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Sulfuric acid and OH in Hyttiälä

T. Petäjä et al.

Sulfuric acid and OH concentrations in a boreal forest site

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Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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. The typical daily maximum concentrations of gas phase sulfuric acid varied from $3 \cdot 10^5$ to $2 \cdot 10^6$ molec cm^{-3} between non-event and event days. Noon-time OH concentrations varied from $3\text{--}6 \cdot 10^5$ molec cm^{-3} and not a clear difference between event and non-events was detected. Since it is still challenging to measure sulfuric acid, and due to its significant role in atmospheric particle formation, three different proxies and one chemical box model calculation were compared to the measured data. The proxies for the sulfuric acid concentration worked reasonably, and with caution, could be applied to other environments.

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

Sulfuric acid and OH in Hyytiälä

T. Petäjä et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



et al., 2004).

As demonstrated in a number of investigations (Kulmala et al., 2004), 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 molecules cm^{-3} has already been available for more than a decade (Eisele and Tanner, 1993). 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 (Sellegrì 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. The

Sulfuric acid and OH in Hyytiälä

T. Petäjä et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Sulfuric acid and OH
in Hyytiälä**

T. Petäjä et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

aim of this study is to present results from a field campaign conducted in Hyytiälä, Finland. 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. 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 field campaign.

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. The measurements were conducted between 24 March and 28 June 2007.

2.1.1 H₂SO₄

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 liters per minute, lpm) to minimize wall losses. From the main inlet flow a sample (typically 10 lpm) is extracted via a thin walled 1.27 cm stainless steel tube.

The sample is then directed to an ion reaction region, where ambient sulfuric acid molecules react with NO₃⁻-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 Am²⁴¹ (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 NO₃⁻ in the outer core of the flow and sample with atmospheric air containing variable amounts of H₂SO₄ 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



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 N₂-molecules leaving the core ion species (NO₃⁻ and HSO₄⁻) (Eisele, 1986).

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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

$$5 \quad [\text{H}_2\text{SO}_4] = C \cdot \frac{\text{HSO}_4^-}{\text{NO}_3^-}, \quad (1)$$

where C is directly measured calibration coefficient (Mauldin III et al., 1999). One measurement cycle is completed in 30 s. A nominal detection limit of the CIMS instrument is $5 \cdot 10^4$ molecule cm^{-3} (Mauldin III et al., 2001) for a 5 min integration period.

2.1.2 OH

10 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 ($\sim 3 \cdot 10^{13}$ molecule cm^{-3}) of isotopically labeled $^{34}\text{SO}_2$ is sprayed to the sample flow with a front injector.

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



20 By using isotopically labeled $^{34}\text{SO}_2$ 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

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



background OH signal, propane is added with the $^{34}\text{SO}_2$ 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 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% (Tanner et al., 1997).

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., detec-

Sulfuric acid and OH in Hyytiälä

T. Petäjä et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



tion limit 0.1 ppb).

Global solar radiation (wavelength $\lambda=0.30\text{--}4.8\ \mu\text{m}$) and UV-B ($\lambda=0.28\text{--}0.32\ \mu\text{m}$) were measured above the forest at 18 m height. The sensors were Reemann TP 3 pyranometer (Astrodata, Toravere, Tartumaa, Estonia) and SL 501A 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., 2005a) 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 generating excited oxygen atoms, which subsequently are either quenched by collisions with N_2 and O_2 , or they react with ambient water vapor to generate OH. A direct proxy for the sulfuric acid utilized measured hydroxyl radical concentrations (e.g. Weber et al., 1997)

$$P_1 = \frac{k_1 \cdot [\text{SO}_2] \cdot [\text{OH}]}{\text{CS}}, \quad (2)$$

Sulfuric acid and OH in Hyytiälä

T. Petäjä et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



where k_1 is rate coefficient of the reaction $\text{OH} + \text{SO}_2 + \text{M} \rightarrow \text{HSO}_3 + \text{M}$, which is the rate-limiting step of sulfuric acid formation. The rate coefficient for this association reaction depends both on temperature and pressure as presented in DeMore et al. (1997). The coefficient was calculated based on 30-min averaged ambient temperature and pressure data logged at the SMEAR II station. The median value for the k_1 was $9.2 \cdot 10^{-13} \text{ cm}^6 \text{ molec}^{-2} \text{ s}^{-1}$ and interquartile range (25%–75%) was 9.1 – $9.3 \cdot 10^{-13} \text{ cm}^6 \text{ molec}^{-2} \text{ s}^{-1}$.

Two additional proxies were calculated using a product of measured SO_2 abundance and solar radiation (in UV-B range and global radiation) divided by sink term (CS) provided by the pre-existing aerosol particle population:

$$P_2 = k_2 \cdot \frac{[\text{SO}_2] \cdot \text{UV} - \text{B}}{\text{CS}} \quad (3)$$

and

$$P_3 = k_3 \cdot \frac{[\text{SO}_2] \cdot \text{Glob}}{\text{CS}}, \quad (4)$$

where scaling factors 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. Only data between 09:00 to 15:00 (local time) was considered in the derivation of the scaling factors, but subsequently applied to all of the available proxy data.

A pseudo-steady state chemical box-model was used to calculate sulfuric acid and OH concentrations. This model was successfully verified against measured sulfuric acid data in Hyytiälä (Boy et al., 2005).

Sulfuric acid and OH in Hyytiälä

T. Petäjä et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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 $2 \cdot 10^6$ molecule cm^{-3} during the measurement campaign in spring-summer 2007. Clearly higher sulfuric acid concentrations are measured during new particle formation event days as 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 to Hyytiälä (Dal Maso et al., 2005b).

Two out of three of the proxy variables utilized solar radiation in the calculations. As the radiation diminishes in the evenings, the proxy estimates lose sensitivity and deviate from the measured concentrations. During night-time these proxies cannot be used due to non-existent radiation. As the nights are shorter in the summer, some proxy data is possible to obtain even during night-time. The proxy-concentrations depend crucially on the scaling factors k_2 and k_3 . These factors were calculated based on the ratios between the proxy and observed sulfuric acid concentrations. Median values for scaling factors were $8.8 \cdot 10^{-7}$ and $2.8 \cdot 10^{-9} \text{ m}^2 \text{ W}^{-1} \text{ s}^{-1}$ for k_2 and k_3 , respectively. The scaling factors were slightly temperature dependent (Fig. 2). Fitting with a form

$$k_{2,3} = 10^{(A \cdot T + B)} \quad (5)$$

was used to calculate the scaling factors as a function of ambient temperature T . The fitted coefficients A and B were 0.0028 and -7 and 0.0067 and -10 for k_2 and k_3 , respectively. Data points obtained between 09:00 and 15:00 (local time) were included in the fitting in order to produce representative daily maximum proxy concentrations.

Overall, the modeled and proxy variables followed the measured concentrations rather well. During evenings, however, we sometimes observed (see e.g. 16 April

Sulfuric acid and OH in Hyytiälä

T. Petäjä et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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 (e.g. OH yield from alpha-pinene with ozone equals 0.7, see University of Leeds Master Chemical Mechanism, 2008) and lead to sulfuric acid production at night.

Median of the daily maximum sulfuric acid are presented in Table 1. Median of the measured sulfuric acid daily maxima was $1.5 \cdot 10^6$ molecule cm^{-3} and the interquartile range from $9.2 \cdot 10^5$ to $2.6 \cdot 10^6$ molecule cm^{-3} in 5-min time resolution. The 30-min averaged values were $1.1 \cdot 10^6$, $6.2 \cdot 10^5$ and $2.2 \cdot 10^6$ molecule cm^{-3} for median, 25% and 75% percentiles, respectively. Modeled daily maximum values were slightly lower, median being $8.7 \cdot 10^5$ molecule cm^{-3} . The proxies relying on the measured OH underestimated the sulfuric acid concentrations by a factor of two whereas the proxies relying on the radiation measurements tended to over-estimate the sulfuric acid. The UV-B proxy reproduced concentrations closer to the measured values, being on average 20% higher than measured 30-min concentrations. This illustrates the importance of the radiation in particular in shorter wavelengths to the atmospheric chemistry. Thus, if applied to the atmospheric conditions, measured UV-B radiation levels instead of global radiation should be used as a basis of the absolute values for the proxy-sulfuric acid.

Measured sulfuric acid concentrations were compared with modeled concentrations as well as proxy results. All the data was averaged to 30 min as this is the time resolution of gas and radiation data utilized in the proxy calculations. The correlations are presented in Fig. 3. Best correlation ($R=0.82$) with the measurements was obtained with the first proxy, which utilized measured OH-concentrations to calculate an estimate for the sulfuric acid concentrations. Proxies with UV-B and global radiation as input parameters performed quite equally both having correlation coefficients of 0.80 and 0.79,

Sulfuric acid and OH in Hyytiälä

T. Petäjä et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



respectively. Based on the data presented in Fig. 3 all of the proxies tend to overestimate the sulfuric acid concentrations on average but are still within the estimated measurement error of 35%. A linear least squares regression to the data indicated a slope of 1.15 for the proxy with UV-B radiation and 1.10 for the proxy with the global radiation in correlation with the measurements. Thus the relative trends in the proxy-sulfuric acid concentration can be estimated either one of the proxies relying on the radiation measurements.

Also the modeled sulfuric acid concentrations correlated fairly well ($R=0.66$, Fig. 4) with the measured concentrations, when day-time (06:00–18:00 local time) are considered. A slightly better correlation ($R=0.68$) is obtained for the whole data set. These correlations are even marginally better than verification results ($R=0.645$) presented in Boy et al. (2005) based on data obtained during spring 2003. Linear least squares regression lines have a slope of 0.70 and 0.99 for day-time data and for all data points, respectively. These results are in good agreement compared to the 2003 analysis with the mean ratio for daytime values of 0.99 (Boy et al., 2005).

During that campaign the mean ratio for the whole period between measured and calculated H_2SO_4 concentrations during the 2003 campaign 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 (Boy et al., 2005).

3.2 OH

The measured and modeled hydroxyl radical concentrations follow each other pretty well (see Fig. 5 for the whole time series). Although qualitatively the diurnal cycle is similar, the measured daily maxima was typically smaller than the modeled OH. Median of the measured daily maximum OH concentration was $4.6 \cdot 10^5$ molecule cm^{-3} whereas the corresponding modeled value was $12.5 \cdot 10^5$ molecule cm^{-3} . The model-measurement difference in the daily maxima is up to 70% (Table 1). The modeled interquartile range was also much smaller than the corresponding range in the mea-

Sulfuric acid and OH in Hyytiälä

T. Petäjä et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



sured OH concentrations.

Correlation between the measured and modeled OH is presented in Fig. 6. Correlation coefficients are 0.31 and 0.51 with day-time data and all data points, respectively. When only day-time data (06:00–18:00 local time) the slope is only 0.25 with a large offset. As all data points are considered, the slope increases to 0.65, but still indicates a strong overestimate of the hydroxyl radical concentrations by the model.

In previous comparisons the model-to-measurement discrepancies in terms of OH concentrations can be as great as 40% (Crosley, 1995; Mauldin III et al., 1998; Shirley et al., 2006) depending on location. In a forested environment this discrepancy stems from the fact that neither all volatile organic compounds nor possible reactions between reaction products with OH are included in the chemical mechanism. Most probably the emissions of complex terpenes like sesquiterpenes are higher during the summer, which leads to higher discrepancies during summer (Tarvainen et al., 2005) as not all sinks are not accounted for in the model. This is indicated also by Fig. 7, which presents the ratio of modeled and measured OH concentrations as a function of ambient temperature. In higher temperatures the overestimation tends to be higher. As the temperature increases the amount of compounds acting as OH sink in the atmosphere increases leading to an increased discrepancy between the model and the measured hydroxyl radical concentrations (Goldstein and Galbally, 2007).

3.3 Diurnal cycles

Sulfuric acid had a clear diurnal cycle as depicted in Fig. 8. Typical daily maximum sulfuric acid concentration was $7\text{--}8\cdot 10^5$ molecules cm^{-3} for 30-min averaged data. During new particle formation event days the sulfuric acid concentration reached higher concentrations, as the grand-averaged mid-day concentration reached values up to $1\cdot 10^6$ cm^{-3} . These event days are typically cloud-free (Sogacheva et al., 2008) with high values of solar irradiance and therefore they favor both higher sulfuric acid production rates and higher new particle formation probability (Nilsson et al., 2001). In a rural continental site of Hohenspeissenberg in Southern Germany, Birmili et al. (2003)

Sulfuric acid and OH in Hyytiälä

T. Petäjä et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



reported that median diurnal cycle during event days reached an order of magnitude higher values up to $1 \cdot 10^7$ molecules cm^{-3} .

During non-event days the amplitude of the diurnal cycle was diminished, reaching only $3\text{--}4 \cdot 10^5$ molecules cm^{-3} . All the proxy sulfuric acid concentrations as well as modeled concentrations revealed similar differences between events and non-event days. Also the night-time concentrations were typically lower during days without new particle production. In the more polluted area of Hohenspeissenberg, Birmili et al. (2003) reported midday sulfuric acid concentrations of $4 \cdot 10^6$ molecules cm^{-3} during non-event days.

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.

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, when sulfuric acid is measured. The OH concentration followed nicely UV radiation, and the sulfuric acid concentrations depended also on SO_2 concentrations and the condensation sink to the pre-existing particles. With the aid of supporting measurements, we were able to derive several proxies for the sulfuric acid concentrations.

Measured sulfuric acid concentrations correlated well with two proxy variables as well as 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 absolute concentrations from the proxy calculations, however, could be site-specific and should be verified against measurements prior utilization.

Sulfuric acid and OH in Hyytiälä

T. Petäjä et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Sulfuric acid and OH
in Hyytiälä**

T. Petäjä et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Clear differences in 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 in depth data analysis is in progress to elucidate the role of sulfuric acid in new particle formation. This data provides an excellent opportunity to do this, since it is the longest available sulfuric acid in Boreal environment.

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**Sulfuric acid and OH
in Hyytiälä**

T. Petäjä et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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**Sulfuric acid and OH
in Hyytiälä**

T. Petäjä et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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**Sulfuric acid and OH
in Hyytiälä**

T. Petäjä et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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8, 20193–20221, 2008

Sulfuric acid and OH in Hyytiälä

T. Petäjä et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Sulfuric acid and OH in Hyytiälä

T. Petäjä et al.

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

	25%	50%	75%
H₂SO₄ [10⁵ molec cm⁻³]			
measured (5-min)	9.2	15.1	25.7
measured (30-min)	5.9	12.2	20.7
modeled	2.5	8.7	17.9
proxy 1	0.9	2.4	6.2
proxy 2	7.9	14.4	22.7
proxy 3	10.8	19.2	30.6
OH [10⁵ molec cm⁻³]			
measured (5-min)	5.9	7.8	10.6
measured (30-min)	2.7	4.6	7.9
modeled	1.3	12.5	20.8

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[I◀](#)
[▶I](#)
[◀](#)
[▶](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)


Sulfuric acid and OH
in Hyytiälä

T. Petäjä et al.

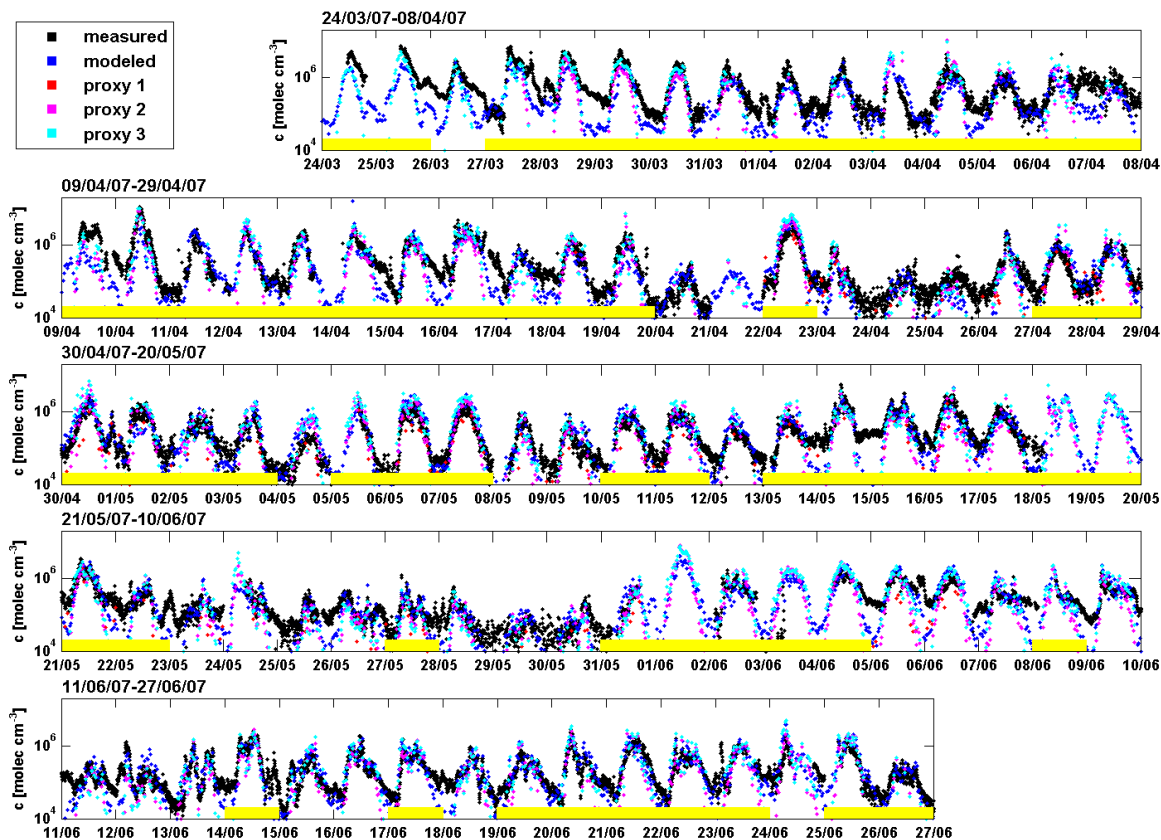


Fig. 1. Timeseries of measured (black), modeled (blue) and proxy-estimated concentrations (red, magenta and cyan) of sulfuric acid from 24 March to 27 June 2007 in Hyytiälä. Days with new particle formation are indicated with yellow bar at the bottom of the graph.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Sulfuric acid and OH
in Hyytiälä

T. Petäjä et al.

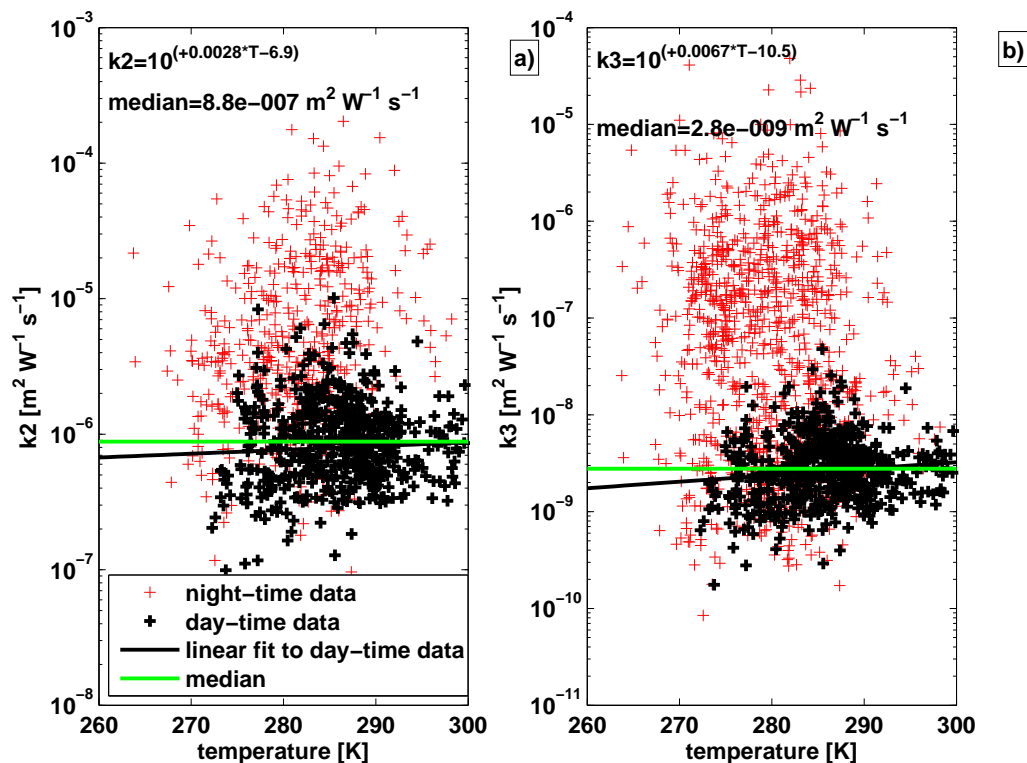


Fig. 2. Temperature dependencies of the proxy scaling factors for (a) UV-B proxy and (b) proxy utilizing global radiation. Black symbols are ratios of the measured and proxy concentrations during 09:00–15:00 (local time) and red symbols are all the ratios during other times.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Sulfuric acid and OH
in Hyytiälä

T. Petäjä et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

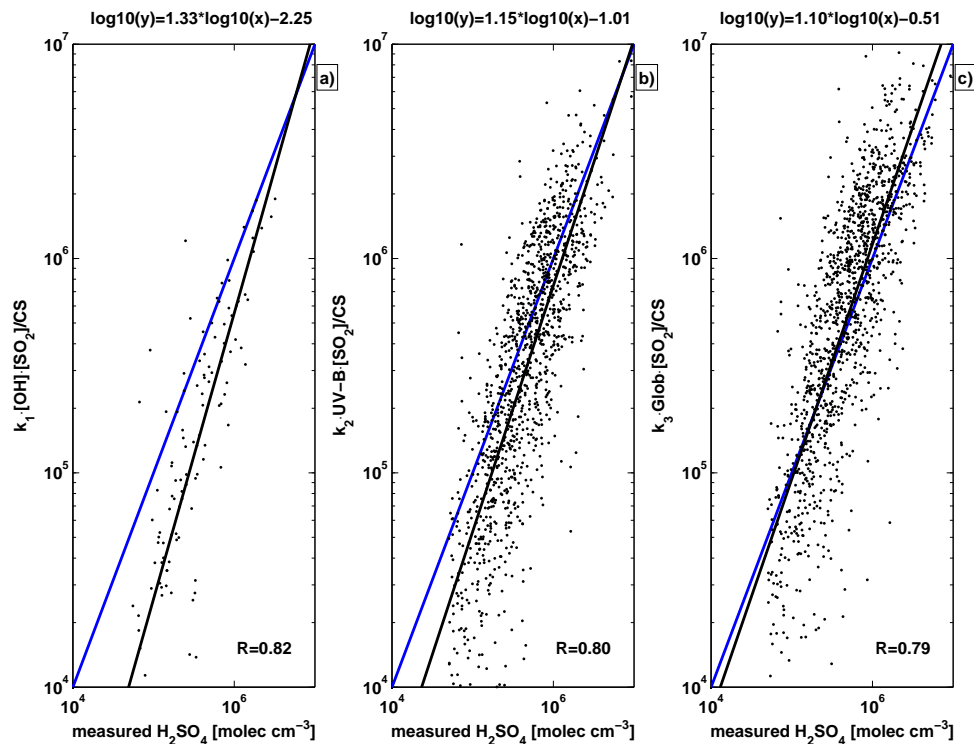


Fig. 3. Correlation and linear least squares fits of measured sulfuric acid concentration with (a) calculated based on measured OH-concentrations, (b) proxy sulfuric acid with UV-radiation and, (c) proxy with global radiation. Blue line is 1:1 line, black line is fitted to data set, which excludes measured concentrations below $5 \cdot 10^4$ molec cm^{-3} and considers only day-time (06:00–18:00 local time).

Sulfuric acid and OH
in Hyytiälä

T. Petäjä et al.

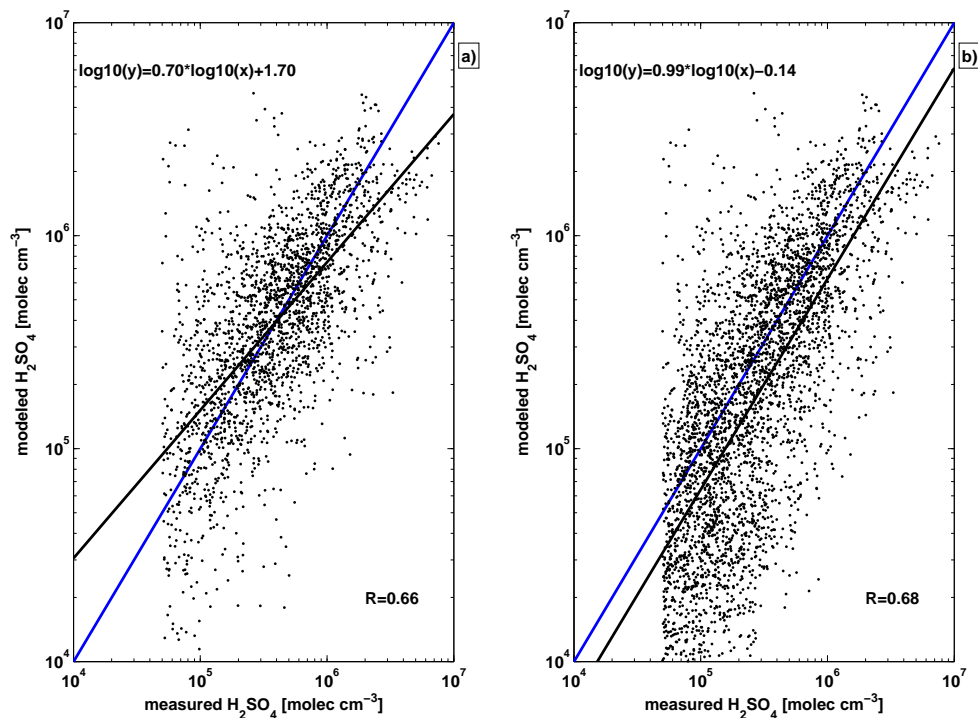


Fig. 4. Correlation and linear least squares fits of measured sulfuric acid concentration with modeled sulfuric acid concentrations for **(a)** day-time data (06:00–18:00 local time) and **(b)** for all data. Blue line is 1:1 line, black line is fitted to data set, which excludes measured concentrations below $5 \cdot 10^4$ molec cm^{-3} .

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Sulfuric acid and OH
in Hyytiälä

T. Petäjä et al.

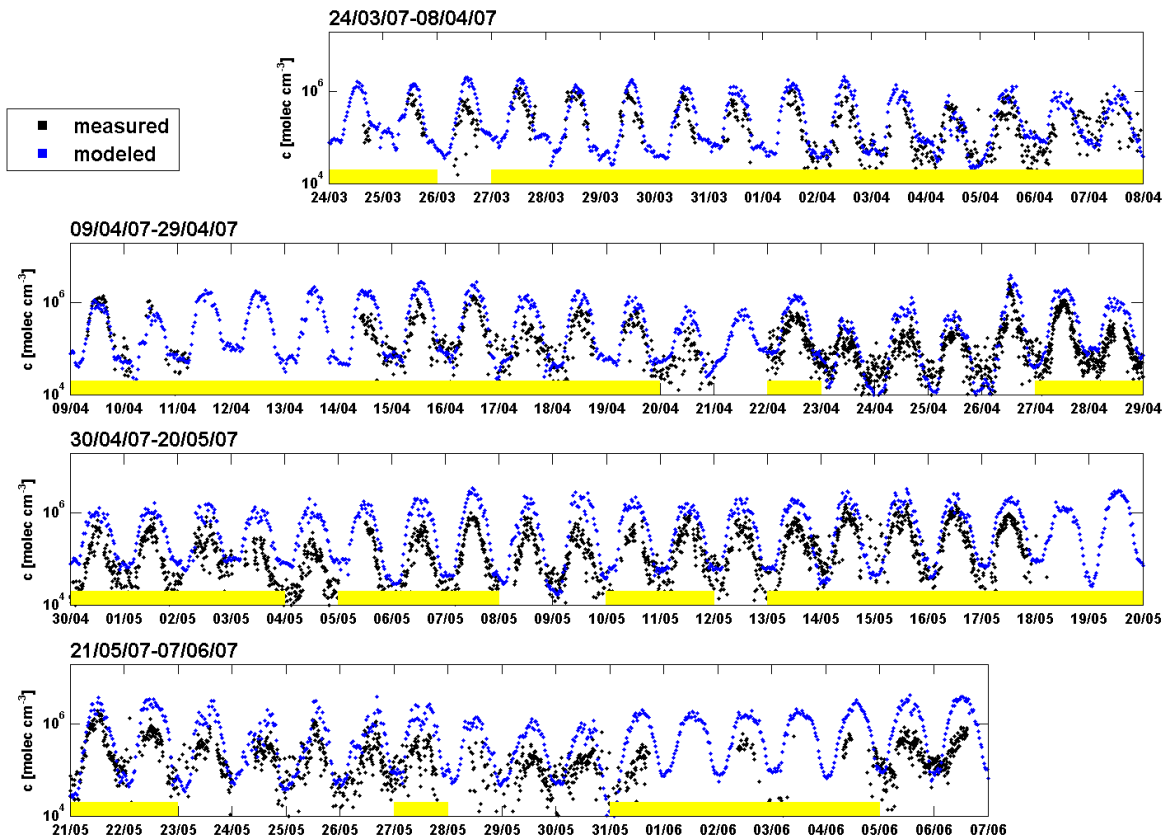


Fig. 5. Timeseries of measured (black) and modeled (blue) concentrations of hydroxyl radical from 24 March to 6 June 2007 in Hyytiälä. Days with new particle formation are indicated with yellow bar at the bottom of the graph.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Sulfuric acid and OH
in Hyytiälä

T. Petäjä et al.

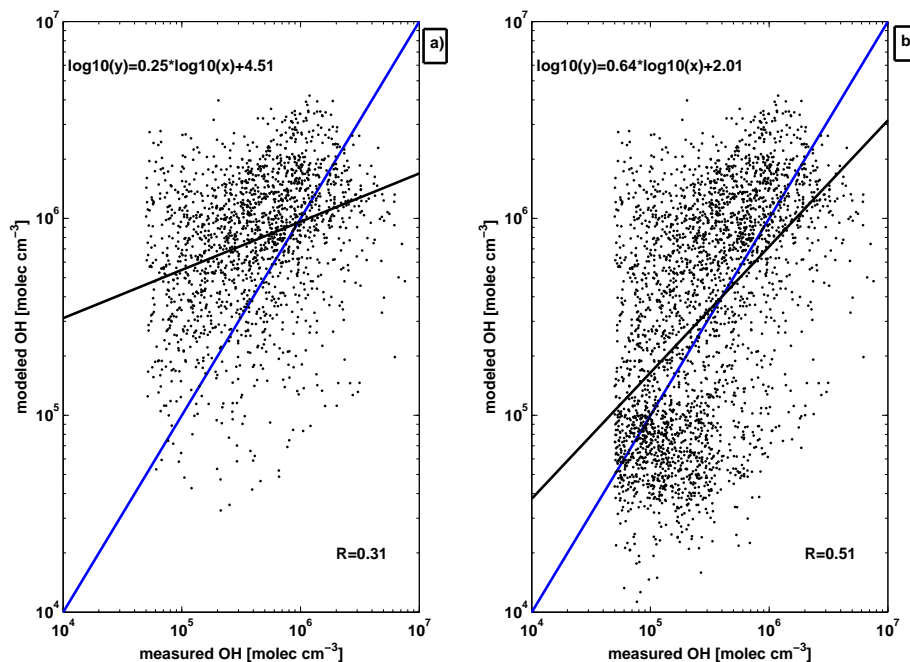


Fig. 6. Correlation and linear least squares fits of measured hydroxyl radical concentration with modeled concentrations for **(a)** day-time data (06:00–18:00 local time) and **(b)** for all data. Blue line is 1:1 line, black line is fitted to data set, which excludes measured concentrations below $5 \cdot 10^4 \text{ molec cm}^{-3}$.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Sulfuric acid and OH
in Hyytiälä

T. Petäjä et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

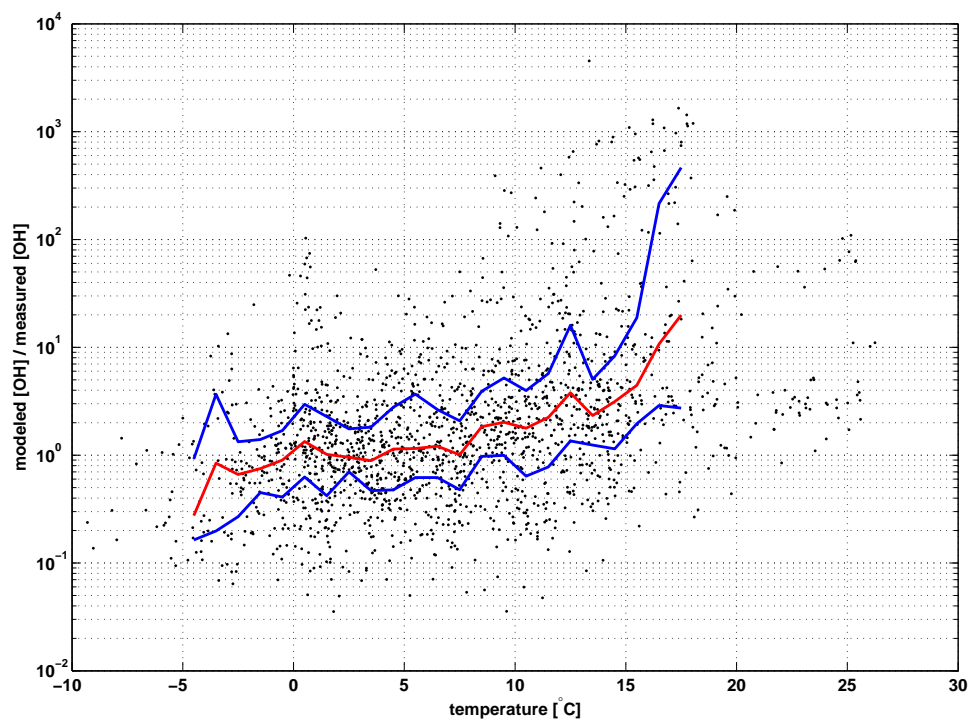


Fig. 7. Temperature dependency of the ratio between the modeled and measured OH radical concentrations (black dots). Red line corresponds to median ratio in a one °C interval and the blue lines correspond to 25% and 75% percentiles of the same interval.

Sulfuric acid and OH
in Hyytiälä

T. Petäjä et al.

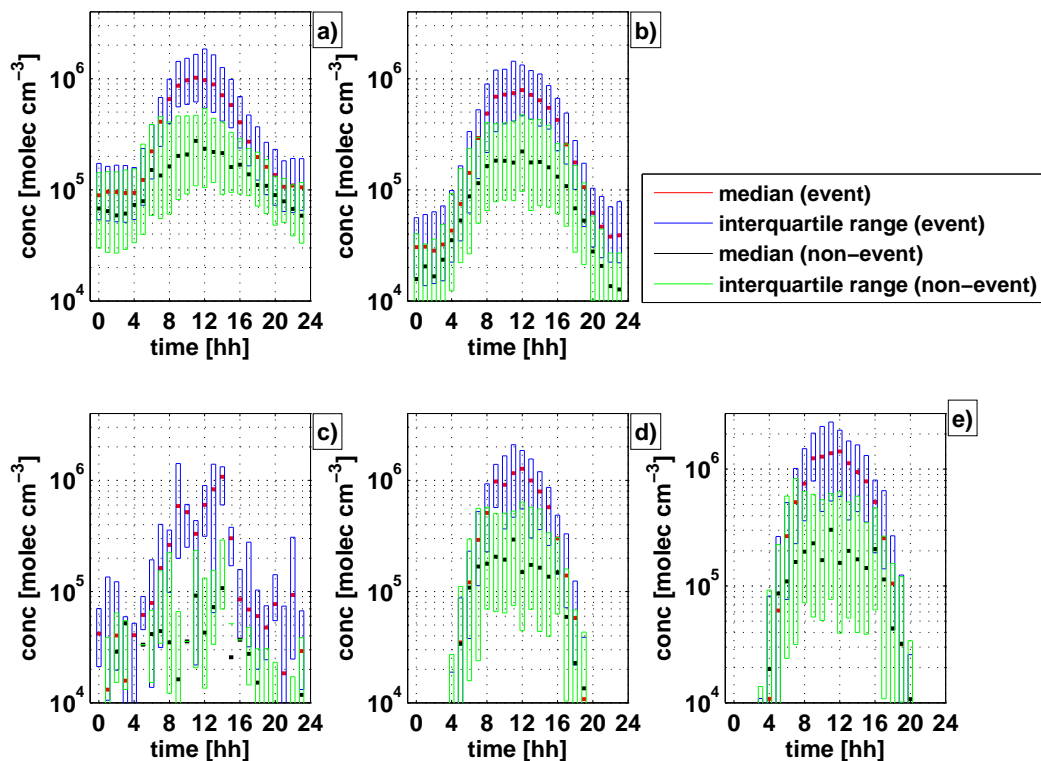


Fig. 8. Median diurnal cycle of (a) measured, (b) modeled, and (c), (d), (e) proxy calculated sulfuric acid during all measurement days during the EUCAARI field campaign in Hyytiälä and after grouping the days into two classes with and without new particle formation. Bar height describes interquartile range (25%–75%) of the concentrations.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Sulfuric acid and OH
in Hyytiälä

T. Petäjä et al.

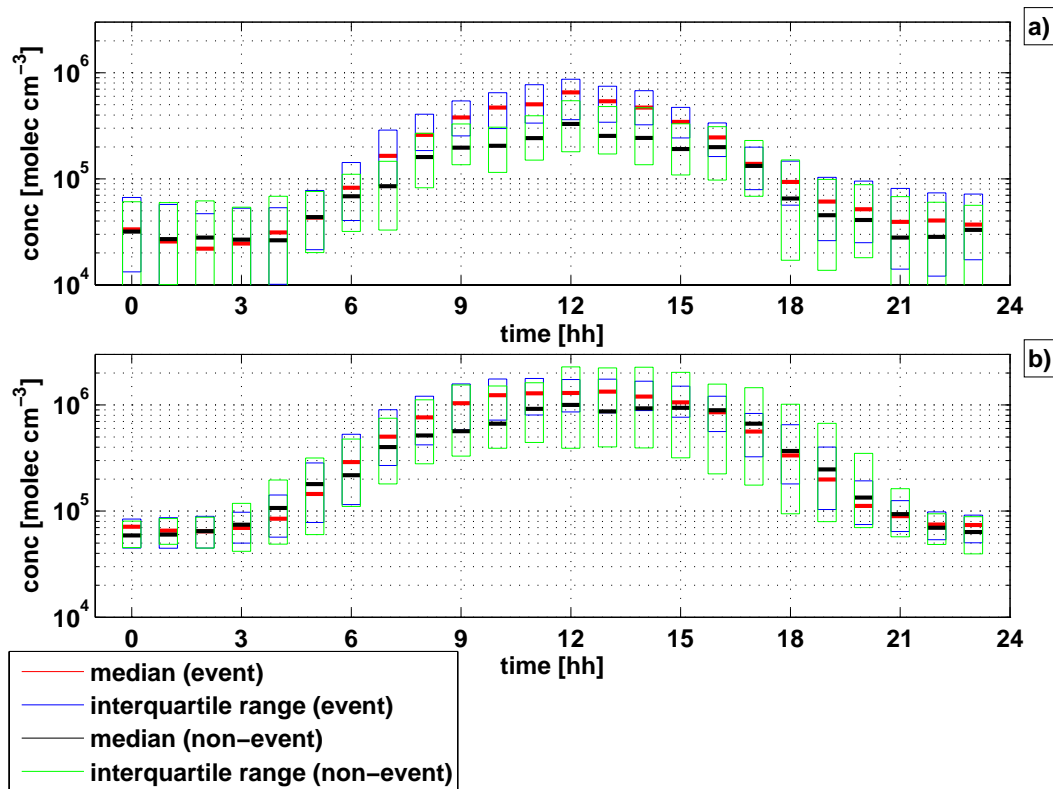


Fig. 9. Median diurnal cycle of (a) measured and (b) modeled hydroxyl radical concentrations during all measurement days during the EUCAARI field campaign in Hyytiälä and after grouping the days into two classes with and without new particle formation. Bar height describes interquartile range (25%–75%)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

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[I◀](#)[▶I](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)