Toward Building a Physical Proxy for Gas-Phase Sulfuric Acid Concentration Based on Its Budget Analysis in Polluted Yangtze River Delta, East China

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ABSTRACT: Gaseous sulfuric acid (H₂SO₄) is a crucial precursor for secondary aerosol formation, particularly for new particle formation (NPF) that plays an essential role in the global number budget of aerosol particles and cloud condensation nuclei. Due to technology challenges, global-wide and long-term measurements of gaseous H₂SO₄ are currently very challenging. Empirical proxies for H₂SO₄ have been derived mainly based on short-term intensive campaigns. In this work, we performed comprehensive measurements of H₂SO₄ and related parameters in the polluted Yangtze River Delta in East China during four seasons and developed a physical proxy based on the budget analysis of gaseous H₂SO₄. Besides the photo-oxidation of SO₂, we found that primary emissions can contribute considerably, particularly at night. Dry deposition has the potential to be a non-negligible sink, in addition to condensation onto particle surfaces. Compared with the empirical proxies, the newly developed physical proxy demonstrates extraordinary stability in all the seasons and has the potential to be widely used to improve the understanding of global NPF fundamentally.

KEYWORDS: sulfuric acid, proxy, budget analysis, primary emission, dry deposition

INTRODUCTION

Atmospheric aerosols play an essential role in air quality,¹ human health,² and climate change.³ New particle formation (NPF), which can be observed worldwide,⁴ determines the global budget of aerosol particles in terms of their number concentrations.⁵ Gaseous sulfuric acid (H₂SO₄) is the key precursor for particle nucleation via a series of processes, including H₂SO₄−H₂O binary nucleation, H₂SO₄−ammonia (NH₃)−H₂O ternary nucleation,⁶,⁷ H₂SO₄−amines−H₂O nucleation,⁸,⁹ H₂SO₄−organic−H₂O nucleation,¹⁰,¹¹ and H₂SO₄−NH₃−organic nucleation.¹² However, measuring gaseous H₂SO₄ has been challenging due to its extremely low atmospheric concentrations. Long-term measurements of ambient H₂SO₄ have only been reported in very few studies,¹³−¹⁸ which limits the understanding of global NPF. Gaseous H₂SO₄ was long believed to be formed only from the reaction between SO₂ and OH. However, more recently, stabilized Criegee intermediates (sCI), formed in the ozonolysis of alkenes, were demonstrated to be able to oxidize SO₂ and contribute to gaseous H₂SO₄.¹⁹,²⁰ This was found to be particularly important for the nighttime H₂SO₄ formation.²¹ In the coastal marine atmosphere, SO₂ oxidation by small Criegee intermediates (CI), produced possibly in photochemical reactions, and SO₃ formed from dimethyl sulfide (DMS) oxidation reaction with water might be non-negligible sources of H₂SO₄.²²,²³ Recently, Olin et al.²⁴ indicated a potential source of H₂SO₄ from traffic emissions in urban Helsinki based on the observed positive correlation between H₂SO₄ and NOₓ concentrations. Because of its weak chemical reactivity, the main sinks for gaseous H₂SO₄ are expected to be condensation onto aerosol particles or dry deposition to the ground or other surfaces.

Several proxies for gaseous H₂SO₄ were developed to enhance our global understanding of H₂SO₄ and NPF. Petäjä et al.²⁵ and Mikkonen et al.²⁶ built such proxies by considering the SO₂−OH reaction as the only source, and condensation onto pre-existing aerosol particles as the only sink, for H₂SO₄. Lu et al.²⁷ took into account O₃ and HONO concentrations to differentiate between OH originating from the O₃ and HONO...
photolysis. Dada et al.\textsuperscript{18} added the reaction of SO\textsubscript{2} with SCI as an additional H\textsubscript{2}SO\textsubscript{4} source to the proxy. These efforts largely improved the understanding of H\textsubscript{2}SO\textsubscript{4} in different environments, however, with obvious limitations. First, they all are empirical proxies based on mainly short-term and site-specific measurements, casting doubts on their general applicability. Second, nighttime H\textsubscript{2}SO\textsubscript{4} is rarely considered in these proxies. Here, we carried out comprehensive measurements of H\textsubscript{2}SO\textsubscript{4} and related parameters during four seasons at the SORPES station, East China, and conducted a budget analysis for gaseous H\textsubscript{2}SO\textsubscript{4} by taking all possible sources and sinks into consideration. We then developed a new physical proxy accordingly and evaluated its stability during different seasons.

\section*{MATERIALS AND METHODS}

\textbf{Field Observations.} The observations were carried out at the Station for Observing Regional Processes of the Earth System (SORPES) in the northeastern part of Nanjing, China (118\textdegree 57'E, 32\textdegree 07'N), which is the regional background station upwind from downtown Nanjing, during winter (from December 11, 2017, to January 17, 2018), spring (from April 13, 2018, to April 23, 2018), summer (from July 11, 2018, to August 9, 2018), and autumn (all of November 2018). The surrounding environment of the site is given in Figure S1 and detailed descriptions can be found elsewhere.\textsuperscript{27\textendash 31}

H\textsubscript{2}SO\textsubscript{4} was measured with a chemical ionization mass spectrometer (CIMS) equipped with a nitrate ionization source.\textsuperscript{32} Ambient H\textsubscript{2}SO\textsubscript{4} molecules were charged by reacting with NO\textsubscript{3}\textsuperscript{–} reagent ions in the reaction chamber of the inlet. Then, the concentration is calculated from the measured ion signals according to:

\begin{equation}
[H_2SO_4] = C \left[ \frac{HSO_4^- + HSO_3^- \cdot HNO_3}{NO_3^- + HNO_3 \cdot NO_3^- + HNO_3 \cdot (HNO_3) \cdot NO_3^-} \right]
\end{equation}

where \(C\) is the calibration coefficient, which was obtained seasonally by the known concentration of H\textsubscript{2}SO\textsubscript{4} calculated from the \text{SO}_{2}\text{OH} reaction here with 33% systematic uncertainty.\textsuperscript{33} Also, this instrument provides a high signal-to-noise ratio and the limit of detection for H\textsubscript{2}SO\textsubscript{4} was reported to be close to \(2 \times 10^3\) mol/cm\textsuperscript{3}.\textsuperscript{32}

During the whole four campaigns, we measured benzene and isoprene by proton-transfer-reaction mass spectrometry\textsuperscript{34} (PTR-ToF-MS). Trace gases (SO\textsubscript{2}, O\textsubscript{3}, NO\textsubscript{x}, and CO) were measured continuously using a Thermo TEI 43i, TEI 49i, TEI 42i, and TEI 48i, respectively. Typical anthropogenic alkenes were obtained by gas chromatography and mass spectrometry\textsuperscript{35} (TT24-2 GCMS) from November 26, 2019, to January 4, 2020. Ultraviolet B (UVB) radiation intensity was measured using a radiometer (Kipp & Zonen UVS-B-T). Wind speeds were measured at six levels using GILL Wind Sonic, and here, we used data from the height of 4 m. The particle number size distribution between 6 and 800 nm was measured using a differential mobility particle sizer (DMPS), and for the sub-6 nm particle and particles larger than 800 nm, a scanning mobility particle sizer (SMPS, 4–495.8 nm) and aerodynamic particle sizer (APS, 0.54–19.8 \mu m) were used respectively from January 1, 2019, to June 30, 2019. In this work, the daytime window was defined from 08:00 to 16:00 and the nighttime window from 20:00 to 04:00 on the following day. In addition to the correlation coefficient (\(R\)), the relative error (RE) is used to evaluate the performance of proxies in the statistical analysis and can be written as follows:

\begin{equation}
RE = \left( \frac{X_{\text{proxy}} - X_{\text{meas}}}{X_{\text{meas}}} \right)_{0.5}
\end{equation}

Here, \(X\) denotes the selected species and the subscript of 0.5 denotes the median number. More details are described in the Supporting Information.

\textbf{Calculation Methods.} The Proxy of Alkenes. Long-term measurement of complex alkenes is challenging, especially for those from anthropogenic sources. In this study, volatile organic compounds (VOCs) were measured simultaneously with H\textsubscript{2}SO\textsubscript{4} during four seasons using PTR-ToF-MS, which is not sensitive to short-chain alkenes. Therefore, we derived a proxy based on a relatively short-term GC–MS measurement, during which ethylene, propene, and 1-butene were the dominating anthropogenic species and correlated linearly to benzene (Figure S3) with the slope of 1.922 and relative error of 28.2%. Since the estimated isoprene emissions are much larger than those of monoterpens over the Yangtze River Delta,\textsuperscript{36} we used isoprene concentration to represent the total biogenic alkenes. Therefore, the total alkene concentration can be obtained by the following equation:

\begin{equation}
[\text{alkenes}] = 1.922[\text{benzene}] + [\text{isoprene}]
\end{equation}

\textbf{Calculation of Dry Deposition.} Dry deposition, as the ultimate path by which trace gases and particles are removed from the atmosphere in the absence of precipitation, is governed by three factors: atmospheric turbulence, the physical and chemical properties of the depositing species, and the nature of the surface. Since simulating such a variety of complex processes is generally impractical, dry deposition is usually simplified as a single parameter, the deposition velocity (\(V_d\)).

Here, a dry deposition resistance model\textsuperscript{37} was used to estimate the deposition losses of H\textsubscript{2}SO\textsubscript{4} indirectly based on measurements by an eddy-covariance system (EC3000, Campbell Scientific) at the height of 3 m. For gases, \(V_d\) in this dry deposition model is computed from a formula analogous to Ohm’s law in electrical circuits:\textsuperscript{38}

\begin{equation}
V_d = (R_a + R_i + R_s)^{-1}
\end{equation}

The term \(R_a\) governed by turbulent transport, represents aerodynamic resistance and \(R_i\) represents the quasi-laminar resistance dependent on molecular properties of the substance and surface characteristics. \(R_s\) is the surface resistance, but it is negligible for H\textsubscript{2}SO\textsubscript{4} due to its extremely high Henry’s law coefficient. The detailed calculation can be found in the Supporting Information.

\textbf{Calculation of Condensation Sink (CS).} CS was calculated using the method proposed by Kulmala et al.\textsuperscript{39} based on measurements of the particle number size distribution between 6 and 800 nm using DMPS. Also, the contribution of sub-6 nm particles and particles larger than 800 nm to CS was estimated to be less than 10% based on measurements of SMPS and APS from January 1, 2019, to June 30, 2019, as described in the Supporting Information.

\textbf{Simulation of Clustering Processes.} Due to the lack of most H\textsubscript{2}SO\textsubscript{4} clusters measurements, a kinetic model was used to estimate clustering processes. The distribution of molecular clusters in acid–base nucleation can be simulated using the
explicit solution of the general dynamic equations. Detailed
descriptions for the model can be found elsewhere.\textsuperscript{40}

\section*{Estimation of Hydroxyl Radical (•OH).} For the difficulty to
measure the \( \text{OH} \) radical continuously, we calculated the
daytime \( \text{OH} \) concentration by applying the empirical formula
proposed by Rohrer and Berresheim,\textsuperscript{41} which demonstrated
that the \( \text{OH} \) radical is linearly correlated to the photolysis
frequency \( J(\text{O}1\text{D}) \). We calculated \( J(\text{O}1\text{D}) \) using the tropo-
spheric ultraviolet and visible (TUV) radiation model and
corrected it by the observed UVB.\textsuperscript{42} Detailed information can
be found in the Supporting Information.

\section*{RESULTS AND DISCUSSION}

\subsection*{Overall Observations and Empirical Formula.} Seasonal
patterns of the daytime \( \text{H}_2\text{SO}_4 \) concentration and related
parameters are illustrated in Figure 1. The median daytime
concentrations of \( \text{H}_2\text{SO}_4 \) were significantly higher in autumn
\((9.02 \times 10^6 \text{ cm}^{-3}) \) and spring \((7.35 \times 10^6 \text{ cm}^{-3}) \) than in
summer \((4.47 \times 10^6 \text{ cm}^{-3}) \) and winter \((1.85 \times 10^6 \text{ cm}^{-3}) \). A
typical diurnal cycle shows the noontime peaks of \( \text{H}_2\text{SO}_4 \) to
follow UVB in spring, autumn, and winter. In summer, \( \text{SO}_2 \)
concentrations, owing to the long-term emission reduction in
China,\textsuperscript{31} were low enough to be the limiting factor for \( \text{H}_2\text{SO}_4 \)
production, and the resulting \( \text{H}_2\text{SO}_4 \) concentration peaked at
about 10:00 am when \( \text{SO}_2 \) had its maximum value. We then
used a traditional approach analogous to most previous works,
developed empirical proxies of \( \text{H}_2\text{SO}_4 \) separately for the four
seasons, and verified their suitability. Note that the traditional
proxy excludes the formation of \( \text{H}_2\text{SO}_4 \) in the oxidation by \text{scI}
and, therefore, we only derived the daytime \( \text{H}_2\text{SO}_4 \) proxy. The
proxy formula is as follows:

\begin{equation}
[\text{H}_2\text{SO}_4] = k_0[\text{SO}_2]^a[\text{CS}^b\text{UVB}^c]
\end{equation}

In Table S1, we summarize the proxy parameters of this
work and previous studies. We can see that the fitting
parameters \( (k_0, a, b, \text{and } c) \) vary remarkably from site to site, as
well as between the different seasons, challenging their general
applicability. For example, the pre-exponential coefficient \( k_0 \)
varied from 0.01 to \( 2.33 \times 10^3 \). To verify this, we used the
proxy obtained from the measurement in one season to the
other three seasons, showing the results and relative errors in
Figure 1 and Table S2. Comparisons between the four proxies
are shown in Figure S5. It is obvious that the empirical proxy
derived from one season cannot capture the variation of \( \text{H}_2\text{SO}_4 \)
in the other three seasons. Especially for Proxy\text{autumn} and
Proxy\text{winter}, they either greatly overestimate or underestimate
the \( \text{H}_2\text{SO}_4 \) concentration for the other campaigns, causing
significant relative errors (even up to 240\%). Furthermore,
since these parameters are obtained from a mathematical
fitting and are not independent of each other, the empirical
proxy would not help understand the budget of \( \text{H}_2\text{SO}_4 \). Our
results suggest that the empirical proxy has strong limitations
and is incapable of being widely used.

\subsection*{Budget Analysis.} Based on current knowledge, gaseous
\( \text{H}_2\text{SO}_4 \) can only be formed from the reactions of \( \text{SO}_2 \) with \text{OH}
or \text{scI}, and it can be lost to aerosol surfaces (condensation
sink), ground surface (dry deposition), and newly formed
particles by forming \( \text{H}_2\text{SO}_4 \) clusters. Given a very short
lifetime, the budget of \( \text{H}_2\text{SO}_4 \) can be described by the following equation

\begin{equation}
\text{Figure 1.} \text{ Daytime variation of UVB, } \text{SO}_2, \text{ measured } \text{H}_2\text{SO}_4, \text{ and calculated } \text{H}_2\text{SO}_4 \text{ by empirical formulas in (a) winter, (b) spring, (c) summer, and (d) autumn. The daytime window is defined from 08:00 to 16:00. The levels of UVB and H}_2\text{SO}_4 \text{ are displayed as their median concentrations. The blue horizontal lines show the median SO}_2, \text{ blue boxes show 25th and 75th percentile values, and whiskers show outlier cutoffs. The red points}
\text{show the mean concentration of SO}_2. \text{ The bottom panel shows measured H}_2\text{SO}_4 \text{ and calculated H}_2\text{SO}_4 \text{ from four proxies based on different seasons. Blue lines, orange dotted lines, yellow dotted lines, purple dotted lines, and green dotted lines denote measured H}_2\text{SO}_4 \text{ and calculated H}_2\text{SO}_4 \text{ based on Proxy}_{\text{winter}}, \text{ Proxy}_{\text{spring}}, \text{ Proxy}_{\text{summer}}, \text{ and Proxy}_{\text{autumn}} \text{ respectively. We provide a time series of related parameters in Figure S2, including UVB, PM}_{10}, \text{ SO}_2, \text{ O}_3, \text{ NO}_x, \text{ and H}_2\text{SO}_4.}
\end{equation}
During the daytime, the H$_2$SO$_4$ formation is dominated by the oxidation of SO$_2$ by OH, which is extremely difficult to be measured but has been demonstrated to be well reproduced by $f$(O’D).$^{41}$ During the nighttime, SO$_2$ oxidation by sCI and OH, produced from the ozonolysis of alkenes, is believed to control the formation of H$_2$SO$_4$.$^{21}$ In polluted urban areas, OH, produced from the ozonolysis of alkenes, is believed to be a “bulk” item, being expressed as $k_1[O_3][\text{alkenes}][SO_2]$. Here, $k_1$ is an apparent reaction rate constant that takes into account the rate constants between O$_3$ and alkenes, the yield of OH radical and sCI, and their reaction with SO$_2$.

Most previous studies considered CS as the only important sink for gaseous H$_2$SO$_4$. However, the measurement site of H$_2$SO$_4$ is usually close to a ground surface (as well as other surfaces) so that dry deposition has the potential to be an important sink. Here, we estimated the loss of H$_2$SO$_4$ via dry deposition with a resistance model. Due to the extremely high Henry’s law coefficient of H$_2$SO$_4$, its dry deposition is limited by atmospheric turbulence. Accurate micrometeorological parameters are needed, especially the friction velocity, which was measured in real time based on the eddy-covariance parameters are needed, especially the friction velocity, which was measured in real time based on the eddy-covariance system in our experiments. We found that the calculated H$_2$SO$_4$ loss onto the ground surface could be up to 30% of that onto aerosol particles with the sampling inlet height of 1.5 m, suggesting a considerable sink for the near-surface H$_2$SO$_4$, particularly during the noontime when the boundary layer mixing tends to decrease CS while, at the same time, enhancing dry deposition (Figure 2).

In addition, clustering processes could be a considerable loss for the H$_2$SO$_4$ monomer but were difficult to be evaluated due to the limitation on measuring most clusters, i.e., (H$_2$SO$_4$)$_2$. $^{21,45}$ Here, we deployed a kinetic model to simulate and estimate the clustering processes. $^{40}$ Given that dimethylamine (DMA) is the crucial stabilizer to form H$_2$SO$_4$ clusters, especially in East China, $^9$ we simulated the daytime clustering processes in four seasons with different DMA concentrations, as well as varied temperatures. The results showed that H$_2$SO$_4$ clustering processes at the SORPES station in summer and winter tended to the 10 ppt DMA scenario, while spring and autumn matched the 5 ppt DMA scenario (Figure S6).

Clustering processes were simplified as $\beta[H_2SO_4]^2$. As shown in Figure 3, higher H$_2$SO$_4$ and DMA concentrations and lower CS and temperature tend to elevate the value of $\beta$. In our study, the majority of data points fall in the left side of the lines in Figure 3, where clustering losses contributed less than 10% of CS on removing the H$_2$SO$_4$ monomer. However, it was non-negligible in some time in spring, autumn, and winter. Therefore, we take this term into consideration in budget analysis, with $\beta$ of 5.69 × 10$^{-10}$ cm$^3$ s$^{-1}$ in winter, 1.37 × 10$^{-10}$ cm$^3$ s$^{-1}$ in spring, 2.55 × 10$^{-11}$ cm$^3$ s$^{-1}$ in summer, and 1.15 × 10$^{-10}$ cm$^3$ s$^{-1}$ in autumn.

By assuming the H$_2$SO$_4$ concentration to be at a pseudo-steady state (the left-hand side of eq 6 can be approximated to be zero), we fitted the data for the four seasons. The coefficients $k_1$ and $k_2$ were in the ranges of 2.21 × 10$^{-30}$ to 5.91 × 10$^{-30}$ cm$^3$ s$^{-1}$ and 5.82 × 10$^{-2}$ to 18.00 × 10$^{-2}$, respectively (Table S3), i.e., they were relatively stable between the different seasons. The SORPES station is located on the southern edge of East China, and it can be influenced by both anthropogenic and biogenic emissions.$^{29,30}$ Since anthropogenic alkenes consist mainly of short-chain alkenes, we could take these three above-mentioned dominating alkenes as representative examples of anthropogenic alkenes, and isoprene as a representative for biogenic alkenes. We could then calculate the derived sCI and SO$_2$ varies in the ranges of 2.4 × 10$^{-11}$ to 6.7 × 10$^{-11}$ cm$^3$ s$^{-1}$ for propene, 9.64 × 10$^{-18}$ cm$^3$ s$^{-1}$ for 1-butenne, and 1.28 × 10$^{-17}$ cm$^3$ s$^{-1}$ for isoprene.$^{44}$ The rate constant of reaction between their derived sCI and SO$_2$ varies from 0.17 to 0.56.$^{47,49}$ The unimolecular decomposition of sCI and reactions between sCI and atmospheric trace gas species, due to its strong chemical reactivity with them, result in a high loss rate of sCI, and we used the value of 32 s$^{-1}$ for this loss rate based on previous studies $^{51,54}$ Here, $k_1$ is considered to vary from 2.03 × 10$^{-31}$ to 2.2 × 10$^{-28}$ cm$^6$ s$^{-1}$ in theory, which well covered coefficients obtained in our experiments and reported in Beijing.$^{21}$ It should be pointed out that in the real atmosphere, $k_1$ can vary over a larger range due to the complexity of sCI chemistry.

$k_2$ is also an apparent coefficient by considering the rate constant of the OH–SO$_2$ reaction ($k_{\text{OH–SO}_2}$) and the pre-exponential coefficient ($a$, see Table S5) of the $f$(O’D)–OH nearly linear relationship, which can be described as [OH] = a × $f$(O’D)/10$^{-5}$ s$^{-1}$. $k_{\text{OH–SO}_2}$ was reported to be in the range from 3.39 × 10$^{-13}$ to 1.24 × 10$^{-12}$ cm$^3$ s$^{-1}$,$^{55,58}$ and the value of coefficient $a$ varied from 2 × 10$^6$ to 4.8 × 10$^6$ cm$^{-3}$ in different observations (see Table S5). Therefore, the theoretical value of $k_2$ should range from 0.068 to 0.595. Here, the fitted $k_2$ varied from 0.058 to 0.18 for the different seasons, mostly within the theoretical value range.

Although the fitted $k_1$ is within the theoretical range, calculations accordingly underestimated the nighttime H$_2$SO$_4$ significantly (Figure 4 and Figure S7) when the reaction of

\[
\frac{d[H_2SO_4]}{dt} = k_1[O_3][\text{alkenes}][SO_2] + k_2f(O’D)[SO_2] - CS[H_2SO_4] - Dep[H_2SO_4] - \beta[H_2SO_4]^2
\]
SO\textsubscript{2} with sCl or OH from ozonolysis of alkenes was assumed to be the major source. This is particularly the truth during winter when simulated H\textsubscript{2}SO\textsubscript{4} was one order of magnitude lower than the measured value.

As shown in Figure 5a, the correlation between the loss of nighttime H\textsubscript{2}SO\textsubscript{4} and [(SO\textsubscript{2})[O\textsubscript{3}][alkenes]] is poor, indicating additional sources other than alkene ozonolysis contributing to the nighttime H\textsubscript{2}SO\textsubscript{4}. We then investigated nighttime H\textsubscript{2}SO\textsubscript{4} events, defined by two criteria: (a) H\textsubscript{2}SO\textsubscript{4} rises, reaching a distinct peak, instead of a continuous decrease from 20:00 to 04:00 in the following day; (b) the maximum concentration exceeds 1 × 10\textsuperscript{6} cm\textsuperscript{-3}. In total, 14 events were selected (Figure S8), only 3 of which can be explained by the source of alkene ozonolysis. However, in 6 events, the H\textsubscript{2}SO\textsubscript{4} concentration correlated strongly with the benzene concentration (Figure S9), indicating a direct emission source related to benzene. Here, we used the toluene-to-benzene (T/B) ratio to indicate the sources of VOCs. The T/B in nighttime benzene-related H\textsubscript{2}SO\textsubscript{4} events has a range of 1–2, very close to road-side and tunnel research studies.\textsuperscript{59,60} SO\textsubscript{2} is a byproduct of the combustion of most fossil fuels and has been reported to be emitted from on-road transportation.\textsuperscript{61} Since OH is also largely produced via burning processes,\textsuperscript{62} H\textsubscript{2}SO\textsubscript{4} is then able to be emitted from vehicles or produced in the freshly emitted plumes by reacting with ambient SO\textsubscript{2}.

To estimate the quantitative contribution from direct emissions, we selected the data points that cannot be explained by the alkene ozonolysis source, locating in the left of the line with \( k = 5 \times 10^{-29} \text{ cm}^6 \text{ s}^{-1} \) in Figure 5a. O\textsubscript{3} concentrations for these data points were very low, probably due to a strong titration by freshly emitted NO. Because of the very short lifetime of gaseous H\textsubscript{2}SO\textsubscript{4} in polluted air, plumes with freshly emitted H\textsubscript{2}SO\textsubscript{4} need to transport quickly enough and have low pre-existing particle loading to overcome the loss of H\textsubscript{2}SO\textsubscript{4} before arriving at the sampling site. Here, we separated the plumes using the wind speed threshold of 1.5 m/s and 0.02 s\textsuperscript{-1} for CS. Under high wind speed and low condensation sink, a positive correlation between the H\textsubscript{2}SO\textsubscript{4} and benzene concentrations was observed (Figure 5b), suggesting that direct emissions related to benzene play an important role in nighttime H\textsubscript{2}SO\textsubscript{4} formation. However, we cannot observe the signal of direct emission at other times. As a matter of fact, the observed H\textsubscript{2}SO\textsubscript{4} concentration from emission is governed by both the intensity of emissions and losses along the transmission path. Since this term was found to be related to benzene, we could assume the intensity of primary emissions to be proportional to the concentration of benzene. Also, with wind speed and condensation sink into consideration, the emission term of H\textsubscript{2}SO\textsubscript{4} can be expressed as

\[
[H_2SO_4]_{\text{emis}} = k_0 [\text{benzene}] \left( \frac{WS}{1 \text{ m s}^{-1}} \right)^a \left( \frac{CS}{0.01 \text{ s}^{-1}} \right)^b
\]

Here, the pre-exponential coefficient, \( k_0 \), reflects the dependence on the intensity of emissions. The exponents \( a \) and \( b \) reflect the effects of wind speed and condensation sink, respectively. We further fitted these coefficients based on the
nighttime data that cannot be explained by the alkene ozonolysis source. The values of $k_0$, $a$, and $b$ were $2.591 \times 10^{-5}$, 1.398, and $-1.404$, respectively. Figure 5c shows the good performance of the proxy; the simulated emission term was well correlated with the unexplainable nighttime H$_2$SO$_4$. It needs to be noted that the contribution of direct emission to the observed H$_2$SO$_4$ concentration should be site/location-dependent. Primary H$_2$SO$_4$ has the potential to be co-emitted with SO$_2$ from power plants, industry, international ships, residential emissions, and transportation on a global scale. Parameters, including the distance of emission sources and meteorological conditions, would have significant impacts on this term.

Proxy Development and Its Stability. Based on the above budget analysis of H$_2$SO$_4$, we developed a physical proxy for H$_2$SO$_4$ as follows, by considering all the above-mentioned sources and sinks:

$$[\text{H}_2\text{SO}_4] = \frac{-\text{CS} + \text{Dep}}{2\beta} + \sqrt{\left\{ \frac{\text{CS} + \text{Dep}}{2\beta} \right\}^2 + \frac{k_1[\text{SO}_2][\text{O}_3][\text{alkenes}] + k_2(\text{O}^\text{D})[\text{SO}_2]}{\beta}} + [\text{H}_2\text{SO}_4]_{\text{min}}$$

(8)

Here, $k_1$ is an apparent reaction rate constant, including the rate constant of the O$_3$–alkenes reaction, the yield of OH radical and sCI, and the fraction and rate constants of their reaction with SO$_2$; $k_2$ is also an apparent coefficient that takes into account the rate constant of the OH–SO$_2$ reaction and the pre-exponential coefficient of the nearly linear relationship between $J(\text{O}^\text{D})$ and OH. We first selected nighttime data points with O$_3$ concentrations higher than 10 ppb in different seasons to obtain $k_1$. As shown in Figure S10, the loss term of nighttime H$_2$SO$_4$ was strongly and positively correlated with the source term ([SO$_2$][O$_3$][alkenes]) at high concentrations of O$_3$, suggesting that the alkene ozonolysis contributed significantly to the nighttime H$_2$SO$_4$ concentration. We then estimated $k_1$ by fitting the 10th percentile data points to eliminate the impact of emissions to the extent possible. The estimated value of $k_1$ ranged from $6.67 \times 10^{-31}$ to $5.27 \times 10^{-30}$ cm$^6$ s$^{-1}$ in different seasons, within the range of the theoretical value. The fitted $k_2$ varied from 0.08 to 0.18 in different seasons (see Table S4), also within the range of the theoretical value.

The developed proxies captured well the measured values in different seasons (Figure S12a–d) and surprisingly correlated with each other very well (Figure S13), with correlation coefficients larger than 0.94, suggesting the strong stability of this method and the possibility to develop a more widely used proxy based on the data from all the seasons. The fitted values of $k_1$ and $k_2$ were $2.49 \times 10^{-30}$ cm$^6$ s$^{-1}$ and 0.15, respectively, so the proxy can be written as

$$[\text{H}_2\text{SO}_4] = \frac{-\text{CS} + \text{Dep}}{2\beta} + \sqrt{\left\{ \frac{\text{CS} + \text{Dep}}{2\beta} \right\}^2 + \frac{2.49 \times 10^{-30}[\text{alkenes}][\text{SO}_2] + 0.15(\text{O}^\text{D})[\text{SO}_2]}{\beta}} + [\text{H}_2\text{SO}_4]_{\text{min}}$$

(9)
This final proxy showed a good performance in such a complex environment (Figure 6a), the simulated values being very close to the measured ones (Figure 6a,b), with a relative error of 58% and the correlation coefficient of 0.71. Given the systematic uncertainty in H₂SO₄ concentration discussed in the method part, our results suggest a nearly close relationship between measurements and proxy. In particular, the simulation of H₂SO₄ in the nighttime and early morning was significantly improved with the consideration of direct emission. Meanwhile, due to negligible clustering processes at most times, the proxy involving the dominant influencing factor can be simplified as eq 10.

\[
[H_2SO_4] = \frac{k_1([O_3][SO_2] + k_2J(O'D)[SO_2])}{CS + Dep} + [H_2SO_4]_{emis}
\]  

We finally investigated the contribution from different sources quantitatively in different seasons based on the newly developed proxy (Figure 6c). As expected, the oxidation of SO₂ by OH dominated the daytime H₂SO₄ formation with a contribution larger than 75% in all the seasons. Therefore, there is a possibility to derive a proxy based on the light-dependent source in the absence of more data. Ozonolysis of alkenes gave a small, about 6% contribution in both summer and autumn and smaller than 4% contribution in winter and spring. In winter daytime, primary emissions contributed considerably by more than 10%. During the nighttime, direct emission contributed much more than alkene ozonolysis, up to more than 90% during winter and about 80% during summer.

**Uncertainty Analysis.** Here, we discussed the uncertainty of the final proxy. For the light-dependent source, the uncertainty of OH calculation consists of two main components: calculation of J(O’D) using the TUV radiation model and the precision of OH calculation based on J(O’D). The relative error between the modeled and measured J(O’D) was estimated to be within 10%, except for the dust event days. Here, we corrected the calculated J(O’D) by the observed UVB to further lower the uncertainty, assuming 5% (the uncertainty of UVB measurement). Also, the precision of the J(O’D) calculation of OH was reported to be 7.8%. Therefore, the total uncertainty of OH estimation should be around 9% (calculated from \(\sqrt{(5\%)^2 + (7.8\%)^2}\)). For the alkene ozonolysis source, the uncertainty mainly comes from the estimation of total alkenes. First, relative precisions of measurements are 12% for isoprene and 10% for benzene. Second, the proxy of anthropogenic alkene causes a relative error of 28%. The relative error of the emission term was estimated as 68% (Figure 5c).

The CS was underestimated by about 8% because we used the particle size distribution from 6 to 800 nm instead of a full range (Figure S3). In the dry deposition model, the extremely high Henry’s law coefficient of H₂SO₄ causes surface resistance, relying heavily on empirical data, which is negligible compared with aerodynamic and quasi-laminar resistance. However, the performance of the large-scale deposition model applied to such local measurements is not clear, and the uncertainty of dry deposition was assumed to be 100%. Direct
measurement of dry deposition is encouraged in the future to compare with the model-based estimation.

**Environmental Implication.** Gaseous sulfuric acid (H$_2$SO$_4$) is essential for new particle formation (NPF) and therefore for the global budget of aerosol particles and cloud condensation nuclei. In situ measurements of H$_2$SO$_4$ are very rare, largely limiting our understanding of global NPF mechanisms. Previous efforts on building empirical proxies for H$_2$SO$_4$ have been demonstrated to be not broadly applicable. A physical proxy was believed to have a wide applicability, e.g., rebuild the long-term variation of H$_2$SO$_4$ in various environments. The detailed budget analysis of H$_2$SO$_4$ can shed some insights into improving the simulation of H$_2$SO$_4$ and nanoparticles, in the current regional and global air quality models that can help improve the global understanding of new particle and aerosol sulfate formation. In addition, a considerable contribution of primary emissions to H$_2$SO$_4$ indicates a new connection between human activities and climate change through anthropogenic H$_2$SO$_4$-induced secondary aerosol formation.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.1c00738.

Detailed descriptions of measurements of H$_2$SO$_4$, estimation of the hydroxyl radical, calculation of condensation sink, and dry deposition; map of the measurement of site (Figure S1); time series of H$_2$SO$_4$ and related parameters in four seasons (Figure S2); relationship between dominating alkenes and benzene (Figure S3); correlation between CS contributed by 6–800 nm particles and CS contributed by 4–19,800 nm particles (Figure S4); relationship between H$_2$SO$_4$ estimated by different proxies based on the empirical formulas in different seasons (Figure S5); comparison between daytime data in four seasons and simulations under different temperatures and DMA concentrations (Figure S6); performance of physical proxy without an emission term (Figure S7); time series of measured H$_2$SO$_4$ simulated H$_2$SO$_4$ and benzene during selected nighttime H$_2$SO$_4$ events (Figure S8); relationship between H$_2$SO$_4$ and benzene in emission cases (Figure S9); development of proxy with an emission term for four seasons (Figures S10 and S11); diurnal variations of measured H$_2$SO$_4$ and H$_2$SO$_4$ obtained from the respective steady-state equilibrium method with emissions into consideration (Figure S12); correlation between H$_2$SO$_4$ estimated by physical proxies in different seasons (Figure S13); development of the final proxy (Figure S14); results of the nonlinear proxy in daytime and comparison with previous works (Table S1); relative errors of traditional proxies (Table S2); coefficients of the physical proxy without an emission term (Table S3); coefficients of proxy based on seasonal data with O$_3$ ≥ 10 ppb (Table S4); summary of the coefficients of the OH–J(O’D) nearly linear relationship in observations (Table S5) (PDF)

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Notes
The authors declare no competing financial interest.

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