Supplemental Information Appendix

Rapid deposition of oxidized biogenic compounds to a temperate forest

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1. Site and Campaign

This research was conducted during the Southern Oxidant and Aerosol Study (SOAS) ground campaign that occurred from June – July 2013 in Alabama and Tennessee. SOAS was part of the larger Southern Atmosphere Study (SAS) campaign, which encompassed many sampling sites and included multiple measurement platforms (tower, ground, and aircraft). Both SOAS and SAS focused on understanding biosphere-atmosphere interactions in the Southeastern United States. The SOAS site was located near Brent, Alabama at the Centreville (“CTR”) Southeastern Aerosol Research and Characterization Study (SEARCH) location managed by the Electric Power Research Institute (Latitude 32.90289 Longitude -87.24968) for the U.S. Environmental Protection Agency, and is hereinafter referred to as CTR. During the campaign, CTR experienced typically humid (RH 50 – 80%) and warm (28 – 30 °C) conditions in the daytime. Winds were observed from all directions; however, the predominant winds were southerly during this experiment. The CTR site was surrounded on three sides (N, W, and E) by a temperate forest that is part of the Talladega National Forest and on the southern side by a grassy field. The forest canopy was comprised of needle-leaf coniferous (shortleaf, longleaf, and loblolly pine) and broad-leaf deciduous (primarily oak, sweetgum, and hickory) tree species. The mean canopy height was approximately 10 m. A 20 m metal walk-up tower was erected in the field several meters from the edge of the forest. The instrument used for this work was stationed at the topmost platform of the tower with the inlet facing north. The measurement height (z) was approximately 22 m, including the sensor heights. Section 2 describes the instrumentation employed in this work in more detail. The mass spectrometers, pumps, and computers were housed in an insulated enclosure that was temperature-controlled with an HVAC unit to protect the components from precipitation and large temperature swings. The sonic anemometer was mounted on top of the instrument enclosure, extending approximately 2 meters north. The sonic was collocated laterally but separated longitudinally from the inlet approximately 0.8 m (see Section 5, standard corrections).

2. Measurements

Chemical ionization mass spectrometry (CIMS): Gas-phase compounds were measured with negative-ion chemical ionization mass spectrometry (CIMS) using CF$_3$O$^-$ as the reagent
ion, described in more detail previously (1-3). The CF$_3$O$^-$ ionization is sensitive toward acids, hydroperoxides, multifunctional nitrates, and multifunctional compounds. Hereinafter the measurement technique will be referred to simply as “CIMS” for brevity. Analytes are generally ionized via two different mechanisms:

$$AH + CF_3O^- \rightarrow A-\cdot HF + CF_2O \quad (1)$$

$$M + CF_3O^- \rightarrow M\cdot CF_2O^- \quad (2)$$

The fluoride transfer mechanism occurs for acidic analytes AH (e.g., nitric or formic acids), resulting in an ion with $m/z = MW + 19$. The cluster formation mechanism occurs for all other analytes M (e.g., H$_2$O$_2$, organic nitrates, hydroxy carbonyls, etc.), resulting in an ion with $m/z = MW + 85$. Weakly acidic analytes will be ionized via both mechanisms, but their fluoride transfer ions are used for quantification due to higher sensitivity and fewer interferences. CIMS calibration and analysis methods are presented in Section 3.

The mass analyzer was a compact time-of-flight (TOF, Tofwerk) spectrometer with mass resolving power of 800 m/$\Delta$m and a mass accuracy of < 100 ppm. The measurement rate of 10 Hz was employed for this work. Ambient air was sampled through a 3.1 cm inner diameter inlet, comprising of a 43 cm long glass section then a 17 cm glass section that both coated with a layer of Fluoropel hydrocarbon film (to minimize wall interactions), at a flow rate of 2000 std. L min$^{-1}$. From the center of the high inlet flow, ~ 180 std. mL min$^{-1}$ was subsampled for the analytical flow, using a moving aperture which was continuously adjusted to maintain 35.0 hPa pressure in a short Fluoropel-coated glass flow tube, as described previously (1). The ambient air stream was diluted a factor of 9 – 11 with dry nitrogen gas before entering the ion-molecule flow region, in order to moderate the effect of water vapor on ionization sensitivity (Section 3). The mixing ratios reported have been corrected for the dilution factor.

An ambient zero background (ambient air that has been scrubbed of reactive volatile compounds by bicarbonate-impregnated nylon wool and Palladium-Alumina catalysts) and a dry zero background (dry nitrogen from liquid N$_2$ boil-off) were recorded every 30 minutes. Ambient calibration (a total flow of 92 std. mL min$^{-1}$ of dry nitrogen carrying calibration gas joined with the ambient zero flow) and dry calibration (the same calibration gas stream joined with the dry zero flow) were recorded every 2 hours. These in-field calibration standards are derived from (a) permeation tubes of isotopically-labeled formic acid
(H$^{13}$COOH), acetic acid (CH$_3^{13}$COOH), and nitric acid (H$^{15}$N$^{18}$O$_3$) kept at 50°C, (b) hydrogen peroxide (H$_2$O$_2$) from a urea hydrogen peroxide ((NH$_2$)$_2$CO·H$_2$O$_2$) standard kept at 0°C, and (c) diffusion vials of deuterium-labeled methyl hydroperoxide (CD$_3$OOH) and peroxyacetic acid (CH$_3$C(O)OOH) kept at 0°C. The calibrations at ambient and dry RH were used to validate laboratory-derived water-dependent calibration factors, which were performed with a larger water vapor range, for the select compounds.

**Sonic Anemometer:** A three-dimensional ultrasonic anemometer (Campbell Scientific, model CSAT3, hereinafter “sonic”) was used to measure the wind speeds and the speed of sound along three non-orthogonal sonic axes. The wind speeds were transformed by the analyzer to the orthogonal wind velocity components $u$, $v$, and $w$. The effects of wind blowing normal to the sonic path were corrected online. The speed of sound in moist air was converted to the sonic virtual temperature offline by applying a temperature- and humidity-dependent correction function (4). The data from the sonic was sampled at 8 Hz frequency.

**Weather Station:** Meteorological conditions were continuously monitored by a weather station (Coastal Environmental Systems Inc, Zeno® 3200) mounted on top of the CIMS enclosure at the top of the tower. Air temperature (T, °C) and relative humidity (RH, %) were monitored by the S1276Z sensor with ±0.4 °C accuracy for T and ±3% for RH. Barometric pressure (P, mBar) was monitored by the S1080Z sensor with ±0.3 mBar accuracy. Solar radiation (W m$^{-2}$) was monitored by the LI-COR LI200SZ pyranometer sensor with ±10% accuracy. Wind speed (m s$^{-1}$) and wind direction (0° – 360°) were measured by the S1146Z cup and vane sensor with accuracy of ±5 m s$^{-1}$ for wind speed and ±5° for direction. Wind direction of 180° is interpreted as northerly.

3. CIMS Calibration and Data Analysis

a. **Sensitivity and water-dependence calibrations** The sensitivities of CIMS to specific analytes are controlled by physical characteristics such as their dipole moments and polarizability (5). There are varying degrees of water-dependence in the ionization of each compound, which becomes more significant for those that form weaker clusters with the anion. For compounds for which authentic standards were commercially available or can be synthesized, a water-dependent sensitivity calibration was performed in the
laboratory prior to ambient measurements. For other compounds, theoretical calculations were performed to estimate the sensitivity, as described in more detail elsewhere (6). The molecular identities, abbreviations used in this work, methods of calibration, and estimated measurement error for each compound are reported in Table S1. Representative traces of CIMS compounds and vertical wind \( w \) are shown in Figure S1, illustrating different propensities toward turbulent transfer for these compounds. The mixing ratio of water is anti-correlated with \( \text{H}_2\text{O}_2 \) and ISOPOOH+IEPOX, visually demonstrating the different directions of their net flux. The magnitude of the fluctuations, e.g., of \( \text{H}_2\text{O}_2 \) (±50\%) and to ISOPN (±15 \%), are indicative of the magnitude of their biosphere-atmosphere exchange velocities.

Authentic standards were used to characterize the dependence of the CIMS sensitivity to water vapor by introducing a gas stream containing a known quantity of the calibrant compound to the CIMS flow region while varying the amount of water vapor that is co-introduced. Variable water vapor content was achieved by mixing different ratios of dry nitrogen with a gas stream containing ~3\% water vapor. The water vapor fraction was characterized by Fourier-transform infrared spectroscopy (FTIR) with a 19 cm pathlength cell. Spectral fitting for water vapor was performed using the HITRAN spectral database (7) and a nonlinear fitting software NLM4 (8). The quantifications of other calibrant gases were performed as follows:

1) HCN was calibrated with a standard gas mixture (6.3 ppmv in N\textsubscript{2}, Scott Specialty Gasses) that was diluted with a known flow rate of dry nitrogen.

2) \( \text{H}_2\text{O}_2 \) was calibrated by flowing dry nitrogen continuously over urea hydrogen peroxide (Aldrich, purity 97\%), kept at 0°C. Absolute \( \text{H}_2\text{O}_2 \) mixing ratio in this stream was quantified by bubbling the equilibrated outflow into ultrapure water (18 M\( \Omega \), Millipore) for a fixed time. The aqueous \( \text{H}_2\text{O}_2 \) was quantified by high-performance liquid chromatography (HPLC) mass spectrometry, as well as a UV-Visible colorimetric technique (3).

3) Formic acid (Aldrich, 98\%) and nitric acid (Aldrich, 70\% in water) were calibrated by flowing dry nitrogen continuously over permeation tubes (Kintec), kept at 50°C.
The permeation rate was determined by gravimetric analysis for formic acid. Nitric acid permeation was calculated by collecting the outflow in ultrapure water and analyzing the solution with ion-chromatography (IC).

PAA (Aldrich, 40% in water) was calibrated by flowing dry nitrogen continuously over custom diffusion vials, kept at 0°C, and collecting the outflow similarly to the protocol for H$_2$O$_2$. The outflow solution was analyzed by HPLC-derivatization fluorescence. Additionally, gas-phase PAA was analyzed with FTIR using the IR cross section from Orlando et al (9).

HMHP was synthesized in the gas phase by the reaction of H$_2$O$_2$ and formaldehyde and characterized by FTIR as described by Fry et al (10).

Hydroxyacetone (Aldrich, 90%) was introduced into an evacuated 500 mL glass bulb by monitoring pressure increase, and backfilled with dry N$_2$ to obtain several ppmv. This mixture was quantified by FTIR using the cross section archived in the Pacific Northwest IR Database (11). The gas in the IR cell was introduced into a ~300 L Teflon bag and diluted with zero air.

The sum of ISOPOOH and IEPOX were observed at the product ion with m/z 203 as they are isobaric (C$_5$H$_{10}$O$_3$). IEPOX was synthesized as reported in Bates et al (12). A measured weight of a standard solution of IEPOX in water was atomized into a 24 m$^3$ FEP Teflon bag alongside hydroxyacetone and toluene as a volume tracer (that was quantified by GC-FID), as reported recently (13). The vapor wall loss and solution-phase decomposition for this method were characterized to be negligible. The combined sensitivity was then determined from a photooxidation experiment, with the assumptions of yields as reported in Paulot et al (14).

ISOPN was synthesized and calibrated as outlined by Lee et al (15). The calibration method relied on the quantitative thermal dissociation of the organic nitrate to NO$_2$ followed by laser-induced fluorescence quantification of NO$_2$ (TDLIF instrument).

PROPNN, and the sum of MACN + MVKN were generated as part of a high-NO isoprene oxidation and separated with a GC column, as described by Lee et al (15).
The outflow of the GC column was directed toward CIMS and the TDLIF instruments, and the calibration technique was similar to that of ISOPN.

b. Measurements of water vapor: High-frequency water vapor mixing ratios for the calculations of latent heat fluxes were determined by CIMS, using the double cluster ion \((H_2O)_2\cdot CF_3O^- \ (m/z \ 121)\). This ion remained linear with respect to the range of water vapor mixing ratios experienced at SOAS while the primary water ion \((H_2O)\cdot CF_3O^-\) was saturated. The \((H_2O)_2\cdot CF_3O^-\) ion had a considerable temperature dependence that was corrected for as a function of the measured flow tube temperatures. Atmospheric water vapor, as measured by the Zeno weather station at 1 Hz, was used as an absolute calibrant. Atmospheric water vapor was calculated from the observed barometric pressure, air temperature, and relative humidity for all dates included in the study (Fig. S2) and the corrected CIMS water vapor measurements compared well to the weather station measurements (Fig. S3.)

4. Eddy Covariance (EC) calculations

a. Data processing: EC fluxes were calculated after the signals of the compounds measured by CIMS \((x, \text{ shown in Table S1})\) were converted to mixing ratios (usually in pptv) by applying all calibrations and corrections. Given the wind velocity vectors \((u, v, w)\) and scalar matrices for species of interest, flux data for virtual temperature \((\overline{w'T'_v})\), momentum \((\overline{w'u'})\), and CIMS-determined compounds including water vapor \((\overline{w'x'})\) were calculated for each ~ 30 minute flux measurement periods, where primes denote deviation from the mean and overbars denote a mean over the flux period. Large spikes in CIMS signals, caused by electronic or temperature instability, were removed by referencing a “quiet” m/z, where no chemical signal is found, and by visual inspection (< 5% of data). For each period: the 8 Hz wind measurement was interpolated onto the time vector of the CIMS measurement, the sonic wind velocity coordinates were rotated by a two-step rotation so that \(\overline{v}=0\) and \(\overline{w}=0\), the sonic data and CIMS data were detrended using a linear detrending algorithm, the correction of inlet lag of the scalar signal of \(x'\) was corrected for lag with respect to \(w'\) by identifying the peak in the lag-covariance function (Fig. S4). Lag times were on the order of 0.1 – 1.1 s. The lag time for \(H_2O\) was
used as the representative lag time for all compounds, which was justified by inspecting the cross covariance spectra for multiple CIMS species for more than 10 daytime flux periods. Using a representative lag time from a compound whose scalar vector has a large covariance with \( w \), was found to decrease the uncertainty of the resulting EC fluxes propagated from the error in locating poorly-defined extrema in the cross covariance spectra for periods of lower flux (e.g., nighttime) or for compounds where the covariance is small (e.g., MTNP). The instantaneous fluxes were then averaged over each flux period. Mean concentrations and solar radiance data were averaged over the same periods.

b. Quality of flux data

The EC fluxes were screened according to the following criteria: i. The upward and downward energy fluxes at the surface should be balanced within the standard deviation of each measurement (~ 15% in the daytime), ii. The spectral analysis should indicate expected behavior of the individual covariances with respect to eddy magnitudes and surface layer theory; iii. The turbulence should be well developed for the day time periods; iv. The stationarity (16) and intermittency (17) conditions should be met. Condition i severely limited the number of useable days within the campaign for calculations of EC fluxes from CIMS. The quality analysis for Conditions ii - iv below pertains mainly to days where EC fluxes were deemed acceptable per Condition i.

i. Energy balance closure condition: The degree of surface energy balance closure provides an important and objective evaluation of the EC fluxes, as conditions that violate EC flux assumptions (e.g., contamination of vertical flux from horizontal wind due to effects of roughness layer inhomogeneity) should affect the turbulent transfer of energy similarly to mass. An external calibration (pyranometer measurements of radiation) was used to constrain the closure condition. The surface energy balance can be written as:

\[
R_n = SH + LE + S + G + Q \quad (3)
\]

where \( R_n \) is the net radiation downward, \( SH \) is the sensible heat flux, \( LE \) is the latent heat flux, \( S \) is the storage heat flux, \( G \) is the soil heat flux, and \( Q \)
collectively represents all other energy fluxes. \( Q \) is generally a small term and was ignored in this work. We also make the assumption that the canopy is closed, so that \( G \) can also be ignored. The revised energy balance equation is written as:

\[
R_n - S = SH + LE \quad (4)
\]

And the heat fluxes are defined as:

\[
SH = \rho_a c_p \overline{w'T_v'} \quad (5)
\]

\[
LE = \rho_a L_v(T) \overline{w'x_{H2O}'} \quad (6)
\]

where \( \rho_a \) is the density of air (kg m\(^{-3}\)), \( c_p \) heat capacity of air (J kg\(^{-1}\) °C\(^{-1}\)) at 1 atm, \( L_v(T) \) is the latent heat of vaporization of air (kJ kg\(^{-1}\)) calculated for the temperatures experienced throughout the flux period, and \( x_{H2O} \) is the water vapor fraction as determined by CIMS (described in Section 3a). The storage term \( S \) was not measured, but was estimated based on measurements at a similar site (18). \( S \) is usually small (- 20 – 50 W m\(^{-2}\)) and thus, error in its estimation does not add significantly to the error of the analysis. Our pyranometer measures solar radiation (shortwave radiation downward) whereas net radiation includes the upwelling and downwelling shortwave and longwave radiation (\( R_n = SW_{up} + SW_{down} + LW_{up} + LW_{down} \)). As longwave radiation was not measured, \( R_n \) was estimated with a method similar to the treatment of satellite data, by exploiting empirical relationships between net radiation and shortwave radiation as developed by Kaminsky et al (19). It was shown that the error in this type of estimation is small (\( r^2 = 0.96 - 0.99 \), root mean square error 18 – 41 W m\(^{-2}\)) compared to the typical magnitude of \( R_n \) (up to 1000 W m\(^{-2}\)).

One of the largest influence on energy balance closure for our work appeared to be wind direction, as southerly winds were typically associated with poor balance closure and northerly winds, even with contributions from winds originating from the west and east, were associated with satisfactory balance closure for the individual day (Fig. S5). This strong impact by wind direction is likely related to the challenges of EC flux measurements from a walk-up tower (e.g., tower and/or instrument enclosure acting as physical barriers that isolate the
inlet and sonic from southerly winds) and the change in roughness element or
topology due to the transition from the forest in the north, west, and east
directions toward the grassy field to the south.

**ii. Spectral analysis:** The cospectra of $x$ and $T_v$ with $w$ in the frequency domain
were calculated by applying a fast Fourier transform to the covariance matrices.
Figure S6 shows the averaged cospectral densities of several CIMS compounds,
chosen for those with higher signal-to-noise to limit error, and $T_v$ with $w$ for the
afternoon local hour 13 on all days included in this flux study. If the
homogeneous fetch is adequate, an underlying assumption for EC, there should be
a development of an “inertial sublayer,” where the fluxes of conserved scalars
(e.g., energy) are roughly independent of vertical height. The spectra show the
expected linear falloff in the inertial subrange frequency ($f > 0.003$ Hz) and, for
the averaged CIMS compounds, the typical slope is similar to the $f^{-7/3}$ slope
predicted by surface layer theory (20). For virtual temperature, the linear fallooffs
for some cospectra were shallower than $f^{-7/3}$, but never shallower than $f^{-5/3}$, such
that the average for all days was most similar to an $f^{-6/3}$ slope.

The plots of cumulative distribution of cospectral density (ogives) indicate
the frequency ranges where most of the flux is captured. Figure S7a shows the
representative ogives for $w$ with several CIMS compounds and $T_v$, for the
afternoon local hours 9 – 15 of all days included in this flux study and Figure S7b
shows the data for JD165. The spectra were normalized to their asymptotic value
in the low-frequency range. As expected, the ogives approach horizontal
asymptotes at both ends of the spectrum. In the high-frequency end, there was no
more flux at approximately 1 Hz, which indicates that the measurement
timescales used in this work (10 Hz for CIMS species and 8 Hz for winds) was
sufficiently fast to capture fluxes carried from the smaller eddies (timescales of 10
s). In the low-frequency end, all of the flux was carried by eddies of frequencies
higher than $1 \times 10^{-3}$ Hz. This indicates that, as an ensemble, our averaging time of
30 minutes was long enough to capture the entirety of the flux. The $w'x'$ ogive
decreases more quickly than the $w'T_v'$ ogive. This is perhaps a real characteristic,
as suggested by an earlier study of acyl peroxynitrate (APN) compounds at BEARPEX (21), because the spectra are similar for compounds whose instrument time response delays were small (Section 5).

Figure S8 shows the frequency-weighted covariance-normalized cospectra plotted against $n = f z/U$, where $z$ is the measurement height and $U$ is the average wind speed for the day. The spectra for (a) JD165 and (b) all days included in the study show one distinct maximum corresponding to $n \sim 0.2 – 0.4$ and few complex turbulent structures, indicating that most of the flux was carried by eddies of timescale $\sim 30$ s. The slope for CIMS compounds was steeper than for $T_v$ in the high frequency domain, also observed for APNs at BEARPEX (21). Combined, the spectral analysis for the species reported in this work provides compelling evidence that the calculated EC fluxes during the daytime hours are accurately represented.

iii. Turbulence: The criterion requiring well-defined turbulence can be accessed by examining the friction velocity $u_*$, calculated in this work from the measured momentum flux ($\tau = -\rho_a w' u'$), where $\rho_a$ is the density of air (kg m$^{-3}$):

$$u_* = |\tau/\rho_a|^{1/2} \quad (7)$$

Figure S9 shows $u_*$ averaged for all days included in this study and errors are one standard deviation from the mean. The determination of turbulent threshold $u_*$ values is subject to debate and may be site-specific. For periods where conditions can be characterized as turbulent, the calculated EC fluxes are affected by substantially fewer errors than for calm periods. Threshold values of 0.1 – 0.3 m s$^{-1}$ have been suggested, and a median value of 0.23 m s$^{-1}$ that was found to be most representative of multiple sites and years (22) was used in our work to qualitatively assess if daytime periods can be characterized as turbulent and further validate the flux data. It was found that, for days with good energy balance, the criterion was satisfied within the standard deviation of the $u_*$ measurement.
iv. **Stationarity and Intermittency:** The stationarity test was performed as suggested by Foken and Wichura (16), where flux data ($F$) were calculated for 5 min averaging periods in addition to 30 min averaging periods. When both calculations were averaged into the same 30 min time bin, the resulting stationarity criterion ($FS < 0.3$), defined as $FS = |F_{30\text{min}} - F_{5\text{min}}|/F_{30\text{min}}$, was satisfied for the majority of points in the day time periods. The stationarity criterion was used as a qualitative assessment and not a discrimination threshold in this work as the available data are sparse. Figure S10 shows the stationarity analysis for $\text{H}_2\text{O}_2$ and sensible heat on JD165, where the 5 min data averaged similarly to the 30 min data did not significantly alter the result. The intermittency criterion (17), defined as $FI = \sigma_{5\text{min}} / F_{30\text{min}}$ where $\sigma_{5\text{min}}$ is the standard deviation in the 5 minute data, was satisfied ($FI < 1$).

5. **EC flux corrections:**

**Standard corrections:** Corrections that are often recommended for EC flux calculations (23) were systematically applied in this work where appropriate. Despiking, time lag, and coordinate rotation were performed as discussed in Section 4a. Cross-wind corrections were applied online within the CSAT3 sonic electronics. The effects of temperature and humidity on the measured air temperature, e.g., buoyancy, were removed in the calculation of the virtual temperature from the sonic speed of sound. Corrections due to flux attenuation at high frequencies were unnecessary as the CIMS measurement was fast enough to capture all the flux in the high-frequency range (Fig. S7a). Webb-Pearman-Leuning (WPL) corrections (24) were unnecessary as we measured the mixing ratio not the partial pressure of chemical species, and temperature and humidity corrections to CIMS sensitivities needed to output count signals to pptv were applied internally as a standard procedure. Transfer functions used to correct for the potential loss of flux due to the separation of the inlet (Fig. S7b) were calculated as suggested by Moore et al (25) but were not applied because the error was estimated to be small ($\sim 3\%$ for CIMS compounds). Corrections often reserved for open-path analyzers were not performed for the closed-system CIMS measurements.
**Instrumental time response correction:** It is challenging to accurately measure compounds that have a propensity to interact with instrument surfaces in complex ways. HNO₃ is of particular concern for our instrument, and we discuss here correction for the loss of flux owing to a “smearing” effect of the HNO₃ signal in time from the interaction with instrument surfaces. The correction was based on observed instrumental responses for HNO₃, and a few other compounds where calibration standards were available in the field during SOAS. An exponential decay curve ($\alpha \cdot \exp(-t/\tau)$) was fit to periods following a pulse of the calibrant gas through the CIMS flow region, where $\tau$ (s) is the inlet time response constant and $\alpha$ is the pre-exponential factor. Figure S11 shows the decay curves for HNO₃ ($\tau = 32, \alpha = 0.55$), formic acid ($\tau = 0.94, \alpha = 0.80$), H₂O₂ ($\tau = 1.3, \alpha = 0.70$), and water vapor ($\tau = 0.22, \alpha = 1.06$) pulses. The fitted parameters for HNO₃ can be used to “degrade” signals with fast time responses (e.g., H₂O₂) and recalculate the fluxes by applying the smearing perturbation to the measured mixing ratios for each $\alpha$ and $\tau$ of interest. The adjusted mixing ratio $C(t)$ can be written as:

$$C(t) = X_t(1 - \alpha) + \alpha \cdot \frac{\int_{t-2\tau}^{t} X_i \cdot \exp\left(-\frac{(t-t_i)}{\tau}\right) \cdot dt_i}{\int_{t-2\tau}^{t} \exp\left(-\frac{(t-t_i)}{\tau}\right) \cdot dt_i}$$ (8)

where $t_i$ is the time in seconds at each iteration $i$, and $X$ is the observed mixing ratio of the chemical species. Figure S12 shows the results of applying various $\tau$, while fixing $\alpha$, to the H₂O₂ mixing ratio vector. A 1s time delay does not visibly change the observed H₂O₂ mixing ratio but longer time responses noticeably degrade the signal such that the high-frequency variations are damped. By design, the smearing function conserves signal.

We applied the smearing perturbation of HNO₃ ($\tau = 32$ s, $\alpha = 0.55$) to the EC calculations of H₂O₂, formic acid, and latent heat. We find that mean chemical mixing ratios do not change more than a few percent until time constants approach 1 or more hours (the timescale of diurnal variation); however, fluxes were affected for time constants on the order of seconds. Figure S13, top panels, shows that the H₂O₂ flux is significantly decreased from a signal degradation in the instrument, the mean concentration remains unperturbed, and, thus, the deposition velocity is significantly suppressed. The ratio of the undamped vs. damped values in $V_d$ and fluxes ranged from 1.5 – 1.8 for multi-day analysis of the formic acid, H₂O₂,
and LE flux (Fig. S13, bottom panels). An average value of 1.62 was used to correct the HNO₃ flux to the value that would have been measured if the time response constant for HNO₃ was τ < 1 s for all of the days included in this study. The mean mixing ratio values were uncorrected. We note that the analysis only includes dampening caused in the CIMS flow tube region, where the majority of the residence time is expected for our instrument. It is possible that the inclusion of the fast flow (~ 2000 L min⁻¹) inlet interaction will require greater dampening corrections; however, we do not have time decay data for compounds through this section of the inlet (the chemical pulse would need to be at the tip of the inlet). The correction for HNO₃ closes the gap between the measured and modeled V_d.

We further explored the effect of the time constant magnitude on the ratio of the undamped vs. damped fluxes using realistic time constants (τ = 1 – 100 s) for CIMS. This time range is also relevant to eddy scales carrying most of the flux we measured, where the loss of flux becomes especially important. Figure S14 shows that as τ increases, the ratio of damped vs. undamped V_d decrease, as expected, but the decrease is not linear (Fig. S14 insert panel). For τ = 1 s, greater than 98% of the H₂O₂ flux is conserved and for τ = 180 s, half of the flux is gone which leads to a significant underestimation in the calculated V_d values. Interestingly, most of that flux was lost between 1 and 32 seconds. Flux loss due to chemical interactions with surfaces is expected to be important for other “sticky” compounds like NH₃ and IEPOX, where a similar correction may be needed.

For most of the CIMS compounds included in this work, time delays are expected to be small (on the order of 1 s) with, perhaps, the exception of IEPOX. Unfortunately, we do not have field calibration sources for all compounds for which to attempt a damping analysis. For the combined ISOPOOH +IEPOX flux, ISOPOOH comprise greater than 66% of the mixing ratio signal for most cases. However, the combined V_d may still be underrepresented by our measurements if the IEPOX has time constant close to that of HNO₃.

6. Resistance Model

Many compounds detectable by CIMS were observed to have relatively high deposition velocities, suggesting a small or negligible resistance to surface uptake by plant stomatal or non-stomatal components such as leaf cuticles. We calculate the expected
contributions to deposition using a parameterization of surface deposition suggested by Weseley and Hicks (29), assuming a resistance-in-series scheme that considers the aerodynamic resistance ($R_a$), molecular diffusion resistance ($R_b$) and surface resistance ($R_c$) to the canopy that is parameterized as a large leaf:

$$V_d = \frac{1}{R_a + R_b + R_c}$$  \hspace{1cm} (9)

$R_a$ describes turbulent transfer of mass in the mixed layer to the surface, and can be parameterized by:

$$R_a = \frac{1}{k u_*} \left[ \frac{k \overline{U(z-d)}}{u_*} - \psi \left( \frac{z}{L} \right) \right]$$  \hspace{1cm} (10)

where $\overline{U(z-d)}$ is the mean wind speed at a height equal to the measurement height ($z$) less the displacement height (d, i.e., thickness of the “leaf”), $u_*$ is the friction velocity (m s$^{-1}$, see Eq. 7), $k$ is the dimensionless von Kármán constant (0.4), $\psi \left( \frac{z}{L} \right)$ is a correction function for the sensible heat and momentum fluxes that is dependent on the dimensionless parameter $z/L$ often used to characterize atmospheric stability. The formulation of $\psi \left( \frac{z}{L} \right)$ for the unstable period (local $h = 9 – 15$) was used to obtain the daytime $R_a$ (30). $L$ is the Monin-Obukhov length, defined as:

$$L = \frac{u_*^3 \overline{\Theta}}{kg \overline{w'\Theta'}}$$  \hspace{1cm} (11)

where $\overline{\Theta}$ is the mean potential temperature (K), i.e., the temperature of an air parcel transported adiabatically to surface pressure as calculated from the measured virtual temperature and atmospheric pressure, $\overline{w'\Theta'}$ is the potential temperature flux, and $g$ is the acceleration due to gravity (m s$^{-2}$).

$R_b$ describes the diffusion of molecules through the quasi-laminar layer at the surface of the roughness element. $R_b$ was modeled following the parameterization suggested by Jensen and Hummelshøj (31, 32) that included a direct dependence on leaf area index (LAI)
and the characteristic leaf thickness scale in the mixed-vegetation canopy \( l \), taken to be 0.001 m (31):

\[
R_b = \frac{\nu}{D_x u_e \left[ (LAI)^2 \nu \right]^{1/3}} \tag{12}
\]

\( \nu \) is the viscosity of air \((m^2 \text{ s}^{-1})\) at the ambient pressure of the measurement height, and \( D_x \) is the diffusivity of a molecule \( x \) in air. \( D_{H_2O_2} \) was taken to be \( 1.56 \times 10^{-5} \text{ m}^2 \text{ s}^{-1} \) at 25°C (scaled from measured values at 60°C (33)), and \( D_x \) for other molecules in this study was calculated from \( D_{H_2O_2} \) using Graham’s Law, where \( D_x = D_{H_2O_2} (MW_{H_2O_2}/MW_x)^{1/2} \). Table S4 shows the diffusivity coefficients and other parameters used in the model for chemical species included in this study and the results of the model.

LAI was measured during the SOAS campaign for the CTR site by coauthor G.M. Wolfe with help from C.J. Groff (Purdue University). Measurements were performed using an upward-looking light sensor (LAI-2000 Plant Canopy Analyzer) that measures the diffuse radiation attenuation, i.e., the fraction of sky blocked by canopy elements, within the canopy at multiple viewing angles. The attenuation is a function of total leaf area and average leaf angle. A representative value (LAI = 4.7) was taken as the mean along three transects at different orientations.

The average \( R_a \) value for the site on day 165 (June 15) was calculated to be \(~ 8 \text{ s m}^{-1}\) and \( R_b \) for \( H_2O_2 \) was \(~ 12 \text{ s m}^{-1}\). From the \( R_a \) and \( R_b \) values calculated, we find that the residual resistance \((1/V_{d, \text{ meas.}} - R_a - R_b)\) is heavily-dependent on the solubility (e.g., the Henry’s Law coefficient \((H)\)), with an additional dependence on the molecular mass of the individual compounds. That the residual resistance depends on solubility suggests that the bulk of this resistance is due to surface uptake. To model the surface resistance, we adjust the original parameterization by Weseley (27). The Weseley parameterization incorporates the dependence of \( R_c \) on molecular mass (e.g., diffusivity) in the stomatal resistance term \( (r_s) \) and on \( H \) in the mesophyll \( (r_m) \) and cuticular \( (r_{cut}) \) resistance terms. The canopy was assumed to be closed, and thus only the surface resistance from the canopy top was considered, i.e., neglecting contributions from the soil and “lower canopy.”
\[ R_c = \left( \frac{1}{r_s + r_m} + \frac{1}{r_{cut}} \right)^{-1} \] (13)

An adjustment to the Weseley parameterization was necessary because the original scheme overestimate \( R_c \) for \( \text{H}_2\text{O}_2 \) and \( \text{HNO}_3 \) in our work (demonstrated by various experimenters and in this work to be less than 5 s m\(^{-1}\) (34, 35)). Other evaluations of observed vs. modeled \( \text{H}_2\text{O}_2 \) flux in a forest (36) similarly concluded that the original Weseley scheme overestimated \( R_c \) for \( \text{H}_2\text{O}_2 \). Coefficients in the parameterizations of \( r_m \) and \( r_{cut} \) were empirically revised to close the discrepancy. We demonstrate that the revised parameterization successfully predicts \( R_c \) for not only \( \text{H}_2\text{O}_2 \) and \( \text{HNO}_3 \), but also for the series of organic and inorganic compounds studied in this work. Further validation is needed before this revised Weseley scheme can be generally applied for all compounds, at all sites, and for all seasons. The resistances to leaf components can be written as:

\[ r_s = \left( \frac{D_{\text{H}_2\text{O}}}{D_x} \right) r_{\text{H}_2\text{O}} \] (14)

\[ r_m = \left( \frac{H}{50RT} + 100f_0 \right)^{-1} \] (15)

\[ r_{cut} = (10^{-4}H/RT + f_0)^{-1} \] (16)

where \( r_{\text{H}_2\text{O}} \) is the stomatal resistance to the diffusion of water, \( H \) is the Henry’s Law coefficient (M atm\(^{-1}\)), \( R \) is the gas constant (atm M\(^{-1}\) K\(^{-1}\)), \( T \) (K) is the air temperature, and \( f_0 \) is a reactivity factor (27) that is defined as 0 = non-reactive, 0.1 = semi-reactive and 1 = reactive as ozone. The values of \( D_x, H \) and \( f_0 \) used in this work are reported in Table S2. Values of \( f_0 \) were used as suggested by Weseley for available compounds, and set as 0 otherwise. The \( r_{\text{H}_2\text{O}} \) term may be dependent on number variables, such as photosynthetically-active radiation, \( \text{CO}_2 \) air mixing ratio and assimilation, water fraction in the leaves and in the air, stomatal density, LAI, and air temperature. In the absence of measurements, only daytime values of \( V_d \) were calculated here, and daytime \( r_{\text{H}_2\text{O}} \) was assumed to be similar to the value computed at the BEARPEX campaign (21).

For many of the multifunctional compounds studied in this work, \( H \) is not known; thus, we estimate \( H \) based on chemical proxies. Uncertainties in \( H \) estimates, which can be >
100% due to the paucity of measurements, are critically important to the $R_c$ term for certain ranges of $H$ (see Fig. S16 and related discussion). Thus, resistance model results should be treated as a rough approximation in this work for compounds with unknown $H$. An example of the large uncertainty in $H$ is the trend with increasing carbon number for the family of hydroxy nitrates. Shepson et al (37) found decreasing $H$ for hydroxy nitrates of increasing carbon number, whereas Treves et al (38) observed the opposite trend. $H$ can be significantly different for different isomers of the same compound; however, the trend of decreasing $H$ with increasing carbon number appears to be more consistent with observations of some chemical families, e.g., in the family of $C_1 – C_9$ straight-chain aldehydes or $C_3 – C_{11}$ straight-chain ketones ((39), and references therein). This trend may be rationalized because the addition of a more hydrophobic alkyl group, while conserving the singular hydrophilic group (e.g., aldehyde) should depress $H$ if all else is equal.

Neither the Shepson et al nor the Treves et al $H$ values can be applied directly, however, as the nitrates we measured were not exclusively alkyl hydroxy nitrates, e.g., ISOPN is a hydroxy nitrate with an alkenyl group, PROPNN is a nitrate with a ketone or aldehyde group, and MACN + MVKN are hydroxy nitrates with a ketone or aldehyde groups. Thus, we used the Shepson et al $H$ values, and extrapolated to higher carbon numbers when necessary. The estimation for INP and MTNP are especially uncertain. As more measurements become available due to greater availability of synthesized authentic standards, the uncertainties in the resistance model can be revised downward. The modeled resistances are shown in Fig. S15. Modeled $R_c$ agree well with previous observations for $HNO_3$ and $H_2O_2\ (0 - 5 \: s \: m^{-1})$, and ROOH $\ (20 - 40 \: s \: m^{-1})$ (34, 35, 40). HCN is both observed and calculated to have the largest total resistance to deposition. Further, $R_c$ is the largest component of the summed resistance for HCN, due to its small $H$ value.

Here we estimate the sensitivity of the resistance model to parameters such as LAI, $u^*$ and leaf thickness. A hypothetical $\pm 200\%$ change in these input parameters modified $R_b$ by $|37 – 58|\%$ and $V_d$ by $\sim |25 – 30|\%$. This $V_d$ model error is similar to standard deviation of the measurements. At SOAS, our measurements of LAI in particular, performed from 6/18/2013 – 6/20/2013 at viewing angles 90 – 270 degrees at three locations within the forest had a 2-sigma uncertainty of 35% (for a confidence level of 95%). This translates to an $R_b$
change of $|18 - 33\%|$ and a $V_d$ change of $|10 - 17\%|$ in the resistance model, which is also within the experimental uncertainty of the measurement. In contrast, $H$ is a parameter where estimates may vary by much larger margins due to the unavailability of direct measurements for most OVOCs. We find that above a threshold value ($H > 3 \times 10^4$ M atm$^{-1}$), the resistance model we used becomes much less sensitive to increases in $H$. We can illustrate this idea by comparing the calculated deposition velocities of two hypothetical water-soluble compounds (X,Y) (high Henry’s Law coefficient, $H$) that are not reactive (low reactivity coefficient, $f_0$). Compound Y is taken as the reference compound with $H = 1 \times 10^5$ M atm$^{-1}$ and $f_0 = 0$. For compound X, $H$ is varied from $1 \times 10^1$ to $1 \times 10^8$ M atm$^{-1}$. The fractional difference in calculated $V_d$ between X and Y is shown in Figure S16. It is clear that uncertainties in $H$ are very important in an intermediate regime (changing $V_d$ by ~ 80%), but at either extremes (i.e., $H \to 0$ and $R_c \to \infty$, or $H \to \infty$ and $R_c \to 0$), the effect is muted.

7. GEOS-Chem Modeling

Global and regional model simulations are performed using the GEOS-Chem global 3-D chemical transport model v9–02 (26). The model is driven by GEOS-FP (“Forward Processing”) assimilated meteorology with hourly resolution. This version of GEOS-Chem implements a new isoprene oxidation mechanism (Mao et al (2013)) based on Paulot et al (2009 a,b). We update this mechanism to include the results of recent studies performed by our group and other groups (Table S3 and corresponding references). Several chemical species measured at the site are not discussed because they are not currently included in the standard mechanism (e.g., HCN, HMHP, HPALD, HDC$_4$, DHC$_4$, INP, and MTNP) or because their dry deposition is not considered (PAA).

GEOS-Chem uses the resistance-based approach described by Weseley 1989 (27) to calculate dry deposition velocities. The performance of this approach depends both on the knowledge of meteorological drivers (e.g., atmospheric stability), surface conditions (e.g., LAI) and the solubility (effective solubility $H^*$) and reactivity (reactivity factor $f_0$) of the compound of interest (Table S4). $f_0$ in the GEOS-Chem model is set to 1 for many VOCs to reflect recent observations from Karl et al (28). We performed two types of simulations for this work:
(1) **Regional simulation:** A set of simulations was performed to calculate dry deposition velocities at CTR site using GEOS-FP meteorology at a horizontal resolution of resolution of (0.25° x 0.33°) over the contiguous US. We find that the GEOS-FP captures well the observed wind speed, friction velocity, latent heat, and sensible heat fluxes at the CTR site. Here we adjust $H^*$ iteratively (Table S4) to improve the model agreement with observations performed on June 15, 2013.

(2) **Global simulation:** Two global simulations (2° x 2.5°) are performed for 2013 to evaluate the impact of our improved dry deposition parameterization on the global budget of selected tracers. The base simulation uses the dry deposition velocities (i.e., the $H^*$) currently used by GEOS-Chem, while our sensitivity simulation arbitrarily increase $H^*$ to match our CTR observations of deposition velocities. Each simulation is preceded by a 4-month spin-up. Monthly deposition fluxes, deposition velocities, and surface concentration of select species are reported as monthly diurnal averages of one hour periods.

The sensitivity simulation suggests that deposition velocities at the CTR site are similar to forests across the southeast and northeast U.S. For example, modeled daytime $V_d$ for H$_2$O$_2$ across the eastern U.S. are 4 – 6 cm s$^{-1}$ (Fig. S18) compared with the 5.2 ± 1.1 cm s$^{-1}$ measured at CTR. Furthermore, the consistency between our observations of H$_2$O$_2$ deposition in a mixed forest in AL and those measured at Canadian Boreal forests (18), German spruce forests (19), and other forested sites in OR and TN (17) suggest that the results obtained here and elsewhere for H$_2$O$_2$ may be representative of forests in general. It is possible that, for compounds like H$_2$O$_2$ where deposition happens with no surface resistance, and where dissociation equilibria on the surface of plants are negligible, characteristics of the specific sites may be unimportant to understanding daytime deposition. Additional flux observations of reactive trace gases will be helpful to validate this suggestion. The year-round sensitivity simulation also shows that deposition velocities and friction velocities observed during the campaign days are typical summer values (Fig. S19) and high deposition rates can extend over much of the period between spring and fall.
Table S1: Molecular identities, abbreviations, and CIMS calibrations of the chemical species included in this study. The molecular structures shown may represent one of many structural isomers that can be characterized as the same chemical species (e.g., IEPOX has 4 isomers) or different chemical species (e.g., DHC4 may be a ketone or aldehyde).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Abbrev.</th>
<th>Representative Structure</th>
<th>CIMS ion</th>
<th>Cal Method (see text)</th>
<th>Sensitivity uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen cyanide</td>
<td>HCN</td>
<td>(\text{HC≡N})</td>
<td>((\text{HCN})\cdot\text{CF}_3\text{O}^-)</td>
<td>Commercial standard gas mixture</td>
<td>30%</td>
</tr>
<tr>
<td>Hydrogen Peroxide</td>
<td>(\text{H}_2\text{O}_2)</td>
<td>(\text{HO}--\text{OH})</td>
<td>((\text{H}_2\text{O}_2)\cdot\text{CF}_3\text{O}^-)</td>
<td>Commercial standard + HPLC</td>
<td>30%</td>
</tr>
<tr>
<td>Formic Acid</td>
<td>Formic</td>
<td>(\text{O}--\text{H}--\text{H})</td>
<td>((\text{HCOOH})\cdot\text{F}^-)</td>
<td>Commercial standard + gravimetric</td>
<td>20%</td>
</tr>
<tr>
<td>Nitric Acid</td>
<td>(\text{HNO}_3)</td>
<td>(\text{O}_2\text{N}--\text{OH})</td>
<td>((\text{HNO}_3)\cdot\text{F}^-)</td>
<td>Commercial standard + IC</td>
<td>30%</td>
</tr>
<tr>
<td>Hydroxy methylhydroperoxide</td>
<td>HMHP</td>
<td>(\text{HOO}--\text{OH}--\text{OH})</td>
<td>((\text{CH}_4\text{O}_3)\cdot\text{CF}_3\text{O}^-)</td>
<td>Synthesized standard + FTIR</td>
<td>40%</td>
</tr>
<tr>
<td>Hydroxy-acetone</td>
<td>HAC</td>
<td>(\text{HO}--\text{C}--\text{O}--\text{H})</td>
<td>((\text{C}_3\text{H}_6\text{O}_2)\cdot\text{CF}_3\text{O}^-)</td>
<td>Commercial standard + FTIR</td>
<td>40%</td>
</tr>
<tr>
<td>Peroxyacetic acid</td>
<td>PAA</td>
<td>(\text{OO}--\text{OH}--\text{O})</td>
<td>((\text{C}_2\text{H}_4\text{O}_3)\cdot\text{CF}_3\text{O}^-)</td>
<td>Commercial standard + FTIR</td>
<td>40%</td>
</tr>
<tr>
<td>(\text{C}_4) Hydroxy dicarboxylic acid</td>
<td>HDC4</td>
<td>(\text{O}--\text{O}--\text{OH}--\text{OH})</td>
<td>((\text{C}_4\text{H}_6\text{O}_3)\cdot\text{CF}_3\text{O}^-)</td>
<td>Calculated</td>
<td>50%</td>
</tr>
<tr>
<td>(\text{C}_4) Dihydroxy carbonyl</td>
<td>DHC4</td>
<td>(\text{O}--\text{OH}--\text{OH}--\text{OH})</td>
<td>((\text{C}_4\text{H}_6\text{O}_3)\cdot\text{CF}_3\text{O}^-)</td>
<td>Calculated</td>
<td>50%</td>
</tr>
<tr>
<td>Isoprene hydroperoxy-aldehyde</td>
<td>HPALD</td>
<td>(\text{HO}--\text{O}--\text{O}--\text{O})</td>
<td>((\text{C}_5\text{H}_8\text{O}_3)\cdot\text{CF}_3\text{O}^-)</td>
<td>Calculated</td>
<td>50%</td>
</tr>
<tr>
<td>Compound Description</td>
<td>Symbol</td>
<td>Chemical Formula</td>
<td>Synthesis/Instrumentation</td>
<td>Yield</td>
<td></td>
</tr>
<tr>
<td>-------------------------------------------------------------------------------------</td>
<td>--------</td>
<td>------------------</td>
<td>--------------------------------------------</td>
<td>-------</td>
<td></td>
</tr>
<tr>
<td>Isoprene hydroxy-hydroperoxide and isoprene dihydroxy-epoxide</td>
<td>ISOPOOH</td>
<td>(C$<em>5$H$</em>{10}$O$_3$)$\cdot$CF$_3$O$^-$</td>
<td>Synthesized standards, NMR + gravimetric</td>
<td>40%</td>
<td></td>
</tr>
<tr>
<td>Propanone nitrate</td>
<td>PROPNN</td>
<td>(C$_3$H$_5$NO$_4$)$\cdot$CF$_3$O$^-$</td>
<td>Separated oxidation mixture + TDLIF</td>
<td>30%</td>
<td></td>
</tr>
<tr>
<td>Isoprene hydroxy nitrate</td>
<td>ISOPN</td>
<td>(C$_5$H$_9$NO$_4$)$\cdot$CF$_3$O$^-$</td>
<td>Synthesized standard + TDLIF</td>
<td>30%</td>
<td></td>
</tr>
<tr>
<td>Methacrolein and Methyl vinyl ketone hydroxy nitrate</td>
<td>MACN/</td>
<td>(C$_4$H$_7$NO$_5$)$\cdot$CF$_3$O$^-$</td>
<td>Separated oxidation mixture + TDLIF</td>
<td>30%</td>
<td></td>
</tr>
<tr>
<td>Methacrolein and Methyl vinyl ketone hydroxy nitrate</td>
<td>MVKN</td>
<td>(C$_4$H$_7$NO$_5$)$\cdot$CF$_3$O$^-$</td>
<td>Separated oxidation mixture + TDLIF</td>
<td>30%</td>
<td></td>
</tr>
<tr>
<td>Isoprene nitroxy hydroperoxide</td>
<td>INP</td>
<td>(C$_5$H$_9$NO$_5$)$\cdot$CF$_3$O$^-$</td>
<td>Calculated</td>
<td>50%</td>
<td></td>
</tr>
<tr>
<td>Monoterpene nitroxy hydroperoxide</td>
<td>MTNP</td>
<td>(C$<em>{10}$H$</em>{17}$NO$_5$)$\cdot$CF$_3$O$^-$</td>
<td>Calculated</td>
<td>50%</td>
<td></td>
</tr>
</tbody>
</table>
Table S2: Inputs for the revised resistance model used in this work for relevant molecules: $H$ is the [a] experimental or [b-d] estimated simple Henry’s Law coefficient, $f_0$ is a reactivity factor, and diffusivity was calculated based on the measured diffusivity of H$_2$O$_2$ as defined in the text.

<table>
<thead>
<tr>
<th>Compound</th>
<th>MW (Da)</th>
<th>Diffusivity ($\text{m}^2 \text{s}^{-1}$)</th>
<th>$H$ ($\text{M atm}^{-1}$)</th>
<th>$f_0$</th>
<th>Calc. $V_d$ (cm s$^{-1}$)</th>
<th>Measured $V_d$ (cm s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCN</td>
<td>27</td>
<td>$1.75 \times 10^{-5}$</td>
<td>10</td>
<td>[a]</td>
<td>0</td>
<td>0.32</td>
</tr>
<tr>
<td>H$_2$O$_2$</td>
<td>34</td>
<td>$1.56 \times 10^{-5}$</td>
<td>$1.1 \times 10^5$ [a]</td>
<td>1</td>
<td>4.78</td>
<td>$5.2 \pm 1.1$</td>
</tr>
<tr>
<td>Formic</td>
<td>46</td>
<td>$1.34 \times 10^{-5}$</td>
<td>$5.6 \times 10^3$ [a]</td>
<td>0</td>
<td>2.05</td>
<td>$1.0 \pm 0.4$</td>
</tr>
<tr>
<td>HNO$_3$</td>
<td>63</td>
<td>$1.15 \times 10^{-5}$</td>
<td>$3.2 \times 10^5$ [a]</td>
<td>1</td>
<td>3.99</td>
<td>$3.8 \pm 1.3$</td>
</tr>
<tr>
<td>HMHP</td>
<td>64</td>
<td>$1.14 \times 10^{-5}$</td>
<td>$1.3 \times 10^6$ [a]</td>
<td>0.1</td>
<td>4.01</td>
<td>$4.1 \pm 1.1$</td>
</tr>
<tr>
<td>HAC</td>
<td>74</td>
<td>$1.06 \times 10^{-5}$</td>
<td>$2 \times 10^3$ [b]</td>
<td>0</td>
<td>1.31</td>
<td>$1.4 \pm 0.5$</td>
</tr>
<tr>
<td>PAA</td>
<td>76</td>
<td>$1.04 \times 10^{-5}$</td>
<td>520</td>
<td>[a]</td>
<td>2.85</td>
<td>$2.7 \pm 0.7$</td>
</tr>
<tr>
<td>HDC$_4$</td>
<td>102</td>
<td>$9.01 \times 10^{-6}$</td>
<td>$2 \times 10^3$ [b]</td>
<td>0</td>
<td>1.21</td>
<td>$1.1 \pm 0.5$</td>
</tr>
<tr>
<td>DHC$_4$</td>
<td>104</td>
<td>$8.92 \times 10^{-6}$</td>
<td>$2 \times 10^3$ [b]</td>
<td>0</td>
<td>1.19</td>
<td>$1.0 \pm 0.4$</td>
</tr>
<tr>
<td>HPALD</td>
<td>116</td>
<td>$8.45 \times 10^{-6}$</td>
<td>$4 \times 10^4$ [b]</td>
<td>0</td>
<td>2.76</td>
<td>$2.4 \pm 0.6$</td>
</tr>
<tr>
<td>ISOPOOH/IEPOX</td>
<td>118</td>
<td>$8.37 \times 10^{-6}$</td>
<td>$7 \times 10^7$ [c]</td>
<td>0</td>
<td>3.25</td>
<td>$2.5 \pm 0.6$</td>
</tr>
<tr>
<td>PROPNN</td>
<td>119</td>
<td>$8.34 \times 10^{-6}$</td>
<td>$1 \times 10^4$ [d]</td>
<td>0</td>
<td>2.00</td>
<td>$1.7 \pm 0.6$</td>
</tr>
<tr>
<td>ISOPN</td>
<td>147</td>
<td>$7.50 \times 10^{-6}$</td>
<td>$5 \times 10^3$ [d]</td>
<td>0</td>
<td>1.47</td>
<td>$1.5 \pm 0.6$</td>
</tr>
<tr>
<td>MACN/MVKN</td>
<td>149</td>
<td>$7.45 \times 10^{-6}$</td>
<td>$6 \times 10^3$ [d]</td>
<td>0</td>
<td>1.56</td>
<td>$1.5 \pm 0.5$</td>
</tr>
<tr>
<td>INP</td>
<td>163</td>
<td>$7.12 \times 10^{-6}$</td>
<td>$5 \times 10^3$ [b]</td>
<td>0</td>
<td>1.32</td>
<td>$1.3 \pm 0.6$</td>
</tr>
<tr>
<td>MTNP</td>
<td>231</td>
<td>$5.98 \times 10^{-6}$</td>
<td>$1 \times 10^3$ [b]</td>
<td>0</td>
<td>0.75</td>
<td>$0.8 \pm 0.4$</td>
</tr>
</tbody>
</table>

[a] Mean experimental values from R. Sander (1999), and references therein
[b] Where empirical data are unavailable, similar compounds from R. Sander (1999) were used as proxies (HAC as C$_3$H$_8$O$_2$, HDC$_4$ and DHC$_4$ as values averaged between butanediol and generic aldehyde, HPALD as a hydroxyaldehyde, INP and MTNP were estimated based on functional groups)
**Table S3:** Revisions to GEOS-Chem mechanism to reflect kinetic data published after the latest revision by Mao et al (2013).

<table>
<thead>
<tr>
<th>Revisions</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Increase ISOPNB +OH rate coefficient by factor of 2.4</td>
<td>Ref. (15)</td>
</tr>
<tr>
<td>Decrease MACRN + OH by factor of 11.46</td>
<td>Ref. (41)</td>
</tr>
<tr>
<td>Include IEPOX formation and change RO₂ branching for ISOPNB + OH:</td>
<td></td>
</tr>
<tr>
<td>- ISOPNB + OH = 0.88 ISOPNBO₂ + 0.12 IEPOX + 0.12 NO₂</td>
<td>Refs. (15, 42)</td>
</tr>
<tr>
<td>Smaller NOx recycling for ISOPNB RO₂ radical:</td>
<td></td>
</tr>
<tr>
<td>- ISOPNBO₂ + NO = 0.249 MVKN + 0.461 MACRN + 0.29 HAC + 0.29 GLYC + 0.71 HCHO + 0.71 HO₂ + 1.29 NO₂</td>
<td>Ref. (15)</td>
</tr>
<tr>
<td>Decrease rate of ISOPNB + O₃ to 3 x 10⁻¹⁹ cm³ molec⁻¹ s⁻¹</td>
<td>Ref. (15)</td>
</tr>
<tr>
<td>Decrease rate of ISOPND + O₃ rate to 2.8 x 10⁻¹⁷ cm³ molec⁻¹ s⁻¹</td>
<td>Ref. (15)</td>
</tr>
<tr>
<td>Increase MACRN photolysis rate to 10*J_ONIT1</td>
<td>Ref. (43)</td>
</tr>
</tbody>
</table>
**Table S4:** Inputs for the base (B) and sensitivity (S) GEOS-Chem simulations, where only the Henry’s law factors were adjusted.

<table>
<thead>
<tr>
<th>Name</th>
<th>Henry’s Index Factor (B) (M atm$^{-1}$)</th>
<th>Henry’s Index Factor (S) (M atm$^{-1}$)</th>
<th>$f_0$</th>
<th>Molec. Weight (kg mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HNO3</td>
<td>1.00E+14</td>
<td>1.00E+14</td>
<td>0</td>
<td>0.063</td>
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<tr>
<td>H2O2</td>
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<td>5.00E+07</td>
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<td>0.034</td>
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<tr>
<td>ISOPND</td>
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<td>2.00E+06</td>
<td>1</td>
<td>0.147</td>
</tr>
<tr>
<td>ISOPNB</td>
<td>1.70E+04</td>
<td>2.00E+06</td>
<td>1</td>
<td>0.147</td>
</tr>
<tr>
<td>PROPNN</td>
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<td>5.00E+05</td>
<td>1</td>
<td>0.119</td>
</tr>
<tr>
<td>HAC</td>
<td>2.90E+03</td>
<td>1.40E+06</td>
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<td>0.074</td>
</tr>
<tr>
<td>GLYC</td>
<td>4.10E+04</td>
<td>2.00E+07</td>
<td>1</td>
<td>0.06</td>
</tr>
<tr>
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<td>2.00E+06</td>
<td>1</td>
<td>0.149</td>
</tr>
<tr>
<td>MVKN</td>
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<td>2.00E+06</td>
<td>1</td>
<td>0.149</td>
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<tr>
<td>RIP</td>
<td>1.70E+06</td>
<td>1.70E+06</td>
<td>1</td>
<td>0.118</td>
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<tr>
<td>IEPOX</td>
<td>1.30E+08</td>
<td>8.00E+07</td>
<td>1</td>
<td>0.118</td>
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</table>
Figure S1: Prime vectors of vertical wind ($w'$, black) and CIMS mixing ratios for water vapor (blue), H$_2$O$_2$ (red), ISOPOOH + IEPOX (magenta) and ISOPN (green) during a ~ 25 minute segment on June 27.
Figure S2: Meteorological parameters on the non-continuous dates included in this study that were used to calculate water vapor fraction for an external calibration of the CIMS water ion measurement.
Figure S3: Water vapor as measured by the CIMS at 10 hz compared to that measured by the Zeno weather station at 1 hz.
Figure S4: Representative lag covariance functions of several CIMS compounds and virtual temperature with \( w \), as a function of lag on JD 165, \( h=14 \). Units are ppmv m/s for \( \text{H}_2\text{O} \), °C m/s for \( T \), and pptv m/s otherwise. Extrema locations indicate optimum lag correction times. Each lag point represents ~ 0.1 s. Lag for virtual temperature with respect to \( w \) is always zero. Lag for CIMS compounds with respect to \( w \) varies from 0.1 – 1.1 s.
Figure S5: Energy balance closure for days where wind is northerly (~ 180 degrees) compared to southerly/southeasterly (320 – 20 degrees).
Figure S6: Representative cospectra for vertical wind (w) with several CIMS compounds and virtual temperature. Cospectra were calculated for hour 13, binned into 150 frequency bins and averaged over all dates included in this study. Dashed black line shows the $f^{-7/3}$ relationship expected for the inertial subrange ($f > 0.003$ Hz) from surface layer theory.
Figure S7: Representative plot of the normalized cumulative sum of unnormalized cospectra (ogive) for vertical wind (w) with several CIMS compounds and virtual temperature calculated for (a) hours 9 – 15, averaged over all of the dates included in this study and (b) for JD 165, superimposed with the normalized transfer function, using mean winds from the day time hours, calculated for the inlet-sonic separation correction (dashed black line). Ogives were normalized to their asymptotic value.
Figure S8: Frequency-weighted covariance-normalized cospectra for vertical wind $w$ with several CIMS compounds and virtual temperature, shown for (a) hours 9 – 15 over the JD 165 where $z/U \sim 7$ s and (b) hours 9 – 15 over all flux days where $z/U$ varies.
Figure S9: Friction velocity, as calculated from the momentum flux (see text), averaged over the dates included in this study. The red line indicates the suggested 0.23 m s⁻¹ threshold over which turbulence can be considered well-developed (44).
Figure S10: Sensible heat flux and H$_2$O$_2$ flux calculated using approximately 30 minute (blue) and approximately 5 min (red) averaging time intervals. Left panels show raw calculated fluxes and right panel show calculated fluxes that have been averaged into the same half-hourly bins.
Figure S11: Decay of CIMS signals from a chemical pulse of individual species, indicating the time response (i.e., “stickiness”) of each species in the CIMS flow region. Time responses were fit with exponential decay functions.
**Figure S12:** Top panel: observed H$_2$O$_2$ mixing ratio. Bottom panel: H$_2$O$_2$ mixing ratio damped with several time response constants.
Figure S13: Top panels (left to right): Hydrogen peroxide flux, mean concentration, and deposition velocities due to applied inlet dampening with time response factor of 32 seconds compared to the undamped measurements. Bottom panels (left to right): Comparisons of the undamped vs. damped values for formic acid $V_d$, H$_2$O$_2$ $V_d$, and latent heat flux (LE).
**Figure S14**: Representative effect of different time response factors (τ) on the EC fluxes (nmol m$^{-2}$ s$^{-1}$) and $V_d$ (cm s$^{-1}$) of H$_2$O$_2$. Mean concentrations did not change within a few percent on this timescale. Insert shows midday flux of H$_2$O$_2$ (h = 12-14) as a function of τ.
Figure S15: Modeled resistances using a resistance-in-series scheme (see text) for the chemical species studied in this work, whose molecular identities are defined in Table S1 and the model inputs are reported in Table S4.
**Figure S16:** Sensitivity of the resistance model to uncertainties in Henry’s Law coefficient \((H)\) for a hypothetical compound \((Y)\) with \(H = 1 \times 10^5\ M\ atm^{-1}\) (water-soluble) and \(f_0 = 0\) (non-reactive). \(H\) was varied by several orders of magnitude for another hypothetical compound \((X, f_0 = 0)\), and the percent change in \(V_d\) was computed with respect to the reference \(V_{d,Y}\). 
Figure S17: Fluxes (left panels) and mean mixing ratios (right panels) for the chemical species for which the data were not shown in the main text. Legends for both panels are shown on the left.
Figure S18: Distribution of 24-h average deposition velocities from the sensitivity simulation for (upper left and clockwise): HNO$_3$, H$_2$O$_2$, ISOPN, and HAC in the Eastern United States grid boxes. Daytime values are approximately twice the 24-h average.
**Figure S19**: Daytime (h = local noon ± 3 h) deposition velocities for HNO$_3$ and H$_2$O$_2$ (right axis) and friction velocity ($u_*$) from GEOS-FP for every day of the year 2013 at the CTR site. Data were obtained from the year-round sensitivity simulation. The measurement period during SOAS is shown in the gray shaded region.
Figure S20: \( \text{H}_2\text{O}_2 \) mixing ratio vertical profile in the base (black) and sensitivity (red) studies for the CTR site during June 2013. The sensitivity study uses daytime deposition velocities measured at CTR during SOAS. The surface altitude (shown as “0” in the plot vertical axis) corresponds to a height of 70 m and values at the measurement height are expected to be 25 – 40% lower than at 70 m. Note the unequal spacing in the vertical axis used to magnify changes in the boundary layer.
Figure S21: SO$_2$ mixing ratio observed by TOF-CIMS during the SOAS Campaign.
References:


