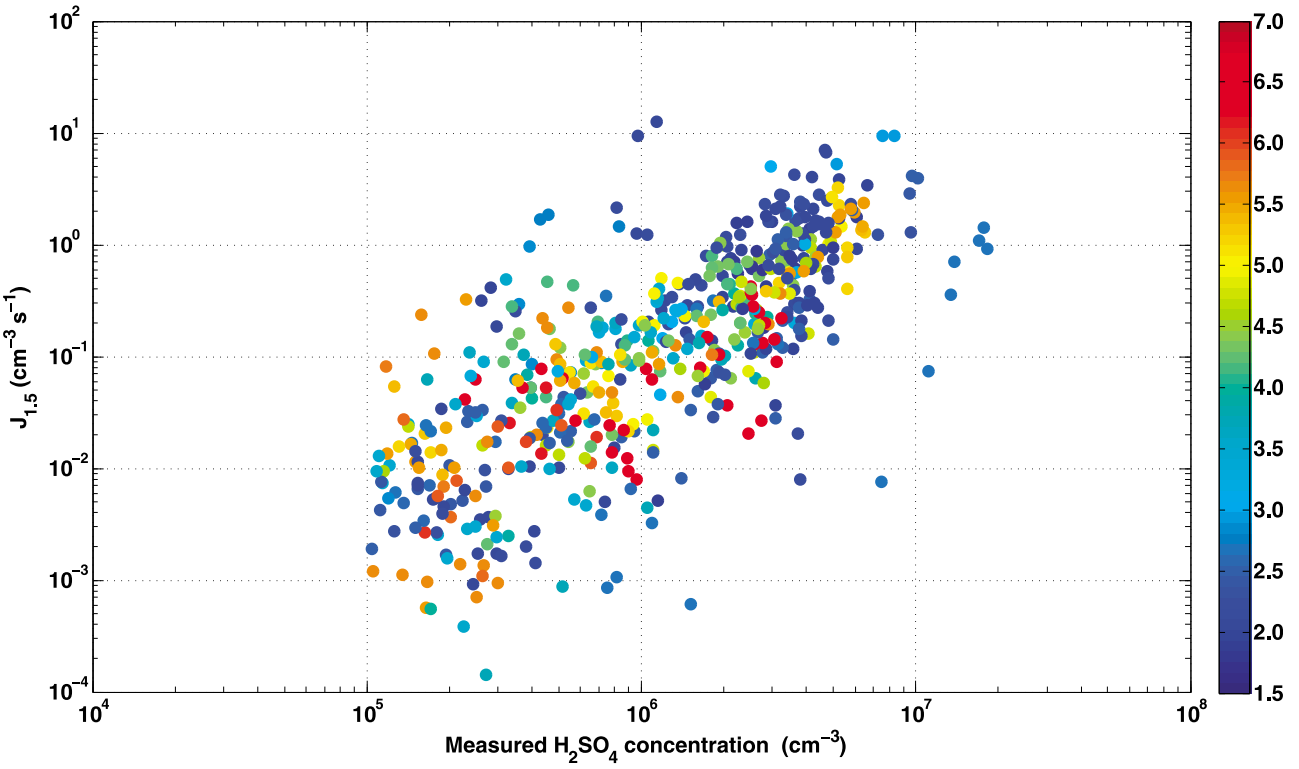

Figure 7. Nucleation rate at 1.5 nm ($J_{1.5}$) versus [H_2SO_4] measured during the 2003 QUEST field campaign in Hyytiälä, Finland. Color coding indicates absolute humidity. Data points represent 10 min averages from 0600 to 1800 LT.

together with some other molecules such as water, ammonia, or some organics, produce stable critical nuclei at a 1 nm mass diameter, which corresponds to ~1.5 nm mobility diameter [*Laaksonen et al.*, 2008; *Kulmala et al.*, 2007]. (2) The critical nuclei start growing by condensation of H_2SO_4 or low volatility organic vapor. (3) If condensable organics have not participated in the growth of the nuclei from 1 nm, it is likely that they start speeding up the growth at some later size when the Kelvin effect has decreased sufficiently, that is, with so-called nano-Köhler mechanisms or via heterogeneous nucleation [*Kulmala et al.*, 2004b]. During the growth toward the detection limit of 3 nm, the growing nuclei are scavenged by coagulation with preexisting aerosol particles. The scavenging efficiency decreases with increasing nucleus size. The following equation [*Lehtinen et al.*, 2007] describes the connection between the actual nucleation rate at 1.5 nm ($J_{1.5}$) and the observed new particle formation rate at 3 nm (J_3):

$$J_3(t+dt) = J_{1.5}(t)\exp\left(-\gamma.D_{1.5}\frac{\mathrm{CoagS}(D_{1.5})}{GR}\right), \qquad (1)$$

where $\gamma = \frac{1}{m+1}\left[\left(\left(\frac{D_3}{D_{1.5}}\right)^{m+1}\right) - 1\right]$ and GR denotes the observed growth rate of the particles (nm h^{-1}). The exponent m depends on the preexisting background size distribution and is given by

$$m = \log\left[\frac{\mathrm{CoagS}(D_3)}{\mathrm{CoagS}(D_{1.5})}\right] \Big/ \log\left[\frac{D_3}{D_{1.5}}\right]. \qquad (2)$$

The CoagS(D_3) and CoagS($D_{1.5}$) are the coagulation sinks of nuclei with diameter 3 nm and 1.5 nm, respectively, onto the preexisting particles.

[20] As with CS, the response of the ambient aerosol to humidity-induced growth must be considered in the calculation of coagulation sink [*Kulmala et al.*, 2001; *Hämeri et al.*, 2000]. In order to get more realistic sink values, the measured particle number size distributions at dry conditions were converted into the ones at ambient conditions by applying the hygroscopic growth law given by *Laakso et al.* [2004].

3.2. Calculations, Results, and Discussion

[21] Here, we discuss theoretically how increases in the coagulation sink at high RH increases the depletion of freshly nucleated particles before they have grown to the observation limit of 3 nm. We make our calculations based on observed variables affecting coagulational scavenging of freshly formed nuclei. We considered two conditions: An average condition (average GR values of the newly formed particles and average CoagS) and a slow growth condition (average CoagS combined with a GR that corresponds to slowest observed values). We use the revised formulation of the relation between J_3 and $J_{1.5}$ presented earlier by *Kerminen and Kulmala* [2002]. The new formula was given by *Lehtinen et al.* [2007], and it has the advantage that coagulation sink is used instead of CS, and thereby no vapor properties enter the equations.

[22] Assuming that the lowest formation rate that can be reliably detected at 3 nm is 10^{-3} cm^{-3} s^{-1}, and that the real nucleation rate ($J_{1.5}$) is a 10^{-2} cm^{-3} s^{-1}, then a 90% loss of

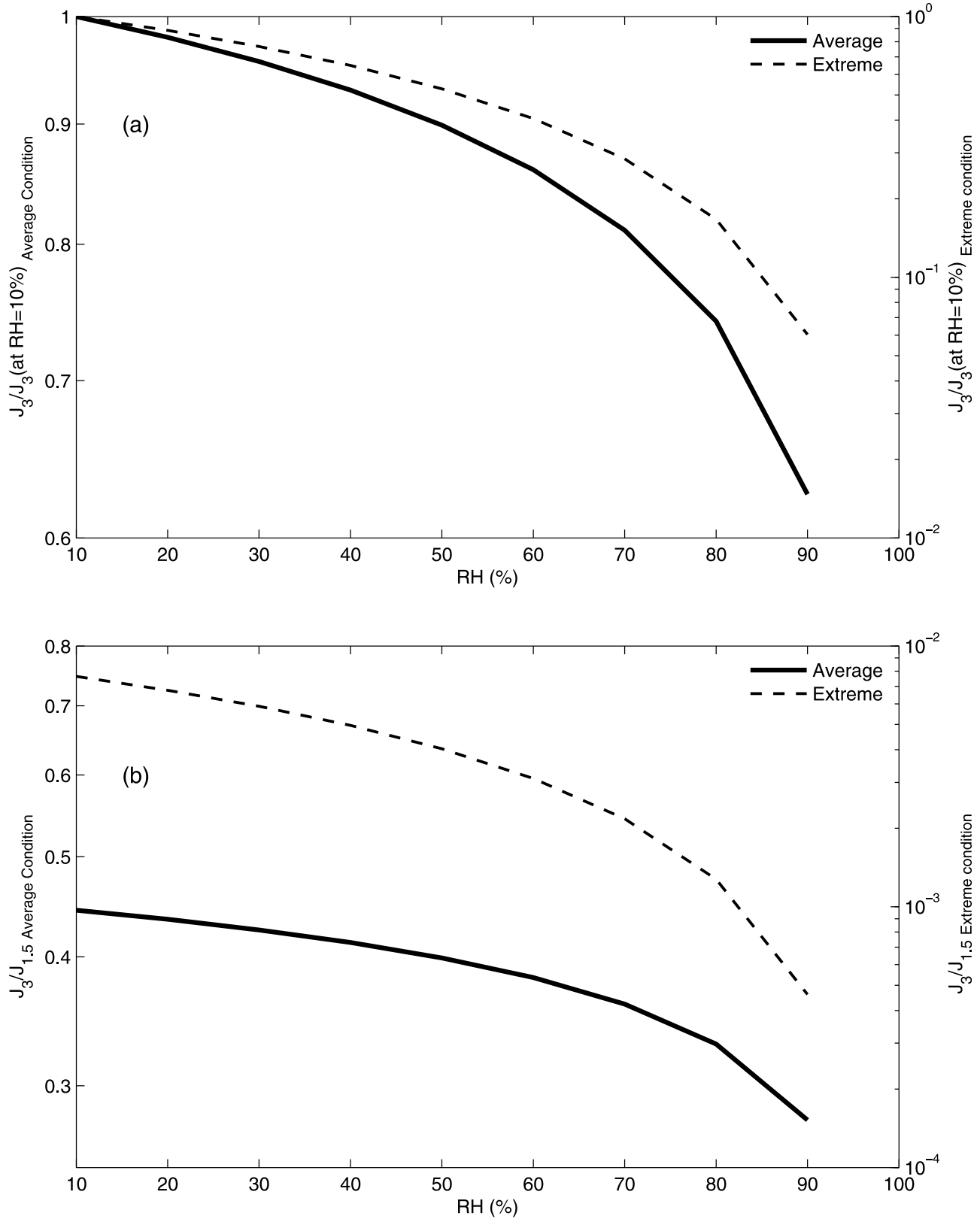

Figure 8. (a) Normalized J_3 (J_3 divided by J_3 at 10% RH) and (b) $J_3/J_{1.5}$ as a function of RH for average (left axis, solid curve) and extreme conditions (right axis, dashed curve). Average conditions correspond to GR = 3 nm h^{-1} and CS = 8.6 h^{-1}, extreme conditions GR = 0.5 nm h^{-1} and CS = 8.6 h^{-1}.

Table 1. Parameters Used in Model Simulations

Variable	Values
SO_2 ($\mu g\ m^{-3}$)	0.5, 5, 50
Organic vapor (cm^{-3})	10^7, 10^8, 10^9
Preexisting particle number (cm^{-3})	50, 500, 5000
A factor (s^{-1})	2E-7, 2E-6, 2E-5

the freshly formed particles by coagulation while they are growing from 1.5 to 3 nm is enough to mask the event from observation. On the other hand, with a $J_{1.5}$ of 10 cm^{-3} s^{-1}, the drop between $J_{1.5}$ and J_3 should be by a factor of 10^4 for the event to become unobservable. The question we want to answer is: If the coagulation sink does not mask a nucleation event at low RH (e.g., 10%), is it possible that such masking would occur solely due to increased coagulation sink if RH increases to a high value (e.g., 90%)? To answer this question, we determine "average" and "extreme" values of particle growth rates and condensation sinks during Hyytiälä nucleation events and calculate (using equation (1)) how much an RH increase from 10 to 90% enhances scavenging of sub-3 nm particles. The average values are taken from *Dal Maso et al.* [2005] who, based on an 8 year dataset of events, found the average GR and CS for dry particle size distribution to be 3 nm h^{-1} and 8.6 h^{-1}, respectively. To define a "slow growth" case (it is clear that a slow GR will lead to enhanced coagulational scavenging of the clusters between 1.5 and 3 nm) we use a growth rate from the low end of observed values (0.5 nm h^{-1}) together with the average CS.

[23] Figure 8a shows how J_3 decreases as a function of RH at the average and slow growth cases. In the average case, J_3 at RH = 90% is 0.63 of its value at 10% RH. Thus, it is quite improbable that high RH values could mask nucleation events very efficiently at average conditions. In the slow growth conditions, on the other hand, J_3 drops by a factor of 15, indicating that masking of nucleation events could take place especially if $J_{1.5}$ is low. Figure 8b reveals that dry coagulation sink alone causes J_3 to be smaller than $J_{1.5}$ by a factor of about 400. Thus, if $J_{1.5}$ is 1 cm^{-3} s^{-1}, the dry sink alone causes J_3 to be 2.5×10^{-3} cm^{-3} s^{-1}, and the event would be barely observable. The increase of the sink at increased RH would then cause complete masking of the event. Thus, it appears that increased coagulation sink, under certain conditions, may cause the observed suppression of NPF events at high RH values. However, the requirements for that are a low nucleation rate at 1.5 nm, a low *GR* (in other words, the event needs to be rather weak to begin with), and an appreciable CoagS. Thus, it appears that the increase of the coagulation sink at high RH is at most a secondary reason for the observed suppression of NPF at high RH values.

[24] The following section discusses how much increased CoagS (as well as increased CS and decreased OH formation) may affect observed new particle formation rates.

4. Numerical Modeling

4.1. Model Description and Setup

[25] The proposed reasons for inhibition of NPF at high RH (i.e., reduced H_2SO_4 formation rate, increased condensation sink, and increased coagulation sink) were further investigated with an aerosol dynamics model UHMA [*Korhonen et al.*, 2004]. This box model has previously been used in several studies of NPF [e.g., *Grini et al.*, 2005; *Tunved et al.*, 2006; *Komppula et al.*, 2006; *Sihto et al.*, 2009].

[26] NPF was simulated for 5 h periods at a wide range of conditions representing both clean and polluted environments. In all the simulations, we assumed activation nucleation [*Kulmala et al.*, 2006] together with coagulation and condensation of H_2SO_4 and a low volatile nonhygroscopic organic compound (saturation concentration of 10^6 cm^{-3}). We calculated explicitly the production of H_2SO_4 from the SO_2 + OH reaction and its loss by condensation and nucleation, whereas the concentration of the organic vapor was assumed constant. The latter assumption may not be true in atmospheric conditions where the condensable organic vapors are likely formed in photooxidation of plant-emitted VOCs. However, using a constant profile instead of an OH-dependent profile in the simulations does not change the conclusions of this study and is thus assumed here to simplify the interpretation of the model result. For each simulation the concentrations of OH and of SO_2 were fixed (however, they varied between the simulations) and thus the H_2SO_4 production rate was constant.

[27] Table 1 lists the different values used for SO_2 concentration (affecting the concentration of H_2SO_4 via the SO_2 + OH reaction), organic vapor concentration (affecting the growth rate of newly formed particles), preexisting particle number concentration (one lognormal mode with geometric mean diameter of 300 nm and a standard deviation of 1.3, affecting the scavenging rate of newly formed particles), and an A factor for activation nucleation (nucleation rate at 1 nm $J = A[H_2SO_4]$), which affects the formation rate of new particles. The chosen preexisting particle concentrations correspond roughly to CS values 2, 20, and 200 h^{-1}. As all the simulations were performed at RH of 10–90%, with 5% increments, we simulated particle formation altogether at 1377 different conditions.

[28] For each of these conditions four model setups were used. For setup 1, the baseline run, OH concentration was set to 10^6 cm^{-3} below RH 60% and assumed to decrease linearly at higher RH (reaching 10^4 cm^{-3} at RH 100%). This assumption is based on a separate analysis with a chemical model [*Boy et al.*, 2005]. For setup 2, the fixed OH run, OH concentration was kept fixed at 10^6 cm^{-3} at all relative humidities. Comparison of this run to the baseline run reveals how much the reduction in the H_2SO_4 production rate affects the nucleation and NPF rates at high RH. Setup 3, the fixed CS run, was the same as the baseline run except that inside the model's condensation routine the particle size was always assumed to be the same as that at RH = 10%. The wet size at simulated RH was used for all other modeled processes. Comparison of this run to the baseline run shows how much the increase in the condensation sink due to higher RH affects the H_2SO_4 concentrations and thus nucleation and NPF rates. Setup 4, the fixed CoagS run, was the same as the baseline run except that inside the coagulation routine the particle size was always assumed to be the same as that at RH = 10%. The wet size at simulated RH was used for all other modeled processes. Comparison of this run to the baseline run shows how much the increase in the coagulation sink due to higher RH affects scavenging of nucleated clusters and thus particle formation rates at 3 nm

Table 2. Variables Used in Model Simulations

	OH (cm^{-3})	RH in CS Calculation (%)	RH in CoagS Calculation (%)
Setup 1	10^4–10^6	10–90	10–90
Setup 2	fixed at 10^6	10–90	10–90
Setup 3	10^4–10^6	fixed at 10	10–90
Setup 4	10^4–10^6	10–90	fixed at 10

(J_3). For each of these conditions we summarize the four setups used in the model simulations and present these in Table 2. It should be noted that while in reality CS and CoagS values are not independent of each other, in the model they can be fixed separately in order to study their relative importance on the inhibition of nucleation.

4.2. Numerical Modeling Results and Discussion

[29] For each of the simulations we calculated the mean H_2SO_4 concentration, nucleation rate (particles formed at 1 nm), and NPF rate (formation rate of 3 nm particles) over the length of the simulation (5 h). It should be noted that although the model assumed that particles form at 1 nm, the conclusions presented below would apply also to particles formed at 1.5 nm.

[30] In Figure 9, we present the ratio of the baseline run mean values to the sensitivity run mean values (model setups 2–4 in the list above). Values below 1 indicate that the mean value in the baseline run is suppressed compared to the sensitivity run. The magnitude of this suppression demonstrates the importance of the RH dependence of OH concentration (setup 2), condensation sink (setup 3) and coagulation scavenging (setup 4) on NPF, respectively. Note that we have left 252 cases out from Figure 9, cases in which the apparent formation rate J_3 in the baseline run was negligibly small (below 10^{-10} cm^{-3} s^{-1}).

[31] In accordance with the data analysis performed above, Figure 9 (top left) shows that high RH affects NPF mainly via reduction of OH concentration which leads on average to 59% less H_2SO_4 at RH = 90% than at RH < 60%. The lowered H_2SO_4 is directly translated to slower cluster formation at 1 nm which together with slower initial growth rate due to H_2SO_4 leads to a reduced NPF rate (Figure 9, middle and Figure 9, bottom, respectively). On average the simulated J_3 is reduced by 81% and it is evident that in many of the cases the nucleation event is suppressed totally.

[32] It is important to notice, however, that the RH effect on the condensation sink (Figure 9, middle) is also of some significance. At high RH the increased CS can reduce

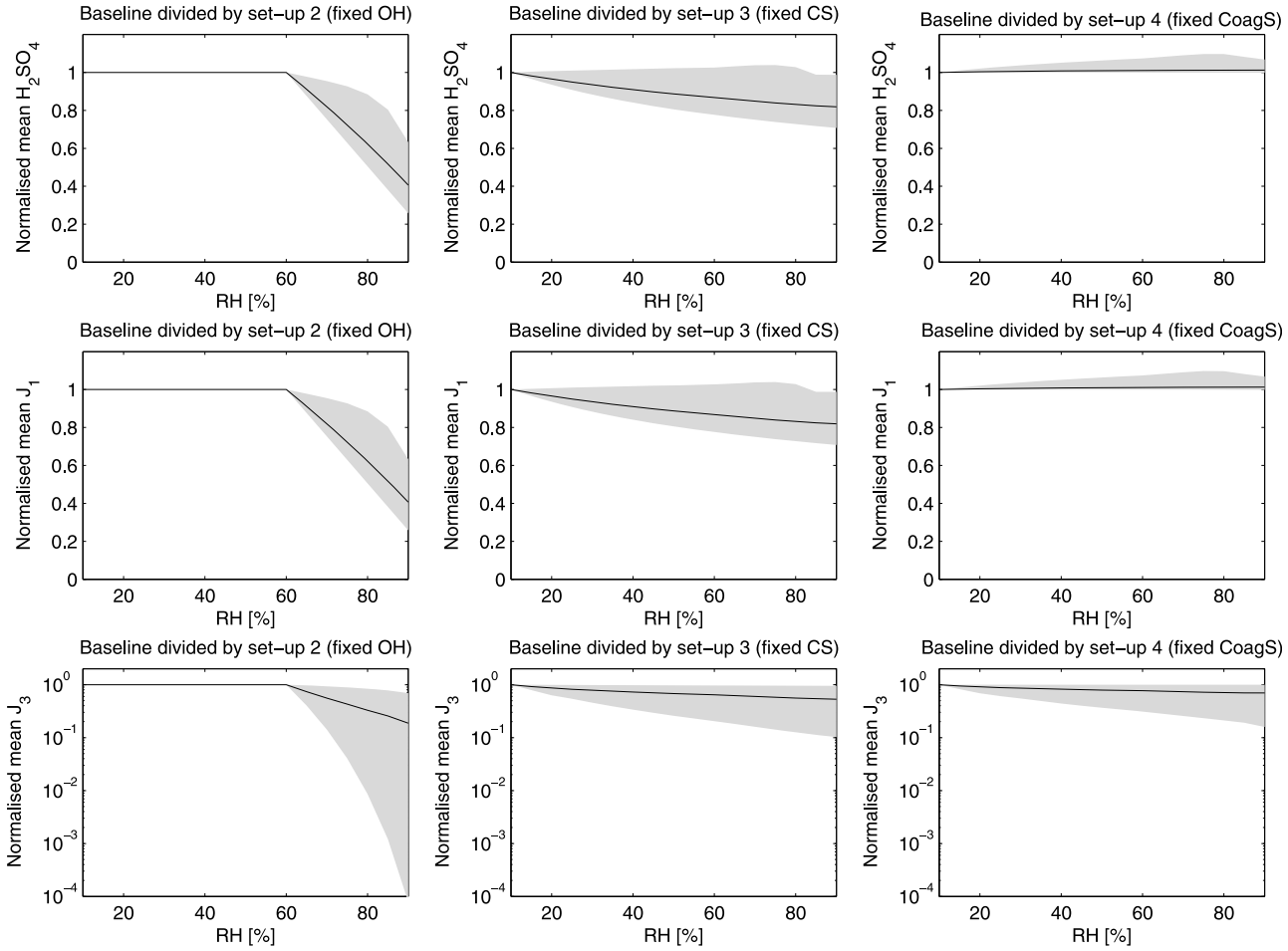

Figure 9. Mean (top) H_2SO_4 concentration, (middle) nucleation rate ($J_{1.5}$), and (bottom) NPF rate (J_3) in the baseline run normalized by the mean values of the sensitivity runs. The shaded area indicates the range of all simulations and the solid curve the mean of the ratios at each relative humidity.

the H_2SO_4 by up to 29% compared to dry atmosphere. On average, this effect leads to 47% lower particle formation rate at RH = 90% than it would were the condensation sink independent of RH. The effect of increased coagulation sink (Figure 9, right) on the NPF rate is of the same magnitude as that of increased CS (mean reduction now 30%). As expected, the effect of the coagulation sink on the H_2SO_4 and J_1 is of minor importance.

[33] Here, the RH dependence of OH concentration was obtained from a separate analysis with a chemical model. However, some observational studies suggest a weaker RH dependence for the OH concentration. For example, should the dependence arise from cloudiness, *Matthijsen et al.* [1998] observed an ~90% drop in OH at surface compared to above cloud values. Therefore, we repeated the model runs at all 1377 conditions assuming that the OH concentration drops to 10^5 cm^{-3} (and not to 10^4 cm^{-3}) at RH = 100%. This change had only a very minor effect on the ratios presented in Figure 9, which suggests that our conclusions are robust regarding the magnitude of OH concentration drop at high relative humidities.

5. Conclusions

[34] There are several reasons why RH has been observed to be anticorrelated with continental NPF: (1) Enhanced coagulational scavenging of sub-3 nm clusters at high RH, (2) diminished solar radiation at high RH leading to diminished gas phase oxidation chemistry, and (3) increased condensation sink of condensable gases due to hygroscopic growth of the preexisting particles. In our study, we used analysis of field measurements (e.g., the QUEST 2003 campaign at Hyytiälä, Finland), theoretical calculations, and box model simulations to examine the role of these factors in detail.

[35] Analysis of the field measurements indicate that sulphuric acid concentrations decreased significantly at RH above 60%. At high RH (>80%) nucleation rates mostly were below 2 cm^{-3} s^{-1} where the H_2SO_4 concentrations were below 3×10^6 cm^{-3}. We then tried to separate the factors contributing to H_2SO_4 formation and loss rates as a function of RH. Overall, there was no significant RH dependence for the measured SO_2 concentration although the maximum SO_2 values decreased slightly with RH during the 2003 QUEST campaign. On the other hand, the UV radiation intensity, which is a proxy for OH concentration, decreased clearly with increasing RH. The interesting finding is that the UV radiation trend was very similar to that of the measured H_2SO_4 concentrations, which suggests that the concentration of H_2SO_4 at high humidities is controlled by the reduced OH formation rate. It must be noted, however, that the sink term for H_2SO_4 increased by a factor of ~3 from 30 to 90% RH, and thus may have played some role in the inhibition of nucleation at high RH.

[36] One reason for the anticorrelation between UV radiation and RH is that their diurnal cycles show opposite trends (while radiation intensity peaks at noon, the RH cycle exhibits a minimum at that time). Moreover, a 30 year data set of cloudiness, RH, and global radiation from the Jokioinen observatory (~100 km from Hyytiälä station) showed that low-level cloud cover correlated with ground level RH, and as a result, global solar radiation is anticorrelated with RH. As a result, RH is anticorrelated with OH production. We therefore conclude that, even though at first glance RH appears to limit NPF, this appearance is due to its anticorrelation with solar radiation. This finding was also supported by the box model simulations.

[37] Further analysis on the role of increased condensation sink and coagulational scavenging was made using theoretical calculations of average and extreme conditions at Hyytiälä as well as box model simulations at a range of clean and polluted conditions. This analysis revealed that while the increased uptake of water by particles does affect the concentration of nucleating vapors and survival of nucleating clusters to some extent, these effects are typically minor in comparison to the reduced OH effect.

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