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Sulfuric acid and OH concentrations in a boreal forest site

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Abstract. As demonstrated in a number of investigations, gaseous sulfuric acid plays a central role in atmospheric aerosol formation. Using chemical ionization mass spectrometer the gas-phase sulfuric acid and OH concentration were measured in Hyytiälä, SMEAR II station, Southern Finland during 24 March to 28 June 2007. Clear diurnal cycles were observed as well as differences between new particle formation event days and non-event days. Typically, the daily maximum concentrations of gas phase sulfuric acid varied from 3×10^5 to 2×10^6 molec cm^{-3} between non-event and event days. Noon-time OH concentrations varied from 3-6×10^5 molec cm^{-3} and not a clear difference between event and non-events was detected. The measured time series were also used as a foundation to develop reasonable proxies for sulfuric acid concentration. The proxies utilized source and sink terms, and the simplest proxy is radiation times sulfur dioxide divided by condensation sink. Since it is still challenging to measure sulfuric acid in ambient concentrations, and due to its significant role in atmospheric particle formation, reasonable proxies are needed. We use all together three different proxies and one chemical box model and compared their results to the measured data. The proxies for the sulfuric acid concentration worked reasonably well, and will be used to describe sulfuric acid concentrations in SMEAR II station, when no measured sulfuric acid data is available. With caution the proxies could be applied to other environments as well.

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1 Introduction

An important phenomenon associated with the atmospheric aerosol system is the formation of new atmospheric aerosol particles. Atmospheric aerosol formation consists of a complicated set of processes that include the production of nanometer-size clusters from gaseous vapors, the growth of these clusters to detectable sizes, and their simultaneous removal by coagulation with the pre-existing aerosol particle population (Kerminen et al., 2001; Kulmala, 2003). It has been proposed, and confirmed by observations, that atmospheric new particle formation depends on the sulfuric acid concentration (Weber et al., 1996, 1997; Kulmala et al., 2006). Recent theoretical and observational results predict that atmospheric clusters (Kulmala et al., 2007) are activated and sulfuric acid is an important player in this process. In addition, large amounts of neutral ammonium bisulfate clusters have been predicted theoretically (Vehkamäki et al., 2004).

As demonstrated in a number of investigations (Kulmala et al., 2004; Kulmala and Kerminen , 2009), gaseous sulfuric acid plays a central role in atmospheric aerosol formation. A technique for measuring the gas-phase sulfuric acid concentration even down to about 10^4 molec cm^{-3} has already been available for more than a decade (Eisele and Tanner, 1993; Berresheim et al., 2000). As a result, a number of field campaigns have been performed that allow us to look at connections between the gas-phase sulfuric acid concentration and aerosol formation rate, both in laboratory and atmospheric conditions.

In the laboratory experiments (Viisanen et al., 1997; Berndt et al., 2005), particle number concentration is found

to have a power-law dependency on the sulfuric acid concentrations having exponents ranging from 4 to 10. On the other hand in the atmospheric conditions this dependency is not as strong (Weber et al., 1996, 1997; Kulmala et al., 2006; Sihto et al., 2006; Riipinen et al., 2007), with an exponent of only 1–2.

In addition to initial formation, sulfuric acid contributes to the growth of aerosol particles. However, there are strong indications that condensing vapors other than sulfuric acid are frequently needed to explain the observed particle growth rates (Kulmala et al., 2001b; Held et al., 2004; Fiedler et al., 2005; Boy et al., 2005; Sihto et al., 2006). Oxidation products of volatile organic compounds (VOCs) are viable candidates to explain the missing growth component (Kulmala et al., 2001a). A few methods are available to estimate source strengths of these compounds. It can be calculated from observed particle growth rates (Kulmala et al., 2005) or by measuring their concentrations directly (Sellegri et al., 2005). Concentrations of potential condensable vapors can also be estimated based on measured VOC emission rates (Tarvainen et al., 2005) then modeling their subsequent oxidation in the boundary layer (Boy et al., 2006). This latter method would benefit from measured hydroxyl radical concentrations as it is together with ozone the main driver of atmospheric oxidation of VOCs during daytime.

In order to obtain reliable information on the relationship of in situ sulfuric acid with new particle formation events and their subsequent growth, atmospheric measurements of sulfuric acid concentrations and also OH concentrations are needed. In the case when no measured data of sulfuric acid concentrations are available also physically sound proxies are needed. The aim of this study is to present results from a field campaign conducted in Hyytiälä, Finland, and to develop physically sound proxies, and investigate their capabilities to predict ambient sulfuric acid concentrations.

We measured gaseous phase sulfuric acid with a Chemical Ionization Mass Spectrometer (CIMS). With the same instrument we also monitored hydroxyl radical concentrations, which is the main day-time oxidizing agent in the atmosphere. Measured concentrations were compared with modeled sulfuric acid and OH abundances. Several proxies for sulfuric acid concentrations were explored. Similar measurements of sulfuric acid and proxy estimates have been performed e.g. at the Hohenpeissenberg meteorological observatory (Rohrer and Berresheim, 2006; Berresheim et al., 2000). The derived proxy in Rohrer and Berresheim (2006) uses the photolysis rate of ozone as a more direct source term in production of sulfuric acid. The measurement of UV-B radiation is, however, more common, and the aim here is to examine a proxy that can be more readily applied. Furthermore, Rohrer and Berresheim (2006) considered in their proxy only the source term of OH. For H_2SO_4 proxy also the sink term is important (e.g. Weber et al., 1997), and the proxies developed here take this into account. Although these proxies cannot capture high frequency variation in the sulfuric acid, they can be used to describe average variability in the sulfuric acid concentrations. With the aid of these proxies we are able to produce a time series of a proxy-sulfuric acid for the time periods without direct measurements of gas phase sulfuric acid.

2 Experimental setup

Measurements presented in this study were conducted at SMEAR II (Station for measuring Forest Ecosystem-Atmosphere Relations) located in Hyytiälä, Southern Finland. The site is surrounded by 42-year-old pine dominated forest (*Pinus Sylvestris* L.). Detailed information about the continuous measurements and the infrastructure can be found elsewhere (Vesala et al., 1998; Kulmala et al., 2001b; Hari and Kulmala, 2005). These observations were done as a part of "European Integrated project on Aerosol Cloud Climate and Air Quality Interactions" (EUCAARI) project (Kulmala et al., 2009) field campaign. The measurements presented in this study were conducted between 24 March and 28 June 2007.

2.1 Selected Ion Chemical Ionization Mass Spectrometer, SICIMS

Sulfuric acid and hydroxyl radical concentrations in the gas phase were measured with a technique utilizing selected chemical ionization and subsequent detection with a mass spectrometer. The technique is described in more detail in Tanner et al. (1997); Mauldin III et al. (1998) and references therein. The CIMS was operated inside a seatainer, approximately 400 m southwest of the main SMEAR II measurement station.

2.1.1 H_2SO_4

Measurement of sulfuric acid with the CIMS consists of several steps. First the sample is drawn inside through an inlet (inner diameter 10.2 cm) with a high flow rate (∼1400 l per min, lpm) to minimize wall losses. From the main inlet flow a sample (typically 10 lpm) is extracted coaxially via a thin walled 1.91 cm stainless steel tube.

The sample is then directed to an ion reaction region, where ambient sulfuric acid molecules react with NO_3^--reagent ions. The reagent ions are generated by adding a small amount of nitric acid to nitrogen flow and then exposing them to an alpha-active Am^{241} (activity 6.67 MBq) radioactive source.

Inside an ion reaction region the sample flow is surrounded by a concentric flow containing the reagent ions. Since the two flows are laminar, the air containing NO_3^- in the outer core of the flow and sample with atmospheric air containing variable amounts of H_2SO_4 do not turbulently mix with each other. The mixing of the sample with the reagent ions is done in a controlled manner by applying voltage between a set

of ion lenses, which generate an electric field pushing the reagent ions towards the centerline of the sample flow in the drift tube.

Inside the ion reaction region the ambient sulfuric acid reacts with the reagent ions

$$H_2SO_4 + NO_3^- \rightarrow HSO_4^- + HNO_3 \quad \text{(R1)}$$

At the end of the ion reaction region the charged ions are directed through a pinhole to a vacuum system by an attractive potential. The ions pass through a layer of dry and clean nitrogen gas flowing across the pinhole. This prevents clustering of the ions in particular with water.

The next stage is a Collision Dissociation Chamber (CDC) inside the vacuum system. The pressure is approximately 13 Pa (0.1 Torr), so the ions are in free expansion. The CDC consists of a set of resistors in series generating an electric field less repulsive to the ions deeper down the vacuum system. Inside the CDC the ions undergo numerous collisions with the N_2-molecules leaving the core ion species (NO_3^- and HSO_4^-) (Eisele, 1986).

The beam of ions is then collimated with conical octopoles operating in 0.13 Pa ($\sim 10^{-3}$ Torr) and directed to a mass filter (quadrupole mass spectrometer). The ions are then detected with a channeltron.

Concentration of H_2SO_4 is calculated from the measured ion signals as

$$[H_2SO_4] = C \cdot \frac{HSO_4^-}{NO_3^-}, \quad (1)$$

where C is directly measured calibration coefficient (Mauldin, III et al., 1999), which was in this study $4.7 \pm 0.5 \times 10^9$ (2σ). One measurement cycle is completed in 30 s. A nominal detection limit of the CIMS instrument is 5×10^4 molec cm^{-3} (Mauldin III et al., 2001) for a 5 min integration period.

2.1.2 OH

The measurement of hydroxyl radical relies on the detection of isotopically labeled sulfuric acid with the method described in the previous section. This technique is discussed in (Eisele and Tanner, 1991, 1993; Tanner et al., 1997) in more detail.

In short, inside the sampling inlet a small amount ($\sim 3 \times 10^{13}$ molec cm^{-3}) of isotopically labeled $^{34}SO_2$ is sprayed to the sample flow with a front injector.

The ambient OH is then titrated into isotopically labeled sulfuric acid via

$$OH + {}^{34}SO_2 + M \rightarrow H{}^{34}SO_3 + M \quad \text{(R2)}$$

$$H{}^{34}SO_3 + O_2 \rightarrow {}^{34}SO_3 + HO_2 \quad \text{(R3)}$$

$${}^{34}SO_3 + 2H_2O + M \rightarrow H_2{}^{34}SO_4 + H_2O + M \quad \text{(R4)}$$

By using isotopically labeled $^{34}SO_2$ one is able to differentiate between naturally occurring sulfuric acid and the labeled sulfuric acid, which is proportional to the OH concentration in the sample air. The labeled sulfuric acid shows at mass 99 in the mass spectrum whereas the ambient sulfuric acid is detected at mass 97. To measure a background OH signal, propane is added with the $^{34}SO_2$ in large enough concentration to remove 98% of the OH present in the sample flow.

To prevent recycling of HO_x and RO_2 back into OH, a second set of injectors is used to inject propane into the the sample flow in high concentration in a continuous basis. The second injector pair is located some 0.05 m downstream from the first set. Propane reacts rapidly with any OH cycled back from the reservoir species (HO_x and RO_2) with O_3 or NO. A more detailed description of the injectors and sampling chemistry can be found in Tanner et al. (1997).

During a CIMS measurement cycle, H_2SO_4 was measured 10 times followed by 20 measurements of combined OH and H_2SO_4 concentrations each lasting typically 30 s. The concentrations were averaged over 5 min.

OH-calibrations were performed every two weeks both to confirm the measured OH-concentrations and to check the overall performance of the instrument. Calibrations were done by photolyzing a controlled amount of water vapor with a mercury lamp producing a light at 184.9 nm wavelength. These energetic photons photolyze water vapor to OH in high quantities. The amount of OH produced depends on water vapor concentration, sample flow rate, intensity of the mercury lamp and H_2O cross section for the 184.9 nm light. During calibrations flow rates and ambient dew point were monitored. The intensity of the mercury lamp was mapped approximately once a month with a solar blind vacuum diode, which was compared with a National Institute of Standards and Technology (NIST) standard diode. Using this calibration method, the overall uncertainty of the OH concentration is 32% and the detection limit in a single measurement is 2×10^5 molec cm^{-3} (Tanner et al., 1997). For a 5-min integrated concentration the detection limit for OH is 5×10^4 molec cm^{-3} (Mauldin III et al., 2001).

2.2 Ancillary data

Several trace gas phase concentrations were measured during the campaign from a 70-m-tall mast from different heights. For characteristic values, mean values of 30 min averages at 16.8-m height were used in the study. Sulfur dioxide was measured with a fluorescence analyzer (Model 43S, Thermo 20 Environmental Instruments Inc., detection limit 0.1 ppb).

Global solar radiation (wavelength λ=0.30−4.8 μm) and UV-B (λ=0.28−0.32 μm) were measured above the forest at 18 m height. The sensors were Reemann TP 3 pyranometer (Astrodata, Toravere, Tartumaa, Estonia) and SL 501 UVB pyranometer (Solar Light, Philadelphia, PA, USA) for global and UV-B, respectively.

Aerosol size distributions were measured with a Differential Mobility Particle Sizer (DMPS). The system (Aalto et al., 2001) measures particles from 3 nm to about 950 nm in diameter in 10 min. The aerosol size distribution was used to classify the days in terms of occurrence of new particle production events. A scheme presented in (Dal Maso et al., 2005) was utilized as the days were divided into 3 sub-groups (event and non-event days and undefined days). In addition, the observed size distributions were used to calculate loss rates of gas-phase sulfuric acid utilizing condensation sink (CS) presented in Kulmala et al. (2001a).

2.3 Proxy calculations and model simulations

Ambient sulfuric acid concentrations are depicted by its sinks and sources. Sulfur dioxide is the main precursor as it oxidizes to sulfuric acid through radical reactions and the main sink is collisions with aerosol particles. To gauge sulfuric acid source rate indirectly, we calculated several proxy concentrations based on measured gaseous phase concentrations, solar radiation and measured aerosol size distribution acting as a condensation sink (Kulmala et al., 2001a) for the sulfuric acid molecules.

The hydroxyl radical is a crucial component in sulfuric acid formation. It is mainly formed via photolysis of ozone by solar radiation in UV-B range (280–320 nm), generating excited oxygen atoms. They are subsequently either quenched by collisions with N_2 and O_2, or they react with ambient water vapor to generate OH. In the following proxies the only source of sulfuric acid concidered is the oxidation of SO_2 by OH and the condensational sink CS is provided by the pre-existing aerosol particle population. A direct proxy for the sulfuric acid utilized measured hydroxyl radical concentrations (e.g. Weber et al., 1997)

$$P_1 = \frac{k_1 \cdot [SO_2] \cdot [OH]}{CS}, \quad (2)$$

and the other two proxies were calculated using solar radiation in UV-B range and global radiation:

$$P_2 = k_2 \cdot \frac{[SO_2] \cdot UVB}{CS} \quad (3)$$

and

$$P_3 = k_3 \cdot \frac{[SO_2] \cdot Glob}{CS}, \quad (4)$$

The scaling factors k_1, k_2 and k_3 are empirically derived factors, which scale the proxy variables to correspond to the measured sulfuric acid concentrations. The scaling factors were derived from the ratios of measured sulfuric acid concentrations and the proxy concentrations, including only the measurements during which the sun was over 15 degrees above the horizon. This minimum solar angle was used to define the day-time in order to diminish the effect of radiation difference between the mast, where the sensors were located, and the forest floor, where the CIMS was operating as well as account for the lengthening of the day as the spring progressed. At the beginning of the measurement campaign these limiting hours were from 8.37 to 16.23 and in the end, few days after the midsummer, from 5.37 to 19.14.

Sulfuric acid proxy based on photolysis rate of ozone would be more accurate in calculating the source term of sulfuric acid. However, proxy based on UV-B or global radiation measurement is more simpler to apply to different measurement settings, as the solar radiation components are more commonly monitored than ozone photolysis rate directly.

A pseudo-steady state chemical box-model was used to calculate sulfuric acid and OH concentrations. This model is described and successfully verified against measured sulfuric acid data in Hyytiälä in Boy et al. (2005). Unlike the proxies, the modeled concentrations could be compared with the measured concentrations also at night. The night hours were selected as those during which the sun was below the horizon.

All the fittings to the data were made with a bivariate fitting method presented by York (1966) and further described by York et al. (2004) and Cantrell (2008). In this method the ratio of the x- and y-dimensional variances of each data point is crucial for having the best possible fit. Because the lowest measured time resolution was 10 min, the resolution of particle measurements providing the condensational sink *CS*, we calculated first 10 min averages of the rest of the data. These values were then used to calculate 30-min averages and further variances and covariances for every data point in order to approximate the propagating errors.

3 Results and discussion

3.1 Sulfuric acid

Figure 1 presents the sulfuric acid data set as a whole. Since sulfuric acid is mainly produced photochemically, a clear diurnal cycle is apparent. Typical maximum measured values reached 2×10^6 molec cm^{-3} during the measurement campaign in spring-summer 2007. Clearly higher sulfuric acid concentrations are measured during new particle formation event days since during these days clear sky prevails, which promote photochemical activity. There is no apparent trend in maximum daily sulfuric acid concentrations from spring to summer. However, the new particle formation events were more frequent during the spring months, which is typical of Hyytiälä (Dal Maso et al., 2005).

In the first proxy the source of sulfuric acid is the oxidation of SO_2 by OH, which both are measured quantities. In the second proxy the OH-concentration is approximated with measured UV-B radiation intensity. The correlation between these two quantities during the whole campaign was good, a correlation coefficient being 0.76. In the third proxy we used global radiation instead of the UV-B radiation.

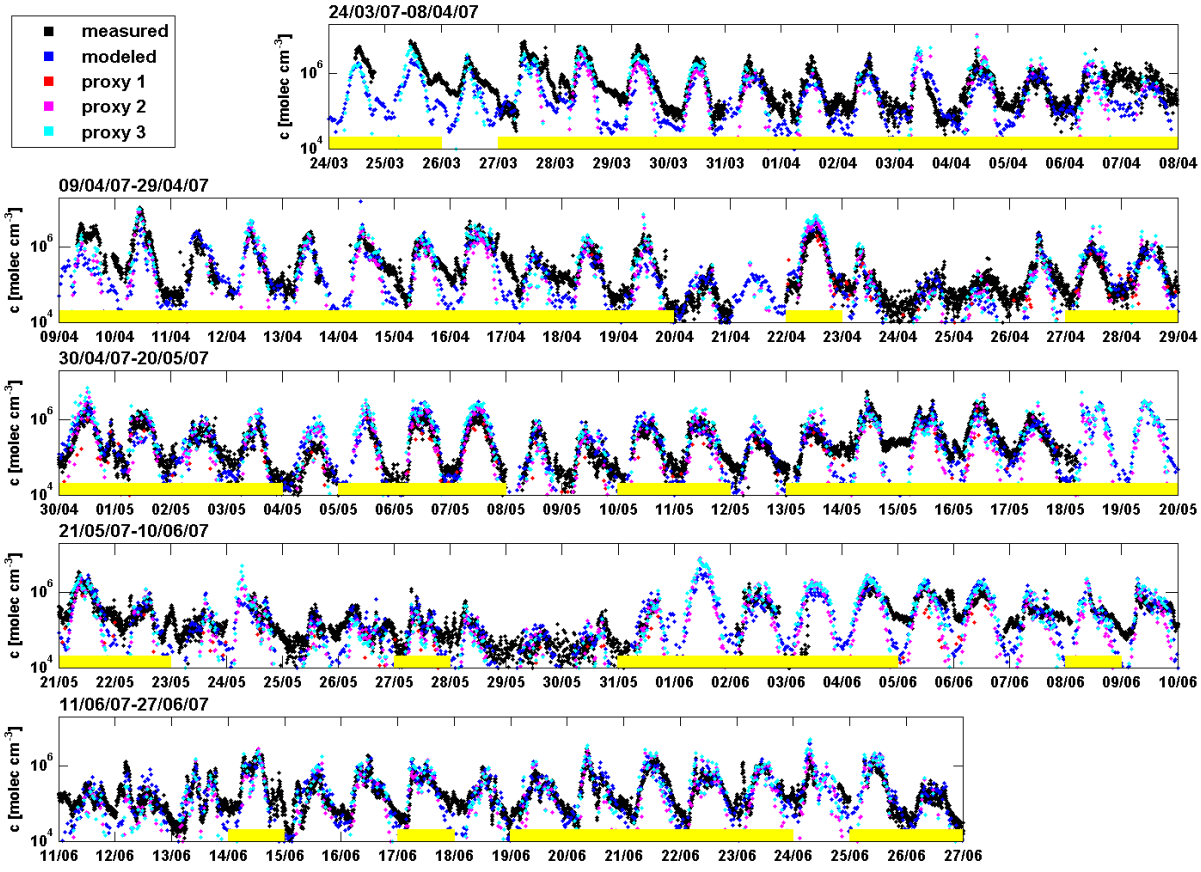

Fig. 1. Timeseries of 30-min averaged measured (black), modeled (blue) and proxy-estimated concentrations (red, magenta and cyan) of sulfuric acid from 24 March to 27 June 2007 in Hyytiälä. Days with new particle formation are indicated with yellow bar at the bottom of the graph.

The proxy concentrations depend crucially on the scaling factors k_1, k_2 and k_3. These factors were calculated from Eqs. (2–4) by replacing the left hand sides of the equations with the measured sulfuric acid concentration. Median values for the scaling factors were 2.2×10^{-12} cm^3 molec^{-1} s^{-1}, 9.9×10^{-7} m^2 W^{-1} s^{-1} and 2.3×10^{-9} m^2 W^{-1} s^{-1} for k_1, k_2 and k_3, respectively. The scaling factors were not significantly dependent on temperature, but all three correlated clearly with the OH concentration or radiation, whichever was used for calculating the coefficient (Fig. 2). Fitting with a form

$$k_i = (A \cdot x_i^B) \quad (5)$$

was used to calculate a scaling factor for each proxy as a function of the OH concentration, UV-B or global radiation as x_1, x_2 and x_3, respectively. The fitted coefficients A and B were 8.6×10^{-10} and -0.48 for k_1, 1.4×10^{-7} and -0.70 for k_2, and 8.4×10^{-8} and -0.68 for k_3.

It is remarkable that the factor k_1 combining the measured sulfuric acid concentration and the proxy utilizing OH measurements had a clear anticorrelation with the measured OH concentration. The factor k_1 should be equal to the rate coefficient of the reaction OH+SO_2+M→HSO_3+M, which is considered as the rate-limiting step of sulfuric acid formation. Median reaction rate coefficient has a value of 9.2×10^{-13} cm^6 molec^{-2} s^{-1} that was calculated according to DeMore et al. (1997). The input parameters used in the calculations were obtained as 30-min averaged data on ambient temperature and barometric pressure data logged at the SMEAR II station. The calculated reaction rate coefficient varied only in a decimal scale. The reason for the factor k_1 being larger than this in almost all the data points can be explained by either too low H_2SO_4 production or too high sink utilized in the proxy. Because the used sink should rather be too low than too high due to e.g. hygroscopic growth of the particle population and as no chemical removal of H_2SO_4, SO_2 or OH is accounted for, we expect that the source term is too low. Furthermore, the increase of the factor k_1 while the measured OH-concentration decreases, implies that the CIMS underestimates the OH concentrations at low concentrations.

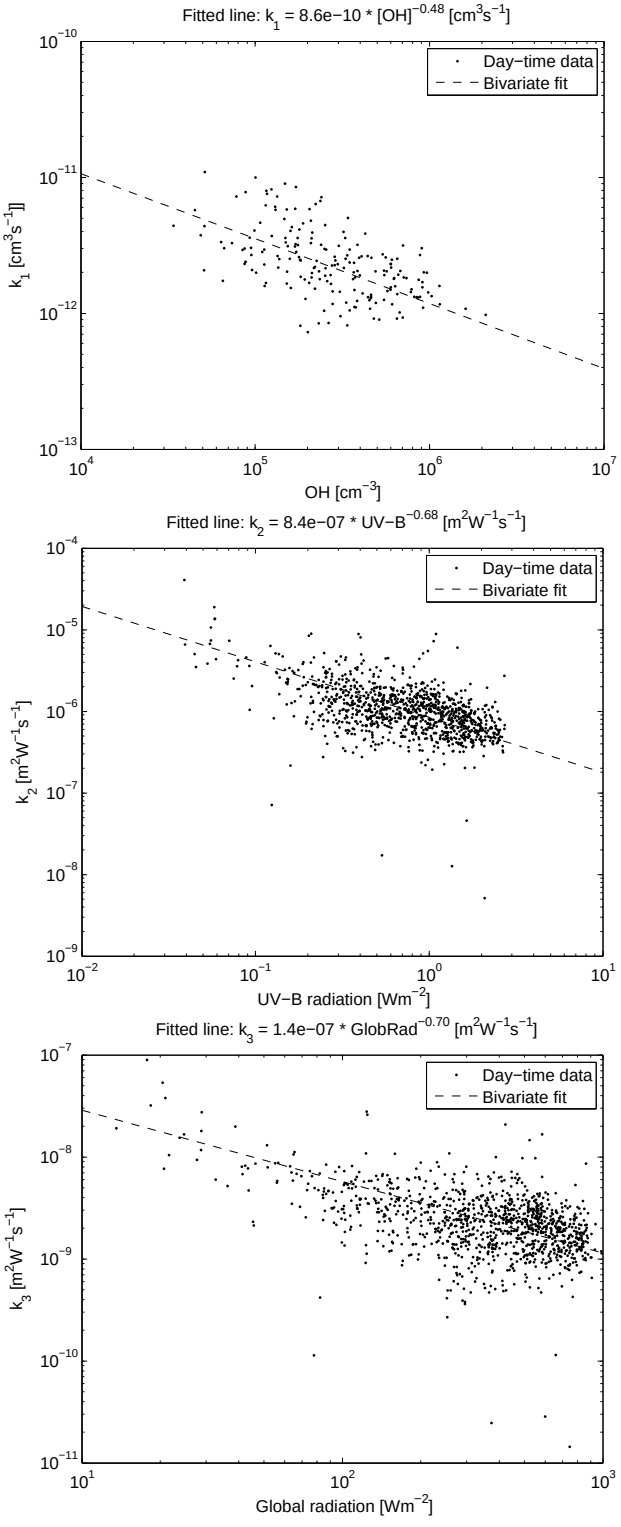

Fig. 2. The sulfuric acid proxy scaling factors, calculated from Eqs. 2–4 by replacing the left hand sides with the measured concentrations, during day-time for **(a)** OH proxy, **(b)** UV-B proxy and **(c)** the proxy utilizing global radiation.

Overall, the modeled and proxy variables followed the measured sulfuric acid concentrations well. During evenings, however, we sometimes observed (see e.g. 16 April 2007) higher sulfuric acid concentrations, which were neither captured by the model nor the proxies. These incidents were typically also accompanied by peaks in sub-20 nm particle concentrations, which indicates that they could be related to processes not included in the model, e.g. local pollution from passing cars or activities in the station. Another plausible explanation are unidentified volatile organic compounds (VOC) not represented in the model. These compounds can act as a missing sink in OH during day-time and while reacting with ozone during night-time can produce OH and lead to sulfuric acid production at night.

The ozone reactions of α- and β-pinene produce on average 0.7 and 0.3 OH-molecules per reaction, respectively (Master Chemical Mechanism, University of Leeds, 2008). In order to prevent the overestimation of night-time OH production in the box-model, the other monoterpenes were modeled to produce 0.1 OH-radicals per ozone reaction, since the quantitative values are not available hitherto. The overall monoterpene concentration was divided into concentrations of specified monoterpenes by roughly estimating the fractions of different monoterpenes in Hyytiälä to be constantly equal to the emissions presented by Tarvainen et al. (2005) including the specific reaction rates.

The only night-time source of H_2SO_4 used in the model was the SO_2 reaction with OH, the source of which is described above. The other possible sources were estimated to be only of a minor importance.

Medians of the daily maximum sulfuric acid concentrations are presented in Table 1. The median of the measured sulfuric acid daily maxima was 1.42×10^6 molec cm^{-3} and the interquartile range from 0.9×10^6 to 2.47×10^6 molec cm^{-3} in 5-min time resolution. The 30-min averaged values were 1.1×10^6, 0.6×10^6 and 2.01×10^6 molec cm^{-3} for the median, 25% and 75% percentiles, respectively. The daily maximum concentrations reproduced with the model and proxies were very close to the measured 30-min averaged values, closest being the OH based proxy with median 1.1×10^6 molec cm^{-3}. The proxies utilizing the UV-B and global radiation data instead of the measured OH-concentration, as well as the model, overestimated the maximum concentrations slightly (medians 1.4×10^6, 1.5×10^6 and 1.3×10^6 molec cm^{-3}, respectively).

Measured sulfuric acid concentrations were compared with the proxy results and the modeled concentrations. All the data was averaged to 30 min in order to have enough data points within the average to calculate covariances used for weighting the errors in x- and y-direction for the fitting procedure. The correlations are presented in Fig. 3. All of the proxies produced concentrations very close to the measured values. Proxies utilizing the measured UV-B and global

Table 1. Daily maximum sulfuric acid and OH concentrations in Hyytiälä between 24 March and 27 June 2007.

	25%	50%	75%
H_2SO_4 [10^5 molec cm^{-3}]			
measured (5-min)	9.0	14.2	24.7
measured (30-min)	6.0	10.4	20.1
modeled	8.7	13.3	21.5
proxy 1	5.1	11.4	22.4
proxy 2	7.4	14.1	21.4
proxy 3	8.2	15.0	24.4
OH [10^5 molec cm^{-3}]			
measured (5-min)	5.7	7.7	10.6
measured (30-min)	4.9	6.3	9.1
modeled	12.9	17.9	23.0

radiation to calculate the estimates for the sulfuric acid concentrations performed quite equally having correlation coefficients of 0.82 and 0.81, respectively. The best correlation (R=0.90) with the measurements was obtained, as expected, with the first proxy using the OH-concentration as the input parameter. Also the slope closest to unity was achieved with OH-based proxy, slope value being 1.03. The slope values for the proxies relying on the UV-B and global radiation were 0.93 and 0.88, respectively. This illustrates the importance of the solar radiation to the atmospheric chemistry. If applied to the atmospheric conditions, both the measured UV-B and the global radiation levels should give reasonably accurate approximation of the concentrations, given that the scaling coefficient is determined reliably against measured sulfuric acid values.

Also the modeled sulfuric acid concentrations correlated fairly well (R=0.58, Fig. 4) with the measured concentrations, when only day-time hours were considered. A slightly better correlation (R=0.65) is obtained for the whole data set. However, the slope of the bivariate regression lines increased from 0.97 during the daytime to 1.44 when all data points were taken into account, due to the underestimation of the nighttime concentrations in the model. The correlation for the entire data set equals to the verification results (R=0.645) presented in Boy et al. (2005) based on data obtained during spring 2003 against a different Chemical Ionization Mass Spectrometer derived sulfuric acid concentrations.

According to Boy et al. (2005) during the 2003 campaign the mean value of the daily averaged (from 9 a.m. to 3 p.m.) ratios between measured and calculated H_2SO_4 concentrations for the whole period reached a value close to unity with a standard deviation of 0.412. The investigated sulfuric acid closure thus achieved a high agreement between the calculated and measured sulfuric acid concentrations. In this work the mean value for the measurement-model ratio for day-time data was 1.4, the median was 1.0 and the standard deviation was 1.3. For the whole data set including night-time

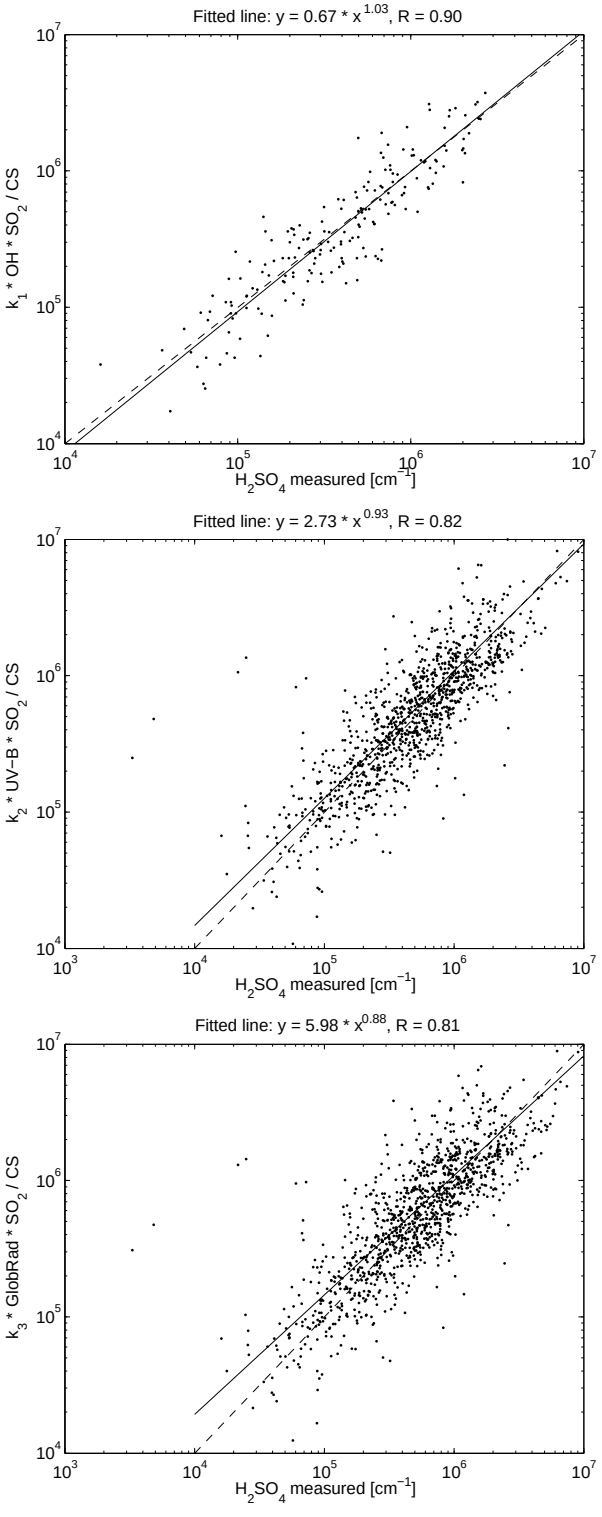

Fig. 3. Correlation and bivariate fits of measured sulfuric acid concentration and proxy utilizing **(a)** measured OH-concentrations, **(b)** UV-radiation and **(c)** global radiation. Blue line is 1:1 line, black line is fitted to data set, which considers only day-time data.

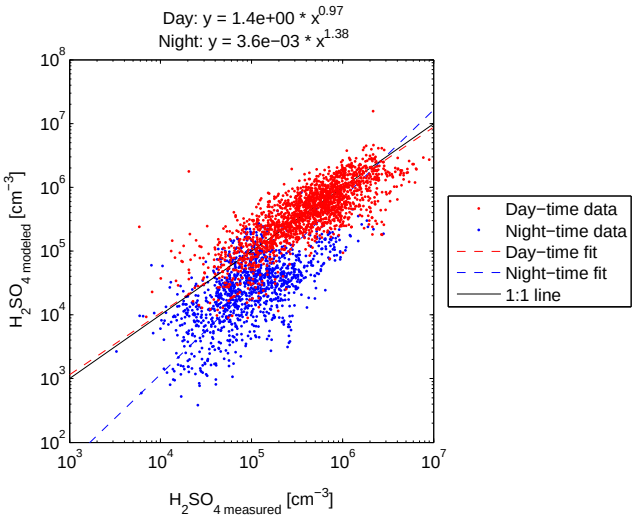

Fig. 4. Correlation and bivariate fits of measured and modeled sulfuric acid concentrations for day-time (red) and night-time (blue) data. Black line is 1:1 line, red and blue lines are fitted to the data sets.

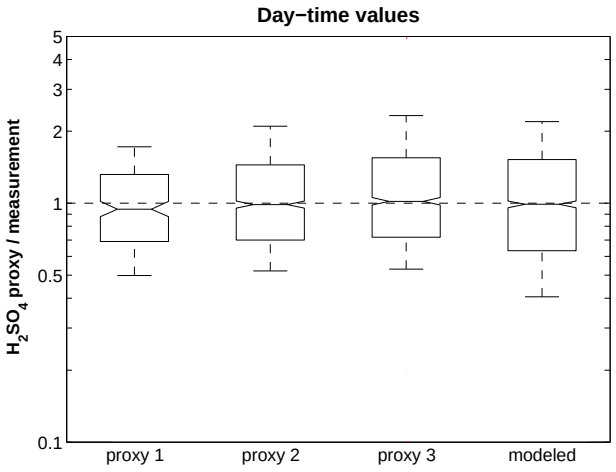

Fig. 5. Variations in the ratios of the proxy and modeled to measured sulfuric acid concentrations. The box illustrates the 25th and 75th percentiles, the line in the box the median value, and the whiskers the 10th and 90th percentiles.

the corresponding values were 3.2, 1.5 and 5.3, respectively. However, we calculated these values taking into account all the data points, not daily averages as Boy et al. (2005).

The medians, interquartile values as well as the 10th and 90th percentile values of the ratios of the proxies and modeled concentration to the measured concentration are presented in Fig. 5. 84% of the concentrations produced with the proxy utilizing the measured OH concentrations were less than a factor of two larger or smaller than the measured sulfuric acid concentration. The corresponding percentage for the UV-B and global radiation based proxies were 80% and 78%, and for the modeled concentrations it was 72%. Thus, the sulfuric acid concentrations in Hyytiälä can be estimated with a reasonable accuracy with either one of the proxies relying on the radiation measurements.

3.2 Typical diurnal cycle of sulfuric acid

The median diel cycle of sulfuric acid is presented in Fig. 6 based on the measured, modeled and proxy variables. The data-set is divided into two classes, which separates the days with new particle formation occurring (event days) from the rest of the days (non-event days). The measured midday maximum sulfuric acid concentration is 1×10^6 molec cm^{-3}. In a rural continental site of Hohenpeissenberg in Southern Germany, Birmili et al. (2003) reported that median diurnal cycle in the summer months during the event days reached an order of magnitude higher values up to 1×10^7 molec cm^{-3}. The concentration sulfuric acid in the gas phase is controlled by its sources and sinks. In order to assess the apparent differences in the event day median concentrations between Hohenpeissenberg and Hyytiälä both have to be taken into account.

Also the new particle formation depends on the interplay with the sinks and the sources (Kulmala et al., 2005). A large sink provided by the pre-existing sink does not necessarily hinder the formation as the events are observed in vastly different, both urban and pristine, environments (Kulmala et al., 2004, 2005). In Hyytiälä the geometric mean dry CS during event days is 1.7×10^{-3} s^{-1} (Dal Maso et al., 2007). On average, the corresponding ambient CS is by a factor of 1.48 larger (Dal Maso et al., 2005), which keeps the median CS during new particle events still below the values typically observed at Hohenpeissenberg during event days (Birmili et al., 2003).

The production of sulfuric acid depends strongly on the precursor (SO_2) concentration as well as the availability of the oxidants and to a small extent due to temperature and pressure dependency of the rate constants. Hohenpeissenberg station has been classified as a representative measurement location for central Europe (Naja et al., 2003), whereas Hyytiälä station represents a boreal forest environment with a less anthropogenic influence. The main boundary layer sources of SO_2 are anthropogenic fossil fuel use whereas naturally it is formed via DMS oxidation, out of which the former is the dominant in both Hyytiälä and in Hohenpeissenberg. Density of human population and industrial activity in general is higher in the region of Hohenpeissenberg, which is reflected also by the NO_x and CO levels mainly originating from north-west (Poland, Chech Republic) to Hohenpeissenberg (Kaiser et al., 2007), which are the major sources also for sulfur dioxide (Vestreng et al., 2007). Main source areas to Hyytiälä are Kola Peninsula, Estonian industry in Narva and long-range transport from central Europe. Although trend in the regional SO_2 emissions are decreasing around Europe (e.g. Vestreng et al., 2007), it is

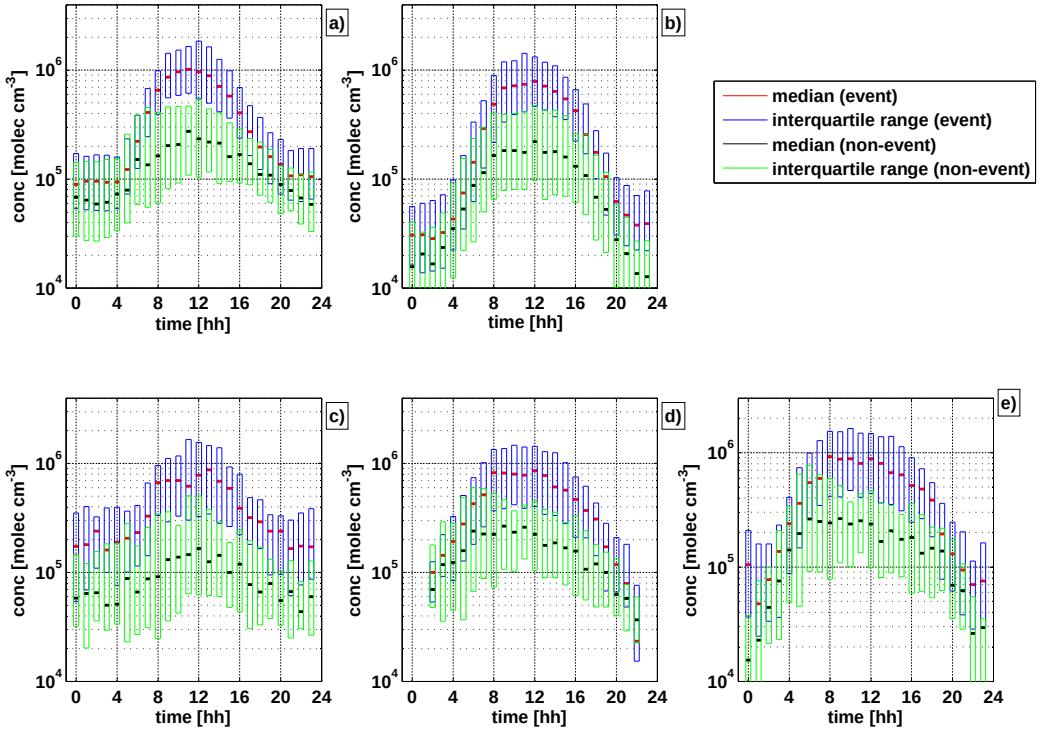

Fig. 6. Median diurnal cycle of **(a)** measured, **(b)** modeled, and **(c)–(e)** proxy calculated sulfuric acid during all measurement days during the EUCAARI field campaign in Hyytiälä and after grouping the days into two classes with and without new particle formation. Bar height describes interquartile range (25%–75%) of the concentrations.

plausible to assume that on average the sulfur dioxide levels are slightly higher in Hohenpeissenberg than in Hyytiälä.

The overall hydroxyl radical levels were higher in Hohenpeissenberg, mid-day maximum being typically 6×10^6 molec cm^{-3} during event days and 4×10^6 molec cm^{-3} during other days, whereas in this study the measured OH was an order of magnitude lower and the modeled OH by a factor of 4–6 lower than observed in Hohenpeissenberg. For more discussion see Sect. 3.3.

As a summary, comparing the diel cycles of sulfuric acid between Hyytiälä and Hohenpeissenberg revealed that in both locations the sulfuric acid was higher during the days when new particle formation was observed than compared with the days without new particle formation. The median concentration levels, however, were different. In Hohenpeissenberg both the event day and non-event day concentrations (1×10^7 molec cm^{-3} and 3×10^6 molec cm^{-3}, respectively) were typically one order of magnitude higher than the concentrations in Hyytiälä (1×10^6 molec cm^{-3} and 2×10^5 molec cm^{-3}, respectively) with a similar classification between the days. In Hyytiälä the modeled and proxies captured these features between the event and non-event days and the concentrations were consistent with the measured values (Fig. 6). The differences between the measured sulfuric acid concentrations between the sites are attributed to the variability of the sink and the source terms. While the sink to the pre-existing particulate population in Hohenpeissenberg seems to be larger, it is compensated by a larger source term due to arguably higher pre-cursor concentrations and to larger oxidation capacity of the atmosphere. Albeit using the same method (CIMS) for the sulfuric acid measurements, there could also be differences stemming from the individual CIMS instruments. Thus, both a more detailed comparison between the sites and an inter-comparison between the individual CIMS instruments is needed in the future.

3.3 OH

The measured and modeled hydroxyl radical concentrations follow each other pretty well (see Fig. 7 for the whole time series). Although qualitatively the diurnal cycle is similar, the measured concentration was typically smaller than the modeled OH. Median of the daily maxima of the 30 min averaged OH concentrations was 6.3×10^5 molec cm^{-3} whereas the corresponding modeled value was 17.9×10^5 molec cm^{-3}. The modeled maximum concentration was on average three times larger than the measured value (median ratio was 2.9, and the 10th and the 90th percentiles 1.5 and 5.9, respectively.

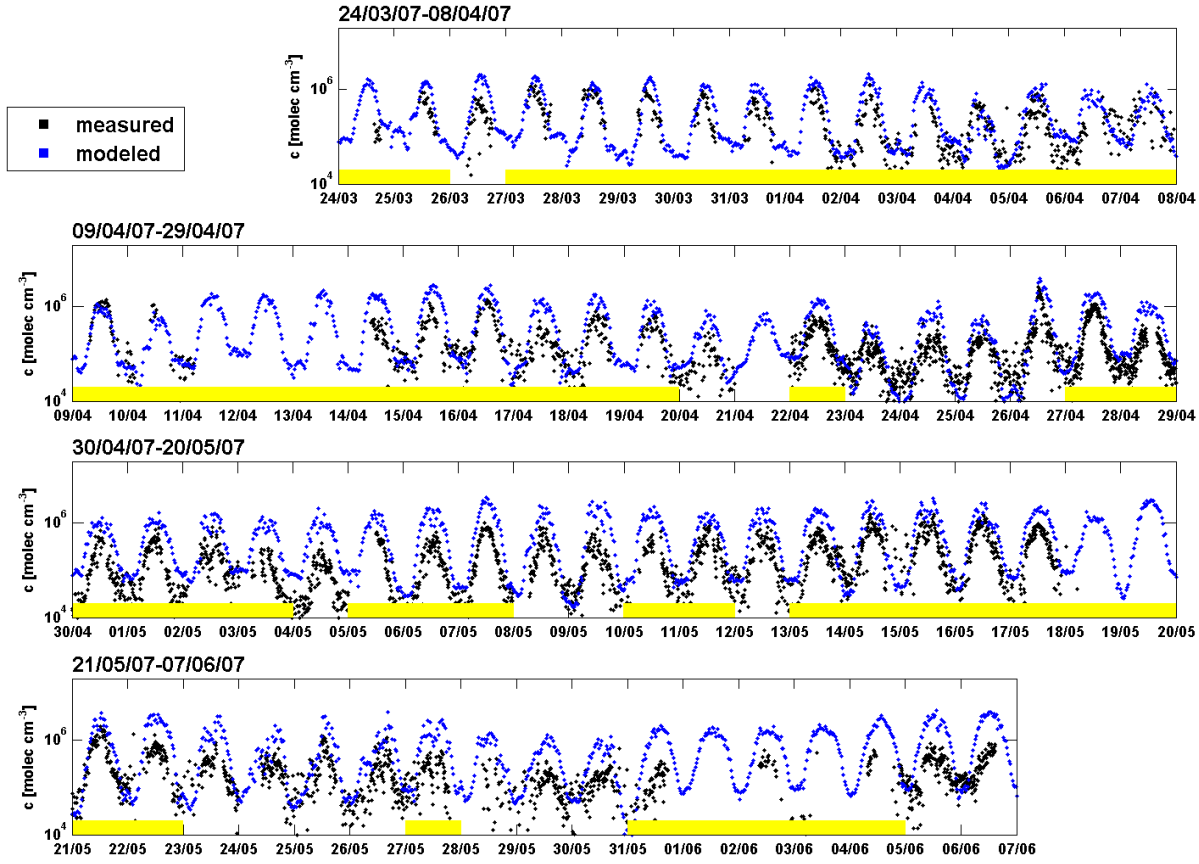

Fig. 7. Timeseries of 30-min averaged measured (black) and modeled (blue) concentrations of hydroxyl radical from 24 March to 6 June 2007 in Hyytiälä. Days with new particle formation are indicated with yellow bar at the bottom of the graph.

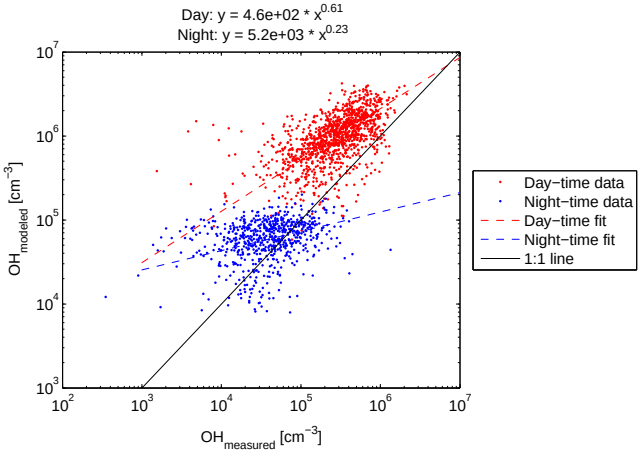

Fig. 8. Correlation and bivariate fits of measured and modeled hydroxyl radical concentrations for day-time (red) and night-time (blue) data. Black line is 1:1 line, red and blue lines are fitted to the data sets.

The correlation between the measured and modeled OH is presented in Fig. 8. The mean and median ratios between modeled and measured concentrations were 5.6 and 3.5 during day-time, and 5.0 and 2.9 when all the data is considered, respectively. The correlation coefficients were 0.56 for day-time data and 0.72 for all the data. The slope fitted to the day-time data points was 0.61. The night-time slope was 0.23, and thus the modeled concentration did not follow the measured concentration as well as during the day, even though the data points were on average closer to one-to-one line. As all data points were considered, the slope value increased to 1.10.

In previous comparisons the model-to-measurement discrepancies in terms of OH concentrations has been up to 40% (Crosley, 1995; Mauldin III et al., 1998; Shirley et al., 2006) depending on the location. Also the model to measurement agreement varies from day-to-day (Handisides et al., 2003). In our study, the ratio between the modeled and measured concentrations correlated during the day with the measured ratio of monoterpene and isoprene concentrations to NO_x (not shown). This suggests that the overestimating feature

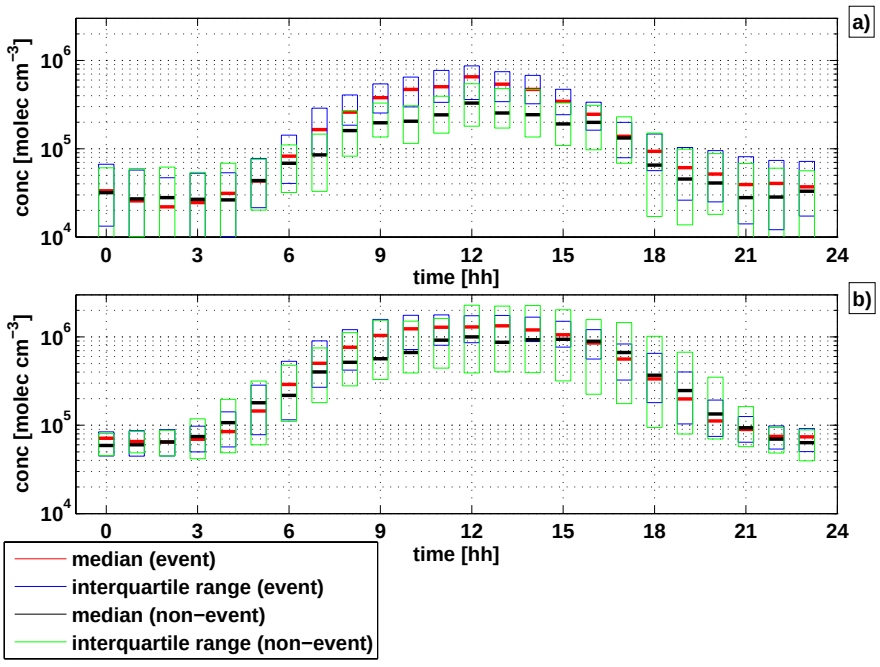

Fig. 9. Median diurnal cycle of **(a)** measured and **(b** modeled hydroxyl radical concentrations during all measurement days during the EUCAARI field campaign in Hyytiälä and after grouping the days into two classes with and without new particle formation. Bar height describes interquartile range (25%–75%) of the concentrations.

of the model is mainly due to missing VOC-chemistry acting as a sink for the hydroxyl radical. During night-time the ratio correlated negatively with the measured NO_x concentration. When the measured OH during night-time was larger than approximately 7×10^4 molec cm^{-3}, the model underestimated the OH concentrations whereas typically the model tended to over-estimated the OH (Fig. 8). These issues need further and more detailed investigations, where the measured and modeled OH concentrations are incorporated with the detailed VOC measurements.

Median hydroxyl radical concentrations were marginally higher during new particle formation event days (Fig. 9). The interquartile ranges of the two sets of data, however, overlapped indicating that the OH concentrations were not different between event and non-event days.

As discussed in Sect. 3.2, the measured sulfuric acid concentrations were typically an order of magnitude higher in Hohenpeissenberg (Birmili et al., 2003). Also the differences in the measured OH concentrations were of one order of magnitude, the values at Hyytiälä being lower. Without a possibility to properly compare day-to-day differences both in the uncertainties of the models and in the instruments as well as the variable characteristic features of the emission potentials of various VOCs and oxidant levels in surroundings of the two measurement sites, only some general remarks can be given, which can affect this difference.

On average, the oxidation capacity in Hohenpeissenberg seems to be slightly larger. Due to southern location and a higher altitude, the intensity of solar radiation is higher. Thus the production rate of OH is larger. Naja et al. (2003) showed that residence time in Europe increased ozone concentrations by about 2 ppb day^{-1} during spring and summer months in Hohenpeissenberg. Typical ozone concentrations in the boundary layer during summer months varied from 45 and 56 ppb, between background and photochemically aged air masses. During this campaign in Hyytiälä the median ozone concentration was 37 ppb. The nitrate radical concentrations in Hohenpeissenberg is estimated to be 6 ppt (Bartenbach et al., 2007) whereas the calculations of Hakola et al. (2003) indicate that the NO_3 levels in Hyytiälä are 2.5–3.5 ppt in the summer months. Thus, on average, the oxidant levels are higher in Hohenpeissenberg than in Hyytiälä.

There are also differences in the VOC concentrations between Hyytiälä and Hohenpeissenberg. According to Hakola et al. (2003), seasonal average for a mid-day mean concentration in summer is in the range of 250 ppt for monoterpenes, alpha-pinene being the largest. From aromatic compounds, benzene and toluene are dominating with seasonal averages in summer being 87 and 55 ppt. The monoterpene concentrations tended to increase from spring to summer whereas the aromatics had the opposite trend (Hakola et al., 2003). In Hohenpeissenberg, the aromatic VOC concentrations are typically higher, being approximately 200–250 ppt

(Birmili et al., 2003). The monoterpene levels, on the other hand, were quite similar to the values from Hyytiälä. In both places there are, however, a lot of day-to-day variability (e.g.Handisides et al., 2003; Rinne et al., 2005; Bartenbach et al., 2007) in the VOC concentrations.

As a summary, the reasons affecting the OH concentrations at the sites originate from the differences in the main oxidant levels and from their diurnal cycles and from the seasonal and diel variability of the VOC emissions. Some of these discrepancies could be addressed utilizing the different instruments in conjunction with several models in a single location.

4 Conclusions

Sulfuric acid and OH were measured with a Chemical Ionization Mass Spectrometer (CIMS) in Hyytiälä, Finland, in March–June 2007. The observation period is currently the longest period in Hyytiälä over which sulfuric acid has been measured. The OH concentration followed nicely UV-B radiation, and the sulfuric acid concentrations depended also on SO_2 concentrations and the condensation sink to the preexisting particles. With the aid of supporting measurements, we were able to derive three proxies for the sulfuric acid concentrations.

Measured sulfuric acid concentrations correlated well with all of the proxies as well as with the detailed pseudo-steady state chemical model results. This gives good indication that these kind of proxies can be used to estimate sulfuric acid concentration and also further the effect of sulfuric acid on new particle formation and subsequent growth. The prefactors enabling the calculation of absolute concentrations from the proxy calculations, however, could be site-specific and should be verified against measurements prior to utilization in other environments. Nevertheless, at Hyytiälä or at a similar kind of site the proxies can be used with caution, since their accuracy seems to be sufficient, 80% of the proxy concentrations were less than a factor of two larger or smaller than the measured concentrations during spring 2007 campaign.

Clear differences in the sulfuric acid concentrations were detected during new particle formation event days and non-event days. The observed results shows that sulfuric acid concentration is clearly higher during event days than in non-event days. More detailed data analysis utilizing the sulfuric acid measurements described in this work is in progress to elucidate the role of sulfuric acid in the new particle formation. This data provides an excellent opportunity to do this, since it is the longest available sulfuric acid data set in Hyytiälä SMEAR II station in the Boreal environment.

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References

Aalto, P., Hämeri, K., Becker, E., Weber, R., Salm, J., Mäkelä, J. M., Hoell, C., O'Dowd, C. D., Karlsson, H., Hansson, H.-C., Väkevä, M., Koponen, I. K., Buzorius, G., and Kulmala, M.: Physical characterization of aerosol particles during nucleation events, Tellus, 53B, 344–358, 2001.

Bartenbach, S., Williams, J., Plass-Dülmer, C., Berresheim, H., and Lelieveld, J.: In-situ measurement of reactive hydrocarbons at Hohenpeissenberg with comprehensive two-dimensional gas chromatography (GC×GC-FID): use in estimating HO and NO_3, Atmos. Chem. Phys., 7, 1–14, 2007, http://www.atmos-chem-phys.net/7/1/2007/.

Berndt, T., Böge, O., Stratmann, F., Heintzenberg, J., and Kulmala, M.: Rapid formation of sulfuric acid particles at near-atmospheric conditions, Science, 307, 698–700, 2005.

Berresheim, H., Elste, T., Plass-Dülmer, C., Eisele, F. L., and Tanner, D. J.: Chemical ionization mass spectrometer for long-term measurements of atmospheric OH and H_2SO_4, Int. J. Mass. Spectrom., 202, 91–109, 2000.

Birmili, W., Berresheim, H., Plass-Dülmer, C., Elste, T., Gilge, S., Wiedensohler, A., and Uhrner, U.: The Hohenpeissenberg aerosol formation experiment (HAFEX): a long-term study including size-resolved aerosol, H_2SO_4, OH, and monoterpenes measurements, Atmos. Chem. Phys., 3, 361–376, 2003, http://www.atmos-chem-phys.net/3/361/2003/.

Boy, M., Kulmala, M., Ruuskanen, T. M., Pihlatie, M., Reissell, A., Aalto, P. P., Keronen, P., Dal Maso, M., Hellen, H., Hakola, H., Jansson, R., Hanke, M., and Arnold, F.: Sulphuric acid closure and contribution to nucleation mode particle growth, Atmos. Chem. Phys., 5, 863–878, 2005, http://www.atmos-chem-phys.net/5/863/2005/.

Boy, M., Hellmuth, O., Korhonen, H., Nilsson, E. D., ReVelle, D., Turnipseed, A., Arnold, F., and Kulmala, M.: MALTE - model to predict new aerosol formation in the lower troposphere, Atmos. Chem. Phys., 6, 4499–4517, 2006, http://www.atmos-chem-phys.net/6/4499/2006/.

Crosley, D.: The measurement of OH and HO_2 in the atmosphere, J. Atmos. Sci., 52, 3299–3314, 1995.

Cantrell, C. A.: Technical Note: Review of methods for linear least-squares fitting of data and application to atmospheric chemistry problems, Atmos. Chem. Phys., 8, 5477–5487, 2008, http://www.atmos-chem-phys.net/8/5477/2008/.

Dal Maso, M., Kulmala, M., Riipinen, I., Wagner, R., Hussein, T., Aalto, P. P. and Lehtinen, K. E. J.: Formation and Growth of Fresh Atmospheric Aerosols: Eight Years of Aerosol Size Distribution Data from SMEAR II, Hyytiälä, Finland, Boreal Environ. Res., 10, 323–336, 2005.

Dal Maso, M., Sogacheva, L., Aalto, P. P., Riipinen, I., Komppula, M., Tunved, P., Korhonen, L., Suur-Uski, V., Hirsikko, A., Kurtén, T., Kerminen, V.-M., Lihavainen, H., Viisanen, Y., Hansson, H.-C., and Kulmala, M.: Aerosol size distribution measurements at four Nordic field stations: identification, analysis and trajectory analysis of new particle formation bursts, Tellus, 59B, 350–361, 2007.

DeMore, W., Sander, S., Golden, D., Hampson, R., Kurylo, M., Howard, C., Ravishankara, A., Kolb, C., and Molina, M.: Chemical kinetics and photochemical data for use in stratospheric modeling, Evaluation 12, JPL Publ, 97-4, 266, 1997.

Eisele, F.: Identification of tropospheric ions, J. Geophys. Res., 91, 7897–7906, 1986.

Eisele, F. and Tanner, D.: Ion-assisted tropospheric OH measurements, J. Geophys. Res., 96, 9295–9308, 1991.

Eisele, F. and Tanner, D.: Measurement of the gas phase concentration of H_2SO_4 and methane sulfonic acid and estimates of H_2SO_4 production and loss in the atmosphere, J. Geophys. Res., 98, 9001–9010, 1993.

Fiedler, V., Dal Maso, M., Boy, M., Aufmhoff, H., Hoffmann, J., Schuck, T., Birmili, W., Hanke, M., Uecker, J., Arnold, F., and Kulmala, M.: The contribution of sulphuric acid to atmospheric particle formation and growth: a comparison between boundary layers in Northern and Central Europe, Atmos. Chem. Phys., 5, 1773–1785, 2005, http://www.atmos-chem-phys.net/5/1773/2005/.

Goldstein, A. and Galbally, I.: Known and unexplored organic constituents in the Earth's atmosphere, Environ. Sci. Technol., 41, 1514–1521, 2007.

Hakola, H., Tarvainen, V., Laurila, T., Hiltunen, V., Hellén, H., and Keronen, P.: Seasonal variation of VOC concentrations above a boreal coniferous forest, Atmos. Environ., 37, 1623–1634, 2003.

Handisides, G. M., Plass-Dülmer, C., Gilge, S., Bingemer, H., and Berresheim, H.: Hohenpeissenberg Photochemical Experiment (HOPE 2000): Measurements and photostationary state calculations of OH and peroxy radicals, Atmos. Chem. Phys., 3, 1565–1588, 2003, http://www.atmos-chem-phys.net/3/1565/2003/.

Hari, P. and Kulmala, M.: Station for Measuring Ecosystem-Atmosphere Relations (SMEAR II), Boreal Environ. Res., 10, 315–322, 2005.

Held, A., Nowak, A., Birmili, W., Wiedensohler, A., Forkel, R., and Klemm, O.: Observations of particle formation and growth in a mountaneous forest region n central Europe, J. Geophys. Res., 109, D23204, doi:10.1029/2004JD005346, 2004.

Kaiser, A., Scheifinger, H., Spangl, W., Weiss, A., Gilge, S., Fricke, W., Ries, L., Cemas, D., and Jesenovec, B.: Transport of nitrogen oxides, carbon monoxide and ozone to the Alpine Global Atmospheric Watch stations Jungfraujoch (Switzerland), Zugspitze and Hohenpeissenberg (Germany), Sonnblick (Austria) and Mt. Krvavec (Slovenia), Atmos. Environ., 41, 9273–9287, 2007.

Kerminen, V. M., Pirjola, L., and Kulmala, M.: How signifigantly does coagulation scavening limit atmospheric particle production?, J. Geophys. Res., 106, 24119–24125, 2001.

Kulmala, M.: How Particles Nucleate and Grow, Science, 302, 1000–1001, 2003.

Kulmala, M., Dal Maso, M., Mäkelä, J. M., Pirjola, L., Väkevä, M., Aalto, P. P., Miikkulainen, P., Hämeri, K., and O'Dowd, C. D.: On the formation, growth and composition of nucleation mode particles, Tellus B, 53, 479–490, 2001a.

Kulmala, M., Hämeri, K., Aalto, P. P., Mäkelä, J. M., Pirjola, L., Nilsson, E. D., Buzorius, G., Rannik, Ü., Dal Maso, M., Seidl, W., Hoffmann, T., Janson, R., Hansson, H.-C., Viisanen, Y., Laaksonen, A., and O'Dowd, C. D.: Overview of the international project on biogenic aerosol formation in the boreal forest (BIOFOR), Tellus B, 53, 324–343, 2001b.

Kulmala, M., Vehkamäki, H., Petäjä, T., Dal Maso, M., Lauri, A., Kerminen, V.-M., Birmili, W., and McMurry, P.: Formation and growth rates of ultrafine atmospheric particles: a review of observations, J. Aerosol Sci., 35, 143–176, 2004.

Kulmala, M., Petäjä, T., Mönkkönen, P., Koponen, I. K., Dal Maso, M., Aalto, P. P., Lehtinen, K. E. J., and Kerminen, V.-M.: On the growth of nucleation mode particles: source rates of condensable vapor in polluted and clean environments, Atmos. Chem. Phys., 5, 409–416, 2005, http://www.atmos-chem-phys.net/5/409/2005/.

Kulmala, M., Lehtinen, K. E. J., and Laaksonen, A.: Cluster activation theory as an explanation of the linear dependence between formation rate of 3 nm particles and sulphuric acid concentration, Atmos. Chem. Phys., 6, 787–793, 2006, http://www.atmos-chem-phys.net/6/787/2006/.

Kulmala, M., Riipinen, I., Sipilä, M., Manninen, H. E., Petäjä, T., Junninen, H., Dal Maso, M., Mordas, G., Mirme, A., Vana, M., Hirsikko, A., Laakso, L., Harrison, R. M., Hanson, I., Leung, C., Lehtinen, K. E. J., and Kerminen, V.: Toward direct measurement of atmospheric nucleation, Science, 318, 89–92, 2007.

Kulmala, M. and Kerminen, V.-M.: On the formation and growth of atmospheric nanoparticles, Atmos. Res., 90, 132–150, 2008.

Kulmala, M., Asmi, A., Lappalainen, H. K., Carslaw, K. S., Pöschl, U., Baltensperger, U., Hov, Ø., Brenquier, J.-L., Pandis, S. N., Facchini, M. C., Hansson, H.-C., Wiedensohler, A., and O'Dowd, C. D.: Introduction: European Integrated Project on Aerosol Cloud Climate and Air Quality interactions (EUCAARI) - integrating aerosol research from nano to global scales, Atmos. Chem. Phys., 9, 2825–2841, 2009, http://www.atmos-chem-phys.net/9/2825/2009/.

Mauldin III, R., Frost, G., Chen, G., Tanner, D., Prevot, A., Davis, D., and Eisele, F.: OH measurements during the First Aerosol Characterization Experiment (ACE 1): Observations and model comparisons, J. Geophys. Res., 103, 16713–16729, 1998.

Mauldin, III, R., Tanner, D., Heath, J., Huebert, B., and Eisele, F.: Observations of H_2SO_4 and MSA during PEM-Tropics-A, J. Geophys. Res., 104, 5801–5816, 1999.

Mauldin III, R., Eisele, F., Tanner, D., Kosciuch, E., Shetter, R., Lefer, B., Hall, S., Nowak, J., Buhr, M., Chen, G., Wang, P., and Davis, D.: Measurements of OH, H_2SO_4, and MSA at the South Pole during ISCAT, Geophys. Res. Lett., 28, 3629–3632, 2001.

Naja, M., Akimoto, H., and Staehelin, J.: Ozone in background and phtochemically aged air over central Europe: analysis of long-term ozonesonde data from Hohenpeissenberg and Payerne, J. Geophys. Res., 108, 4063, doi:10.1029/2002JD002477, 2003.

Nilsson, E., Rannik, Ü., Kulmala, M., Buzorius, G., and ODowd, C.: Effects of the continental boundary layer evolution, convec-

tion, turbulence and entrainment on aerosol tormation, Tellus, 53B, 441–461, 2001.

Rinne, J., Ruuskanen, T. M., Reissell, A., Taipale, R., Hakola, H., and Kulmala, M.: On-line PTR-MS measurements of atmospheric concentrations of volatile organic compounds in a European boreal forest ecosystem, Boreal Environ. Res., 10, 425–436, 2005.

Riipinen, I., Sihto, S.-L., Kulmala, M., Arnold, F., Dal Maso, M., Birmili, W., Saarnio, K., Teinilä, K., Kerminen, V.-M., Laaksonen, A., and Lehtinen, K. E. J.: Connections between atmospheric sulphuric acid and new particle formation during QUEST IIIIV campaigns in Heidelberg and Hyytiälä, Atmos. Chem. Phys., 7, 1899–1914, 2007, http://www.atmos-chem-phys.net/7/1899/2007/.

Rohrer, F. and Berresheim, H.: Strong correlation between levels of tropospheric hydroxyl radicals and solar ultraviolet radiation, Nature, 442, 184–187, 2006.

Sellegri, K., Hanke, M., Umann, B., Arnold, F., and Kulmala, M.: Measurements of organic gases during aerosol formation events in the boreal forest atmosphere during QUEST, Atmos. Chem. Phys., 5, 373–384, 2005, http://www.atmos-chem-phys.net/5/373/2005/.

Shirley, T. R., Brune, W. H., Ren, X., Mao, J., Lesher, R., Cardenas, B., Volkamer, R., Molina, L. T., Molina, M. J., Lamb, B., Velasco, E., Jobson, T., and Alexander, M.: Atmospheric oxidation in the Mexico City Metropolitan Area (MCMA) during April 2003, Atmos. Chem. Phys., 6, 2753–2765, 2006, http://www.atmos-chem-phys.net/6/2753/2006/.

Sihto, S.-L., Kulmala, M., Kerminen, V.-M., Dal Maso, M., Petäjä, T., Riipinen, I., Korhonen, H., Arnold, F., Janson, R., Boy, M., Laaksonen, A., and Lehtinen, K. E. J.: Atmospheric sulphuric acid and aerosol formation: implications from atmospheric measurements for nucleation and early growth mechanisms, Atmos. Chem. Phys., 6, 4079–4091, 2006, http://www.atmos-chem-phys.net/6/4079/2006/.

Sogacheva, L., Saukkonen, L., Nilsson, E., Dal Maso, M., Schultz, D., De Leeuw, G., and Kulmala, M.: New aerosol particle formation in different synoptic situations at Hyytiälä, Southern Finland, Tellus B, 60, 485–494, 2008.

Tanner, D., Jefferson, A., and Eisele, F.: Selected ion chemical ionization mass spectrometric measurement of OH, J. Geophys. Res., 102, 6415–6425, 1997.

Tarvainen, V., Hakola, H., Hellén, H., Bäck, J., Hari, P., and Kulmala, M.: Temperature and light dependence of the VOC emissions of Scots pine, Atmos. Chem. Phys., 5, 989–998, 2005, http://www.atmos-chem-phys.net/5/989/2005/.

University of Leeds: The Master Chemical Mechanism website, http://mcm.leeds.ac.uk/MCM/, last access: 30 September 2009, cited June, 2008.

Vehkamäki, H., Napari, I., Kulmala, M., and Noppel, M.: Stable ammonium bisulphate clusters in the atmosphere, Phys. Rev. Lett., 93, 148501, doi: 10.1103/PhysRevLett.93.148501, 2004.

Vesala, T., Haataja, J., Aalto, P., Altimir, N., Buzorius, G., Garam, E., Hämeri, K., Ilvesniemi, H., Jokinen, V., Keronen, P., Lahti, T., Markkanen, T., Mäkelä, J., Nikinmaa, E., Palmroth, S., Palva, L., Pohja, T., Pumpanen, J., Rannik, Ü., Siivola, E., Ylitalo, H., Hari, P., and Kulmala, M.: Long-term field measurements of atmosphere-surface interactions in boreal forest combining forest ecology, micrometeorology, aerosol physics and atmospheric chemistry, Trends in Heat, Mass & Momentum Transfer, 4, 17–35, 1998.

Vestreng, V., Myhre, G., Fagerli, H., Reis, S., and Tarrasón, L.: Twenty-five years of continuous sulphur dioxide emission reduction in Europe, Atmos. Chem. Phys., 7, 3663–3681, 2007, http://www.atmos-chem-phys.net/7/3663/2007/.

Viisanen, Y., Kulmala, M., and Laaksonen, A.: Experiments on gas-liquid nucleation of sulfuric acid and water, J. Chem. Phys., 107, 920–926, 1997.

Weber, R. J., Marti, J., McMurry, P. H., Eisele, F., Tanner, D. J., and Jefferson, A.: Measured atmospheric new particle formation rates: implications for nucleation mechanisms, Chem. Eng. Commun., 151, 53–64, 1996.

Weber, R. J., Marti, J. J., McMurry, P. H., Eisele, F. L., Tanner, D. J., and Jefferson, A.: Measurements of new particle formation and ultrafine particle growth rates at a clean continental site, J. Geophys. Res., 102, 4373–4385, 1997.

York, D.: Least-squares fitting of a straight line, Can. J. Phys., 44, 1079–1086, 1966.

York, D., Evensen, N. M., López Martinez, M., and De Basabe Delgado, J.: Unified equations for the slope, intercept, and standard errors of the best straight line, Am. J. Phys., 72(3), 367–375, 2004.