This work is on a Creative Commons Attribution 4.0 International (CC BY 4.0) license, https://creativecommons.org/licenses/by/4.0/. Access to this work was provided by the University of Maryland, Baltimore County (UMBC) ScholarWorks@UMBC digital repository on the Maryland Shared Open Access (MD-SOAR) platform.

Please provide feedback

Please support the ScholarWorks@UMBC repository by emailing scholarworks-group@umbc.edu and telling us what having access to this work means to you and why it’s important to you. Thank you.
Text S1. Adjustment of Lab-Reported ERs

As noted in Sect. 2.4 of the main text, we adjust the emission ratios of acrolein and biacetyl downward by factors of 2.3 and 10, respectively, relative to the values reported by Koss et al. (2018). Here we provide some justification for these modifications.

For acrolein, instrument inter-comparisons during and after FIREX-AQ recently revealed a factor of 2.3 error in the quantification of the NOAA acrolein gas standard (personal communication, A. Wisthaler and M. Coggon, 2021). This is the same standard used in Koss et al. (2018).

For biacetyl (2,3-butanedione), it is likely that the work of Koss et al. (2018) did not account for all potential isomers in the PTR-ToF-MS interpretation. The molecular formula for this compound is C_4H_6O_2. Using GC-CIMS data, Koss et al. (2018) inferred contributions to this PTR-ToF-MS signal from biacetyl (87%), methacrylate (5%), and other unidentified compounds (8%). Previous work has suggested the presence of additional isomers that are not easily detected by GC. In one study of pine burning emissions,
2-oxobutanal emissions were 3 times greater than those of biacetyl (Schauer et al., 2001). 1,4-butanedial has also been observed in significant amounts in tobacco smoke (personal communication, A. Wisthaler, 2021). Based on the likely presence of these compounds, we conservatively reduce biacetyl by a factor of 10.

These adjustments reduce model over-prediction for APAN (produced solely from acrolein oxidation) and PAN (where biacetyl is a major precursor) in sensitivity simulations described in the main text.

Text S2. Other oVOC

Figure S13 shows the age progression of several other oVOC. Methanol is long-lived, and variability may reflect changing emissions or background conditions (Fig. S13a). A sharp rise in the methanol NEMR at 2 h may be another indicator of biogenic influence. Acetone and propanal are isomers (C₃H₆O) and are reported as a sum in the SEAC⁴RS dataset. Acetone is likely the dominant isomer given the short lifetime of propanal, and this is consistent with the small NEMR variability as the lifetime of acetone against oxidation is weeks (Fig. S13b). The hydroxyacetone NEMR is relatively constant with age, and model values agree with observations within uncertainties (Fig. S13c). The sum of MVK and MACR tells a story similar to acetaldehyde, with a biogenic signature at ~2 h and an over-rapid decline in the base simulation (Fig S13d). Results from other simulations are discussed in the main text, when relevant.

Text S3. Additional NOₓ Details

Several studies have noted potential positive artifacts in NO₂ measurements due to decomposition of thermally unstable gases in the sample inlet or instrument (Browne et al., 2011; Silvern et al., 2018; Nault et al., 2015). This is unlikely to explain the discrepancy between observed and modeled NOₓ in simulations M0 and M1 (Fig. 2i) for several reasons. First, such an interference would need to affect both the TDLIF and chemiluminescence NO₂ measurements similarly, as these two measurements are strongly correlated: \( \text{NO}_2(\text{TDLIF}) = 1.2 \times \text{NO}_2(\text{CL}) - 0.12 \text{ ppbv}, r^2 = 1.00 \). Second, if the artifact were due to known NOₓ reservoirs, the conversion efficiency would need to be substantial. The difference between observed and modeled NO₂ in simulation M1 is 260 ± 100 pptv at ages beyond 5 h. Mean observed PAN and total PNs are 1.3 and 2.1 ppbv, respectively. Thus a conversion efficiency of 10% or more would be required to fully explain the model-measurement difference, and this is unlikely given typical aircraft cabin and inlet temperatures (< 40 °C). Modeled HO₂NO₂ and CH₃O₂NO₂ are < 5 pptv and < 1 pptv, respectively. We cannot rule out the potential influence of yet-unidentified NOₓ reservoirs, though previous work suggests such artifacts are likely limited to the upper troposphere (Silvern et al., 2018).

In addition to PAN (discussed in the main text), the SEAC⁴RS dataset includes observations of several other speciated peroxy nitrates (PNs) and a total PN measurement. Other speciated PNs, shown in Fig. S14, include peroxypropionyl nitrate (PPN), peroxyacryloyl nitrate (APAN), and peroxyisobutyryl nitrate (PiBN). In the base simulation, early PPN NEMR growth is under-predicted, but the model and observations converge after 2h. APAN and PiBN are generally under-predicted, due in part to a lack of VOC precursors in the base simulation. Changes in model PNs in simulation M1 reflect increases in VOC precursors. In particular, APAN is produced solely through oxidation of acrolein. All PNs increase upon
addition of initial HONO or pNO$_3^{-}$ photolysis due to more RO$_2$ and NO$_2$. Conversely, heterogeneous NO$_2$ conversion to HONO has essentially no effect on PN NEMRs. In this case, decreasing NO$_2$ and increasing NO offsets the increase in RO$_2$.

Model-measurement comparison with the ΣPN observations tell a qualitatively similar story to the speciated data (Fig. S15a). This measurement (via thermal dissociation and laser-induced fluorescence detection of NO$_2$) is typically higher than the sum of speciated PN measurements (via thermal dissociation and detection of the peroxyacyl radicals), and in the first few hours this difference exceeds the combined uncertainty of the measurements. The reasons for this difference are unclear.

Alkyl nitrates (ANs) are minor products of the reaction of organic peroxy radicals (RO$_2$) with NO. The observed ΣAN NEMR is variable with no clear trend (Fig. S15b). The simulated ΣAN NEMR is relatively constant throughout each simulation, and all simulations fall within the variability of observed NEMRs.

References

Akagi, S. K., Yokelson, R. J., Wiedinmyer, C., Alvarado, M. J., Reid, J. S., Karl, T., Crounse, J. D., and Wennberg, P. O.: Emission factors for open and domestic biomass burning for use in atmospheric models, 11, 4039–4072, https://doi.org/10.5194/acp-11-4039-2011, 2011.

Browne, E. C., Perring, A. E., Wooldridge, P. J., Apel, E., Hall, S. R., Huey, L. G., Mao, J., Spencer, K. M., Clair, J. M. S., Weinheimer, A. J., Wisthaler, A., and Cohen, R. C.: Global and regional effects of the photochemistry of CH$_3$O$_2$NO$_2$: evidence from ARCTAS, 11, 4209–4219, https://doi.org/10.5194/acp-11-4209-2011, 2011.

Gustafson, W. and Yu, S.: Generalized approach for using unbiased symmetric metrics with negative values: normalized mean bias factor and normalized mean absolute error factor, 13, 262–267, https://doi.org/10.1002/asl.393, 2012.

Koss, A. R., Sekimoto, K., Gilman, J. B., Selimovic, V., Coggon, M. M., Zarzana, K. J., Yuan, B., Lerner, B. M., Brown, S. S., Jimenez, J. L., Krechmer, J., Roberts, J. M., Warneke, C., Yokelson, R. J., and de Gouw, J.: Non-methane organic gas emissions from biomass burning: identification, quantification, and emission factors from PTR-ToF during the FIREX 2016 laboratory experiment, 18, 3299–3319, https://doi.org/10.5194/acp-18-3299-2018, 2018.

Nault, B. A., Garland, C., Pusede, S. E., Wooldridge, P. J., Ullmann, K., Hall, S. R., and Cohen, R. C.: Measurements of CH$_3$O$_2$NO$_2$ in the upper troposphere, 987–997, https://doi.org/10.5194/amt-8-987-2015, 2015.

Schauer, J. J., Kleeman, M. J., Cass, G. R., and Simoneit, B. R. T.: Measurement of Emissions from Air Pollution Sources. 3. C1–C29 Organic Compounds from Fireplace Combustion of Wood, Environ. Sci. Technol., 35, 1716–1728, https://doi.org/10.1021/es001331e, 2001.

Silvern, R. F., Jacob, D. J., Travis, K. R., Sherwen, T., Evans, M. J., Cohen, R. C., Laughner, J. L., Hall, S. R., Ullmann, K., Crounse, J. D., Wennberg, P. O., Peischl, J., and Pollack, I. B.: Observed NO/NO$_2$ Ratios in the Upper Troposphere Imply Errors in NO-NO$_2$-O$_3$ Cycling Kinetics or an Unaccounted NO$_x$ Reservoir, 45, 4466–4474, https://doi.org/10.1029/2018GL077728, 2018.
Toon, O. B., Maring, H., Dibb, J., Ferrare, R., Jacob, D. J., Jensen, E. J., Luo, Z. J., Mace, G. G., Pan, L. L., Pfister, L., Rosenlof, K. H., Redemann, J., Reid, J. S., Singh, H. B., Thompson, A. M., Yokelson, R., Minnis, P., Chen, G., Jucks, K. W., and Pszenny, A.: Planning, implementation, and scientific goals of the Studies of Emissions and Atmospheric Composition, Clouds and Climate Coupling by Regional Surveys (SEAC4RS) field mission, 121, 4967–5009, https://doi.org/10.1002/2015JD024297, 2016.
Table S1. SEAC4RS measurement details.

| Measurement                              | Instrumenta | Accuracy  |
|------------------------------------------|-------------|-----------|
| Pressure                                 | MMS         | < 1%      |
| Temperature                              |             |           |
| H₂O                                      | DLH         | 5%        |
| Photolysis frequencies                   | CAFS        | 12 – 20%b|
| O₃                                      | NOyO₃       | 3%        |
| NO                                       |             | 4%        |
| NO₂                                      |             | 7%        |
| NO₃                                      | TDLIF       | 5%        |
| H₂O₂                                     | CIT-CIMS    | 30%       |
| HNO₃                                     |             | 30%       |
| HCN                                      |             | 50%       |
| Peroxyacetic acid                        |             | 50%       |
| Hydroxyacetone                           |             | 50%       |
| Hydroxymethyl hydroperoxide              |             | 50%       |
| Ethene hydroxynitrate                    |             | 50%       |
| Propene hydroxynitrate                   |             | 30%       |
| Butene hydroxynitrate                    |             | 50%       |
| Ethanal nitrate                          |             | 50%       |
| Propanone nitrate                        |             | 50%       |
| Isoprene hydroxynitrate                  |             | 30%       |
| CO                                       | DACOM       | 2%        |
| PAN                                      | GT-CIMS     | 15%       |
| PPN                                      |             | 20%       |
| APAN                                     |             | 40%       |
| PiBN                                     |             | 40%       |
| ΣPN                                      | TDLIF       | 10%       |
| ΣAN                                      |             | 15%       |
| Particulate nitrate                      | AMS         | 17%       |
| VOCc                                     | WAS         | 5%        |
| CH₃CN                                    | PTR-MS      | 15%       |
| CH₃OH                                    |             | 15%       |
| CH₃CHO                                   |             | 15%       |
| Acetone + propanal                      |             | 5%        |
| MVK + MACR                               |             | 10%       |
| Isoprene + Furan                         |             | 5%        |
| Methanol                                 |             | 15%       |
| HCHO                                     | ISAF        | 10%       |
|                                      | CAMS        | 4%        |
| Aerosol surface area                     | LAS         | 20%       |
| Solar irradiance                         | BBR         | 5%        |

aSee Toon et al. (2016) for details and references.
bVaries based on uncertainties in recommended cross sections and quantum yields.
cMethyl nitrate, ethyl nitrate, isopropyl nitrate, n-propyl nitrate, 2-butyl nitrate, 3-methyl-2-butyl nitrate, 3-pentyl nitrate, 2-pentyl nitrate, methane, ethane, propane, n-butane, isobutene, n-pentane,
isopentane, n-hexane, 2-methyl pentane, 3-methyl pentane, 2,3-dimethylbutane, n-heptane, ethene, propene, 1-butene, cis-2-butene, trans-2-butene, isobutene, 1,3-butadiene, 1-pentene, propadiene, benzene, toluene, ethyl benzene, o-xylene, m-xylene + p xylene (measured as sum, assumed 50%/50% distribution), isoprene, α-pinene, β-pinene.
Table S2. MCM assignments for unmeasured VOC.

| Koss ID                  | Koss Formula | MCM Name              | Emission Ratio (ΔX/ΔCO) |
|--------------------------|--------------|-----------------------|-------------------------|
| **Species with direct MCM analogues** |              |                       |                         |
| Acetic acid + glycolaldehyde | C2H4O2H     | CH3CO2H               | 10.7633                 |
| Acetic acid + glycolaldehyde | C2H4O2H     | HOCH2CHO              | 5.3013                  |
| HONO                     | HNO2H        | HONO                  | 3.2765                  |
| 2-furfural + 3-furfural + other HCO2 | C5H4O2H     | FURFURAL2             | 3.2625                  |
| Formic acid              | CH2O2H       | HCOOH                 | 3.2024                  |
| 2-(3H)Furanone           | C4H4O2H      | BZFUONE               | 1.8951                  |
| 5-Methyl furfural + Benzene diols (=catechol, resorcinol) | C6H6O2H | MFURFURAL             | 1.8749                  |
| 5-Methyl furfural + Benzene diols (=catechol, resorcinol) | C6H6O2H | CATECHOL              | 1.8749                  |
| Guaiacol (=2-methoxyphenol) | C7H8O2H     | GUAIACOL              | 1.8696                  |
| Acrolein                 | C3H4O4H      | ACR                   | 1.8446                  |
| 2-Methylphenol (=o-cresol) + anisol | C7H8O2H | CRESOL                | 1.7222                  |
| Phenol                   | C6H6O4H      | PHENOL                | 1.7124                  |
| 2-Methoxy-4-methylphenol (= creosol) | C8H10O2H | MGAUAIACOL            | 1.1605                  |
| 2-methylfuran + 3-methylfuran + general HCO | C5H6O4H | M2F                   | 0.9074                  |
| methyl acetate + ethyl formate + hydroxyacetone | C3H6O2H | METHACET              | 0.9060                  |
| Pyruvaldehyde (=methyl glyoxal) + acrylic acid | C3H4O2H | MGLYOX                | 0.7083                  |
| Pyruvaldehyde (=methyl glyoxal) + acrylic acid | C3H4O2H | AC2O2H                | 0.7083                  |
| Glyoxal                  | C2H2O2H      | GLYOX                 | 0.7048                  |
| MEK + butanal + 2-methylpropanal | C4H8O2H | MEK                   | 0.5282                  |
| MVK + methacrolein + crotonaldehyde | C4H6O2H | C4ALDB                | 0.5053                  |
| Quinone (=p-Benzoquinone) | C6H4O2H     | PBZQONE               | 0.4795                  |
| Ethanol                  | C2H6O2H      | C2H5OH                | 0.4481                  |
| 2,5-dimethyl furan + 2-ethylfuran + other C2 substituted furans | C6H8O2H | DIM25FURAN            | 0.4226                  |
| C2 Phenols + methyl anisol | C8H10O2H | OXYLOL                | 0.4222                  |
| methyl acetate + ethyl formate + hydroxyacetone | C3H6O2H | ETHFORM               | 0.3624                  |
| Acetic anhydride          | C4H6O3H      | METHCOACET            | 0.3198                  |
| Benzaldehyde             | C7H6O2H      | BENZAL                | 0.1962                  |
| 2-methylfuran + 3-methylfuran + general HCO | C5H6O2H | M3F                   | 0.1779                  |
| 2,3-butanedione + methyl acrylate + other HCO2 | C4H6O2H | BIAZET                | 0.1650                  |
| Styrene                  | C8H8H        | STYRENE               | 0.1625                  |
| 2-furfural + 3-furfural + other HCO2 | C5H4O2H | FURFURAL3             | 0.1554                  |
| Syringol                 | C8H10O3H     | SYRINGOLA             | 0.1485                  |
| Tolualdehyde             | C8H8O2H      | PXYLAL                | 0.0900                  |
| Tolualdehyde             | C8H8O2H      | MXYLAL                | 0.0900                  |
| 3-methyl-2-butanone + 2-methylbutanal+3-methylbutanal+2-pentanone +3-pentanone | C5H10O2H | MIPK                  | 0.0877                  |
| Species                                                                 | Molecular Formula | OH Reaction Rate Coefficient |
|------------------------------------------------------------------------|-------------------|------------------------------|
| MEK + butanal + 2-methylpropanal                                       | C4H8O2H           | 0.0062                       |
| Tolualdehyde                                                           | C8H8O2H           | 0.0072                       |
| 3-methyl-2-butane + 2-methylbutanal + 3-methylbutanal + 2-pentanone + 3-pentanone | C5H10O2H          | 0.0063                       |
| Methyl benzoic acid                                                    | C8H8O2H           | 0.0065                       |
| Sesquiterpenes                                                         | C15H24H           | 0.0065                       |
| Methyl benzoic acid                                                    | C8H8O2H           | 0.0065                       |
| 3-methyl-2-butane + 2-methylbutanal + 3-methylbutanal + 2-pentanone + 3-pentanone | C5H10O2H          | 0.0042                       |
| Pyruvic acid                                                           | C3H4O2H           | 0.0040                       |
| heptanal + 2,3-dimethyl-3-pentanone + heptanone                        | C7H14O2H          | 0.0031                       |
| heptanal + 2,3-dimethyl-3-pentanone + heptanone                        | C7H14O2H          | 0.0032                       |
| Dimethyl sulfide                                                       | C2H6SH            | 0.0011                       |
| hexanal + hexanones                                                    | C6H12O2H          | 0.0007                       |
| MEK + butanal + 2-methylpropanal                                       | C4H8O2H           | 0.0062                       |
| hexanal + hexanones                                                    | C6H12O2H          | 0.0005                       |
| 3-methyl-2-butane + 2-methylbutanal + 3-methylbutanal + 2-pentanone + 3-pentanone | C5H10O2H          | 0.0041                       |
| Species mapped to MCM using OH reaction rate coefficient and molecular formula |
| 2-furanmethanol + other HCO2                                            | C5H6O2H           | MEKAOH 1.7325                |
| 5-(hydroxymethyl)-2-furfural                                           | C6H6O3H           | C12O2OH 1.0774               |
| 5-hydroxymethyl-2(3H)-furanone                                         | C7H6O3H           | C12O2OH 0.9055               |
| 2-hydroxy-3-methyl-2-cyclopenten-1-one                                 | C6H8O2H           | HEX3ONDOOH 0.7753            |
| Product of levoglucosan dehydration (pyrolysis)                       | C6H8O4H           | M3HEXANO3 0.6436             |
| 2,5-di(hydroxymethyl)furanan + Methyl hydroxy dihydrofurfural          | C6H8O3H           | CO1M22CHO 0.5730             |
| Methyl methacrylate + other HCO2                                       | C5H8O2H           | HO2CO4CHO 0.5689             |
| 3-methyl-3-butene-2-one + cyclopentanone + HCO1                        | C5H8O2H           | PEBOH 0.5685                 |
| 5-Hydroxy 2-furfural/2-furoic acid                                     | C5H4O3H           | C4DBDIKET 0.4838             |
| 2,4-Cyclopentadiene-1-one + 2 other HCO isomers                       | C5H4O2H           | HO2SC6 0.4779                |
| Vanillin                                                               | C8H4O3H           | C7CO4EBB 0.4712              |
| Methyl propanoate                                                     | C4H4O2H           | MAE 0.4602                   |
| Vinyl guaiaicol                                                        | C9H10O2H          | LIMKET 0.3705                |
| Acetamide                                                             | C2H5NOH           | ACO2H 0.3637                 |
| 5-hydroxymethyl tetrahydro 2-furanone + 5-hydroxy tetrahydro 2-furfural | C5H8O3H          | CO2M33CO3H 0.3543            |
| 3 furan + various HCO                                                  | C7H10O2H          | HO2SC7 0.3052                |
| 1-Buten-3-yne                                                         | C4H4H             | ACR 0.2894                   |
| pyrrole + butene nitrile isomers                                       | C4H5NH            | C5H8 0.2417                  |
| Compound                                      | Formula      | Database | TIC (%) |
|----------------------------------------------|--------------|----------|---------|
| Eugenol + isoeugenol                        | C10H12O2H    | LIMKET   | 0.2415  |
| Nitromethane                                 | CH3NO2H      | ACR      | 0.2091  |
| 2-propynal                                   | C3H2OH       | ACR      | 0.2091  |
| Dihydro furandione                           | C4H4O3H      | HMACO3H  | 0.2083  |
| Hydroxy benzoquinone                         | C6H4O3H      | M3HEXANO3| 0.2058  |
| 2-hydroxybenzaldehyde (=Salicylaldehyde)     | C7H6O2H      | HO3C5CHO | 0.1526  |
| Pyridine + pentadienonitrites                | C5H5NH       | M23C4    | 0.1432  |
| Naphthalene                                  | C10H8H       | UDECOH   | 0.1388  |
| C9 Aromatics                                 | C9H12H       | DECOH    | 0.1255  |
| methane thiol                                | CH4SH        | CHL2CHO  | 0.1243  |
| Methyl benzofuran                            | C9H8OH       | NOPINAOH | 0.1191  |
| C6 Diones + C6 1-DBE esters                 | C6H10O2H     | IEB4CHO  | 0.1141  |
| Acrylonitrile                                | C3H3NH       | DICLETOH | 0.1138  |
| Methyl thiophenes                            | C5H6SH       | ETBE     | 0.1098  |
| 1,3-Cyclopentadiene                         | C5H6H        | ME2BUT2ENE| 0.1055  |
| dimethylbenzofuran                           | C10H10OH     | NOPINAOH | 0.1045  |
| Methyl cyclopentanone + cyclohexanone + other ketones | C6H10OH     | M3PECOOH | 0.0927  |
| methyl isocyanate + hydroxyacetonitrile      | C2H3NOH      | ETPOX    | 0.0871  |
| 3-methylacetophenone                         | C9H10OH      | C8BCCO   | 0.0870  |
| Methyl propenyl benzene + ethyl styrene      | C10H12H      | C7MOCOCO3H| 0.0860  |
| Formamide                                    | C3H3NOH      | CCL3CHO  | 0.0842  |
| Indane + methyl styrenes + propenyl benzenes | C9H10H      | APINENE  | 0.0820  |
| Benzofuran                                   | C8H6OH       | NOPINAOH | 0.0819  |
| Propane nitrile                              | C3H5NH       | CH3CL2OH | 0.0797  |
| C10 Aromatics                                | C10H14H      | NC9H20   | 0.0792  |
| Methyl pyrrole isomers + Pentene nitrile isomers | C5H7NH     | ME2BUT1ENE| 0.0743  |
| C6 esters                                    | C6H12O2H     | EMPHCOME | 0.0690  |
| Benzonitrile                                 | C7H5NH       | MC6OTKETOH| 0.0685  |
| Thiophene                                    | C4H4SH       | IBUTOL   | 0.0610  |
| 2-methyl pyridine + 3-methylpyridine         | C6H7NH       | MIPK     | 0.0603  |
| Dihydronaphthalene                           | C10H10H      | C108NO3  | 0.0574  |
| Dihydropyrole + butane nitrile               | C4H7NH       | CL12PRCHO| 0.0570  |
| Methyl naphthalene                           | C11H10H      | C129CO   | 0.0552  |
| Propionic acid                               | C3H2O2H      | ALLYLOH  | 0.0542  |
| Methyl chavicol (estragole)                  | C10H12OH     | PINAL    | 0.0522  |
| Ethylcyclopentanone                          | C7H12OH      | HM33C4OH | 0.0497  |
| 1,3-dimethylnaphthalene                     | C12H12H      | NC1313OH | 0.0493  |
| Indene + propynyl benzene isomer             | C9H8H        | BPINENE  | 0.0488  |
| 4-pyridinol                                  | C5H5NOH      | TBUACET  | 0.0427  |
| Camphor + other oxygenated monoterpenes      | C10H16OH     | C828PAN  | 0.0396  |
| 2-ethenyl benzofuran                         | C10H8OH      | NOPINAOH | 0.0379  |
| Compound Description                                                                 | Formula       | Ref.  |
|-------------------------------------------------------------------------------------|---------------|-------|
| 2,5-dimethyl pyrrole + 1-ethylpyrrole + other C2 substituted pyrroles               | C6H9NH        | 0.0366|
| Ethenamine                                                                          | C2H5NH        | 0.0346|
| Nitrobenzene                                                                        | C6H5NO2H      | 0.0325|
| Pentanenitriles                                                                     | C5H9NH        | 0.0314|
| Phenylacetylene                                                                     | C8H6H         | 0.0276|
| Nitrotoluene                                                                        | C7H7NO2H      | 0.0246|
| dihydroxy pyridine + methyl maleimide                                              | C5H5NO2H      | 0.0225|
| pyridine aldehyde + methylfuranitrile + nitrosobenzene                              | C6H5NOH       | 0.0211|
| benzeneacetonitrile                                                                 | C8H7NH        | 0.0207|
| C11 aromatics                                                                       | C11H16H       | 0.0197|
| ethylindene                                                                         | C11H12H       | 0.0194|
| 2-furancarbonitrile + 3-furancarbonitrile                                          | C5H3NOH       | 0.0189|
| Trimethylamine                                                                       | C3H9NH        | 0.0181|
| dimethyl pyridine + ethylpyridine + heptylnitriles                                  | C7H9NH        | 0.0172|
| C7 acrylonitrile                                                                    | C7H11NH       | 0.0169|
| Acenaphthylene                                                                      | C12H8H        | 0.0164|
| Propene amine                                                                       | C3H7NH        | 0.0158|
| Cineole + other oxygenated monoterpenes                                             | C10H18OH      | 0.0137|
| C12 aromatics                                                                       | C12H18H       | 0.0113|
| 4-methylpentanenitrile                                                              | C6H11NH       | 0.0109|
| Carbon suboxide                                                                     | C3O2H         | 0.0104|
| Methyl benzeneacetonitrile                                                           | C9H9NH        | 0.0104|
| Dimethyl disulfide                                                                  | C2H6S2H       | 0.0098|
| C13 aromatics                                                                       | C13H20H       | 0.0097|
| butene nitrates                                                                     | C4H7NO3H      | 0.0078|
| Vinylpyridine                                                                       | C7H7NH        | 0.0066|
| decanal                                                                             | C10H20OH      | 0.0065|
| Nitrofuran                                                                          | C4H3NO3H      | 0.0064|
| Methanimine                                                                         | CH3NH         | 0.0062|
| Propionitrile (=propyne nitrile)                                                    | C3HNH         | 0.0058|
| Butene amine                                                                        | C4H9NH        | 0.0055|
| nitroethene                                                                         | C2H3NO2H      | 0.0054|
| Ethynlypyrrole                                                                      | C6H6N         | 0.0046|
| methane diol                                                                        | CH4O2H        | 0.0041|
| Nitroethane or ethane nitrite                                                       | C2H5NO2H      | 0.0035|
| Ethylamine + dimethylamine                                                          | C2H7NH        | 0.0030|
| Dihydro pyridine                                                                    | C8H9NH        | 0.0029|
| Nitropropanes                                                                       | C3H7NO2H      | 0.0018|
| Cyanoallene isomers                                                                 | C4H3NH        | 0.0013|
| C8 nitriles                                                                         | C8H15NH       | 0.0012|
| Dimethyl trisulfide                                                                 | C2H6S3H       | 0.0011|
| n-sulfinyl methanamine                                                              | CH3NOSH       | 0.0003|
Figure S1. DC-8 sampling temperature (a), atmospheric pressure (b), and altitude above ground level (c, cyan circles) as a function of plume Lagrangian Age. The dashed line in (c) denotes the boundary layer height relative to ground level based on output from the two meteorological datasets used for trajectory analysis.
Figure S2. Dilution factor for each WAS plume sample, calculated as the ratio of initial to sample-time background-corrected CO.
Figure S3. Comparison of normalized excess mixing ratios (NEMR) from the “source” sample of this study and the Rim Fire emission ratios (ER) reported by Liu et al. (2017). Both NEMR and ER values are normalized to excess CO. In the species-specific plot, positive values correspond to species with a higher ratio in long-axis source sample, and values with ER $< 10^{-4}$ ppbv / ppbv are excluded. In the inset, the solid line is the 1:1 relationship and dashed lines are ±50%.
Figure S4. Modified combustion efficiency (MCE) (a) and NEMRs for formonitrile and acetonitrile (b). MCE is defined as $\Delta CO_2 / (\Delta CO + \Delta CO_2)$. Gray dashed lines in (a) denote the range of 0.8 – 1 typical of wildfires (Akagi et al., 2011).
Figure S5. Gaussian dilution timescale for each model puff, calculated from observations of the decay of CO and Eqn. (2) as described in the main text.
Figure S6. Observed and derived aerosol-related properties as a function of plume age: AMS-observed particulate nitrate mass concentration (a), LAS-observed aerosol surface area (b), calculated reactive uptake coefficient for NO$_2$ conversion to HONO (c), and calculated first order rate coefficient for the same (d).
Figure S7. (top) Comparison of particulate nitrate observed by the AMS and SAGA instruments. The AMS has a size cut of ~1 micron, while SAGA samples up to 4 microns. AMS data are averaged over the SAGA sampling interval (~5 minutes) for all Rim Fire observations. Data is shown on both a log (left) and linear (right) scale. (bottom) Comparison of aerosol surface area observed by the LAS and UHSAS instruments. Low bias in the LAS results from the use of PSLs for size calibration instead of ammonium sulfate (P. Campuzano-Jost, personal communication, 2021).
Figure S8. Linear relationship between solar zenith angle and total (up + down) solar irradiance from the broadband radiometer (BBR) instrument. The red line represents an ordinary least-squares fit, used to estimate irradiance for the parameterization of NO\textsubscript{2} reactive uptake.
Figure S9. Age evolution of NEMRs for all observed VOC. Black circles and gray triangles are observations from the WAS and PTR-MS, respectively, with their corresponding uncertainty due to measurement accuracy and age. Species, in order from a) to u), are: ethane, propane, n-butane, i-butane, toluene, benzene, ethyl benzene, o-xylene, m-xylene + p-xylene, ethene, propadiene, propene, 1-butene, furan, 1-pentene, methyl propene (isobutene), 1,3-butadiene, cis-2-butene, trans-2-butene, α-pinene + β-pinene, and isoprene. Colored lines are model output from the base simulation (M0, blue), addition of unmeasured VOC (M1, red), and addition of unmeasured VOC and primary HONO (M2c, yellow) or secondary HONO via pNO$_3^-$ photolysis (M3b, purple). Note that the furan observation is the difference between PTR-MS (furan + isoprene) and WAS isoprene.
Figure S10. Normalized mean bias NMB modeled VOC profiles compared to observations. For each simulation and each VOC, NMB is computed with model output shown in the previous figure following (Gustafson and Yu, 2012). Negative bias means that the model is lower than observations, on average. Vertical dotted lines demarcate the four groups discussed in the main text.
Figure S11. Age evolution of model-predicted OH concentration (a) and HO$_2$ mixing ratio (b). Colors are as described in Fig. S9.
Figure S12. Age evolution of NEMRs for oxygenated VOC. Black circles are observations with their corresponding uncertainty due to measurement accuracy and age. Colored lines are as described in Fig. S9.
Figure S13. Age evolution of NEMRs for speciated peroxynitrates. Black circles are observations with their corresponding uncertainty due to measurement accuracy and age. Colored lines are as described in Fig. S9.
Figure S14. Age evolution of NEMRs for total peroxy nitrates (a), total alkyl nitrates (b), and nitric acid (c). Black circles are observations with their corresponding uncertainty due to measurement accuracy and age. Colored lines are as describe in Fig. S9. MCM PN and AN species are identified using simplified molecular-input line-entry system (SMILES) strings and SMILES filtering code provided with FOAM. Model HNO₃ NEMRs deviate significantly from observations because the model does not account for gas-to-particle nitrate partitioning.
Figure S15. Age evolution of absolute ozone mixing ratio. Symbols and lines are as described Fig. S9. The grey dashed line denotes the estimated O_3 background mixing ratio.
Figure S16. Comparison of NO\textsubscript{X} NEMRS for observations (symbols), simulations M0/M1 (solid lines), and sensitivity perturbations where initial NO\textsubscript{X} is doubled (dashed lines). For observations, black circles and gray triangles represent NO\textsubscript{X} calculated with two different NO\textsubscript{2} measurements and the same NO measurement (from the NOyO3 instrument). Error bars denote uncertainty due to age estimation. Uncertainty due to measurement accuracy is small (4%).
Figure S17. Age evolution of simulated HONO NEMRs (a) and absolute HONO mixing ratios (b). Colored lines are as described in Fig. S9.
Figure 18. Age evolution of NEMRs for sensitivity simulations to assumed initial HONO concentration. Black circles are observations with their corresponding uncertainty due to measurement accuracy and age. Colored lines are model output from the base simulation (M0, blue), addition of unmeasured VOC (M1, red), and addition of unmeasured VOC plus primary HONO at mixing ratios of 5, 15, and 25 ppbv (yellow, purple, and green, respectively).
Figure 19. Age evolution of NEMRs for sensitivity simulations to particulate nitrate photolysis. Black circles are observations with their corresponding uncertainty due to measurement accuracy and age. Colored lines are model output from the base simulation (M0, blue), addition of unmeasured VOC (M1, red), and addition of unmeasured VOC plus pNO$_3^-$ photolysis with rate multipliers of 0.5, 1, and 2 (yellow, purple, and green, respectively). See Sect. 2.4.2 and Table 1 in the main text for further details.
Figure 20. Age evolution of NEMRs for sensitivity simulations to heterogeneous reaction of NO$_2$. Black circles are observations with their corresponding uncertainty due to measurement accuracy and age. Colored lines are model output from the base simulation (M0, blue), addition of unmeasured VOC (M1, red), and addition of unmeasured VOC plus NO$_2$ heterogeneous reaction with rate multipliers of 1 and 1000 (yellow and purple, respectively). See Sect. 2.4.2 and Table 1 in the main text for further details. Note that there is no visible difference in model output for simulations M1 and M4a.
Figure S21. NMB of NEMRs for ozone (a-e), NOx (f-j), and PAN (k-o) for the sensitivity simulations described in Sect. 2.4.3 and Sect. 3.4. Simulations involve iteratively scaling unmeasured VOC (x-axis), pNO3- photolysis (y-axis), and initial HONO (columns) by factors of 0, 0.25, 0.5, 0.75, and 1. Shading indicates NMB of simulation NEMRs against observations, ranging from negative (blue) to positive (red) values. Dashed lines indicate interpolated contours for NMB of zero, corresponding to values shown in Figs. 5 and S22.
Figure S22. Isopleths for net-zero values of the normalized mean bias (NMB) for NEMRs of NO\textsubscript{x} (a) and PAN (b). Each colored dotted line represents a fixed scaling factor for initial HONO mixing ratios. The x-y coordinates for a point on a given line represent a combination of VOC and pNO\textsubscript{3}\textsuperscript{-} photolysis scaling factors that minimize the O\textsubscript{3} NEMR NMB. Isopleths are based on interpolation of results from the optimization simulations (Fig. S21).
Figure S23. Fractional contributions to production of peroxyacetyl radical in simulation M3b.