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Oxidation of SO_2 by stabilized Criegee Intermediate (sCI) radicals as a crucial source for atmospheric sulphuric acid concentrations

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Abstract

The effect of increased reaction rates of stabilised Criegee Intermediates (sCI) with SO_2 to produce sulphuric acid is investigated using data from two different locations, SMEAR II, Hyytiälä, Finland and Hohenpeissenberg, Germany. Results from MALTE, a zero dimensional model, show that using previous values for the rate coefficients of sCI + SO_2, the model underestimates gas phase H_2SO_4 by up to a factor of two when compared to measurements. Using the rate coefficients recently calculated by Mauldin et al. (2012) increases sulphuric acid by 30–40 %. Increasing the rate coefficient for formaldehyde oxide (CH_2OO) with SO_2 by a factor of ten further increases the H_2SO_4 yield by 16 %. Taken together, these increases lead to the conclusion that, depending on their concentrations, the reaction of stabilized Criegee intermediates with SO_2 could contribute as much as 50 % to atmospheric sulphuric acid gas phase concentrations at ground level. Using the SMEAR II data, results from SOSA, a one-dimensional model, show that contribution from sCI reactions to sulphuric acid production is most important in the canopy where the concentration of organic compounds are the highest, but can have significant effects on sulphuric acid concentrations up to 100 m. The recent findings that the reaction of sCI + SO_2 is much faster than previously thought together with these results show that the inclusion of this new oxidation mechanism is crucial in regional, as well as, global models.

1 Introduction

New particle formation in the troposphere is important for the global concentration of cloud condensation nuclei (CCN) (Merikanto et al., 2010). Recently Makkonen and co-workers (2012) presented the effect of new particle formation on anthropogenic climate forcing in present-day and future (year 2100) conditions and concluded that with total aerosol forcing diminishing in response to air pollution controls taking effect (especially reductions in sulphur dioxide (SO_2)), warming from increased greenhouse

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gas concentrations can potentially increase at a very rapid rate. According to several studies (e.g. Kulmala et al., 2000; Paasonen et al., 2010; Sipilä et al., 2010; Zhao et al., 2010; Lauros et al., 2011) sulphuric acid (H_2SO_4) is one of the initial or required molecules in the nucleation mechanism. In order to quantify future atmospheric sulphuric acid concentrations a complete understanding of the sink and source terms is crucial. Although the precursors for sulphuric acid (at least some of them), as well as the main sink term (condensation on atmospheric aerosols) have been measured in several places, the closure between measured and calculated sulphuric acid concentrations has rarely been investigated (Eisele et al., 1993; Weber et al., 1997; Boy et al., 2005).

Criegee Intermediate (CI) radicals can play a crucial role in tropospheric oxidation as suggested more than a decade ago by Calvert et al. (2000). The CI formation mechanism starts from the ozonolysis of alkenes, with an addition of ozone to the double bond forming a primary ozonide with high excess energy. The excess energy causes the primary ozonide to decompose instantaneously to the Criegee intermediate, which will still posses excess energy. In order to release it's excess energy, the Criegee intermediate either decompose into different products or collisionally stabilize (we refer to the latter as a stabilized Criegee intermediate). The stabilized CI can then react with various atmospheric compounds, particularly H_2O, NO_x, SO_2, CO and many others.

Recently, Welz et al. (2012) pointed out that ozonolysis of unsaturated hydrocarbons (e.g. terpenes) is a major removal process in the troposphere for organic compounds and proceeds via Criegee Intermediate radicals. In their work, Welz and co-workers reported more than three orders of magnitude higher reaction rate constant for formaldehyde oxide (CH_2OO) with sulphur dioxide than was reported in the literature until today ($k = 3.9 \times 10^{-11} \pm 0.7 \times 10^{-11}$ cm^3 s^{-1} at 298 K and 4 torr). The laboratory conditions for their outstanding findings were in the low pressure regime and therefore are not applicable to tropospheric conditions. However, the potential for different CI's to oxidize compounds like SO_2 is much stronger than previously expected and is thus crucial to be included in all chemical models.

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New atmospheric observations supported by laboratory experiments and theoretical considerations point to the existence of compounds (most probably stabilized CI's) which have significant capacities to oxidize atmospheric trace gases like sulphur dioxide (Mauldin III et al., 2012). These authors claimed rate constants for Criegee Intermediate radicals originating from the ozonolysis of α-pinene and limonene to be $6 \times 10^{-13}\,cm^3\,s^{-1}$ and $8 \times 10^{-13}\,cm^3\,s^{-1}$, respectively. These new rate constants are about one order of magnitude higher than assumed as for example in the Master Chemical Mechanism published by the University of Leeds, Great Britain (http://mcm.leeds.ac.uk/MCM/).

In this work we investigated the effect of increased reaction rate constants of SO_2 with Criegee Intermediate radicals on the atmospheric concentrations of sulphuric acid for two different stations: SMEAR II, Hyytiälä, Finland and Hohenpeissenberg, Germany. Our results show that depending on the concentrations of the organic compounds their contribution via the reaction of stabilized Criegee Intermediates to atmospheric gas phase sulphuric acid concentrations is crucial at ground level. We further studied the role of this new oxidation mechanism in the lower troposphere (up to 2 km) with the one-dimensional chemical-transport model SOSA for the Finnish station SMEAR II. In the last section we will present a short discussion about the uncertainties in the calculations of the condensational sink term and the CI-chemistry.

2 Measurements

For our model investigations, we used data from two different stations. These data included: measured concentrations of volatile organic compounds (VOC), hydroxyl radical (OH), sulphuric acid, and other inorganic gases in addition to particle size distributions and basic meteorological data. The next three subsections will present information about the stations and the used data sets.

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2.1 Hyytiälä

Measurements in Hyytiälä were performed at the University of Helsinki's SMEAR II station (Station for Measuring Ecosystem-Atmosphere Relations; Hari and Kulmala (2005); 61° 51′ N, 24° 17′ E). The surroundings of the station are a rather homogeneous Scots pine (*Pinus sylvestris*) forest, which was sown in 1962. The station is equipped with permanent instrumentation for measuring basic meteorological parameters, aerosol concentrations, photosynthesis and soil properties. In this work, we utilize measurements of temperature, wind speed, spectral irradiance, global and diffuse solar radiation intensity, SO_2, CO, NO, NO_x, O_3, VOC, OH and H_2SO_4 concentrations. Furthermore, particle size number concentrations from DMPS (Differential Mobility Particle Sizer) and APS (Aerodynamic Particle Sizer) are included. A detailed description of the station and instrumentation (name, branch and detection limit) can be found under Kulmala et al. (2001a) and at http://www.atm.helsinki.fi/SMEAR/index.php.

For Hyytiälä we first selected 7 days (29 July to 4 August) during the HUMPPA-COPEC-2010 (Hyytiälä United Measurement of Photochemistry and Particles – Comprehensive Organic Particle and Environmental Chemistry) campaign which took place in July and August 2010 (Williams et al., 2011). For the results in Sect. 4.3 we used measurements from the whole year 2010.

2.2 Hohenpeissenberg

The measurements at Hohenpeissenberg in rural Southern Germany were conducted at the Meteorological Observatory Hohenpeissenberg (47° 48′ N, 11° 0′ E, e.g. Birmili et al., 2003, Rohrer and Berresheim, 2006). The observatory is operated by German Weather Service (DWD) and is located atop the Hohenpeissenberg Mountain, at an altitude of 985 m a.s.l. and about 300 m above the surrounding terrain, which consists mainly of meadows and forests. At night, the site is generally above the nocturnal boundary layer and local emissions from surrounding vegetation and anthropogenic sources do not reach the site. Data utilized from this station were global and diffuse

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radiation intensity, SO_2, CO, NO, NO_x, O_3, VOC, OH and H_2SO_4 concentrations. In addition, we used particle size number concentrations from a DMPS system.

For Hohenpeissenberg a long-term data-set from the year 2000 recorded during the HAFEX-campaign (Birmili et al., 2003) covering the period January to August was available. However, the organic compounds, which are crucial for our studies were only measured at certain times per day. Based on the measurements for these parameters in combination with the availability of all other requested data we selected 7 days where at least seven measurement-points of VOC's concentrations were performed during the day. These selection criteria limited our studies to the following days: the 9, 10, 27 and 28 April and the 18 to 20 June, 2000.

2.3 OH, H_2SO_4 and VOC concentration measurements at the two stations

The sulphuric acid and OH concentrations were measured with a Chemical Ionization Mass Spectrometer (CIMS, Berresheim et al., 2000; Petäjä et al., 2009). The CIMS instruments applied in Hyytiälä (Petäjä et al., 2009) and in Hohenpeissenberg (Berresheim et al., 2000 see also http://www.dwd.de/luftchemie) are of slightly different design but calibrated with a similar procedure. The uncertainty of the CIMS instruments at 2σ-level has been estimated to be 39 % for sulphuric acid and 54 % for OH concentration (Mauldin, III et al., 1999; Berresheim et al., 2000; Plass-Dülmer et al., 2011).

The measurements of monoterpene concentrations at the two sites were performed using different instruments. At Hyytiälä the total monoterpene concentration was obtained with Proton Transfer Reaction Mass Spectrometry (PTR-MS, DeGouw and Warneke, 2007) whereas at Hohenpeissenberg the total monoterpene concentration is calculated as a sum of the single monoterpene concentrations measured using a Gas Chromatography Mass Spectrometry (GC-MS, Plass-Duelmer and Berresheim, 2007). The monoterpenes detected with the applied GC-MS were α-thujene, tricyclene, α-pinene, camphene, sabinene, myrcene, β-pinene, α-phellandrene, Δ^3-carene, α-trepinene, limonene and β-phellandrene.

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3 Methods

In this work we used two different models, MALTE (Model to predict new Aerosol formation in the Lower TropospherE; Boy et al., 2006, 2008; Lauros et al., 2011) and SOSA (model to Simulate the concentrations of Organic vapours and Sulphuric Acid; Boy et al., 2011; Mogensen et al., 2011). Although MALTE – similar to SOSA – is a one dimensional chemistry-transport model, we used the latter to investigate the effect of the studied oxidation schemes on temporal trends in concentration profiles. This exploration can only be done with SOSA because the model is parallelized and runs on a computer cluster, so that the chemistry in different atmospheric layers can be computed in parallel. In the next two sections we will discuss the two models briefly and in Sect. 3.3 we will define the selected chemistry scenarios in particular.

3.1 MALTE

The one-dimensional model MALTE (Model to predict new Aerosol formation in the Lower TropospherE) is described in detail by Boy et al. (2006, 2008) and Lauros et al. (2011). The model reproduces the diurnal variation of boundary layer meteorology, chemistry, emissions and particle formation. Here, we used the zero-dimensional version of the model with different chemistry scenarios but without any aerosol dynamics.

The chemistry is calculated using the Kinetic PreProcessor (KPP) (Damian et al., 2002) and selected organic reactions from the Master Chemical Mechanism v3.2 (Jenkin et al., 1997; Saunders et al., 2003) via website: http://mcm.leeds.ac.uk/MCM/. We included photochemical and inorganic reactions from the Master Chemical Mechanism v3.2 and from Atkinson et al. (2004), together with spectral irradiance measurements from the SMEAR II station (Boy and Kulmala, 2002). Measured inorganic gas concentrations (NO_x, SO_2 and CO), OH and VOC concentrations from SMEAR II are used as input. The condensation sink for vapours was calculated from aerosol number

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size distributions measured with the twin-DMPS and APS using the method presented by Kulmala et al. (2001b).

3.2 SOSA

The one-dimensional chemistry-transport model SOSA is described in detail by Boy et al. (2011) and Mogensen et al. (2011), thus we will only give a brief overview of the model here. SOSA consists of three modules dealing with meteorology, emissions and chemistry. The measured input data are obtained from SMEAR II and includes inorganic gas concentrations (NO_x, SO_2 and CO) together with condensation sinks for sulphuric acid and nitric acid, based on DMPS and APS data (Boy et al., 2003).

The meteorological module is described by a 1-D version of the coupled plant-atmosphere boundary-layer model SCADIS (Sogachev et al., 2002, 2005; Sogachev and Panferov, 2006; Sogachev, 2009; Boy et al., 2011). SCADIS employs a 1.5-turbulent kinetic energy – specific dissipation closure scheme (including the Reynolds averaged Navier–Stokes equations for flow) using a number of parameterizations. The model is capable of describing the physical processes forming the meteorological regime within and above the forest canopy under different environmental conditions. The model describes the atmospheric boundary layer evolution and the mixing of the chemical species within a model domain of a flexible amount of layers. A resolution of 100 layers is used in this study. The separation between the model layers increase logarithmically from the bottom to the top of the column (3000 m). Meteorological data from the European Centre for Middle range Weather Forecast (ECMWF) were used for nudging the model variables towards the observations and upper boundary meteorological conditions at 3000 m.

The emissions of biogenic organic vapours from the canopy are calculated with an implemented modification of the MEGAN model (Model of Emissions of Gases and Aerosols from Nature), version 2.04 (Guenther et al., 2006). MEGAN uses estimates of plant species composition, representative species-specific emission factors, and information about leaf temperature and solar radiation on sun and shade leaves at

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different canopy levels, to simulate landscape average emissions. We have assumed a Scots pine forest environment and used 16 different canopy characteristics, such as leaf data together with scattering and reflection coefficients, to describe the conifer forest. Included also are standard emission potentials (SEP) for isoprene, α-pinene, β-pinene, Δ^3-carene, limonene, sabinene, ocimene farnesene, β-caryophyllene, 2-methyl-3-buten-2-ol, cineole, linalool and unspecified monoterpenes and sesquiterpenes (Hakola et al., 2006). The emission scheme has been verified by comparing VOC gas concentrations in the papers by Boy et al. (2011) and Mogensen et al. (2011).

The chemistry module is similar to the one used in MALTE. However, the concentrations of the hydroxyl radical and the organic vapours are predicted by the model SOSA, whereas measurements are used as input in MALTE.

3.3 Selected chemistry scenarios

To investigate the quantitative contribution of the stabilized Criegee Intermediates to the oxidation of sulphur dioxide we ran MALTE with 5 different chemistry scenarios which will be explained in detail below:

Scenario A: Tropospherically relevant inorganic reactions selected from the Master Chemical Mechanism and Atkinson et al. (2004) were used.

Scenario B: The same inorganic chemistry as under scenario A plus additional organic reactions for isoprene and monoterpenes from the MCM. As the MCM currently only includes full chemistry pathways for the terpenes α-pinene, β-pinene and limonene, we adopted rate constants from Atkinson et al. (1994) for Δ^3-carene, sabinene, myrcene and camphene with OH, O_3 and NO_3. The further chemical steps for the first order reaction products of Δ^3-carene, sabinene, myrcene and camphene with OH, O_3 and NO_3 have been approximated with the chemical path for α-pinene, β-pinene and limonene depending on their mixing ratios and location of the double bond(s). We have approximated the chemical path for Δ^3-carene, which is a bicyclic monoterpene with an endocyclic double bond, with α-pinene, which is also a bicyclic monoterpene with an endocyclic double bond. The chemical path for sabinene and

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camphene which are both bicyclic monoterpenes with an exocyclic double bond, has been approximated with the chemistry path for β-pinene that is likewise a bicyclic monoterpene with an exocyclic double bond. Myrcene, an acyclic monoterpene with three double bonds was also added to the β-pinene-path. By limiting our chemistry for the monoterpenes to these 7 compounds, we are able to cover generally more than 95 % of the observed monoterpene concentrations in Hyytiälä and Hohenpeissenberg (Plass-Dülmer and Berresheim, 2007; Bäck et al., 2012).

Scenario C: In this scenario we used the same chemical reactions as described in scenario B, but we increased the reaction rates of the sCI's with SO_2 based on the new values recently suggested by Mauldin III and co-workers (2012). Currently the MCM assumes a reaction constant of 7×10^{-14} cm^3 s^{-1} for all sCI's with SO_2, but with different compound-specific stabilization and loss rates for the different Criegee Intermediates. Equations (1)–(3) present the crucial reactions for the oxidation of sulphur dioxide based on the MCM scheme and Table 1 gives the original and modified reaction rate constants.

$$\alpha\text{-pinene} + O_3 \xrightarrow{k1} \text{APINOOB} \xrightarrow{k2} \text{APINBOO} + SO_2 \xrightarrow{k3} SO_3 \quad (1)$$

$$\beta\text{-pinene} + O_3 \xrightarrow{k1} \text{NOPINOOA} \xrightarrow{k2} \text{NOPINOO} + SO_2 \xrightarrow{k3} SO_3 \quad (2)$$

$$\text{limonene} + O_3 \xrightarrow{k1} \text{LIMOOB} \xrightarrow{k2} \text{LIMOO} + SO_2 \xrightarrow{k3} SO_3 \quad (3)$$

Combining the formation and the stabilization rates of the Criegee Intermediates (multiplication of the yields of the two steps reactions) results in nearly equal values for α-pinene, β-pinene and limonene with 0.2, 0.102 and 0.135, respectively. However, the rates of the sCI's (not presented in Table 1) with water vapour (sometimes called water channel) show two-times higher loss for APINBOO and LIMOO compared to NOPINOO. This would lead to remarkable higher sulphur dioxide oxidation if high concentrations of β-pinene are present (which is not the case for the two selected stations).

Scenario D: In this scenario we investigate the effect of the stabilized Criegee Intermediate formaldehyde oxide (CH_2OO) which is formed by the ozonolysis of isoprene

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and β-pinene (see Eq. 4). We increased the reaction rate of this sCI by a factor of 10 according to the other monoterpene derived sCI's. The combined formation and stabilization rate originated from isoprene is only 0.066 with a similar water channel as for the other terpenes. However, it should be considered that isoprene is the most abundant VOC in the atmosphere and due to its high concentrations isoprene could still have a remarkable effect in the oxidation of SO_2.

$$\text{isoprene} + O_3 \xrightarrow{k1} CH_2OOE \xrightarrow{k2} CH_2OO + SO_2 \xrightarrow{k1} SO_3 \quad (4)$$

Scenario W: Our last scenario reflects exactly the chemistry as in scenario D with the exception that we used the rate constant for the reaction of formaldehyde oxide with SO_2 ($k3$ in Eq. 4) published by Welz and co-workers (2012). These authors reported a reaction rate at 298 K (and 4 torr) of 3.9×10^{-11} cm^3 s^{-1}.

4 Results and discussion

The results of our investigation of the oxidation capacity of sCI's to form sulphuric acid will be presented in three subsections. In the first we discuss the ambient measured conditions of several relevant parameters including the concentrations of OH and H_2SO_4. In the following subsection our zero-dimensional model results for the two stations will be presented and in the last we show the average seasonal and yearly effect of the new oxidation mechanism in the lower part of the troposphere over the SMEAR II station in Hyytiälä.

4.1 Ambient conditions at the two stations

Figure 1 shows the temperature and radiation (global and diffuse) for the selected days at Hyytiälä and Hohenpeissenberg. During the days at the SMEAR II exceptionally warm air-masses with both the lowest and highest temperatures of 12.8 and 32.7 °C were present. Most of the time clouds formed during the day which is visible in the small

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difference between the values of these two measured radiation parameters (Williams et al., 2011). At Hohenpeissenberg three different meteorological periods can be categorized: at the beginning of April cold air masses with temperatures always below 10.4 °C but high solar irradiance with values up to 800 $W m^{-2}$ were observed; followed by a more cloudy but warmer period at the end of April and a clear sky period with temperatures between 10 and 26 °C in June.

The condensation sink (CS) and the concentrations of sulphur dioxide for both stations are presented in Fig. 2. These two parameters are crucial in the production of H_2SO_4: CS is the most important sink term for sulphuric acid and proportional to the surface area of the existing atmospheric aerosols, while SO_2 is one of its precursors. The most obvious finding from the figure is that the values of both parameters are similar at both stations. Daily variations are not pronounced, however the presence of more or less polluted air masses in Hyytiälä and Hohenpeissenberg can also be recognised as well. At the SMEAR II station we observed relatively high concentrations of CS and SO_2 on the first day followed by much cleaner air over the next two days. During the last four days both parameters are similar to values in the first three days with the exception of the last evening when the CS-value decreased towards its lowest value of 0.0008 s^{-1}. Compared to Hyytiälä, Hohenpeissenberg has smaller variations both in and between the three different periods. It seems that during all selected days at this station no air-mass changes with dramatic increases or decreases of pollution occurred.

A relatively strong difference in the daily pattern at the two stations can be found when observing the concentrations of organic compounds, hydroxyl radicals and sulphuric acid, which are presented in Fig. 3. The sum of the monoterpenes and isoprene measured at the SMEAR II station shows only a very small distinctive diurnal trend. This observation is in contrast with earlier studies at the same location were night time values were a factor of 2–3 higher than during the day and the absolute concentrations were clearly higher compared to our selected days (e.g. Mogensen et al., 2011). One reason could be the nearly constant high temperatures during the selected period

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causing the closing of the stomata of the plants to decrease evaporation and loss of water. Also the positive temperature dependence of the mixing layer height is probably affecting this pattern: even though the monoterpene emissions during the warmer day are higher, the concentration is more effectively diluted through the higher mixing layer. A completely different picture appears for Hohenpeissenberg with a clearly pronounced daily pattern for all three parameters. However, the ratio between day-and-night concentrations of the organic compounds are vice versa as is normally observed at Hyytiälä. Day-time concentrations are larger by up to a factor of 10, but the absolute concentrations are similar to those measured at the SMEAR II station. Measured VOC's are emitted at lower altitudes in the surroundings and then transported to the site by updrafts during convective meteorological conditions (high solar irradiance). At night, the observatory at the Hohenpeissenberg Mountain is above the mixing layer, and thus the monoterpenes emitted in the surroundings do not reach the station before the increase of the mixing layer height in the morning. The reader should also remember that the volatile organic compounds in Hohenpeissenberg were not measured continuously with a PTR-MS as was in the case of the SMEAR II, but by online GC-MS (see Sect. 2.3). For this reason only time-space point measurements are available for the station in Germany with linear interpolation being used to retrieve the daily variation.

The same discrepancy as for the organics can also be observed in the daily patterns between the two stations for the OH and H_2SO_4 concentrations. At both stations the profiles of these two parameters show a similar behaviour, but the increase during daytime is more pronounced at Hohenpeissenberg. However, at daytime the absolute values of the parameters are in the same range as would be expected at least for sulphuric acid by comparing the sink and source terms. We should also remember that at this time of the year the amount of day-light in Hyytiälä is around 18 h and that photochemistry is only inactive for a very short period during night. In Hyytiälä there exist strong differences between the hydroxyl radical and sulphuric acid concentrations on the first day which could point to an extra source term of H_2SO_4 related to the observed

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much more highly polluted air-mass during this time (see Fig. 2). Most probably the reaction products of organic compounds contribute to the oxidation of SO_2 which will be investigated in detail in Sect. 4.2.

4.2 Process-study near the ground at the two stations

In this subsection we used the zero-dimensional version of the model MALTE to investigate the oxidation capacity of the stabilized CI described in Sect. 3.3 to form sulphuric acid at the two selected stations, Hyytiälä and Hohenpeissenberg. During the simulations we kept the concentrations of the OH radicals and the VOC's constrained by the measurements. All other organic compounds and H_2SO_4 were calculated by the model. This setup was used to minimize the errors resulting from the model and to receive the best estimates for our study.

Figure 4 shows a scatter plot for the concentrations of the four Criegee Intermediates using scenario D for the chemistry against the missing sulphuric acid concentrations calculated by subtracting the measured sulphuric acid concentrations from those predicted by MALTE running the chemistry scenario B. For the Hyytiälä-plot we see a very similar trend for formaldehyde oxide and the sum of the three CI resulting from the ozonolysis of the monoterpenes. This reflects the nearly identical behaviour of the precursors during the chosen period presented in Fig. 3. At Hohenpeissenberg the behaviour of the precursors is more pronounced with larger increases of the monoterpene concentrations during the day. However, at both stations the sCI's from the monoterpene ozonolysis are larger by a factor 3–5 compared to CH_2OO. The important observation from this figure is the trend between the two plotted variables. With increasing concentrations of the stabilized Criegee Intermediates we see a larger number of sulphuric acid molecules which cannot be predicted using the model chemistry from the MCM with unchanged reaction rates for the oxidation of sulphur dioxide with the sCI's. This linear dependency can be observed at both stations and could indicate the possible participation of the sCI's in SO_2 oxidation.

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The next step in our study was to run the model with the different chemistry scenarios explained in Sect. 3.3 to predict the contributions of each different sulphur dioxide oxidation mechanism. Table 2 shows the mean measured and modelled sulphuric acid concentrations together with the correlation coefficient and the coefficient of variation of the root-means-square error – CV(RMSE) – between the measurements and simulations for each scenario and station. In Table 3 we present the percentage contribution of the different reactions schemes described in Sect. 3.3 in relation to the measured concentrations. If we compare the measured and modelled sulphuric acid concentrations at each station we realize that for both locations the model underestimates the measurements by approximately a factor of 2 using the chemistry from the Master Chemical Mechanism as explained under scenario B. If we consider the new reaction rates for the sCI's resulting from the ozonolysis of the monoterpenes (scenario C) we increase calculated H_2SO_4 concentrations between 30–40 %. By also including the new reaction rate from formaldehyde oxide as in scenario D, we increase the simulated sulphuric acid concentrations for both stations by 16 %. Adding all the different factors together we find the model underestimates measured concentrations of H_2SO_4 in Hyytiälä by 14 % and overestimates them by 14 % for Hohenpeissenberg. In the case of scenario W, the model produces very large values with sulphuric acid concentrations that are more than 100 % too high. Including the measured reaction rate constant for formaldehyde oxide with NO_2 from the manuscript by Welz and co-workers (2012) decrease the lifetime of this sCI but still leads to unrealistic high sulphuric acid concentrations with 320 % and 165 % for Hyytiälä and Hohenpeissenberg, respectively.

All scenarios except scenario W show a very high correlation between the modelled and measured values with $R \geq 0.88$. This correlation shows that there is a similar trend in the two data sets, but it gives no information about the difference between both data sets. For this reason we calculated the RMSE (sometimes also called root-mean-square deviation – CV(RMSD)) to measure the difference between our predicted and measured sulphuric acid concentrations. At the last step we normalized these values with the mean measured concentrations and present the values in percentage in

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Table 2. It is obvious that scenarios C and D have the lowest CV(RMSE) values compared to all other runs and that the root-mean-square error is reasonably smaller at Hohenpeissenberg.

Figures 5 and 6 show the measured and modelled (scenarios B and D) sulphuric acid concentrations for Hyytiälä and Hohenpeissenberg, respectively. For Hyytiälä, it is obvious that the inclusions of the new reaction rates for the sCI's nearly always dramatically improves the simulated sulphuric acid concentrations. Only at the end of our selected period does the model overestimate the measurements continuously for several hours. At Hohenpeissenberg the situation differs for the three different periods. During the first two days, the difference between the measured sulphuric acid concentrations and the one modelled without using the improved reaction rates for the sCI's is very small. However, the concentrations of the monoterpenes and isoprene are reasonably smaller, thus the contributions of the new oxidation path for sulphur dioxide is very small. If we now consider the last three days in this plot we see a much greater difference between measured and modelled concentrations for scenario B. This difference becomes smaller when we use the new reaction rates of the sCI's on all days. The contribution of these mechanisms seems to be crucial for Hohenpeissenberg especially during the night-time when the isoprene and monoterpene concentrations reach a certain value. Scatter plots for both stations of the measured and modelled (scenario D) H_2SO_4 concentrations presented in Fig. 7 show that for both stations most of the values are in the 50 % interval, which could be explained by taking the uncertainty of all the measurements into account. During time periods with sulphuric acid concentrations below 3×10^5 molecules cm^{-3} the model still seems to underestimate compared to the measured concentrations. This divergence could be related to the fact that we only changed the rates for four reactions of stabilized Criegee Intermediates for our model investigations and very likely many more exist in the real atmosphere, which are not currently included.

Figures 8 and 9 give the contributions, as a percentage, of the different chemical path ways for the entire periods at the two stations. The "H_2SO_4 by SO_2 and CIs" data

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were calculated by first running the model with scenario D and then subtracting the values predicted by a run with scenario B. In this case only the difference between the new and old reaction rate constants for the sCI's are considered as a source term for the concentrations of sulphuric acid. The difference in the contributions at the two stations is remarkable. While in Hyytiälä both mechanisms seem to be active at all times with nearly similar contributions, the situation appears completely different at Hohenpeissenberg. Here we recognise a clear dominance of the OH-path during daytime and conversely at nights when the sCI's contribute between 50 and 80 % depending on the precursor concentrations. As mentioned in Sect. 2 the meteorological situation of the summer 2010 in Hyytiälä was very exceptional during the HUMPPA-COPEC campaign and would not be considered the normal situation for this station. In the next subsection we will show that there is also in Hyytiälä this clear trend of OH-generated H_2SO_4 during daytime and sCI-generated H_2SO_4 at night is valid. The selected period shown for Hyytiälä was abnormal and gave a good opportunity to test the new chemical paths under extreme conditions and investigate if the results are still valid.

4.3 Vertical seasonal impact at Hyytiälä

In this last section we will investigate the seasonal impact of the oxidation of SO_2 by sCI's on the sulphuric acid concentrations in the lower part of the troposphere at Hyytiälä during 2010 using the chemistry-transport model SOSA. In contrast with the model MALTE in the previous subsection where measured values were used, OH and VOC's will now be calculated online and not taken from measurements. This change is necessary because no long-term (over a season or year) vertical measurements for these compounds exist, but are necessary to do this type of study.

After the run we calculated for every time-step and for every day in 2010 the H_2SO_4 production ratio. We define the H_2SO_4 production ratio as the ratio between H_2SO_4 produced only by OH oxidation of SO_2 divided by H_2SO_4 produced both by OH oxidation of SO_2 and also by reactions of stabilized Criegee intermediates with SO_2. We can

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write this ratio, R, as:

$$R = \frac{[H_2SO_4]_{OH}}{[H_2SO_4]_{OH} + [H_2SO_4]_{sCI}} \quad (5)$$

This ratio is calculated for every height layer and averaged seasonally over the year 2010 with spring season being March, April and May, summer June, July and August, autumn September, October and November and winter January, February and December.

Figure 10 presents the sulphuric acid production ratio in the lowest 500 m for all seasons at the SMEAR II station at Hyytiälä and Table 4 gives the average values for different height levels from the ground to the height mentioned in the first column. In spring, summer and autumn the situations are quite similar with a contribution from the stabilized Criegee Intermediates to the total sulphuric acid production decreasing from 15–21 % in the lowest 20 m to 6–8 % when considering the first 500 m. However, nearly double the contribution of the sCI's is observed during winter due to the low solar irradiance at this high latitude station during the months of December to February. One remarkable result from the plots in Fig. 10 is the expected daily distribution with relatively low sulphuric acid production ratios during night times. As already mentioned above this observation reflects exactly the monoterpene concentrations measured at this station in earlier studies (Mogensen et al., 2011) and stands in contrast with the terpene profiles recorded during the HUMPPA-COPEC campaign.

The last figure of our study (Fig. 11) shows the sulphuric acid production ratio for two different height intervals (500 m and 50 m) averaged over the whole year 2010 at the SMEAR II station. In the first plot we see that up to a height of 100 m the average daily contribution of the sCI's can be around 20 % with higher contributions during night times. Above this height the OH-production-term dominates and the ozonolysis of the monoterpene contributes only with a very small fraction to the total sulphuric acid production. The second plot also shows one short coming of the model SOSA, or rather the emission module used, which is that it currently does not include any

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parameterization of VOC-emissions from the soil or floor of the canopy. For this reason the H_2SO_4 production ratio increased quite strongly in the lowest 3 m compared to the upper part of the canopy. Overall our results show that the effect of sCI's can have a significant impact in the lowest part of the troposphere (first 100 m) when calculating the sulphuric acid concentrations. Considering that most of the H_2SO_4 measurements are performed at ground level the inclusion of this new oxidation mechanism is crucial. However, when we consider the vertical dependence over the SMEAR II station (up to 2 km), the model shows a decreasing importance with only some percent of the produced sulphuric acid concentrations (5 % up to 2 km) originating from the reaction of sulphur dioxide with stable Criegee Intermediates.

5 Uncertainties

The aerosol condensational sink (CS) determines how rapidly molecules will condense onto pre-existing aerosols (Kulmala et al., 2001b). In these calculations we use measured particle number concentrations from the smallest sizes at around 3 nm up to several µm. However, the uncertainty of the predicted CS-values due to potentially different hygroscopic growth behaviour depending on the chemical composition of the particles is difficult to estimate and could have a significant effect for the simulated sulphuric acid concentrations.

The Criegee chemistry has been investigated both experimentally as well as theoretically, but is still somewhat unexplored and leaves us with a lot to wish for concerning the chemical mechanisms, pathways, products, stabilisations and yields, thermal life times, pressure dependency and reaction rate coefficients. Donahue et al. (2011) gives a great general overview of the dependences on conditions in atmospheric Criegee chemistry. Below we will briefly touch those uncertainties that influence the results gained in the presented manuscript.

Firstly, it should be emphasised that CIs have not been directly observed in the gas phase until very recently, by Welz et al. (2012). Instead its presence, lifetime and

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reaction rate coefficients have been estimated based on indirect measurements; by investigating changes in the products of ozonolysis of specific alkenes upon addition of different reagents or scavengers (e.g. Alam et al., 2011; Presto and Donahue, 2004).

Chemical paths: The CI chemistry of simple alkenes is still not fully understood, but the situation gets still worse for more complex systems. E.g. α-pinene and limonene (endocyclic terpenes) produce two excited CI's, both with a carbonyl and a carbonyl oxide functional group. This structure gives the possibility for intra-molecular reactions, which is not well investigated. Furthermore, limonene also has an exocyclic double bond, where we would also expect an ozone addition (Leungsakul et al., 2005; Jiang et al., 2010); however this is not included in the MCM.

Stabilisation: In order to react with other molecules, the CI must be collisionally stabilized. MCM assumes that one stable CI is formed for each alkene (including dienes). Browsing through the literature, one finds that there also here seems to be some disagreement concerning the yields of the sCI produced from various alkenes; e.g. for α-pinene yields of 0.34 (Zhang and Zhang, 2005) and 0.15 (Drozd and Donahue, 2011) have been reported, while for β-pinene the yields are given as 0.37 (Nguyen et al., 2009) and 0.22 (Zhang and Zhang, 2005).

Thermal lifetime: After stabilisation of the CI, the CI must have a long enough thermal lifetime in order to react with other molecules. Again, direct measurements of the lifetimes of the stabilized intermediates have not been possible so far, and reported values span orders of magnitudes (e.g. Welz et al., 2012; Olzmann et al., 1997).

Reaction rate coefficients: The stabilised CI is assumed to react with SO_2, CO, NO, NO_2 and H_2O. Direct measurements, indirect determinations via measurements and computational calculations of specific CI's reaction rate coefficients with these various compounds spans several orders of magnitudes and must be thought to be extremely uncertain (e.g. Welz et al., 2012; Mauldin III et al., 2012; Johnson and Marston, 2008; Hatakeyama et al., 1986, 1994; Kurtén et al., 2011). Measurements of the reaction rate coefficients are often done under low (and tropospherically irrelevant) pressure due to practical issues. When applying reaction rate coefficients measured under low pressure

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conditions one has to bear in mind that reaction rate coefficients under tropospheric conditions can be pressure- and temperature-dependent, reactions are commonly affected by the presence of water, and if the reactions have a substantial stabilization component, the rate constants could be substantially larger at atmospheric pressure (Welz et al., 2012). In our study we have only changed the reaction rate coefficients for reaction between Cl and SO_2. However, the large uncertainty on the Cl reaction rate coefficients is not only thought to be for reactions with SO_2, but must also be expected for reaction with the other trace gases. Hypothetically speaking; if the reaction rate coefficients for reaction between Cl and SO_2, CO, NO, NO_2 and H_2O are all several orders of magnitude larger than previously assumed, then the amount of Cl available to react with SO_2 will decrease significantly, which will decrease the amount of produced H_2SO_4 that we have shown in this study.

6 Conclusions

This study dramatically change the current understanding of atmospheric sulphuric acid production: we have shown that oxidation of SO_2 by stabilized Criegee Intermediate radicals can be a crucial source for atmospheric sulphuric acid production in VOC rich environments. Depending on the concentrations of several investigated organic compounds (reaction products from ozone oxidation of isoprene and monoterpenes) their contribution via the reaction of stabilized Criegee Intermediates to atmospheric sulphuric acid gas phase concentrations could be as high as 50 % at ground level. Taking into account that most of the H_2SO_4 measurements are performed at ground level, the inclusion of this new oxidation mechanism is crucial in regional, as well as, global models.

Our model investigations of the boundary layer in Hyytiälä showed that the contribution from the sCI to sulphuric acid production is, as expected, most important in the canopy where the concentration of organic compounds are highest. However, our

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overall results show that the effect of sCI's up to 100 m is very important to consider when calculating the sulphuric acid concentration.

We were not able to reproduce the measured sulphuric acid concentration when including the reaction rate coefficient for reaction of formaldehyde oxide with SO_2 by Welz et al. 2012. Instead we overestimated the sulphuric acid concentration with more than 100 %.

We assume that other stabilized Criegee Intermediate radicals produced from ozone oxidation of other unsaturated organic compounds exist and contribute in the production of sulphuric acid and we urge for more investigation into this field.

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Table 1. Reaction rates for the most crucial chemical equations presented under Eqs. (1)–(4).

	$k1$ ($cm^3\,s^{-1}$)	$k2$ (s^{-1})	$k3$ (MCM) ($cm^3\,s^{-1}$)	$k3$ (new) ($cm^3\,s^{-1}$)
α-pinene	$6.3 \times 10^{-16} \cdot \exp(-580/T) \cdot 0.4$	$1 \times 10^{6} \cdot 0.5$	7×10^{-14}	6×10^{-13}
β-pinene	$1.5 \times 10^{-17} \cdot 0.6$	$1 \times 10^{6} \cdot 0.17$	7×10^{-14}	6×10^{-13}
limonene	$2.95 \times 10^{-15} \cdot \exp(-783/T) \cdot 0.27$	$1 \times 10^{6} \cdot 0.5$	7×10^{-14}	8×10^{-13}
isoprene	$1.03 \times 10^{-14} \cdot \exp(-1995/T) \cdot 0.3$	$1 \times 10^{6} \cdot 0.22$	7×10^{-14}	7×10^{-13}

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Table 2. Statistical analysis between measured and modelled sulphuric acid concentrations for Hyytiälä and Hohenpeissenberg (RMSE – root mean square error).

	Hyytiälä				Hohenpeissenberg			
	Mean meas.	Mean model	Corr. Coef.	CV(RMSE) (%)	Mean meas.	Mean model	Corr. Coef.	CV(RMSE) (%)
Scenario A	1.2 E6	3.3 E5	0.98	137.4	1.3 E6	7.4 E5	0.91	47.1
Scenario B	1.2 E6	4.3 E5	0.96	119.9	1.3 E6	8.3 E5	0.92	41.8
Scenario C	1.2 E6	7.6 E5	0.95	77.4	1.3 E6	1.2 E6	0.89	32.2
Scenario D	1.2 E6	9.1 E5	0.94	65.6	1.3 E6	1.4 E6	0.88	33.8
Scenario W	1.2 E6	2.1 E6	0.86	112	1.3 E6	2.9 E6	0.71	136.1

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Table 3. Contribution of the different chemical paths to form sulphuric acid in the atmosphere.

	Hyytiälä	Hohenpeissenberg
Inorganic chemistry (scenario A)	28.9 %	49.5 %
Organic chemistry from MCM (scenario B)	9.1 %	10.2 %
sCI's from Monoterpenes with increased reaction rate (scenario C)	31.7 %	38.1 %
sCI's from CH200 with increased reaction rate (scenario D)	16.1 %	16.4 %
Underestimation by scenario D	14.1 %	−14.2 %

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Table 4. Seasonal mean values of the sulphuric reaction ratio averaged from the ground up to different heights calculated according to Eq. (5).

Season Height	Spring	Summer	Autumn	Winter
22 m	0.84	0.85	0.79	0.60
56 m	0.85	0.86	0.80	0.62
108 m	0.87	0.87	0.82	0.69
225 m	0.91	0.90	0.87	0.79
505 m	0.94	0.93	0.92	0.88
2001 m	0.96	0.96	0.95	0.94

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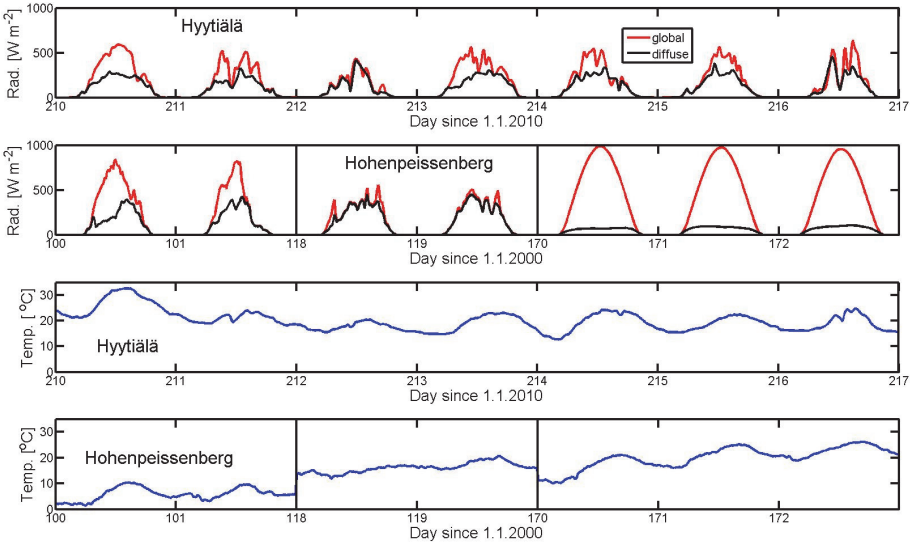

Fig. 1. Measured temperature, global and diffuse radiation for the selected time periods at both stations.

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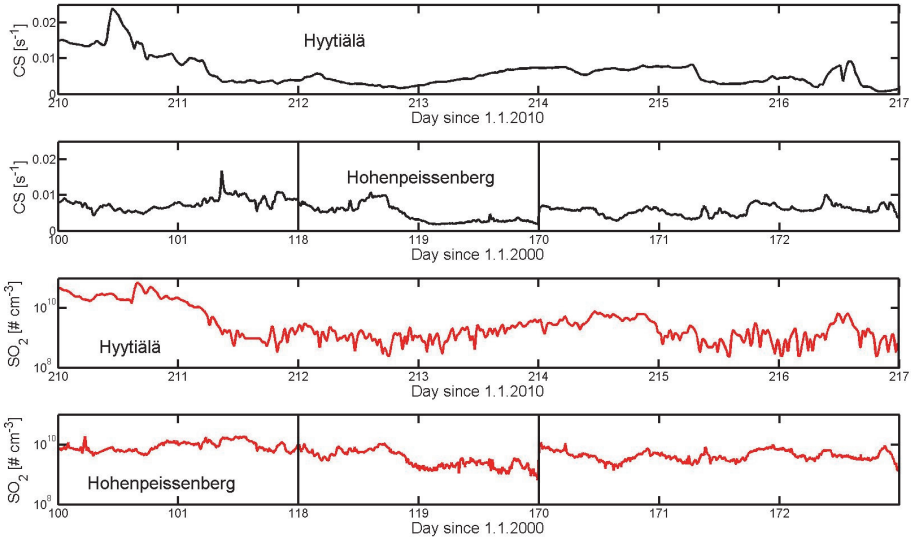

Fig. 2. Measured condensational sink and sulphur dioxide concentrations for the selected periods at both stations.

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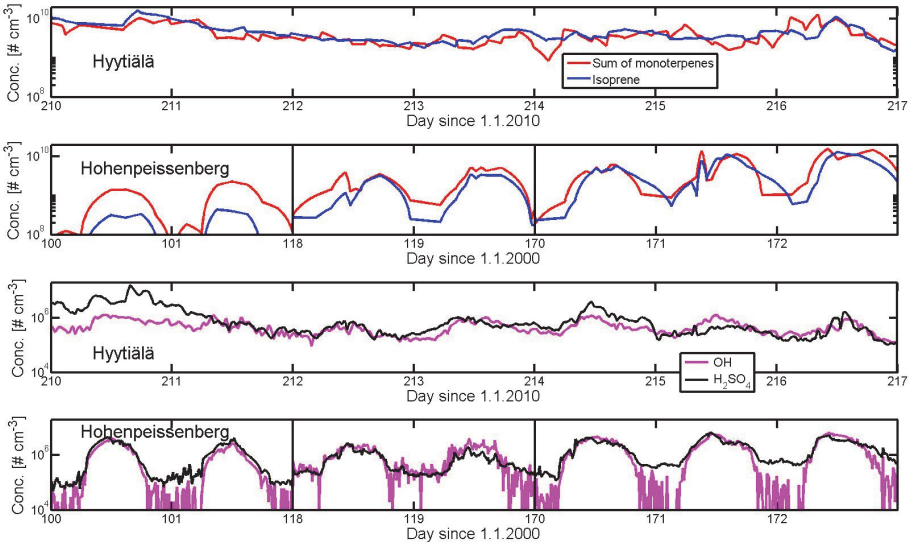

Fig. 3. Measured concentrations of different organic vapours, hydroxyl radical and sulphuric acid for the selected periods at both stations.

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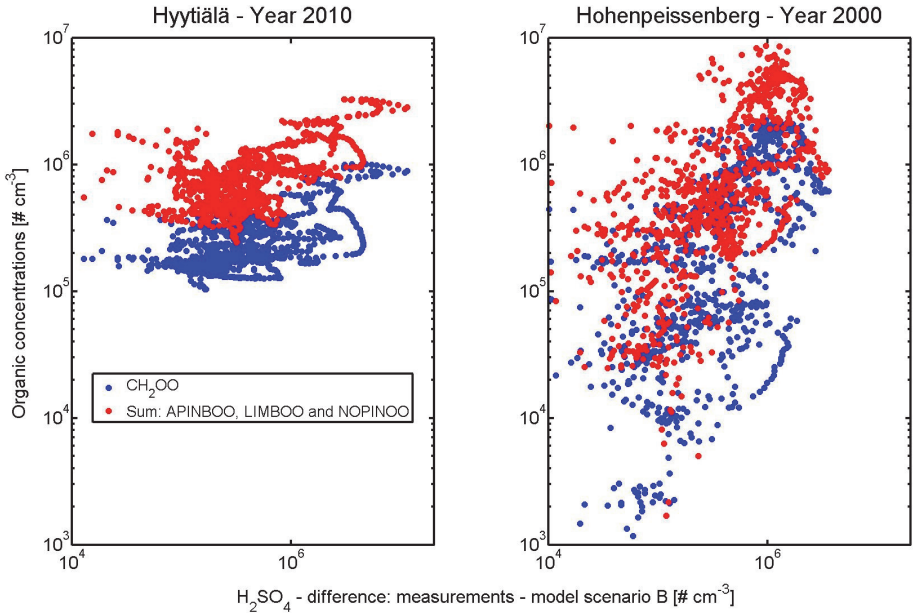

Fig. 4. Scatter plot of organic vapours against the missing sulphuric acid concentrations for the selected periods at both stations.

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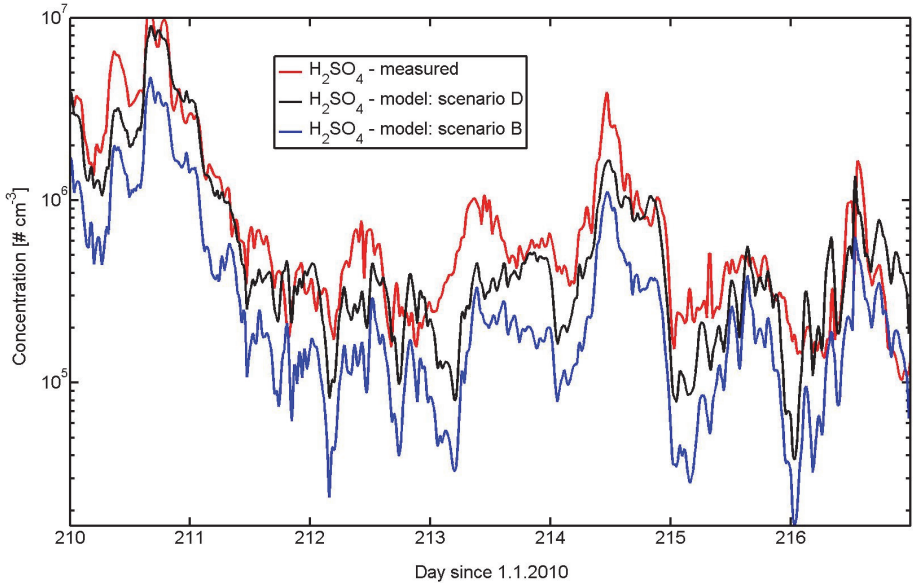

Fig. 5. Measured and modelled sulphuric acid concentrations for Hyytiälä; the definitions of the different model scenarios are presented in Sect. 3.3.

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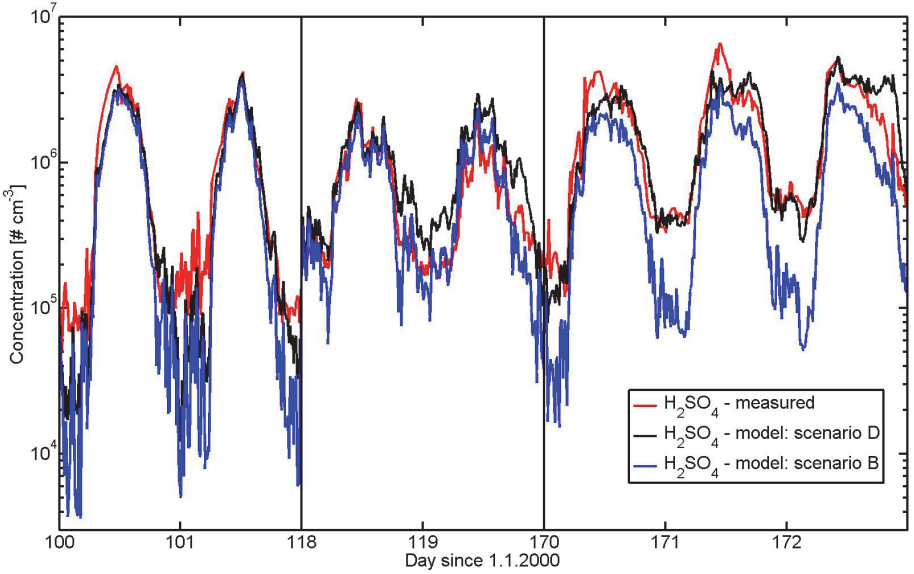

Fig. 6. Measured and modelled sulphuric acid concentrations for Hohenpeissenberg – the definitions of the different model scenarios are presented in Sect. 3.3.

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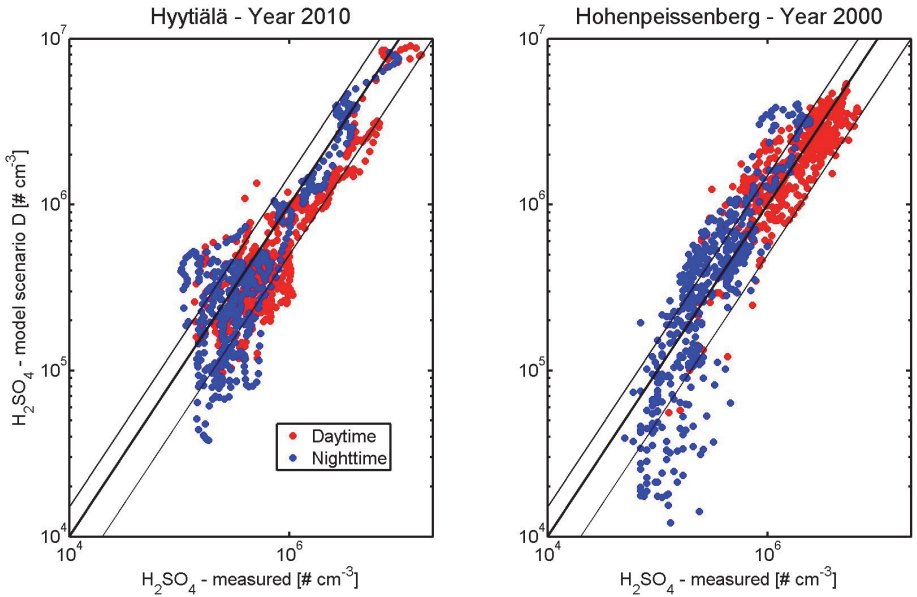

Fig. 7. Scatter plot of measured against modelled sulphuric acid concentrations for the selected periods at both stations based on simulation with scenario D (for the definition of the scenarios see Sect. 3.3); black thick lines indicate the 1 : 1 range and black thin lines the 50 % uncertainty interval.

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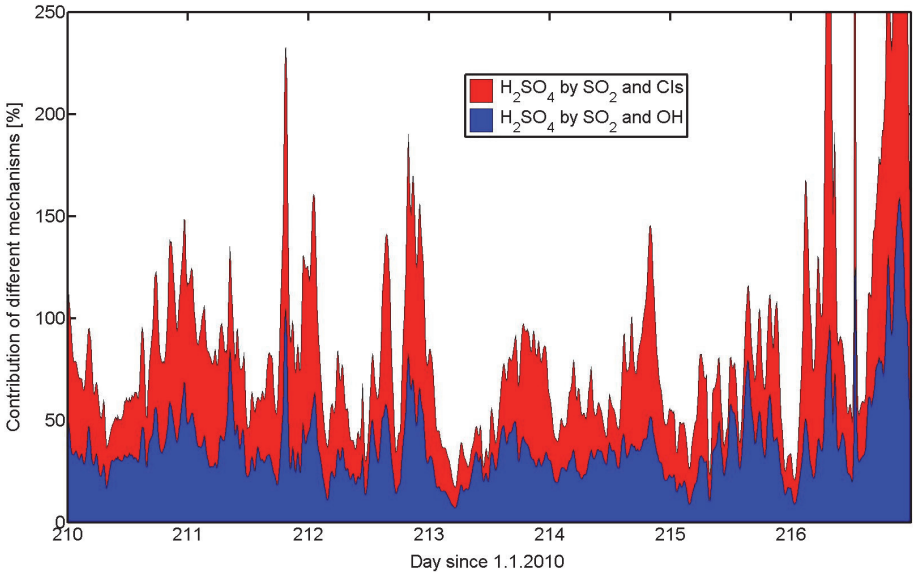

Fig. 8. Cumulative percentage contribution of the different SO_2 oxidation mechanisms for Hyytiälä.

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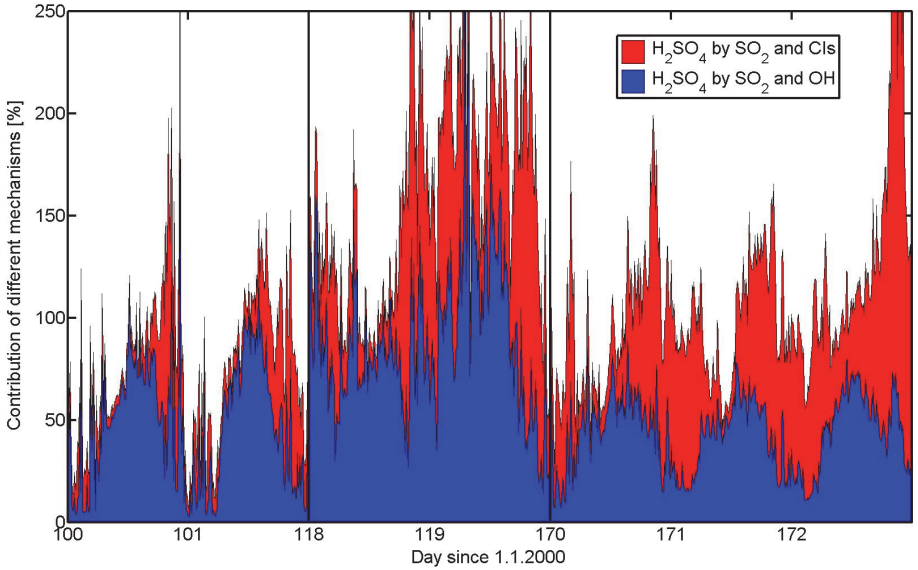

Fig. 9. Cumulative percentage contribution of the different SO_2 oxidation mechanisms for Hohenpeissenberg.

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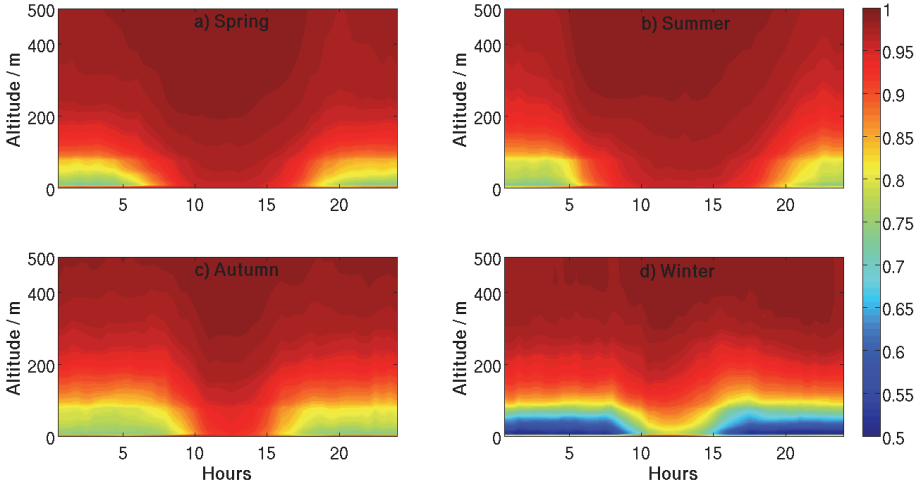

Fig. 10. Seasonal average values over the first 500 m above the surface at SMEAR II for model simulations with the chemistry model from scenario B divided by scenario D (for the definition of the scenarios see Sect. 3.3). The colour bar gives the ratio as described in Eq. (5).

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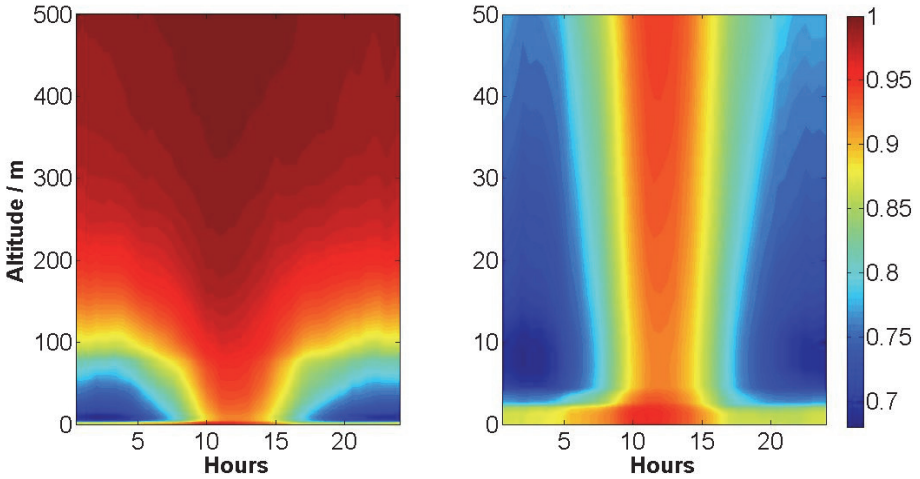

Fig. 11. Yearly average values for 50 and 500 m above the surface at SMEAR II for model simulations with the chemistry model from scenario B divided by scenario D (for the definition of the scenarios see Sect. 3.3). The colour bar gives the ratio as described in Eq. (5).

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