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Atmospheric Chemistry and Physics Discussions

Sources and sinks driving sulphuric acid concentrations in contrasting environments: implications on proxy calculations

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Abstract

Sulphuric acid has been shown to be a key driver for new particle formation and subsequent growth in various environments mainly due to its low volatility. However, direct measurements of gas-phase sulphuric acid are oftentimes not available, and the current sulphuric acid proxies cannot predict for example its nighttime concentrations or result in significant discrepancies with measured values. Here, we define the sources and sinks of sulphuric acid in different environments and derive a new physical proxy for sulphuric acid to be utilized in locations and during periods when it is not measured. We used H_2SO_4 measurements from four different locations: Hyytiälä, Finland; Agia Marina, Cyprus; Budapest, Hungary; and Beijing, China, representing semi-pristine boreal forest, rural environment in the Mediterranean area, urban environment and heavily polluted megacity, respectively. The new proxy takes into account the formation of sulphuric acid from SO_2 via OH oxidation and other oxidation pathways, specifically that via stabilized Criegee Intermediates. The sulphuric acid sinks included in the proxy are its condensation sink (CS) and atmospheric clustering starting from H_2SO_4 dimer formation. Indeed, we found that the observed sulphuric acid concentration can be explained by the proposed sources and sinks with similar coefficients in the four contrasting environments where we have tested it. Thus, the new proxy is a more flexible and an important improvement of previous proxies. Following the recommendations in the manuscript, a proxy for a specific location can be derived.

Keywords: sulphuric acid, proxy, boreal, rural, urban, megacity

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1. Introduction

Atmospheric New Particle formation (NPF) events and their subsequent growth have been observed to take place almost everywhere in the world (Kulmala et al., 2004; Kerminen et al., 2018; Chu et al., 2019). Many of these observations are based on continuous measurements and some include more than a year of measurement data (Nieminen et al., 2018). The importance of NPF events on the global aerosol budget and cloud condensation nuclei formation has been well established (Spracklen et al., 2008; Merikanto et al., 2009; Spracklen et al., 2010; Kerminen et al., 2012; Gordon et al., 2017). Recently, the contribution of NPF to haze formation, which was still controversial, is being investigated in an increasing number of studies from Chinese megacities (Guo et al., 2014; Zamora et al., 2019).

Sulphuric acid (H_2SO_4), which has a very low saturation vapor pressure, has been found to be the major precursor of atmospheric NPF (Weber et al., 1996; Kulmala et al., 2004; Sihto et al., 2006; Sipilä et al., 2010; Erupe et al., 2011; Lehtipalo et al., 2018; Ma et al., 2019). However, atmospheric measurements of gas-phase sulphuric acid are rare, mainly due to its low concentration (10^6–10^7 molecules cm^{-3} or below) that can only be measured using state-of-the art instruments (Mikkonen et al., 2011) such as the Chemical Ionization atmospheric pressure interface time of flight spectrometer (CI-APi-ToF) (Eisele and Tanner, 1993; Jokinen et al., 2012). Therefore, a physically and chemically sound proxy is needed to estimate H_2SO_4 concentrations in various environments where NPF events are observed but H_2SO_4 concentrations are not continuously measured.

Due to its important participation in clustering and thus in the NPF process, several studies have tried to produce proxies for H_2SO_4 in order to fill gaps in data. For example, Petäjä et al. (2009) developed an approximation of gas-phase H_2SO_4 concentration in Hyytiälä, southern Finland, using its source from reactions between SO_2 and OH radicals, and its loss by condensation onto pre-existing particles (condensation sink, CS). Later, Mikkonen et al. (2011) developed H_2SO_4 proxies based on measurements at six urban, rural and forest areas in European and North American sites. Proxies developed by Mikkonen et al. (2011) suggested that the sulphuric acid concentration depends mostly on the available radiation and SO_2 concentration, with little influence by CS. However, Lu et al. (2019), who developed a daytime proxy based on measurement in Beijing China, proved the need of taking into account the CS when approximating gaseous H_2SO_4, especially in areas where the condensational sink can be relatively high. The proxy developed by Lu et al. (2019) takes into consideration the formation pathways of H_2SO_4 via OH radicals from both the conventional photolysis of O_3 and from the photolysis of HONO, as well as, the loss of H_2SO_4 via CS.

Here, we derive a new proxy which takes into account the production of gaseous sulphuric acid from SO_2 with oxidation by OH and stabilized Criegee Intermediates (Mauldin et al., 2012) reactions, and its losses onto pre-existing aerosol particles (condensation sink) and due to molecular cluster formation. In order to evaluate the accuracy of the our hypothesized sources and sinks and the goodness of our new proxy, we utilize measurements from four different locations: (1) Hyytiälä, Finland, (2) Agia Marina, Cyprus, (3) Budapest, Hungary and (4) Beijing, China, representing a semi-pristine boreal forest environment, rural environment in the Mediterranean area, urban environment and heavily polluted megacity, respectively. We further compare the coefficients of production and losses in each environment in order to understand the prevailing mechanism of the H_2SO_4 budget in each of the studied environments. As a result of this investigation, a well-defined sulphuric acid

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concentration can be derived for multiple areas around the world and even extended in time during times when it was not measured (such as: gap filling, forecast, prediction, estimation, etc.).

2. Measurement locations, observations and instrumentation

2.1. Locations

Semi-pristine boreal forest environment: Hyytiälä, Finland

Measurements were conducted at the SMEAR II-station, located in Hyytiälä (61.1° N, 24.17°E, 181 m a.s.l. (Hari and Kulmala, 2005)), southern Finland. Here we used measurements from August 18, 2016 to April 16, 2017 and from March 8, 2018 to February 28, 2019. The measurements were performed at a tower 35 m above the ground level. A summary for all locations and instrumentation is given in Table S1.

Rural background site: Agia Marina, Cyprus

Measurements were conducted at the Cyprus Atmospheric Observatory (CAO) (35.03 N, 33.05° E; 532 m a.s.l.), a rural background site located close to Agia Marina Xyliatou village, between February 22 and March 3, 2018. For more details, see for example Pikridas et al. (2018).

Urban location: Budapest, Hungary

The measurements took place at the Budapest platform for Aerosol Research Training (BpART) Research Laboratory (N 47° 28' 30", E 19° 03' 45", 115 m a.s.l.) of the Eötvös University situated on the bank of the Danube between March 21 and May 2, 2018. The site represents a well-mixed average atmosphere of the city centre Salma et al. (2016).

Polluted megacity: Beijing, China

Here the observations were performed during December 1, 2018 to January 31, 2019, at the west campus of Beijing University of Chemical Technology (39.94° N, 116.30° E). The sampling took place from outside the window at the 5th floor of a university building adjacent to a busy street. For more details, see for example Lu et al. (2019); Zhou et al. (2020).

2.2. Instrumentation

Trace Gases

A summary for all locations and instrumentation is given in Table S1. In all four locations, the sulphuric acid concentrations were measured using a Chemical Ionization atmospheric pressure interface time of flight spectrometer (CI-APi-ToF) (Eisele and Tanner, 1993; Jokinen et al., 2012) with NO_3^- as a reagent ion and analyzed using a tofTools package based on MATLAB software (Junninen et al., 2010). In Hyytiälä and Beijing, the SO_2 and O_3 concentrations were measured using an SO_2 analyzer (Model 43i, Thermo, USA), with a detection limit of 0.1 ppbv, and O_3 analyzer (Model 49i, Thermo, USA), respectively. In Cyprus, SO_2 and O_3 are monitored using Ecotech Instruments (9850 and 9810, respectively). Concentrations of SO_2 in Budapest were measured by UV

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fluorescence (Ysselbach 43C) with a time resolution of 1 h at a regular station of the National Air Quality Network located in 1.7 km in the upwind prevailing direction from the BpART site. It was shown earlier that the hourly average SO_2 concentrations (See Figure S1) in central Budapest are ordinarily distributed without larger spatial gradients (Salma and Németh, 2019).

Particle number Size Distribution

The condensation sink (CS) was calculated using the method proposed by Kulmala et al. (2012) from number size distribution measurements. In Hyytiälä, the particle number size distribution was measured using a twin differential mobility particle sizer (DMPS) (Aalto et al., 2001). Hygroscopic growth correction (Laakso et al., 2004) was included when calculating the CS in Hyytiälä (Figure S2). In Agia Marina, the particle number size distribution between 2 and 800 nm was reconstructed from two instruments: an Airel NAIS (Neutral cluster and Air Ion Spectrometer, 2-20 nm) and TSI SMPS (Scanning Mobility Particle Sizer, 20-800 nm). In Budapest, the particle number size distributions were measured by a flow-switching type DMPS in a diameter range from 6 to 1000 nm in the dry state of particles (RH<30%) in 30 channels with a time resolution of 8 min (Salma et al., 2016b). In Beijing, the particle number size distribution between 3 nm and 850 nm was measured using a Particle Size Distribution System (PSD,(Liu et al., 2016)).

Radiation

In Hyytiälä, Global radiation (GlobRad) was measured using a SK08 solar pyranometer until August 24, 2017 and after that using a EQ08-S solar pyranometer. The measurements were relocated from 18-m height to 37-m height on February 14, 2017. Global Radiation from the Agia Marina is monitored using a weather station (Campbell Scientific Europe). In Budapest, global radiation was measured by an SMP3 pyranometer (Kipp and Zonnen, The Netherlands) on the roof of the building complex with a time resolution of 1 min. Its operation was checked by comparing the measured data with those obtained from regular radiation measurements performed by a CMP11 pyranometer (Kipp and Zonnen, The Netherlands) at the Hungarian Meteorological Service (HMS) in a distance of 10 km. The annual mean GlobRad ratio and SD of the 1-h values for the BpART and HMS stations were 1.03±0.23 for GlobRad > 100 W m^{-2}, which changed to 1.01±0.05 when considering additionally clear sky conditions. In Beijing, GlobRad intensity was measured at the rooftop of the 5-floor building using a Vaisala Weather station data acquisition system (AWS310, PWD22, CL51), Metcon.

Alkenes

Volatile organic compounds (VOCs) were measured with a proton transfer reaction quadrupole mass spectrometer (PTR-MS, Ionicon Analytik GmbH) in Hyytiälä. Ambient mixing ratios are measured every third hour from several different measurement heights. In this study, we use data from 16.8 m height. The instrument is calibrated regularly with standard gas (Apel-Riemer Environmental, Inc.) (Taipale et al., 2008).
In Beijing, VOCs were measured using single photon ionization time-of-flight mass spectrometer (SPI-MS 3000R, Hexin Mass Spectrometry) with unit mass resolution (UMR) (Gao et al., 2013) from September 27, 2018 and May 28, 2019. The alkenes included here are propylene, butylene, butadiene, isoprene, pentene and hexene. As the instrument cannot distinguish conformers, the pentene and

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hexene could also be cyclopentene and cyclohexene. Correlation coefficients between the different variables used in our study in all four locations are shown in Figures S3-S7.

3. Derivation of the new proxy

We applied the following equation to describe the time-evolution of gas-phase sulphuric acid concentration:

$$\frac{d[H_2SO_4]}{dt} = k_0[OH][SO_2] + k_2[O_3][Alkene][SO_2] - CS[H_2SO_4] - k_3[H_2SO_4]^2 \qquad (1)$$

Here, k_o represents the coefficient of H_2SO_4 production term due to the well-known SO_2 - OH reaction (Petäjä et al., 2009) and k_2 is the coefficient of H_2SO_4 production via stabilized Criegee Intermediates (sCI) produced by the ozonolysis of alkenes (Mauldin et al., 2012). Here we use available monoterpene concentration (MT) as a proxy for alkenes in Hyytiälä as they are the dominating species in the boreal forest environment (Hakola et al., 2012; Hellén et al., 2018; Rinne et al., 2005). For Beijing, we use urban dominating aromatic alkenes. As no VOC measurements are performed in neither Agia Marina nor Budapest, we evaluate the proxy without the stabilized Criegee Intermediate source term. It is important to note here that the coefficient for sCI is a "bulk" term, and it varies from place to place due to the differences in sCI structures and different production efficiency from different alkene species (Novelli et al., 2017; Sipilä et al., 2014). The third term in Equation 1 represents the loss of H_2SO_4 to pre-existing aerosol particles, known as condensation sink (CS). The fourth term in Equation 1 takes into account the additional loss of H_2SO_4 due to cluster formation not included in the term containing CS. This is necessary because CS is only inferred from size-distribution measurements at maximum down to 1.5 nm, i.e. not containing any cluster concentrations and hence losses onto these clusters. This term is written in the form of sulphuric acid dimer production, which seems to be the first step of cluster formation once stabilized by bases (Kulmala et al., 2013; Almeida et al., 2013; Yao et al., 2018).

Since measuring the OH concentration is challenging, we first replaced it with the UVB radiation intensity, which has been shown to be a good proxy for the OH concentration (Berresheim et al., 2002; Lu et al., 2019; Rohrer and Berresheim, 2006). Unfortunately, UVB was not measured in all the field studies considered here. Alternatively, GlobRad, a commonly measured quantity, tends to correlate well with UVB and can generally replace it, as used previously by Petäjä et al. (2009). We confirmed the strong correlation between UVB radiation and Global radiation in two locations, Hyytiälä and Beijing (Figure S8-S9). Accordingly, the coefficient k_1 here replaces the coefficient of H_2SO_4 production k_o terms (Equation 2). We proceed here using only GlobRad in the proxy to be consistent with the two other locations where UVB was not measured (Agia Marina and Budapest).

$$\frac{d[H_2SO_4]}{dt} = k_1 GlobRad[SO_2] + k_2[O_3][Alkene][SO_2] - CS[H_2SO_4] - k_3[H_2SO_4]^2 \qquad (2)$$

By assuming a steady state between H_2SO_4 production and loss, the H_2SO_4 concentration can be solved directly from Equation (2):

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$$[H_2SO_4] = -\frac{CS}{2k_3} + \sqrt{\left(\frac{CS}{2k_3}\right)^2 + \frac{[SO_2]}{k_3}(k_1 GlobRad + k_2[O_3][Alkene])} \quad (3)$$

In order to evaluate the importance of each of the source terms in determining the change in sulphuric acid concentration, we refitted the data after excluding the stabilized Criegee intermediates source pathway as shown in Equation 4.

$$\frac{d[H_2SO_4]}{dt} = k_1 GlobRad[SO_2] - CS[H_2SO_4] - k_3[H_2SO_4]^2 \quad (4)$$

In order to evaluate the importance of each of the sink terms in determining the sulphuric acid concentration, we refitted the data after excluding the loss of sulphuric acid via the cluster formation pathway using Equation 5.

$$\frac{d[H_2SO_4]}{dt} = k_1 GlobRad[SO_2] + k_2[O_3][Alkene][SO_2] - CS[H_2SO_4] \quad (5)$$

we also refitted the data using the simple proxy proposed by Petäjä et al. (2009) by excluding the formation of sulphuric acid via stabilized Criegee intermediates source pathway and loss of sulphuric acid via the cluster formation pathway using Equation 6 and evaluated it by comparing to the original proxy.

$$\frac{d[H_2SO_4]}{dt} = k_1 GlobRad[SO_2] - CS[H_2SO_4] \quad (6)$$

$$\frac{d[H_2SO_4]}{dt} = 1.4x\ 10^7 x\ GlobRad^{-0.7}[SO_2] - CS[H_2SO_4] \quad \textit{(See Petäjä et al. 2009)} \quad (7)$$

The fitting coefficients were obtained by minimizing the sum of the squared logarithm of the ratio between the proxy values and measured sulphuric acid concentration using the method described by Lagarias et al. (1998), a build-in function *fminsearch* of MATLAB, giving the optimal values for the coefficients. The data was subject to boot strapping when getting the *k* values as a measure of accuracy in terms of bias, variance, confidence intervals, or prediction error (Efron and Tibshirani, 1994). The median, 25th percentile and 75th percentiles of the coefficients are shown in for all locations together with the median *k* values in Table 1. Figures S3-S5 present the correlation matrix between the different variables participating in H_2SO_4 formation and loss in all locations. In Beijing, the Alkenes (AVOCs) have different patterns in day and night which forces us to have two separate equations for daytime and nighttime. The goodness of the fit and the probability of overfitting or under-fitting was evaluated using the Akaike information criterion (Figure S10), which also compares the proxies given in equations 2, 4, 5 and 6. The criterion uses the sample size (number of points), the number of parameters (terms in the equation) and the sum of squared estimate of errors (SSE: deviations predicted from actual empirical values of data) to estimate the quality of each model, relative to each of the other models and thus provides means for model selection (McElreath, 2018).

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4. Results and Discussions

4.1. The sulphuric acid proxy for Hyytiälä SMEAR II station

Figure 1 shows the scatter plot between the observed H_2SO_4 concentrations and that derived by the proxy using the full Equation 2. The correlation coefficient was 0.85 (2089 data points). The data were related to 3-hour medians, as the monoterpene concentration was measured only every third hour. In Figure 1B-D, the proxy is refitted after removing one of the source or sink terms (Equations 4-6), in order to evaluate the sensitivity of the proxy to each of the terms and to show the improvement of the proxy using the additional source and sink (Figure 1A) in comparison to the simple proxy that was used by Petäjä et al. (2009) (Figure 1D). Our results show that the integration of additional terms of H_2SO_4 formation (i.e. the stabilized Criegee Intermediates) and loss (atmospheric cluster formation) gives the new proxy the ability to accurately capture the diurnal variation of the H_2SO_4 concentration, demonstrating a clear improvement over the earlier physical proxy (Petäjä et al., 2009). In Figure 1B the corresponding data are shown without the alkene term (Equation 4). The correlation is significantly weaker (0.73) than with the full equation. Even more importantly, we cannot estimate the contribution of the alkene term to the sulphuric acid concentration (Figure 2 – Fit 2) as the fit results also in an unphysical coefficient for cluster formation (Kürten et al., 2015) and the fit fails to capture the diurnal pattern during dark hours after 16:00 (Figure 2 – Fit 2). When fitting the data without the cluster source term (Equation 5), the correlation coefficient is high (Figure 1C), yet the goodness of the fit is not as good as when the cluster source term is taken into account (Figure S10).

The fit was able to reproduce the sulphuric acid concentration in such clean environment without the cluster term (Figure 2 – Fit 3), perhaps due to low concentrations of bases participating in clustering in Hyytiälä (Jen et al., 2014). Finally, the corresponding data without both the alkene source term and cluster formation source term (Equation 6, Figure 1D) shows a weaker correlation between the measured and modelled sulphuric acid concentration (0.73), but more importantly, it deviates far from the 1:1 line during both daytime and nighttime (Figure 2 – Fit 4). It is important to note here that when deriving the Petäjä proxy (Petäjä et al. 2009), the model relied on summer data between April and June 2007 which could explain the misfit with the current data from Hyytiälä which spans the whole year. In general, using all four terms in equation 2 shows improvement over all other combinations (Equations 4-6) in terms of not only correlation coefficients and accurate diurnal cycle between measured and calculated concentrations of sulphuric acid as shown in Figures 1 and 2, but also show a better goodness of the fit as shown in Figure S10 when using the AIC statistical method.

4.2. Sulphuric Acid Proxy at a Rural Site: Agia Marina, Cyprus

Since there were no direct measurements of alkenes in Agia Marina, we had to exclude the formation of H_2SO_4 in the oxidation by sCI from the proxy, and therefore we derived only the daytime H_2SO_4 proxy concentration. The correlation between the measured and proxy concentration of H_2SO_4 was 0.88 (96 data points) which proves the truthfulness of this proxy (Figure 3). However, the slope deviates from the 1-to-1 line which could be attributed to the additional formation mechanisms that we could not include with the current data. However, the addition of the cluster loss mechanism shows a noticeable improvement over the simple proxy, in Figure 3B (R = 0.80). The cluster loss term starts to become more important in this rural environment in comparison to the boreal forest, which could be due to a higher concentration of stabilizing bases in Agia Marina compared with Hyytiälä.

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Although both fits, Equation 4 and 6, show similar diurnal patterns (Figure 4, Fits 2 and 4), the loss term due to H_2SO_4 cluster formation improved the precision of the new proxy (Figures 3). According to the statistical AIC method, the goodness of the fit has improved from 161 to 71, with and without the clustering term, respectively, as shown in Figure S10. Also, even without the alkene term, the new coefficients derived improved the proxy in comparison to Petäjä et al. (2009) Figure 4.

4.3. **Proxy for urban environment: Budapest, Hungary**

Next we try to understand the mechanisms of sulphuric acid formation and losses in an even more complex environment, such as urban Budapest (Figures 5 & 6). Since there were no direct measurements of alkenes there, neither its proxies such as monoterpenes or anthropogenic volatile organic compounds, we derived the sulphuric acid proxy excluding the formation due to stabilized Criegee Intermediate pathway, as in Equation 4. In comparison to the simple proxy (Figure 5B; R = 0.49; 262 data points), the correlation between the measured and proxy concentration of H_2SO_4 improved with the addition of the loss term due to cluster formation, R = 0.59 (Figure 5A). The correlation between measured and modelled values of sulphuric acid became weaker in Budapest in comparison to Hyytiälä and Agia Marina, which could be attributed to a more complex environment, and additional pathways of sulphuric acid formation and losses. Additionally, we observed a sudden SO_2 concentration change in the middle of the campaign, possibly due to sudden change in local meteorology and airmass transport, which could also explain the weaker correlation (See Figure S1). The loss term due to H_2SO_4 dimerization improved the precision of the new proxy in comparison to the simple model as well as the Petäjä et al. (2009) derivation, as shown in Figure 6. We think that the overestimation in the Petäjä proxy is because of its dependence on the SO_2/CS ratio. The proxy is originally derived in Hyytiälä and when we apply the same coefficients to Budapest it gives higher estimated concentration compared to the measured since SO_2/CS ratio is smaller in Budapest (Figure 10). It is also visible from Figures 5 and 6, that the addition of the dimerization term was capable of better capturing the lower H_2SO_4 concentrations in comparison to fitting the data without the dimerization term. In comparison to both Hyytiälä and Agia Marina, the coefficient associated with dimerization in Budapest is slightly higher, which can be attributed to the availability of a possibly facilitated clustering due to higher abundance of stabilizing bases such as amines and ammonia (discussed in the later section 4.5).

4.4. **Proxy for Megacity: Beijing, China**

In megacities, in our case Beijing, the sulphuric acid concentration is particularly high during nighttime, which confirms the need for determining the contribution of sources other than OH (radiation) to its formation. Our observations emphasize the contribution of the alkene pathway, as without considering this route we would not replicate morning hours correctly. During daytime, there is enhanced dimerization and cluster formation due to the abundance of stabilizing bases (Yao et al., 2018). In addition, alkenes or volatile organic compounds during daytime are different from those during nighttime, which could be attributed to a different fleet composition during those times (Yang et al., 2019). For that purpose, we had to divide the data for Beijing into two groups: daytime (GlobRad >= 50 W/m^2) and nighttime (GlobRad<50 W/m^2). Besides, in such a complex environment, sulphuric acid might originate from sources other than the ones we accounted for in our calculation, for example through the hydrolysis of SO_3 formed from non-photochemical processes (Yao et al.,

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2020, In Prep.). As a result, we derived two separate sets of equations, as shown in Table 1. Results of a combined equation are shown in Figures S11 and S12.

In Figure 7, we see an improvement of the new proxy (Equation 2) in comparison to the simple proxy (Equation 6) derived by Petäjä et al. (2009) as the former takes into the account the additional sources and sinks of H_2SO_4 which were not considered in previous works (See also Figure S10). Introducing the alkene production term improved the accuracy of the H_2SO_4 concentration slightly for daytime and significantly during nighttime (Figures 7 and 8), which supports our assumption that H_2SO_4 formation during nighttime is driven by stabilized Criegee Intermediates. In Figure 7B we show the proxy without the alkene term. Although the correlation improves, this is only because the nighttime values are not captured. In Figure 9, we see the importance of all sources and sinks predicted for sulphuric acid, as Fit 1 (Equation 2) predicts best the measured sulphuric acid concentration. Additionally, according to the statistical AIC method, using the full equation has the least probability of inaccuracy and error in estimating the sulphuric acid concentration (Figure S10). Moreover, it is clear that the addition of the cluster sink term in Megacity environment is required due to it large contribution as a sink for H_2SO_4 especially due to higher concentrations of stabilizing molecules, the cluster mode (sub-3 nm) particle concentration, are the highest in Chinese Megacities (Zhou et al., 2020).

4.5. **Sensitivity of the proxy to the H_2SO_4 sources and sinks**

The variations of coefficients related to Equation 3 can be used to get insights into the general chemical behavior under current atmospheric conditions, as well as into the mechanisms of sulphuric acid formation and losses in various environments. The contribution of different terms in different locations seem to vary significantly. The new loss term taking into account clustering starting from dimer formation needs to be taken into account in all the environments in daytime. On the other hand, without alkene term it is in practice impossible to get nighttime concentrations right.

In Table 1 we have presented the fitted coefficients (Equation 3) for all our sites, whereas the contributions of the different terms in the balance equation are given during daytime in Figure 9 and Table 2. The variability of the coefficients (Table 1), as well as the relative contributions of each term to the total sulphuric acid concentration (Table 2), could give valuable information on the mechanisms resulting in sulphuric acid formation and losses. At steady state (Equation 2), the sources and sinks are in balance with each other during both daytime and nighttime, but there were clear differences in the individual contributions. For instance, a variation in k_1 could be due to variations in OH sources and sinks. Although in urban locations OH sinks are expected to be higher and therefore k_1 to be lower, additional sources of OH are available in such locations, for example HONO (Zhang et al., 2019). The alkene/Criegee intermediate term was found to be an important H_2SO_4 source (Figures 1, 2, 7 and 8), as without it we are not able predict night or morning concentrations of H_2SO_4 properly. The alkene source term contributed up to almost 100% of the H_2SO_4 sources during nighttime in Beijing and up to 82% of the sources during nighttime in Hyytiälä (Table 2). The alkene term is, however, not only important during nighttime but also during daytime, as it contributed to the sources by a median of 41% during daytime in Beijing. It is important to note here that Criegee intermediates vary between locations, they also form in different yield percentages from different alkenes (Novelli et al., 2017; Sipilä et al., 2014). These stabilized Criegee intermediates also react differently under different environmental conditions.

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The CS term had the highest contribution to the total sink in Hyytiälä. Its contribution decreased when moving towards more polluted environments (Figure 10), to become in Beijing, regardless of the relatively high condensation sink in Megacities (Laakso et al., 2006; Monkkonen et al., 2005; Monkkonen et al., 2004; Yao et al., 2018), smaller than that of the cluster sink term. This observation might be attributed to decreased effectiveness of condensation sink in more polluted environments (Kulmala et al., 2017), but also to increased contribution of the clustering sink term in such environments where the concentration of stabilizing bases is highest, particularly in daytime (Yao et al., 2018; Yan et al., 2018). It should be noted that measurements of ammonia and similar bases are rare, so their exact contribution is difficult to estimate..

5. Conclusions and recommendations

Sulphuric acid is a key gas-phase compound linked to secondary aerosol production in the atmosphere. The concentration of sulphuric acid in the gas phase is governed by source and sink terms. In this paper we define the sources and sinks of H_2SO_4 and derived a physically and chemically sound proxy for the sulphuric acid concentration using measurements at 4 different locations, including boreal forest environment (Hyytiälä, Finland), a rural Mediterranean site (Cyprus), an urban area (Budapest) and a megacity (Beijing). When describing the change in gas phase sulphuric acid concentration, we took into account two source terms: 1) photochemical oxidation of sulfur dioxide and 2) sulphuric acid originating from alkene and ozone reactions and associated stabilized Criegee radical pathway. For the sink terms, we considered 3) the loss rate to the pre-existing aerosol described by condensation sink, and 4) loss rate of sulphuric acid monomer due to clustering process.

In general, the variation in the environmental conditions and difference in concentrations of air pollutants affects the coefficients derived and therefore it is important to derive location specific coefficients. The derived coefficients give insights into the general chemical behavior and into the mechanisms of sulphuric acid formation and losses in various environments. As improvements from previously derived proxies, without the alkene H_2SO_4 formation pathway, it is in practice impossible to get nighttime concentrations. On the other hand, the additional loss term taking into account clustering starting from dimer formation needs to be taken into account in all the environments especially those with higher cluster formation probabilities due to availability of stabilizing bases.

The coefficients derived do not differ substantially between the different locations. The proxy could therefore be used at locations with no prior H_2SO_4 measurements, provided that the environmental conditions are approximately similar to those in one of the four sites described here. More specifically, the proxies could be utilized to derive long-term data sets for H_2SO_4 concentrations, which would be essential in performing various kinds of trend analyses. In order to derive the long term sulphuric acid concentrations, we recommend deriving in-house coefficients in case sulphuric acid concentrations are directly measured rather than using the ones from already derived studies. The choice of equation depends on the availability of the data on site. In case alkenes or their proxies are measured and sulphuric acid is measured, derivation of the coefficients should be based on Equation 2. In case neither alkenes nor their proxies are measured but sulphuric acid is measured, the coefficients and therefore the proxy for daytime only can be derived, using Equation 4. In case, sulphuric acid is not measured, one can calculate the sulphuric acid proxy using the Equation 2 or Equation 4, depending on whether the alkene data is available or not, respectively, using the coefficients suggested in Table

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1 which are relevant to the site of interest. In order to make the best choice for the coefficients, Figure 10 can be followed in order to decide which description fits the location of interest best. For instance, in case the condensation sink is between 2 x 10^{-3} and 6 x 10^{-3} s^{-1}, and the SO_2 concentration is lower than 2 x 10^9 molecules. cm^{-3}, coefficients of Hyytiälä or the boreal forest are to be used.

Data availability

The data used in the manuscript and the MATLAB code which provides the k values are available from the first author at lubna.dada@helsinki.fi.

Author contributions

MK came up with the idea, LD, IY, CL, RB analyzed the data, YG, CD, RY, CY, LY, JJ, YL, BC performed the measurements in Beijing and pre-processed the raw data, NS, TJ, MS, TP performed the measurements in Hyytiälä and pre-processed the raw data, LD, TN, JK, KRD, DS, TH, PP, FB, VMK, MK provided useful discussion and ideas, IS, TW, RB, TJ performed the measurements in Budapest and pre-processed the raw data, MP, JS, RB, TJ performed the measurement in Agia Marina and pre-processed the raw data. LD, VMK and MK wrote the manuscript. All co-authors contributed to reviewing the manuscript and to the discussions related to it.

Competing interests

All authors declare no competing interests.

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Tables and Figures

Table 1: Coefficients used in the proxy equation in all four environments. Numbers in parenthesis represent the 25th and 75th percentiles of boot strapped data, respectively.

Location	***GlobRad (W/m²)***	$k_1(10^{-8}\ m^2\ W^{-1}\ s^{-1})$	$k_2(\cdot 10^{-29}\ cm^6\ s^{-1})$	$k_3\ (\cdot 10^{-9}\ cm^3\ s^{-1})$
Hyytiälä	>=0	1.21(1.15-1.24)	10.3(10.0-10.61)	5.98(5.58-5.99)
Agia Marina	>= 50	0.92(0.78-1.13)	N/A	2.32(1.47-3.63)
Budapest	>= 50	0.14(0.13-0.15)	N/A	7.90(7.90-7.91)
Beijing	>= 50	5.20(4.62 – 5.78)	1.45(1.09 – 1.88)	5.76(4.30 – 7.0)
Beijing	<50	1.35(1.09 – 1.64)	4.39(4.24 – 4.59)	7.0(6.99 – 7.0)

Table 2: Fraction of each source and sink term to total H_2SO_4 concentration. Median of boot strapping results and their 25th and 27th percentiles are shown.

	GlobRad (W/m^2)	Source Terms		Sink Terms	
		$k_1 Glob[SO_2]$	$k_2[O_3][A][SO_2]$	$-k_3[H_2SO_4]^2$	$-CS[H_2SO_4]$
Hyytiälä	>=0	0.31 (0.08-0.43)	0.18 (0.06-0.41)	0.16 (0.06-0.29)	0.34 (0.21-0.44)
Agia Marina	>= 50	0.5 (0.48-0.52)	0	0.20 (0.15-0.32)	0.30 (0.18-0.33)
Budapest	>= 50	0.5 (0.48-0.51)	0	0.22 (0.15-0.29)	0.28 (0.21-0.35)
Beijing	>= 50	0.29 (0.24 – 0.35)	0.21 (0.15 – 0.26)	0.29 (0.18 – 0.34)	0.21 (0.14 – 0.30)
	<50	0.06 (0.02 – 0.13)	0.44 (0.36 – 0.48)	0.24 (0.11-0.35)	0.26 (0.15-0.39)

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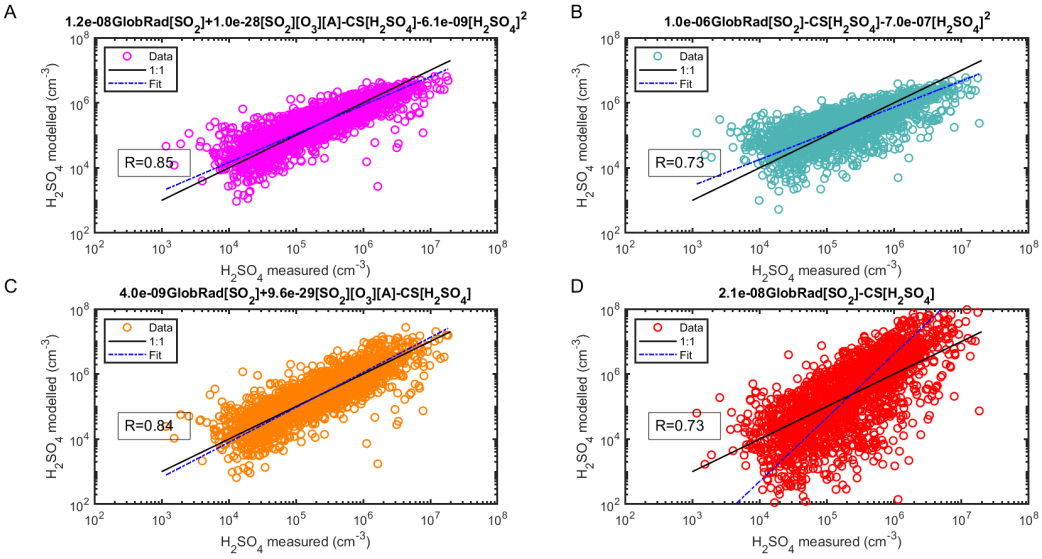

Figure 1: Sulphuric acid proxy concentration as a function of measured sulphuric acid. Observation at SMEAR II station, Hyytiälä Finland. The observed concentrations are measured 2016-2019 using CI-APi-ToF and are 1-hour medians resulting in a total of 2089 data points. In (A), the full Equation 2 is used, in (B) the equation without the Stabilized Criegee Intermediates source (Equation 4), in (C) the equation without the cluster sink term (Equation 5) and in (D) the equation without both the Stabilized Criegee Intermediates source and the cluster sink term (Equation 6). The 'Fit' refers to the fitting between the measured and the proxy calculated sulphuric acid concentration.

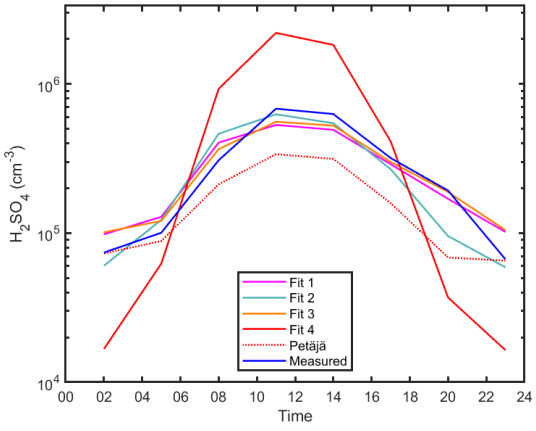

Figure 2: The diurnal variation of sulphuric acid proxy concentrations using different fits and observed concentrations at SMEAR II in Hyytiälä, Finland. Median values are shown. Fits 1,2, 3 and 4 corresponds to the Equations 2, 4, 5, and 6, respectively. Petäjä fit shown is applied using the coefficients reported in Petäjä et al. 2009 (Equation 7).

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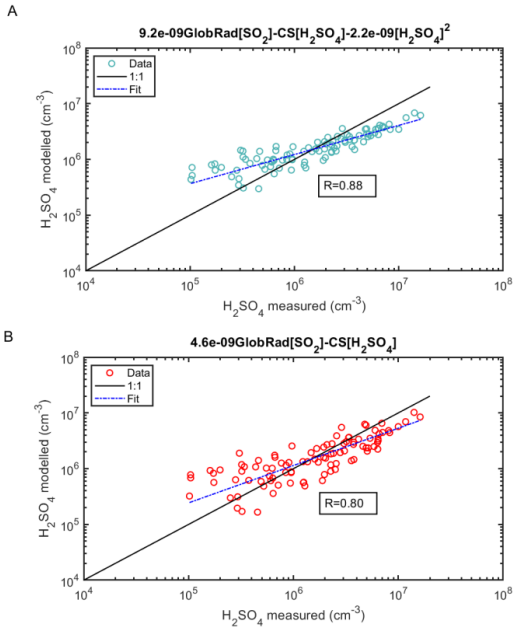

Figure 3: Sulphuric acid proxy concentration as a function of measured sulphuric acid. Observation at Agia Marina, Cyprus, excluding the Alkene term. The observed numbers concentrations are measured during Feb- Mar 2018 using CI-APi-ToF and are hourly medians resulting in a total of 96 data points. Sulphuric acid proxy concentration as a function of measured sulphuric acid. In (A), the equation without the Stabilized Criegee Intermediates source (Equation 4) and in (B) the equation without both the Stabilized Criegee Intermediates source and the cluster sink term (Equation 6).

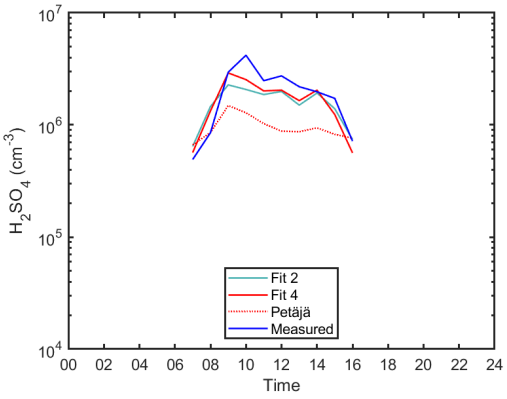

Figure 4 The diurnal variation of sulphuric acid proxies and observed concentrations in Agia Marina, Cyprus. Hourly median values are shown. Fits 2 and 4 corresponds to the Equations 4 and 6, respectively, See also Figure 3A and B, respectively. Petäjä fit shown is applied using the coefficients reported in Petäjä et al. 2009 (Equation 7).

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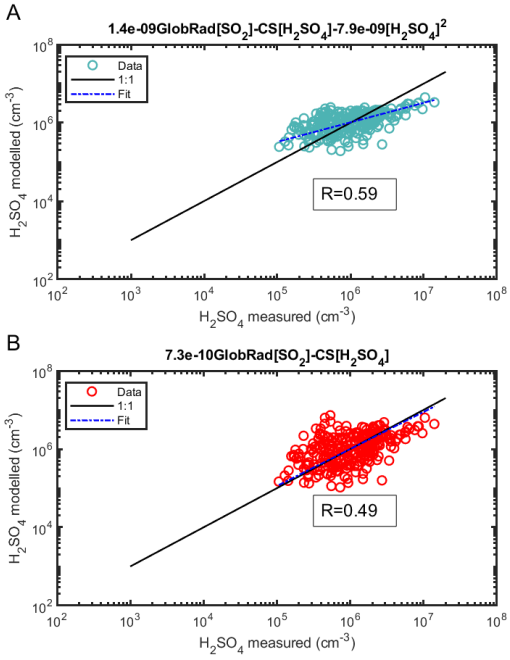

Figure 5 Sulphuric acid proxy as a function measured sulphuric acid at Budapest station, excluding the Alkene term. The observed numbers are measured during spring 2018 using CI-APi-ToF and are 1-hour medians coinciding with the measurement of trace gases and Global radiation every one hour resulting in a total of 262 data points. In (A), the equation without the Stabilized Criegee Intermediates source (Equation 4) and in (B) the equation without both the Stabilized Criegee Intermediates source and the cluster sink term (Equation 6).

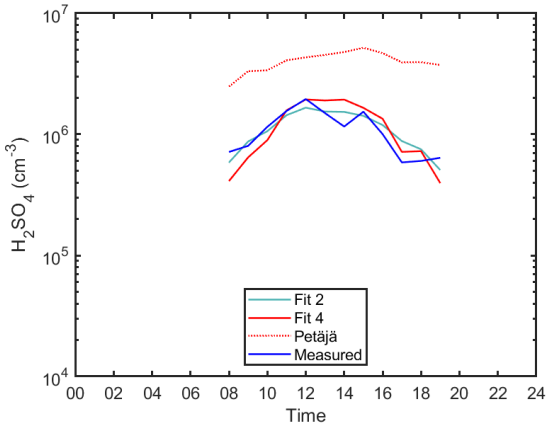

Figure 6 The diurnal variation of sulphuric acid proxies and measured concentrations in Budapest. Hourly median values are shown. Fits 2 and 4 corresponds to the Equations 4 and 6, respectively. Petäjä fit shown is applied using the coefficients reported in Petäjä et al. 2009 (Equation 7).

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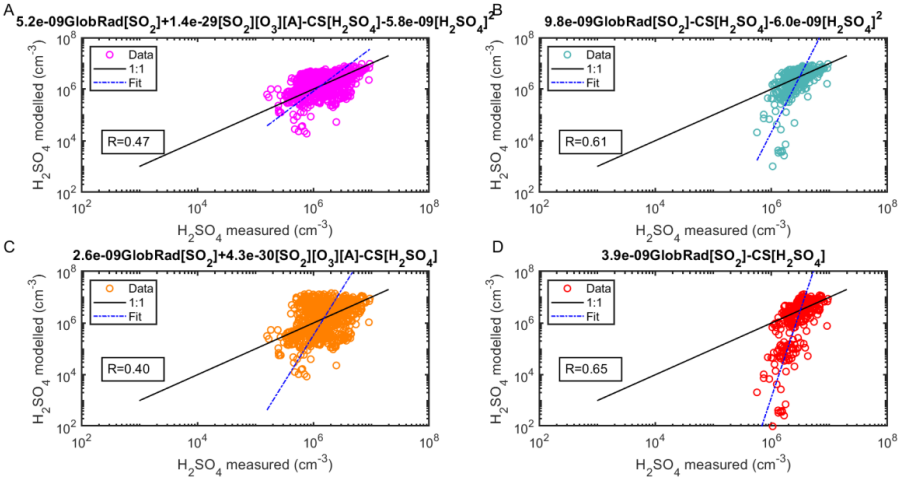

Figure 7 (A) Sulphuric acid proxy concentration using Globrad as a function of measured sulphuric acid. Observation at Beijing, China. The observed numbers concentrations are measured between 2018-2019 using CI-APi-ToF and are 1-hour medians resulting in a total of 875 data points. In (A), the full Equation 2 is used, in (B) the equation without the Stabilized Criegee Intermediates source (Equation 4), in (C) the equation without the cluster sink term (Equation 5) and in (D) the equation without both the Stabilized Criegee Intermediates source and the cluster sink term (Equation 6). Coefficients shown on top of the subplots relate to the daytime values.

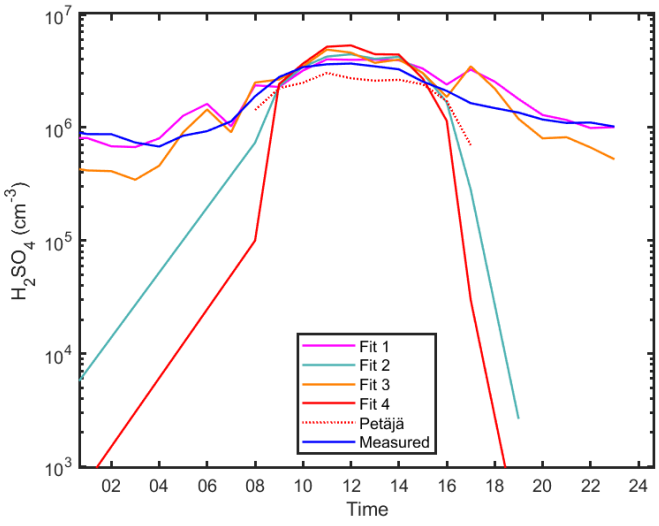

Figure 8 The diurnal variation of sulphuric acid proxy concentrations using different fits and observed concentrations at Beijing China, Finland. Median values are shown. Fits 1,2, 3 and 4 corresponds to the Equations 2, 4, 5, and 6, respectively. Petäjä fit shown is applied using the coefficients reported in Petäjä et al. 2009 (Equation 7).

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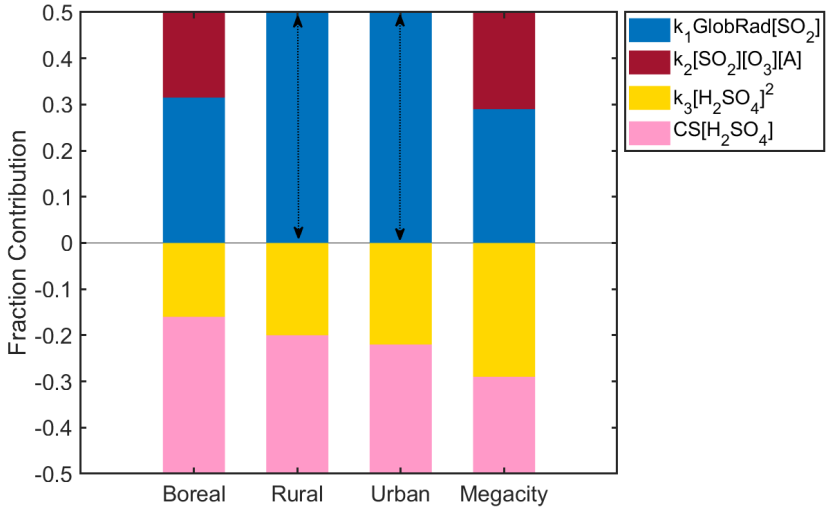
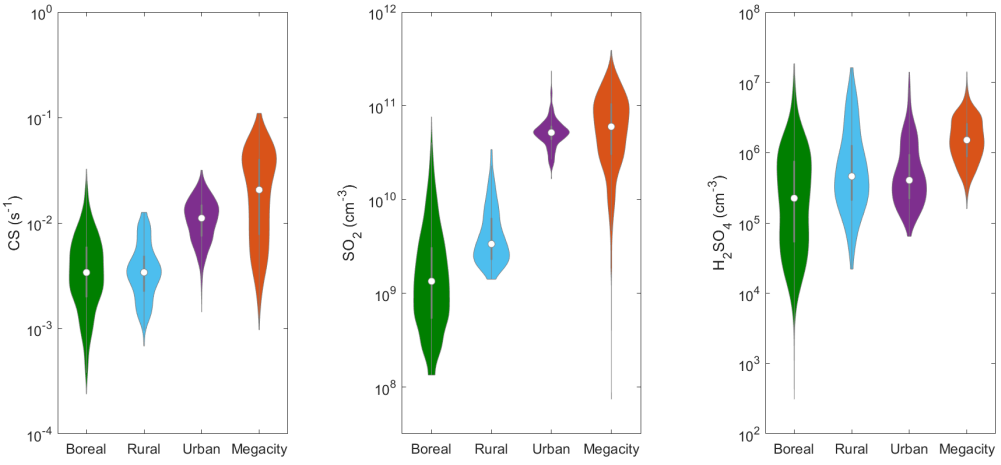


Figure 9 Fraction of each source and sink term to the change in H_2SO_4 concentration during daytime. Figure 9 is complementary to Table 2. The boreal, rural, urban and megacity labels refer to Hyytiälä, Agia Marina, Budapest and Beijing sites, respectively. Note that the fraction of the alkene term contribution is not zero for the rural or urban sites, but is due to unavailable alkene data from the Budapest and Cyprus sites.



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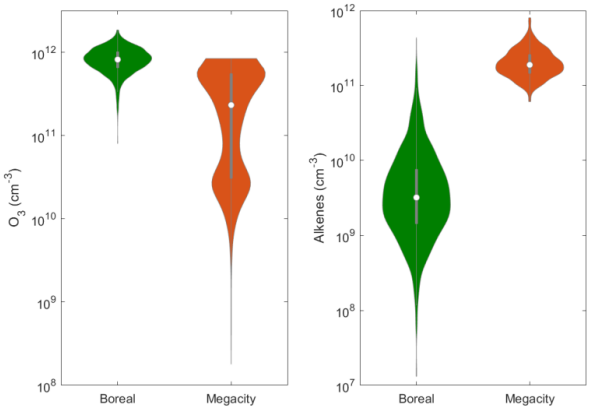

Figure 10 Condensation Sink, SO_2 and H_2SO_4 concentrations in diffrerent environements and O_3 and Alkenes in the boreal forest (Hyytiälä) and megacity (Beijing) environments. This figure could be used in order to choose the coefficients for calculating the proxy. The alkenes in the boreal environment are monoterpenes(e.g. alpha-pinene) and in the Megacity are anthropogenic volatile organic compounds (propylene, butylene, butadiene, isoprene, pentene and hexene). The concentrations are displayed as violin plots which are a combination of boxplot and a kernel distribution function on each side of the boxplots. The white circles define the median of the distribution and the edges on the inner grey boxes refer to the 25th and 75th percentiles respectively. Daytime data (GlobRad > 50 W/m^2) is shown in Figure S11-S12. The correlations between the different variables at each site are shown in Figures S3 – S7.

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