Bidirectional ecosystem-atmosphere fluxes of volatile organic compounds across the mass spectrum: How many matter?

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Supporting Information

Table S1; Figures S1-S6.

Table S1. Parameters for certified compressed VOC standards used in the field[a]

Compound	Cylinder #	Mixing ratio (ppb)	Uncertainty (%)
Acetaldehyde	1	1050	±5%
Methanol	1	4944	±5%
Isoprene	1	2497	±5%
Acetone	1	2457	±5%
Acetonitrile	1	1008	±5%
Methyl ethyl ketone	1	1052	±5%
Benzene	1	1070	±5%
Hydroxyacetone	1	1558	±5%
Toluene	1	1057	±5%
m-Xylene	1	1028	±5%
1,3,5-Trimethylbenzene	1	955	±5%
1,2,4,5-Tetramethylbenzene	1	1018	±5%
Propene	2	990	±5%
Furan	2	1033	±5%
Dimethylsulfide	2	1072	±5%
Methacrolein	2	1047	±5%
2-Methyl-3-buten-2-ol	2	1046	±5%
3-Hexanone	2	1008	±5%
β-Pinene	2	1012	±5%
Propyne	3	982	±5%
1-Butene	3	974	±5%
Ethanol	3	1005	±5%
Methyl vinyl ketone	3	976	±5%
3-Methylfuran	3	930	±5%
3-Pentanone	3	1031	±5%
Ethylbenzene	3	998	±5%
α-Pinene	3	1005	±5%

[a]Cylinders prepared by Apel-Reimer Environmental Inc.

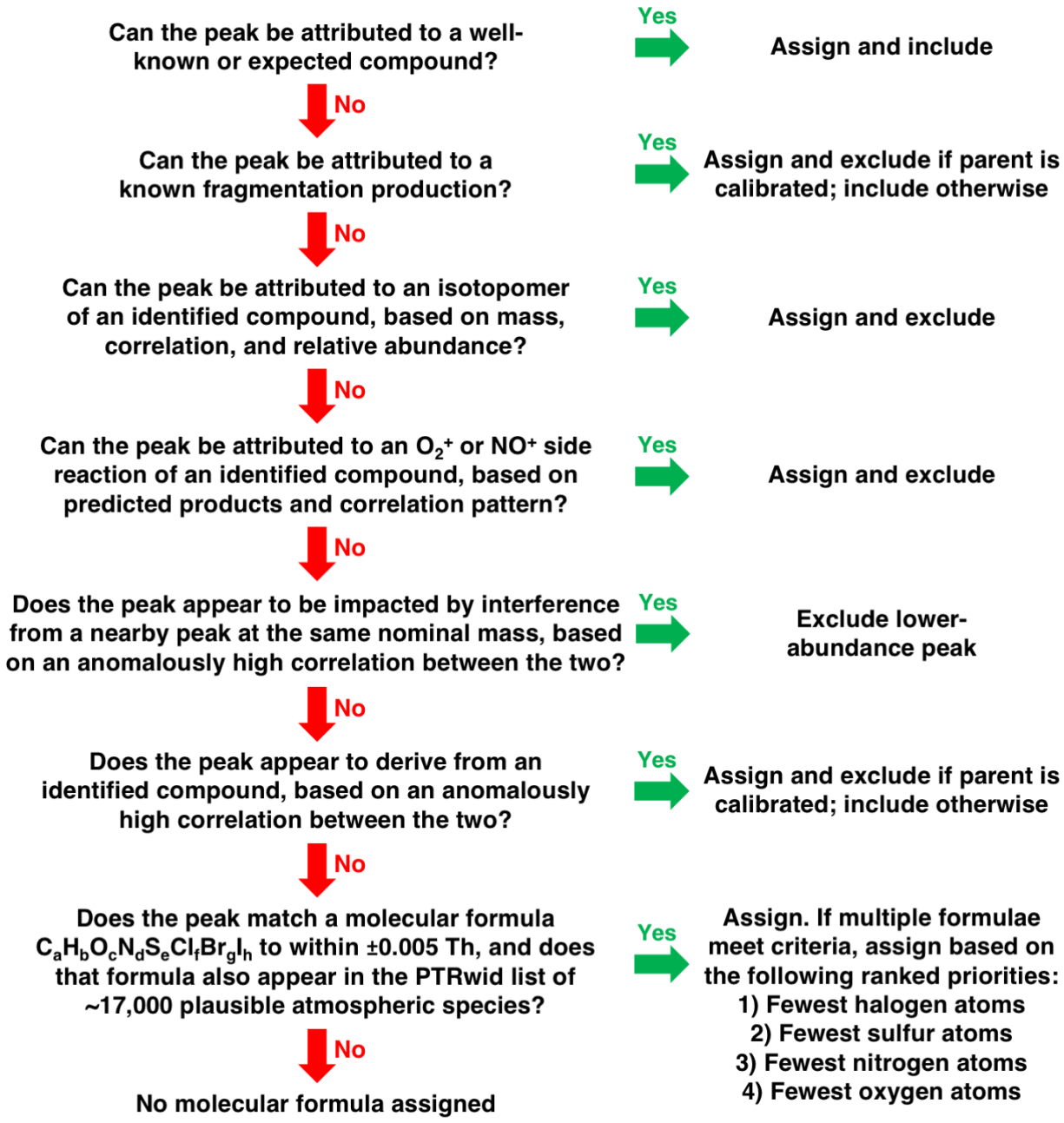

Figure S1. Workflow for assigning molecular formulae to detected ion peaks.

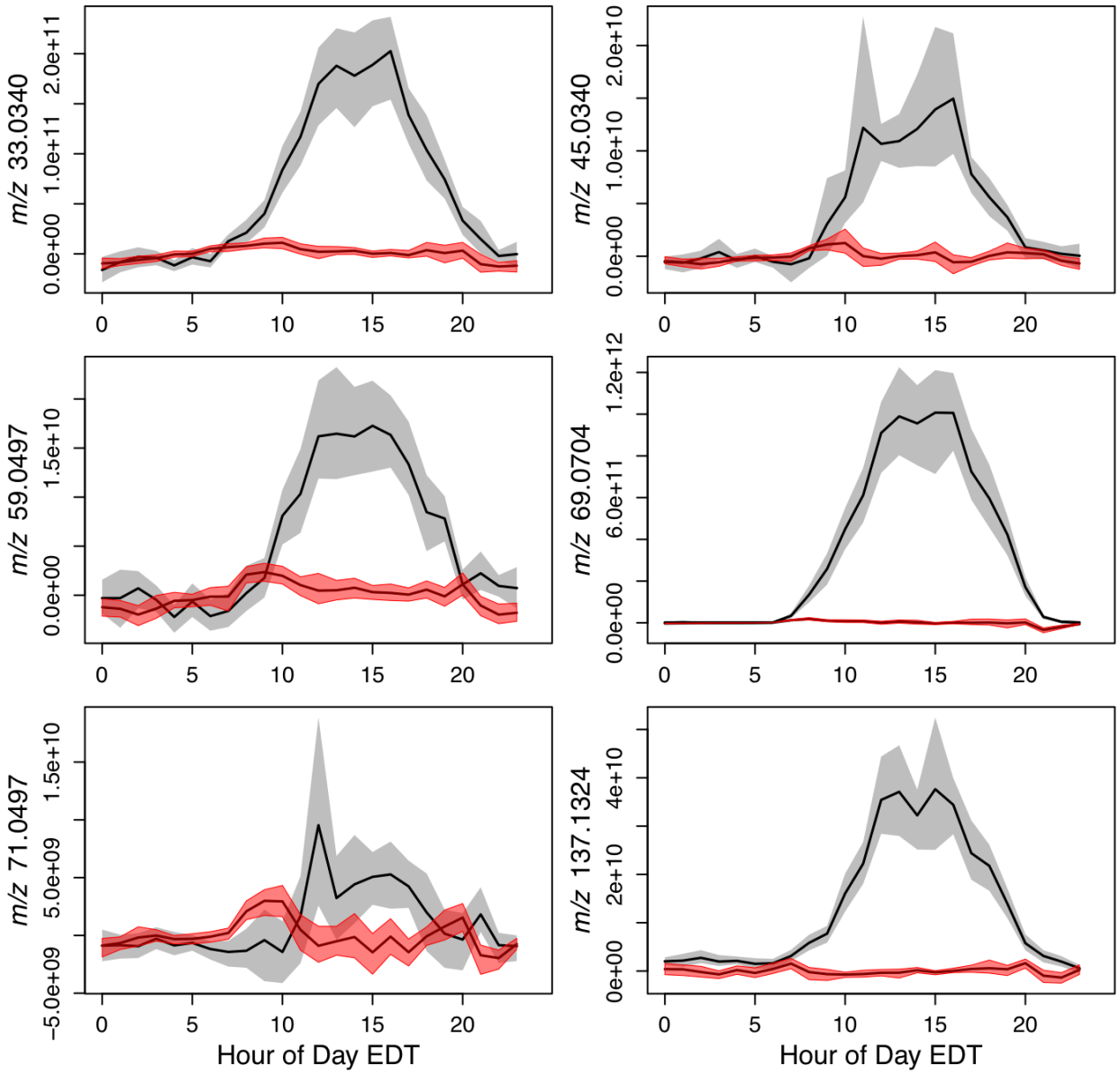

Figure S2. Mean diel cycle of above-canopy (black) and canopy storage (red) fluxes as measured at PROPHET-AMOS for selected compounds (*m*/*z* 33.0340: methanol; *m*/*z* 45.0340: acetaldehyde; *m*/*z* 59.0497: acetone; *m*/*z* 69.0704: isoprene; *m*/*z* 71.0497: methyl vinyl ketone (MVK) + methacrolein (MACR); *m*/*z* 137.1324: monoterpenes). Solid lines and shaded regions show the mean observed fluxes and associated 95% confidence intervals, respectively.

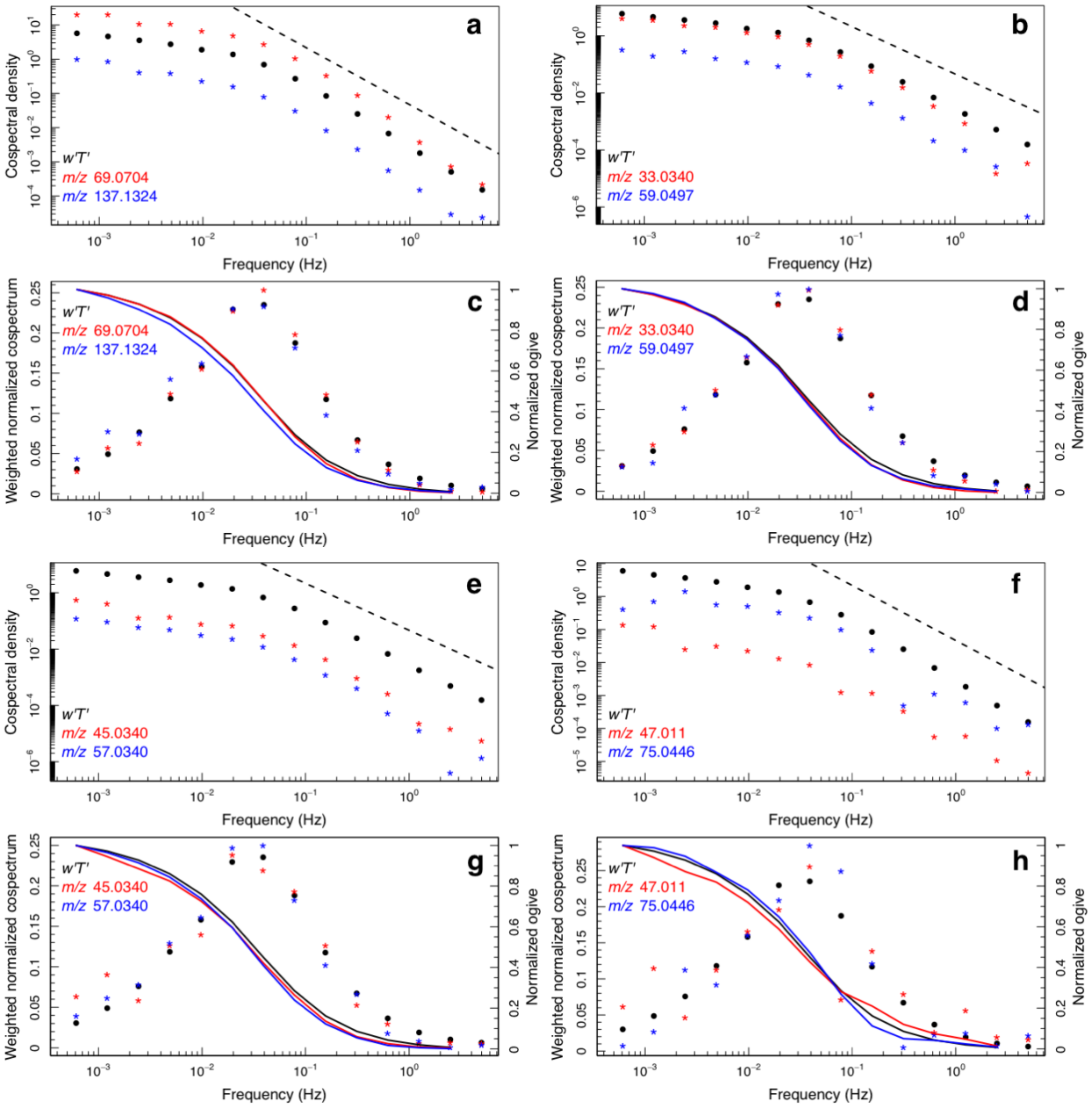

Figure S3. Spectral analysis for example *m/z* ratios. Ensemble co-spectral densities are shown for (a) *m/z* 69.070 ($C_5H_9^+$, isoprene) and 137.132 ($C_{10}H_{17}^+$, monoterpenes); (b) *m/z* 33.034 (CH_5O^+, methanol) and 59.050 ($C_3H_7O^+$, acetone+propanal); (e) *m/z* 45.034 ($C_2H_5O^+$, acetaldehyde) and 57.034 ($C_3H_5O^+$, acrolein); (f) *m/z* 47.011 ($CH_3O_2^+$, formic acid) and 75.045 ($C_3H_7O_2^+$, hydroxyacetone+propanoic acid). Black points and dashed lines show the *w'T'* co-spectral density and the -5/3 slope predicted by theory, respectively. Panels (c), (d), (g), and (h) show the corresponding frequency-weighted covariance-normalized co-spectra (points) and normalized ogives (lines). Data shown reflect the ensemble average spectra for daytime turbulent periods (11am-4pm EDT; $u^* > 0.3$ m/s) with winds that are not from the direction of the tower.

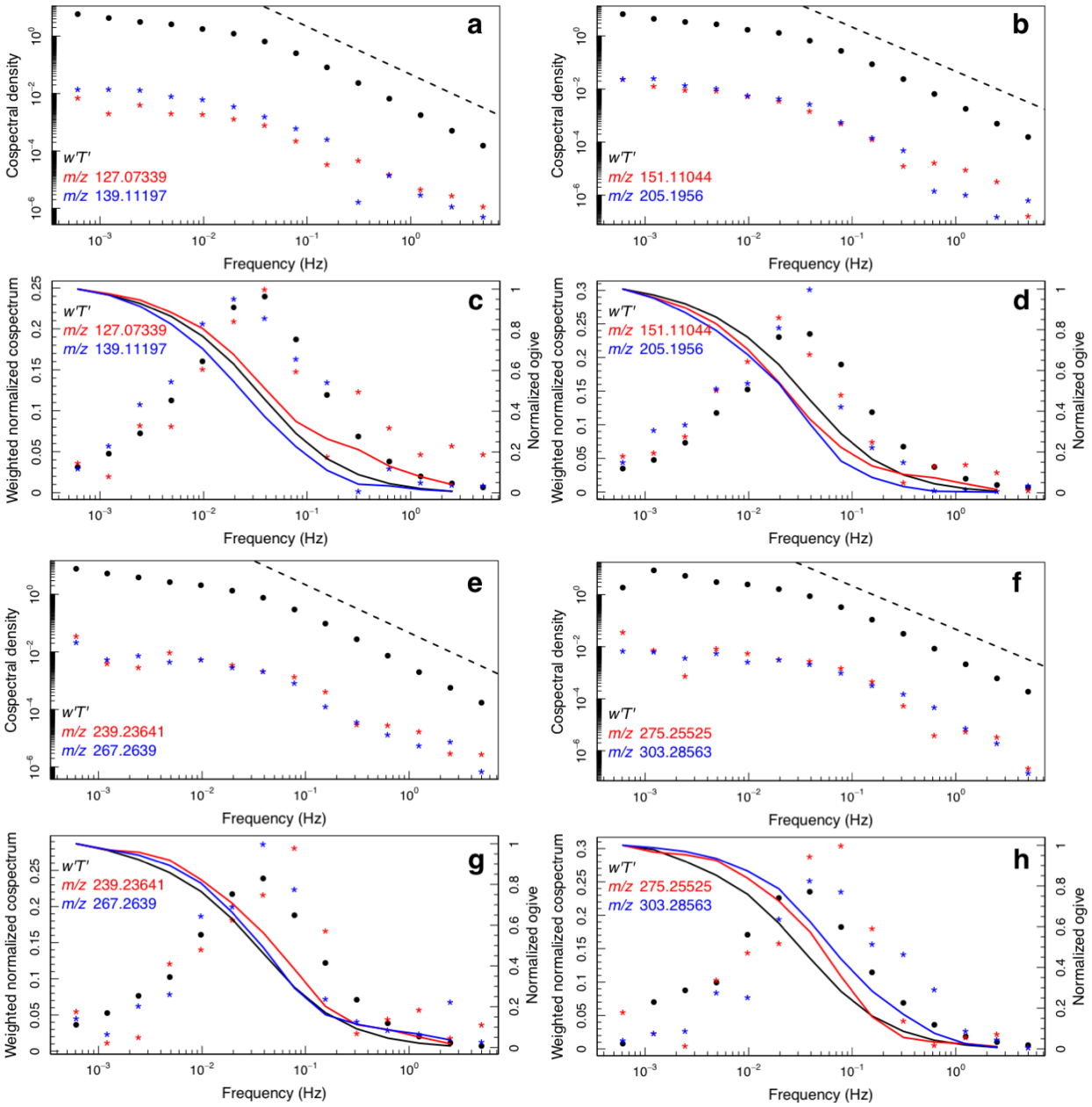

Figure S4. Same as Figure S2, but for: (a) and (c) *m/z* 127.073 ($C_7H_{11}O_2^+$) and 139.112 ($C_9H_{15}O^+$), both corresponding to likely terpene oxidation products; (b) and (d) *m/z* 151.110 ($C_{10}H_{15}O^+$) and 205.120 ($C_{15}H_{25}^+$), corresponding to a likely terpene oxidation product and sesquiterpenes, respectively; (e) and (g) *m/z* 239.236 (assigned to $C_{16}H_{31}O^+$) and 267.264 (assigned to $C_{18}H_{35}O^+$); (f) and (h) *m/z* 275.255 (assigned to $C_{16}H_{35}O_3^+$) and 303.286 (assigned to $C_{18}H_{39}O_3^+$).

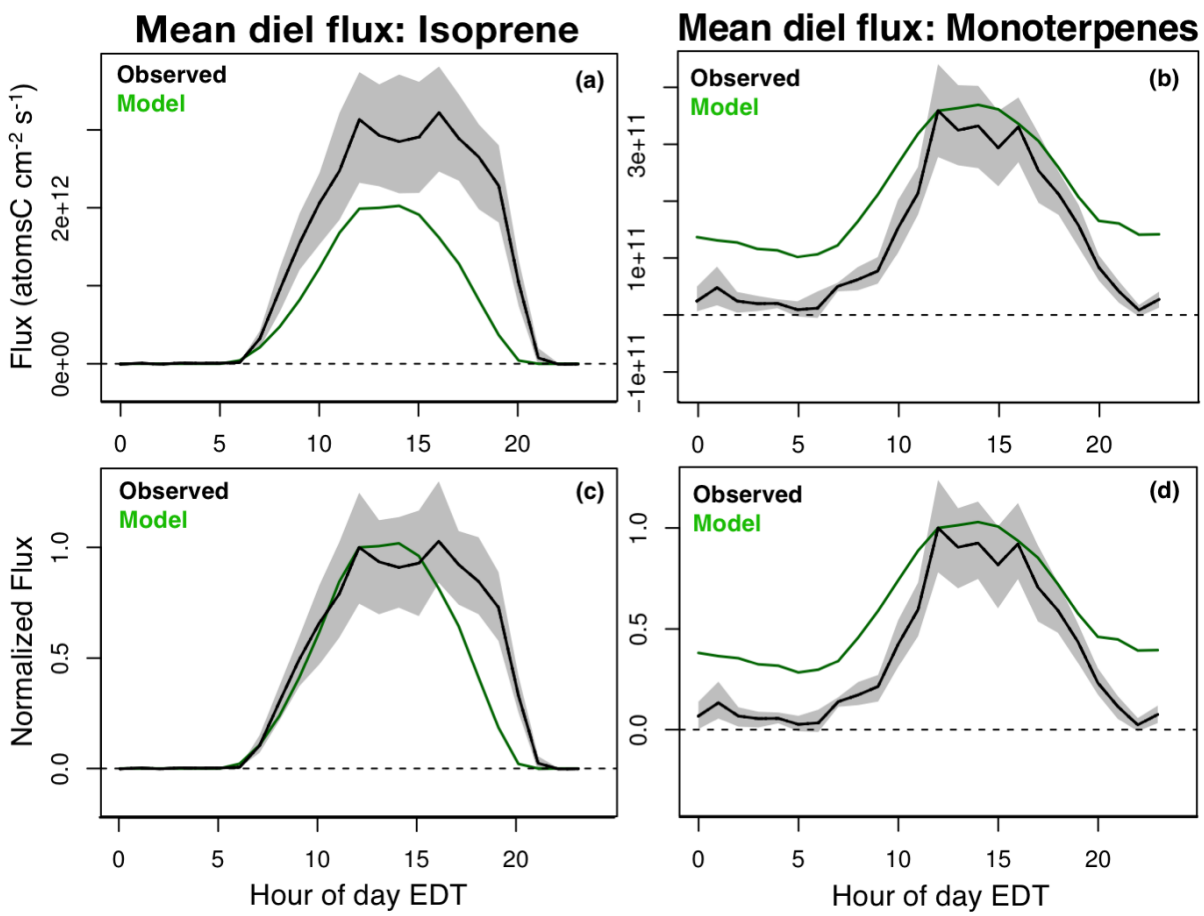

Figure S5. Mean diel cycle of isoprene (a) and monoterpene (b) fluxes. The black solid line and shaded gray region show the mean observed flux and associated 95% confidence interval. The green line shows the simulated emission from GEOS-Chem. The normalized diel cycle (with respect to the noontime value) is shown in panel (c) for isoprene and panel (d) for monoterpenes.

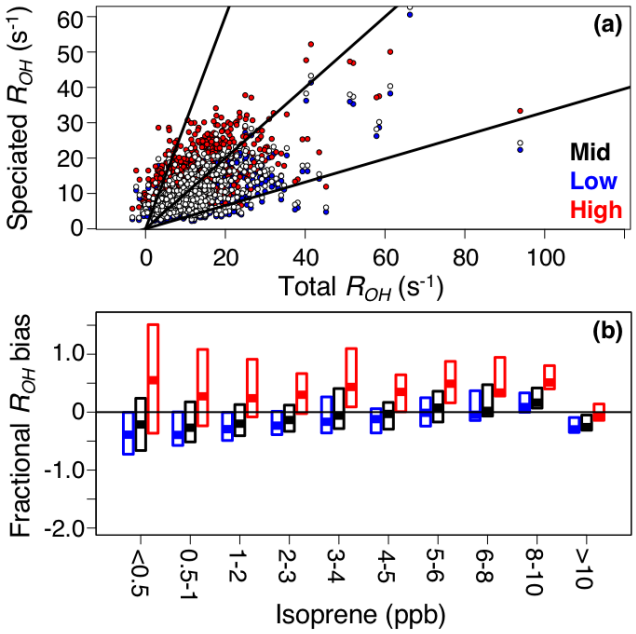

Figure S6. Panel (a): speciated versus total OH reactivity (R_{OH}). Lines illustrate the 3:1, 1:1, and 1:3 relationships. Panel (b): fractional bias in the speciated R_{OH} binned by the observed isoprene mixing ratio, with boxes displaying the median and interquartile range of the bias for each bin. In both panels the black, blue, and red symbols show results using the best-guess, lower-limit, and upper limit rate coefficients as described in the text.