# Supplementary Information: The Global Importance of Gas-phase $RO_2$ Dimerization Reactions

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*Table S1. Species constrained in the SOAS box models, along with corresponding names in the MCM and GEOS-Chem mechanism. Lumped species, where the sum of species measurements are assigned to one model species, are indicated by merged table entries.*

| Species Name | MCM Name | GEOS-Chem Name |
|---|---|---|
| Formaldehyde | HCHO | CH2O |
| Isoprene | C5H8 | ISOP |
| α-pinene | APINENE | MTPA |
| β-pinene | BPINENE | |
| Limonene | LIMONENE | LIMO |
| Ethane | C2H6 | C2H6 |
| Ethene | C2H4 | C2H4 |
| Ethyne | C2H2 | C2H2 |
| Benzaldehyde | BENZAL | BALD |
| Benzene | BENZENE | BENZ |
| Ethanol | C2H5OH | EOH |
| Propane | C3H8 | C3H8 |
| Propene | C3H6 | PRPE |
| Acetone | CH3COCH3 | ACET |
| Methanol | CH3OH | MOH |
| Toluene | TOLUENE | TOLU |
| Ethylbenzene | EBENZ | EBZ |
| i-butane | IC4H10 | ALK4 |
| i-pentane | IC5H12 | |
| n-butane | NC4H10 | |
| n-pentane | NC5H12 | |
| n-hexane | NC6H14 | ALK6 |
| n-decane | NC10H22 | |
| o-xylene | OXYL | XYLE |
| 1,3,5-trimethylbenzene | TM135B | |
| 1,2,4-trimethylbenzene | TM124B | |

*Table S2. SIMLES strings assigned to each GEOS-Chem RO2 for input to the GECKO-A tool.*

| GEOS-Chem $RO_2$ | Assigned SMILES |
|---|---|
| A3O2 | CCCO[O] |

| | |
|---|---|
| ACRO2 | OCC(O[O])C=O |
| ACO3 | [O]OC(=O)C=C |
| ALK4N1 | CC(O[O])CC(ON(=O)=O)C |
| ALK4O2 | CC(CCC)O[O] |
| ATO2 | CC(=O)O[O] |
| B3O2 | OCC(C)O[O] |
| BENZO2 | [O]OCc1ccccc1 |
| BUTO2 | OCC(O[O])C=C |
| BZCO3 | [O]OC(=O)c1ccccc1 |
| C4HVP1 | CC(O[O])=CCO |
| C4HVP2 | CC(CO)=CO[O] |
| ETOO | OCCO[O] |
| ETO2 | CCO[O] |
| HPALD1OO | CC(C=O)(O[O])C(O)COO |
| HPALD2OO | CC(O)(COO)C(C=O)O[O] |
| ICHOO | CC(CO)(O[O])C(=O)CO |
| ICNOO | O=CC(O)C(C)(O[O])CON(=O)=O |
| IDHNBOO | CC(CO)(O[O])C(CON(=O)=O)OO |
| IDHNDOO1 | CC(CON(=O)=O)(O[O])C(O)COO |
| IDHNDOO2 | CC(CON(=O)=O)(O)C(O[O])COO |
| IDNOO | CC(CON(=O)=O)(O[O])C(O)CON(=O)=O |
| IEPOXAOO | CC(C=O)(O[O])C(O)CO |
| IEPOXBOO | CC(C=O)(O[O])C(O)CO |
| IHOO1 | C/C(=C/CO[O])CO |
| IHOO4 | C/C(=C/CO)CO[O] |
| IHPNBOO | CC(CO)(O[O])C(CON(=O)=O)OO |
| IHPNDOO | CC(CON(=O)=O)(O[O])C(O)COO |
| IHPOO1 | CC(CO)(O[O])C(CO)OO |
| IHPOO2 | CC(O)(COO)C(CO)O[O] |
| IHPOO3 | CC(OO)(CO)C(CO)O[O] |
| INO2B | C=CC(C)(CON(=O)=O)O[O] |
| INO2D | [O]OCC=C(C)(CON(=O)=O) |
| ISOPNOO1 | CC(CO)(ON(=O)=O)C(CO)O[O] |
| ISOPNOO2 | CC(CO)(O[O])C(CO)ON(=O)=O |
| KO2 | [O]OCCC(=O)C |
| LIMO2 | [O]OC1(C)CCC(CC1O)C(=C)C |
| APINO2 | [O]OC1(C)C(O)CC2CC1C2(C)C |
| PINO3 | [O]OC(=O)CC1CC(C(=O)C)C1(C)C |
| C96O2 | [O]OCC1CC(C(=O)C)C1(C)C |
| BPINO2 | OCC1(O[O])CCC2CC1C2(C)C |
| BPINOO2 | [O]OC1CC(=O)C2CC1C2(C)C |

| | |
|---|---|
| LIMKO2 | O=CCC(CCC(=O)C)C(C)(CO)O[O] |
| LIMO3 | [O]OC(=O)CC(CCC(=O)C)C(=C)C |
| MACR1OO | CC(=C)C(=O)O[O] |
| MACRNO2 | [O]OC(=O)C(C)(CO)ON(=O)=O |
| MCO3 | CC(=O)O[O] |
| MCROHOO | CC(C=O)(CO)O[O] |
| MEKCO3 | CCC(=O)O[O] |
| MO2 | CO[O] |
| MVKOHOO | CC(=O)C(O[O])CO |
| NRO2 | [O]OC2C=Cc1ccccc1C2O |
| OTHRO2 | CCO[O] |
| PIO2 | [O]OC1CC2CC(C1(C)O)C2(C)C |
| PO2 | OCC(O[O])C |
| PRN1 | CC(CON(=O)=O)O[O] |
| R4N1 | CCC(ON(=O)=O)C(O[O]) |
| R4O2 | CCCC(O[O]) |
| R7O2 | CCCC(CC)O[O] |
| R7N1 | CCC(O[O])C(CC)ON(=O)=O |
| RCO3 | CCC(=O)O[O] |
| TLFUO2 | [O]OC1(C)C(=O)OC(C)C1(C)O |
| ZRO2 | [O]OC1C=CC2(C)OOC1C2O |
| C2BZRO2 | [O]OCC(O)c1ccccc1 |
| BPINNRO2 | OCC1(CC(O[O])C2CC1C2(C)C)ON(=O)=O |
| TOLURO2 | [O]OC1C=CC2(C)OOC1C2O |
| PHENRO2 | [O]OC1(O)C=CC2OOC1C2O |
| SQTP3RO2 | O=CCCC(CO)(O[O])C1CC(C)(C)C1CCC(=O)C |
| PLIMALO2 | [O]OC1(C)CCC(CC1O)C(=C)C |
| MCTO2 | [O]Oc1ccccc1O |
| PIPO2 | [O]OC1(C)C(O)CC2CC1C2(C)C |
| LIMRO2 | O=CCC(CCC(=O)C)C(C)(CO)O[O] |
| BENZRO2 | [O]OC1C=CC2OOC1C2O |
| SQTP2RO2 | O=CCCC(CO)(O[O])C1CC(C)(C)C1CCC(=O)C |
| CSLO2 | [O]OC1(O)C=CC2(C)OOC1C2O |
| EBZRO2 | [O]OC1C=CC2(CC)OOC1C2O |
| TMBRO2 | [O]OC1C(=CC2(C)OOC1(C)C2O)C |
| PINRO2 | OCC1(CC(O[O])C2CC1C2(C)C)ON(=O)=O |
| MYRCORO2 | O=CCC(CC(=O)C(=O)C)C(C)(C)O[O] |
| SQTNO2 | [O]OC1(C)CCC2C(CC2(C)C)C(=C)CCC1O[N+](=O)[O-] |
| SQTO2 | [O]OC1(C)CCC2C(CC2(C)C)C(=C)CCC1O |
| PMYRCOO2 | O=CCC1CC(O[O])(C(=O)C)C1(C)C |
| TMB2RO2 | [O]OCc1cc(C)cc(C)c1 |

| | |
|---|---|
| SQTP4RO2 | O=CCCC(CO)(O[O])C1CC(C)(C)C1CCC(=O)C |
| PMEKRO2 | OCC1CC(O[O])(C(=O)C)C1(C)C |
| APINNRO2 | OCC1(CC(O[O])C2CC1C2(C)C)ON(=O)=O |
| XYLERO2 | [O]OC1(C)C=CC2OOC1(C)C2O |
| OLND | [O]OC1(C)C(ON(=O)=O)CC2CC1C2(C)C |
| OLNN | [O-][N+](=O)OC1CC(CCC1(C)O[O])C(=C)C |
| GCO3 | OCC(=O)O[O] |
| AROMCO3 | [O]OC(=O)COC(=O)C(=O)C |

*Table S3. Non-accretion reactions added and removed from the GEOS-Chem mechanism for modified runs*

| **Added Sesquiterpene Chemistry** | |
|---|---|
| **Reaction** | **Rate** |
| FARN + OH = SQTO2 | 2.25d-10 |
| FARN + O3 = 0.89SQTO + 0.16MVK + 0.33ACET + 0.02CH2O + 0.1OH | GCARR_ac(3.5d-12, -2590.0d0) |
| FARN + NO3 = SQTNO2 | 2.15d-11 |
| BCAR + OH = SQTO2 | 2.0d-10 |
| BCAR + O3 = SQTO + 0.08OH | 1.2d-14 |
| BCAR + NO3 = SQTNO2 | 1.9d-11 |
| OSQT + OH = SQTO2 | 2.1d-10 |
| OSQT + O3 = SQTO + 0.1 OH | 6.3d-15 |
| OSQT + NO3 = SQTNO2 | 2.0d-11 |
| SQTO2 + HO2 = SQTO | GCARR_ac(2.9d-13, 1300.0d0) |
| SQTO2 + NO = 0.25SQTN + 0.75NO2 + 0.75HO2 + 0.75SQTO | GCARR_ac(2.7d-12, 360.0d0) |
| SQTO2 + MO2 = SQTO + HO2 + 0.75CH2O + 0.25MOH | GCARR_ac(2.5d-14, -300.0d0) |
| SQTO2 + NO3 = SQTO + NO2 + HO2 | 2.3d-12 |
| SQTNO2 + HO2 = SQTN | GCARR_ac(2.9d-13, 1300.0d0) |
| SQTNO2 + NO = SQTN + NO2 + HO2 | GCARR_ac(2.7d-12, 360.0d0) |
| SQTNO2 + MO2 = SQTN + HO2 + 0.75CH2O + 0.25MOH | GCARR_ac(2.5d-14, -300.0d0) |
| SQTNO2 + NO3 = SQTN + NO2 + HO2 | 2.3d-12 |
| SQTN + OH = SQTP2RO2 | 6.2d-11 |
| SQTN + O3 = 0.1OH + 0.5SQTP4RO2 + 0.15ACET + 0.075MVK + 0.2MYRCO + 0.15CH2O + 0.10CH2OO + 0.3SQTP | GCARR_ac(3.42d-15, -570.0d0) |
| SQTN + NO3 = SQTP2RO2 | 3.3d-13 |
| SQTO + OH = SQTP2RO2 | 6.2d-11 |

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|---|---|
| SQTO + O3 = 0.1OH + 0.5SQTP4RO2 + 0.15ACET + 0.075MVK + 0.2MYRCO + 0.15CH2O + 0.10CH2OO + 0.3SQTP | GCARR_ac(3.42d-15, -570.0d0) |
| SQTO + NO3 = SQTP2RO2 | 3.3d-13 ; |
| SQTP + OH = SQTP3RO2 | 1.0d-11 ; |
| SQTP + O3 = 0.1OH | 1.0d-16 ; |
| SQTP + NO3 = HNO3 + SQTP3RO2 | 5.0d-14 ; |
| SQTP2RO2 + HO2 = SQTP + OH + HO2 | 2.91d-13 * EXP( 1300.0d0 / TEMP ) * 0.82d0; |
| SQTP2RO2 + NO = SQTP + NO2 + HO2 | GCARR_ac(2.60d-12, 365.0d0); |
| SQTP2RO2 + NO3 = SQTP + NO2 + HO2 | 2.30d-12; |
| SQTP3RO2 + HO2 = OH + HO2 | 2.91d-13 * EXP( 1300.0d0 / TEMP ) * 0.82d0; |
| SQTP3RO2 + NO = NO2 + HO2 | GCARR_ac(2.60d-12, 365.0d0); |
| SQTP3RO2 + NO3 = NO2 + HO2 | 2.30d-12; |
| SQTP4RO2 + HO2 = OH + HO2 | 2.91d-13 * EXP( 1300.0d0 / TEMP ) * 0.82d0; |
| SQTP4RO2 + NO = NO2 + HO2 | GCARR_ac(2.60d-12, 365.0d0); |
| SQTP4RO2 + NO3 = NO2 + HO2 | 2.30d-12; |
| **Replaced Aromatic & BVOC Chemistry** | |
| **Reaction** | **Rate** |
| STYR + OH = 0.300ZRO2 + 0.700AROMRO2 + 0.700HO2 + CH2O + 0.700BALD | 5.8d-11; |
| STYR + NO3 = AROMRO2 + NO2 + CH2O + BALD | 1.5d-12; |
| EBZ + OH = 0.813AROMRO2 + 0.250CH2O + 0.070ZRO2 + 0.180CSL + 0.400ALD2 + 0.400AROMP5 + 0.800AROMP4 + 0.1800HO2 | 7.0d-12 |
| EBZ + NO3 = AROMRO2 + HNO3 + CH2O + BALD | 1.2d-16 |
| TMB + OH = 0.930AROMRO2 + 0.120CH2O + 0.050ZRO2 + 0.030CSL + 0.600AROMP5 + 0.375AROMP4 + 0.250MGLY + 0.100GLYX + 0.500RCOOH + 0.120CO + 0.030HO2 + 0.150TLFUONE | 3.92d-11 |
| TMB + NO3 = AROMRO2 + HNO3 + 0.400AROMP5 + BALD | 1.4d-15 |
| BENZ + OH = BRO2 + 0.54PHEN + 0.54HO2 + 0.46AROMRO2 + 0.18GLYX + 0.2CO +0.55AROMP4 | GCARR_ac(2.3d-12, -193.0d0) |
| TOLU + OH = TRO2 + 0.19CSL + 0.19HO2 + 0.81AROMRO2 + 0.06BALD + 0.12GLYX + 0.12MGLY + 0.27CO + 0.04MVK + 0.3AROMP5 + 0.68AROMP4 | GCARR_ac(1.8d-12, 340.0d0) |
| XYLE + OH = XRO2 + 0.15CSL + 0.15HO2 + 0.85AROMRO2 + 0.06BALD + 0.1GLYX + 0.2MGLY + 0.3CO + 0.04MVK + 0.56AROMP5 + 0.28AROMP4 + 0.45RCOOH | 1.7d-11 |

| | |
|---|---|
| AROMRO2 + HO2 = OH + HO2 | 2.91d-13 * EXP( 1300.0d0 / TEMP ) * 0.82d0 |
| AROMRO2 + NO = NO2 + HO2 | GCARR_ac(2.60d-12, 365.0d0) |
| AROMRO2 + NO3 = NO2 + HO2 | 2.30d-12 |
| AROMRO2 + MO2 = CH2O + HO2 + HO2 | GCARR_ac(1.70d-14, 220.0d0) |
| AROMRO2 + MCO3 = MO2 + HO2 + CO2 | GCARR_ac(4.20d-14, 220.0d0) |
| PHEN + OH = 0.06BENZO + 0.06GLYX + 0.18AROMP4 + 0.14AROMRO2 + 0.8MCT + 0.8HO2 | GCARR_ac(4.70d-13, 1220.0d0) |
| CSL + OH = 0.727MCT + 0.727HO2 + 0.2AROMRO2 + 0.073BENZO + 0.44AROMP5 | 4.7d-11 |
| CSL + NO3 = 0.5NPHEN + 0.2AROMRO2 + 0.5HNO3 + 0.3BENZO + 0.44AROMP5 | 1.4d-11 |
| MCT + OH = 0.3BENZO + 0.7AROMRO2 + 1.05AROMP4 | 2.0d-11 |
| MCT + NO3 = 0.5NPHEN + 0.5HNO3 + 0.3BENZO + 0.2AROMRO2 + 0.3AROMP4 | 9.9d-11 |
| LIMO + O3 = 0.865OH + 0.15CO + 0.15AROMRO2 + 0.27LIMAL + 0.715LIMO3 | GCARR_ac(2.95d-15, -783.0d0) |
| MTPO + O3 = 0.5ACET + 0.8OH + 0.1CH2O + 0.5MEK + 0.15MVK + 0.4MYRCO + 0.5AROMRO2 + 0.05HO2 + 0.3KO2 + 0.3RCHO | GCARR_ac(2.7d-15, -520.0d0) |
| APINN + OH = 0.5PINAL + 0.5NO2 + 0.5HO2 + 0.5C96N + 0.5CH2O + 0.5AROMRO2 | 5.50d-12 |
| C96O2 + NO = 0.16C96N + 0.84NO2 + 0.84AROMRO2 + 0.84ACET + 0.84CH2O + 0.84RCO3 + 0.42MEK | GCARR_ac(2.7d-12, 360.0d0) |
| C96O2 + NO3 = NO2 + AROMRO2 + ACET + CH2O + RCO3 + 0.5MEK | 2.3d-12 |
| C96O2 + MO2 = HO2 + 0.75CH2O + 0.25MOH + 0.25C96O2H + 0.75AROMRO2 + 0.75ACET + 0.75CH2O + 0.75RCO3 + 0.375MEK | GCARR_ac(3.75d-13, 500.0d0) |
| C96O2H + OH = 0.5C96O2 + 0.5AROMRO2 + 0.5ACET + 0.5CH2O + 0.5RCO3 + 0.25MEK | 2.6d-11 |
| C96N + OH = 0.5NO2 + 0.5MONITS + 0.55AROMRO2 + 0.4ACET + 0.4CH2O + 0.4RCO3 + 0.3MEK | 2.88d-12 |
| BPINN + OH = 0.5BPINON + 0.5AROMRO2 + CH2O + 0.5NO2 + 0.5HO2 + 0.5BPINO | 4.7d-12 |
| LIMAL + NO3 = AROMRO2 + LIMNB | 2.6d-13 |
| LIMKET + NO3 = LIMNB + AROMRO2 | 9.4d-12 |
| LIMN + NO3 = NO2 + LIMNB + AROMRO2 | 2.6d-13 |

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|---|---|
| PIP + OH = 0.3OH + 0.7AROMRO2 + 0.3MVK + 0.3ACET + 0.1CH2O + 0.78MYRCO | GCARR_ac(6.05d-12, 440.0d0) |
| PIP + O3 = 0.3OH + 0.7AROMRO2 + 0.3MVK + 0.3ACET + 0.1CH2O + 0.78MYRCO | GCARR_ac(1.35d-15, -520.0d0) |
| PIP + NO3 = 0.5OLNN + 0.5NO2 + 0.15OH + 0.35AROMRO2 + 0.15MVK + 0.15ACET + 0.05CH2O + 0.39MYRCO | GCARR_ac(1.06d-12, 490.0d0) |
| PIN + OH = 0.7AROMRO2 + 0.7MONITU + 0.3NO2 + 0.3MYRCO | GCARR_ac(6.05d-12, 440.0d0) |
| PIN + O3 = 0.7AROMRO2 + 0.7MONITU + 0.3NO2 + 0.3MYRCO | GCARR_ac(1.35d-15, -520.0d0) |
| PIN + NO3 = 0.5OLNN + 1.15NO2 + 0.35AROMRO2 + 0.35MONITU + 0.15MYRCO | GCARR_ac(1.06d-12, 490.0d0) |
| MYRCO + OH = HO2 + AROMRO2 + 1.5CH2O + MEK + 0.5ACET + 0.5MVK + 0.5GLYC | GCARR_ac(6.05d-12, 440.0d0) |
| MYRCO + O3 = OH + AROMRO2 + 1.5CH2O + MEK + 0.5ACET + 0.5MVK + 0.5GLYC | GCARR_ac(1.35d-15, -520.0d0) |
| MYRCO + NO3 = 0.5OLNN + 0.5NO2 + 0.5HO2 + 0.5AROMRO2 + 0.75CH2O + 0.5MEK + 0.25ACET + 0.25MVK + 0.25GLYC | GCARR_ac(1.06d-12, 490.0d0) |
| C96O2H + hv = OH + AROMRO2 + ACET + CH2O + RCO3 + 0.5MEK | PHOTOL(172) |
| **Replacement Aromatic and BVOC Chemistry** | |
| **Reaction** | **Rate** |
| STYR + OH = 0.300ZRO2 + 0.700C2BZRO2 + 0.700HO2 + 0.3CH2O | 5.8d-11 |
| STYR + NO3 = C2BZRO2 + NO2 | 1.5d-12 |
| EBZ + OH = 0.75EBZRO2 + 0.070ZRO2 + 0.180CSL + 0.1800HO2 | 7.0d-12 |
| EBZ + NO3 = C2BZRO2 + HNO3 | 1.2d-16 |
| TMB + OH = 0.050ZRO2 + 0.030CSL + 0.030HO2 + 0.92TMBRO2 | 3.92d-11 |
| TMB + NO3 = TMB2RO2 + HNO3 | 1.4d-15 |
| BENZ + OH = BRO2 + 0.54PHEN + 0.54HO2 + 0.46BENZRO2 | GCARR_ac(2.3d-12, -193.0d0) |
| TOLU + OH = TRO2 + 0.19CSL + 0.19HO2 + 0.81TOLURO2 | GCARR_ac(1.8d-12, 340.0d0) |
| XYLE + OH = XRO2 + 0.15CSL + 0.15HO2 + 0.85XYLERO2 | 1.7d-11 |
| PHEN + OH = 0.06BENZO + 0.14PHENRO2 + 0.8MCT + 0.8HO2 | GCARR_ac(4.70d-13, 1220.0d0) |

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|---|---|
| CSL + OH = 0.727MCT + 0.727HO2 + 0.2CSLO2 + 0.073BENZO | 4.7d-11 |
| CSL + NO3 = 0.5PHEN + 0.5HNO3 + 0.2CSLO2 + 0.3BENZO | 1.4d-11 |
| MCT + OH = 0.3BENZO + 0.7MCTO2 | 2.0d-11 |
| MCT + NO3 = 0.5NPHEN + 0.5HNO3 + 0.3BENZO + 0.2MCTO2 | 9.9d-11 |
| C2BZRO2 + HO2 = CH2O + BALD + OH + HO2 | 2.91d-13 * EXP( 1300.0d0 / TEMP ) * 0.82d0 |
| C2BZRO2 + NO = CH2O + BALD + NO2 + HO2 | GCARR_ac(2.60d-12, 365.0d0) |
| C2BZRO2 + NO3 = CH2O + BALD + NO2 + HO2 | 2.30d-12 |
| EBZRO2 + HO2 = 0.333CH2O + 0.533ALD2 + 0.533AROMP5 + 1.067AROMP4 + OH + HO2 | 2.91d-13 * EXP( 1300.0d0 / TEMP ) * 0.82d0 |
| EBZRO2 + NO = 0.333CH2O + 0.533ALD2 + 0.533AROMP5 + 1.067AROMP4 + NO2 + HO2 | GCARR_ac(2.60d-12, 365.0d0) |
| EBZRO2 + NO3 = 0.333CH2O + 0.533ALD2 + 0.533AROMP5 + 1.067AROMP4 + NO2 + HO2 | 2.30d-12 |
| TMBRO2 + HO2 = 0.13CH2O + 0.13CO + 0.652AROMP5 + 0.408AROMP4 + 0.272MGLY + 0.109GLYX + 0.543RCOOH + 0.163TLFUONE + OH + HO2 | 2.91d-13 * EXP( 1300.0d0 / TEMP ) * 0.82d0 |
| TMBRO2 + NO = 0.13CH2O + 0.13CO + 0.652AROMP5 + 0.408AROMP4 + 0.272MGLY + 0.109GLYX + 0.543RCOOH + 0.163TLFUONE + NO2 + HO2 | GCARR_ac(2.60d-12, 365.0d0) |
| TMBRO2 + NO3 = 0.13CH2O + 0.13CO + 0.652AROMP5 + 0.408AROMP4 + 0.272MGLY + 0.109GLYX + 0.543RCOOH + 0.163TLFUONE + NO2 + HO2 | 2.30d-12 |
| TMB2RO2 + HO2 = 0.400AROMP5 + BALD + OH + HO2 | 2.91d-13 * EXP( 1300.0d0 / TEMP ) * 0.82d0 |
| TMB2RO2 + NO = 0.400AROMP5 + BALD + NO2 + HO2 | GCARR_ac(2.60d-12, 365.0d0) |
| TMB2RO2 + NO3 = 0.400AROMP5 + BALD + NO2 + HO2 | 2.30d-12 |
| BENZRO2 + HO2 = 0.391GLYX + 0.434CO + 1.196AROMP4 + OH + HO2 | 2.91d-13 * EXP( 1300.0d0 / TEMP ) * 0.82d0 |
| BENZRO2 + NO = 0.391GLYX + 0.434CO + 1.196AROMP4 + NO2 + HO2 | GCARR_ac(2.60d-12, 365.0d0) |
| BENZRO2 + NO3 = 0.391GLYX + 0.434CO + 1.196AROMP4 + NO2 + HO2 | 2.30d-12 |

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| TOLURO2 + HO2 = 0.074BALD + 0.148GLYX + 0.148MGLY + 0.332CO + 0.05MVK + 0.37AROMP5 + 0.84AROMP4 + OH + HO2 | 2.91d-13 * EXP( 1300.0d0 / TEMP ) * 0.82d0 |
| TOLURO2 + NO = 0.074BALD + 0.148GLYX + 0.148MGLY + 0.332CO + 0.05MVK + 0.37AROMP5 + 0.84AROMP4 + NO2 + HO2 | GCARR_ac(2.60d-12, 365.0d0) |
| TOLURO2 + NO3 = 0.074BALD + 0.148GLYX + 0.148MGLY + 0.332CO + 0.05MVK + 0.37AROMP5 + 0.84AROMP4 + NO2 + HO2 | 2.30d-12 |
| XYLERO2 + HO2 = 0.07BALD + 0.118GLYX + 0.235MGLY + 0.351CO + 0.047MVK + 0.65AROMP5 + 0.32AROMP4 + 0.5RCOOH + OH + HO2 | 2.91d-13 * EXP( 1300.0d0 / TEMP ) * 0.82d0 |
| XYLERO2 + NO = 0.07BALD + 0.118GLYX + 0.235MGLY + 0.351CO + 0.047MVK + 0.65AROMP5 + 0.32AROMP4 + 0.5RCOOH + NO2 + HO2 | GCARR_ac(2.60d-12, 365.0d0) |
| XYLERO2 + NO3 = 0.07BALD + 0.118GLYX + 0.235MGLY + 0.351CO + 0.047MVK + 0.65AROMP5 + 0.32AROMP4 + 0.5RCOOH + NO2 + HO2 | 2.30d-12 |
| PHENRO2 + HO2 = 1.288AROMP4 + 0.424GLYX + OH + HO2 | 2.91d-13 * EXP( 1300.0d0 / TEMP ) * 0.82d0 |
| PHENRO2 + NO = 1.288AROMP4 + 0.424GLYX + NO2 + HO2 | GCARR_ac(2.60d-12, 365.0d0) |
| PHENRO2 + NO3 = 1.288AROMP4 + 0.424GLYX + NO2 + HO2 | 2.30d-12 |
| CSLO2 + HO2 = 1.4AROMP5 + OH + HO2 | 2.91d-13 * EXP( 1300.0d0 / TEMP ) * 0.82d0 |
| CSLO2 + NO = 1.4AROMP5 + NO2 + HO2 | GCARR_ac(2.60d-12, 365.0d0) |
| CSLO2 + NO3 = 1.4AROMP5 + NO2 + HO2 | 2.30d-12 |
| MCTO2 + HO2 = 1.5AROMP4 + OH + HO2 | 2.91d-13 * EXP( 1300.0d0 / TEMP ) * 0.82d0 |
| MCTO2 + NO = 1.5AROMP4 + NO2 + HO2 | GCARR_ac(2.60d-12, 365.0d0) |
| MCTO2 + NO3 = 1.5AROMP4 + NO2 + HO2 | 2.30d-12 |
| LIMO + O3 = 0.865OH + 0.15CO + 0.15PLIMALO2 + 0.12LIMAL + 0.715LIMO3 | GCARR_ac(2.95d-15, -783.0d0) |
| MTPO + O3 = 0.5PMYRCOO2 + 0.5ACET + 0.8OH + 0.5MEK + 0.15MVK + 0.05HO2 + 0.3KO2 | GCARR_ac(2.7d-15, -520.0d0) |
| APINN + OH = 0.5PINAL + 0.5NO2 + 0.5HO2 + 0.5APINNRO2 | 5.50d-12 |
| C96O2 + NO = 0.16C96N + 0.84NO2 + 0.84PMEKRO2 | GCARR_ac(2.7d-12, 360.0d0) |
| C96O2 + NO3 = NO2 + PMEKRO2 | 2.3d-12 |

| | |
|---|---|
| C96O2 + MO2 = HO2 + 0.75CH2O + 0.25MOH + 0.25C96O2H + 0.75PMEKRO2 | GCARR_ac(3.75d-13, 500.0d0) |
| C96O2H + OH = 0.5C96O2 + 0.5PMEKRO2 | 2.6d-11 |
| C96N + OH = 0.5NO2 + 0.5MONITS + 0.5PMEKRO2 | 2.88d-12 |
| BPINN + OH = 0.5BPINNRO2 + 0.5CH2O + 0.5NO2 + 0.5HO2 + 0.5BPINO | 4.7d-12 |
| LIMAL + NO3 = LIMRO2 | 2.6d-13 |
| LIMKET + NO3 = LIMRO2 | 9.4d-12 |
| LIMN + NO3 = NO2 + LIMRO2 | 2.6d-13 |
| PIP + OH = 0.3OH + 0.7PIPO2 + 0.09MVK + 0.09ACET + 0.03CH2O + 0.234MYRCO | GCARR_ac(6.05d-12, 440.0d0) |
| PIP + O3 = 0.3OH + 0.7PIPO2 + 0.09MVK + 0.09ACET + 0.03CH2O + 0.234MYRCO | GCARR_ac(1.35d-15, -520.0d0) |
| PIP + NO3 = 0.5OLNN + 0.5NO2 + 0.15OH + 0.35PIPO2 + 0.045MVK + 0.045ACET + 0.015CH2O + 0.117MYRCO | GCARR_ac(1.06d-12, 490.0d0) |
| PIN + OH = 0.7PINRO2 + 0.3NO2 + 0.3MYRCO | GCARR_ac(6.05d-12, 440.0d0) |
| PIN + O3 = 0.7PINRO2 + 0.3NO2 + 0.3MYRCO | GCARR_ac(1.35d-15, -520.0d0) |
| PIN + NO3 = 0.5OLNN + 1.15NO2 + 0.35PINRO2 + 0.15MYRCO | GCARR_ac(1.06d-12, 490.0d0) |
| MYRCO + OH = HO2 + MYRCORO2 + 0.5CH2O + 0.5ACET + 0.5MVK + 0.5GLYC | GCARR_ac(6.05d-12, 440.0d0) |
| MYRCO + O3 = OH + MYRCORO2 + 0.5CH2O + 0.5ACET + 0.5MVK + 0.5GLYC | GCARR_ac(1.35d-15, -520.0d0) |
| MYRCO + NO3 = 0.5OLNN + 0.5NO2 + 0.5HO2 + 0.5MYRCORO2 + 0.25CH2O + 0.25ACET + 0.25MVK + 0.25GLYC | GCARR_ac(1.06d-12, 490.0d0) |
| C96O2H + hv = OH + PMEKRO2 | PHOTOL(172) |
| APINNRO2 + HO2 = C96N + CH2O + OH + HO2 | 2.91d-13 * EXP( 1300.0d0 / TEMP ) * 0.82d0 |
| APINNRO2 + NO = C96N + CH2O + NO2 + HO2 | GCARR_ac(2.60d-12, 365.0d0) |
| APINNRO2 + NO3 = C96N + CH2O + NO2 + HO2 | 2.30d-12 |
| PMEKRO2 + HO2 = ACET + CH2O + RCO3 + 0.5MEK + OH + HO2 | 2.91d-13 * EXP( 1300.0d0 / TEMP ) * 0.82d0 |
| PMEKRO2 + NO = ACET + CH2O + RCO3 + 0.5MEK + NO2 + HO2 | GCARR_ac(2.60d-12, 365.0d0) |
| PMEKRO2 + NO3 = ACET + CH2O + RCO3 + 0.5MEK + NO2 + HO2 | 2.30d-12 |
| BPINNRO2 + HO2 = BPINON + CH2O + OH + HO2 | 2.91d-13 * EXP( 1300.0d0 / TEMP ) * 0.82d0 |
| BPINNRO2 + NO = BPINON + CH2O + NO2 + HO2 | GCARR_ac(2.60d-12, 365.0d0) |
| BPINNRO2 + NO3 = BPINON + CH2O + NO2 + HO2 | 2.30d-12 |
| LIMRO2 + HO2 = LIMNB + OH + HO2 | 2.91d-13 * EXP( 1300.0d0 / TEMP ) * 0.82d0 |
| LIMRO2 + NO = LIMNB + NO2 + HO2 | GCARR_ac(2.60d-12, 365.0d0) |

| | |
|---|---|
| LIMRO2 + NO3 = LIMNB + NO2 + HO2 | 2.30d-12 |
| PINRO2 + HO2 = MONITU + OH + HO2 | 2.91d-13 * EXP( 1300.0d0 / TEMP ) * 0.82d0 |
| PINRO2 + NO = MONITU + NO2 + HO2 | GCARR_ac(2.60d-12, 365.0d0) |
| PINRO2 + NO3 = MONITU + NO2 + HO2 | 2.30d-12 |
| MYRCORO2 + HO2 = CH2O + MEK + OH + HO2 | 2.91d-13 * EXP( 1300.0d0 / TEMP ) * 0.82d0 |
| MYRCORO2 + NO = CH2O + MEK + NO2 + HO2 | GCARR_ac(2.60d-12, 365.0d0) |
| MYRCORO2 + NO3 = CH2O + MEK + NO2 + HO2 | 2.30d-12 |
| PLIMALO2 + HO2 = LIMAL + OH + HO2 | 2.91d-13 * EXP( 1300.0d0 / TEMP ) * 0.82d0 |
| PLIMALO2 + NO = LIMAL + NO2 + HO2 | GCARR_ac(2.60d-12, 365.0d0) |
| PLIMALO2 + NO3 = LIMAL + NO2 + HO2 | 2.30d-12 |
| PMYRCOO2 + HO2 = 0.6RCHO + 0.2CH2O + 0.8MYRCO + OH + HO2 | 2.91d-13 * EXP( 1300.0d0 / TEMP ) * 0.82d0 |
| PMYRCOO2 + NO = 0.6RCHO + 0.2CH2O + 0.8MYRCO + NO2 + HO2 | GCARR_ac(2.60d-12, 365.0d0) |
| PMYRCOO2 + NO3 = 0.6RCHO + 0.2CH2O + 0.8MYRCO + NO2 + HO2 | 2.30d-12 |
| PIPO2 + HO2 = 0.3ACET + 0.3MVK + 0.1CH2O + 0.78MYRCO + OH + HO2 | 2.91d-13 * EXP( 1300.0d0 / TEMP ) * 0.82d0 |
| PIPO2 + NO = 0.3ACET + 0.3MVK + 0.1CH2O + 0.78MYRCO + NO2 + HO2 | GCARR_ac(2.60d-12, 365.0d0) |
| PIPO2 + NO3 = 0.3ACET + 0.3MVK + 0.1CH2O + 0.78MYRCO + NO2 + HO2 | 2.30d-12 |

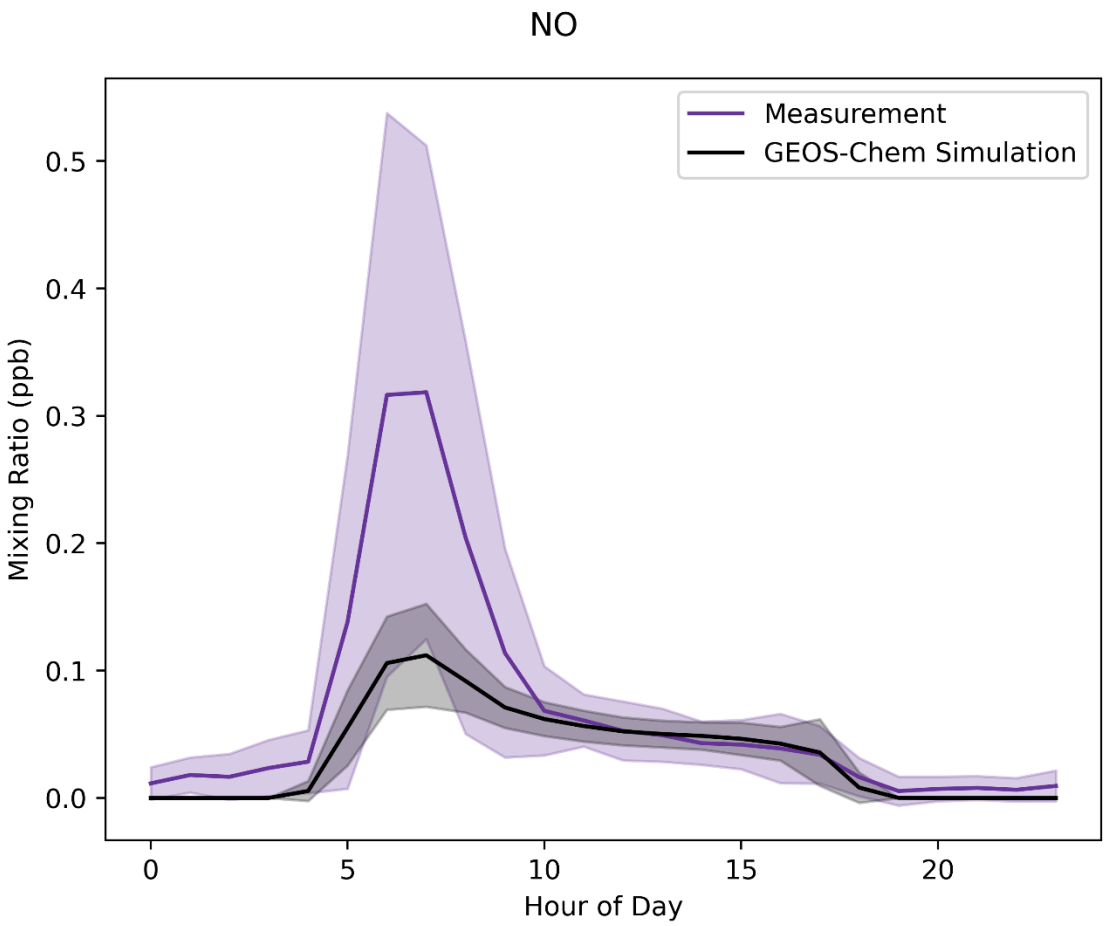


*Figure S1. Comparison of simulated NO concentrations in the GEOS-Chem grid-box corresponding to the SOAS measurement location to measured mixing ratios. Each of the box models are constrained to the measured NO mixing ratios. The solid lines show the mean for each hour across the campaign, with the shaded regions showing one standard deviation above and below the mean.*

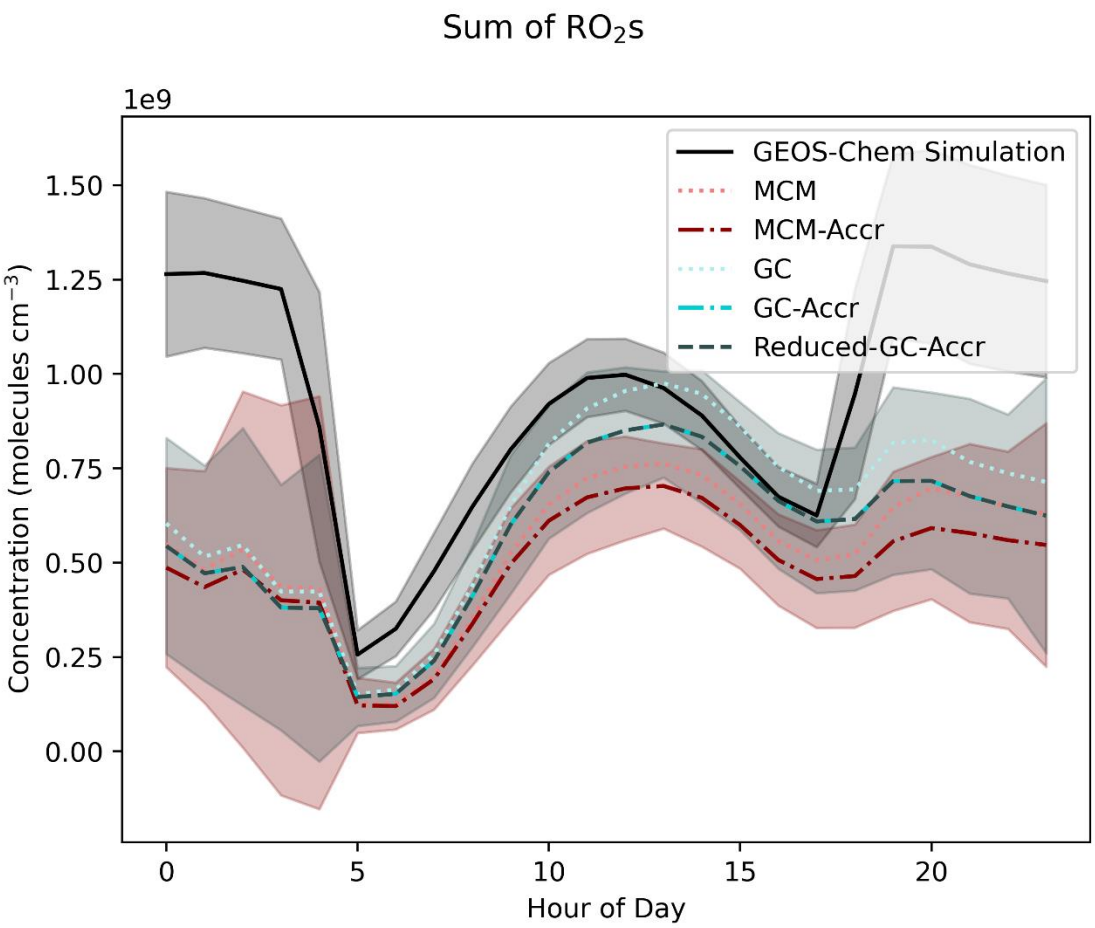


*Figure S2. Comparison of simulated $RO_2$ concentrations in each of the SOAS box models and the GEOS-Chem grid-box corresponding to the SOAS measurement location. The solid lines show the mean for each hour across the campaign, with the shaded regions showing one standard deviation above and below the mean.*

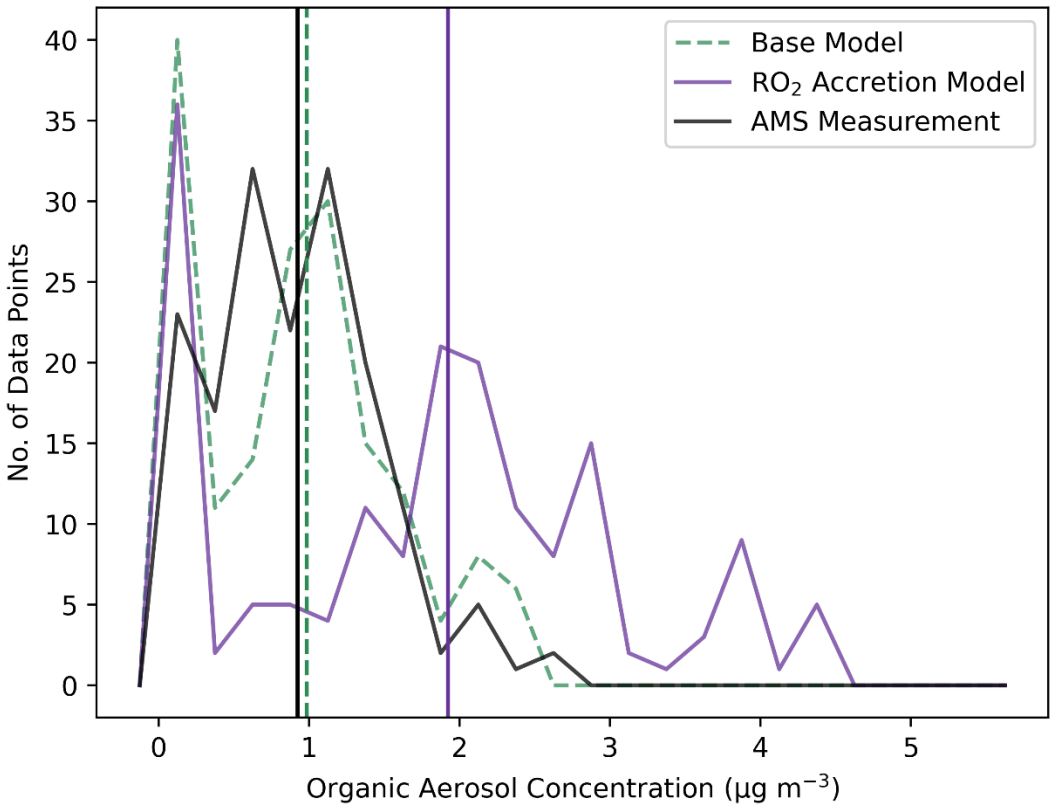


*Figure S3. Distribution of measured organic aerosol concentrations (solid black line) compared to organic aerosol concentrations in the GEOS-Chem models over the course of the GOAMAZON flights. Vertical lines show the median of each distribution.*

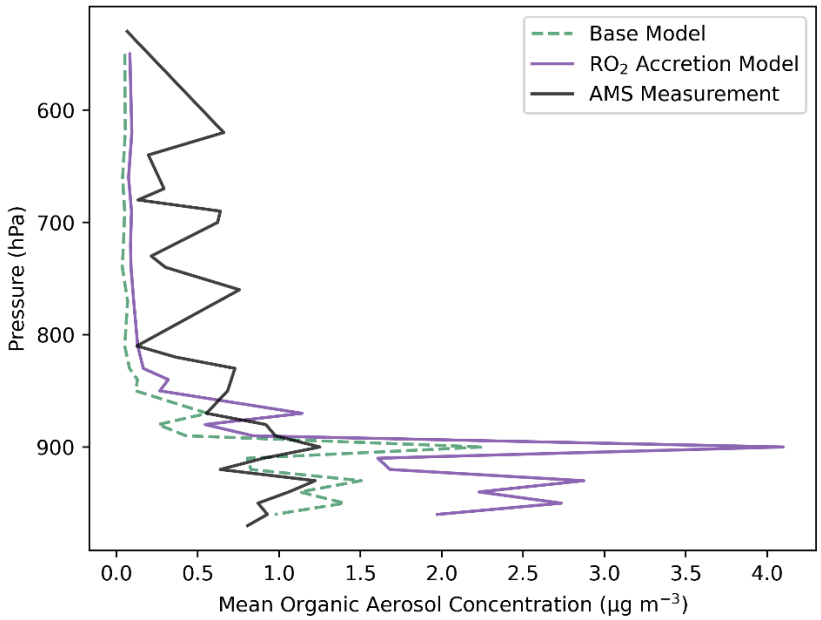


*Figure S4. Vertical profile of measured organic aerosol concentrations (solid black line) compared to organic aerosol concentrations in the GEOS-Chem models. Data is binned into 10 hPa groups and the mean value token throughout the GOAMAZON flight trajectory.*

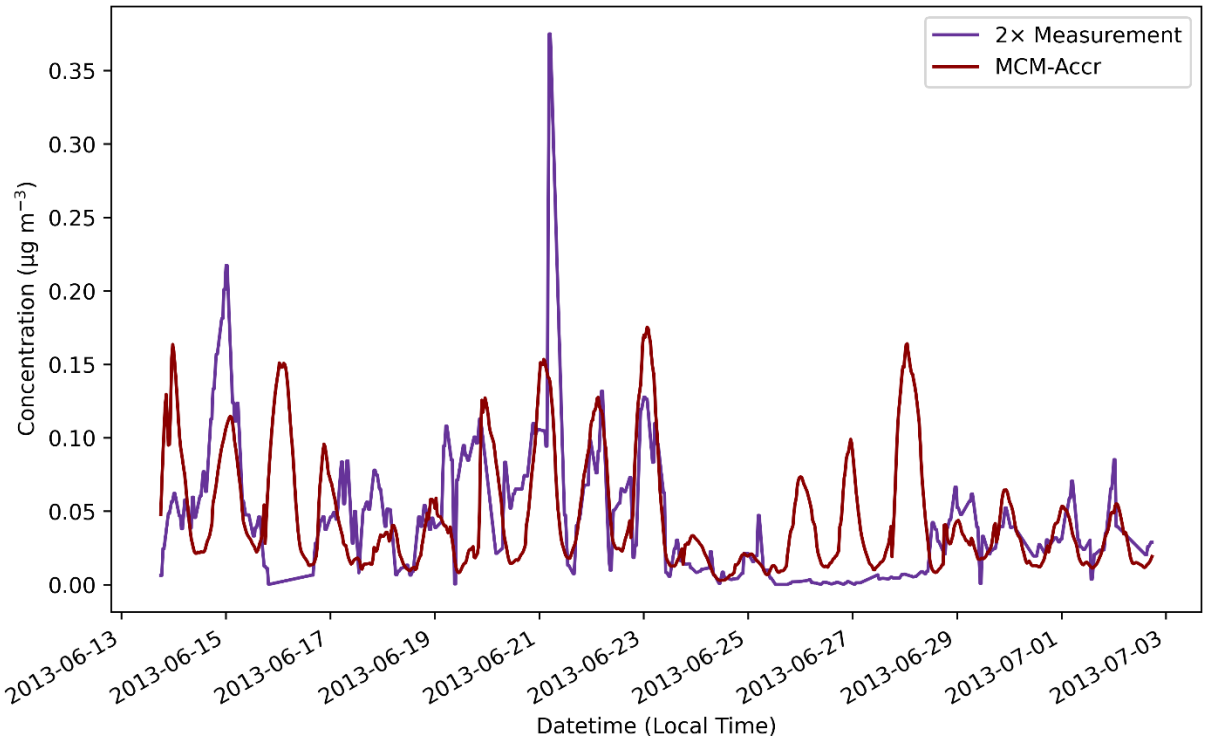


*Figure S5. Aerosol-phase concentrations of selected accretion products corresponding to the 41 selected CIMS signals. The red line shows the simulated concentrations from the MCM-Accr model, with the purple line showing measured concentrations multiplied by 2.*

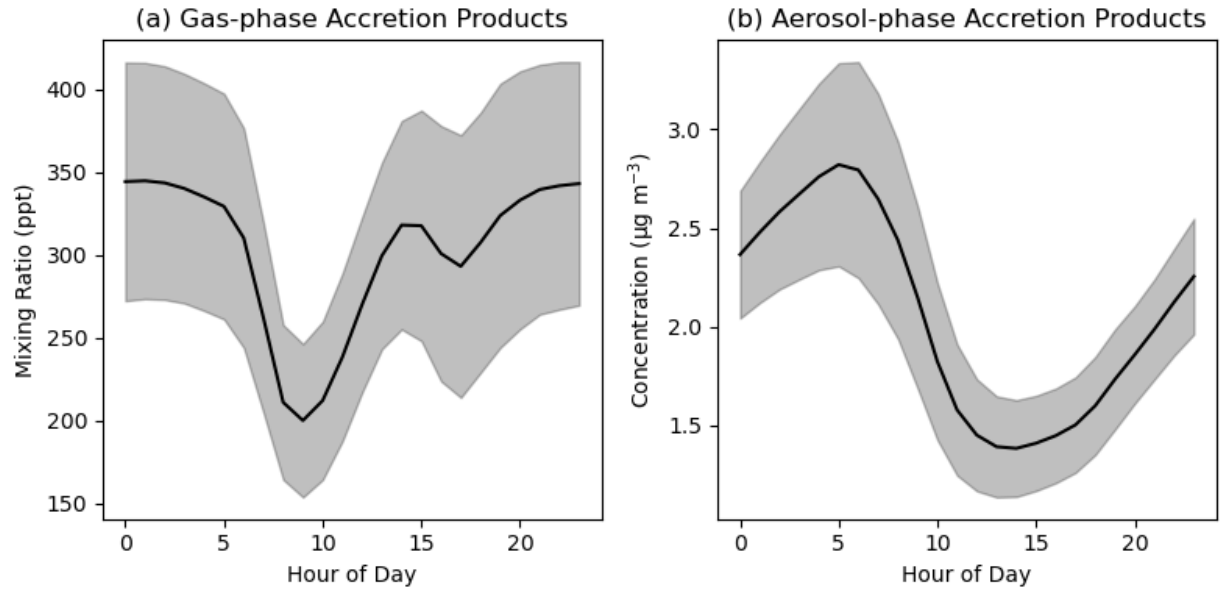


*Figure S6. Average modelled ground-level gas-phase (a) and aerosol-phase (b) accretion product concentrations during the GOAMAZON period (2014-02-21 and 2014-03-25) between latitude-longitude coordinates of (-4.0, 62.5) and (0.0, -57.5). The solid lines show the mean for each hour across the campaign, with the shaded regions showing one standard deviation above and below the mean.*

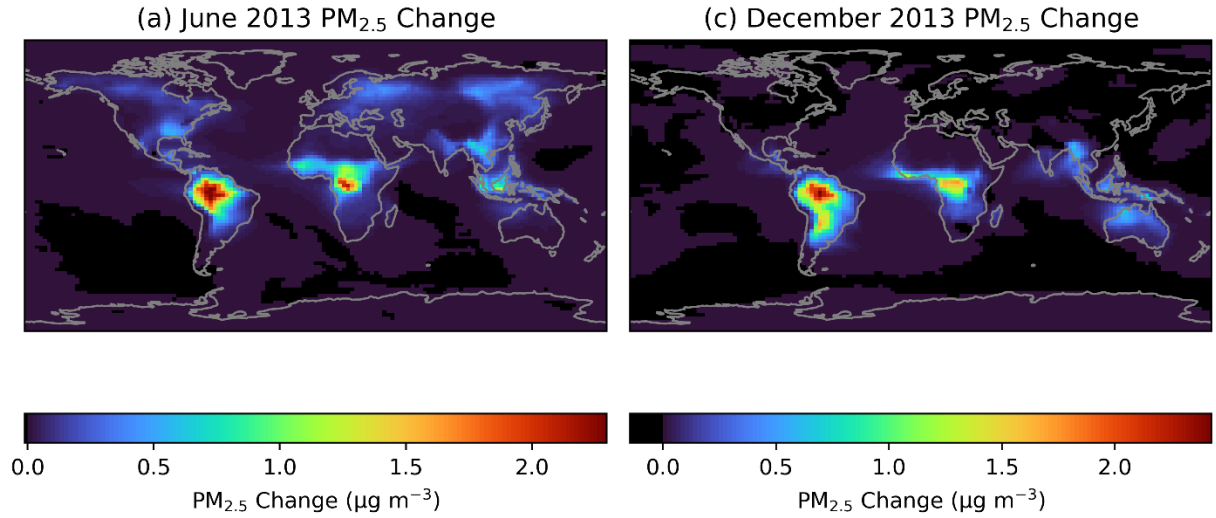


*Figure S7. The change in $PM_{2.5}$ concentrations in the first 10 vertical levels when adding $RO_2$ accretion reactions to GEOS-Chem. (a) and (c) show the absolute change in $PM_{2.5}$ mass concentration in June and January, respectively. (b) and (d) show the change as a percentage of $PM_{2.5}$ in the base model in June and January, respectively.*

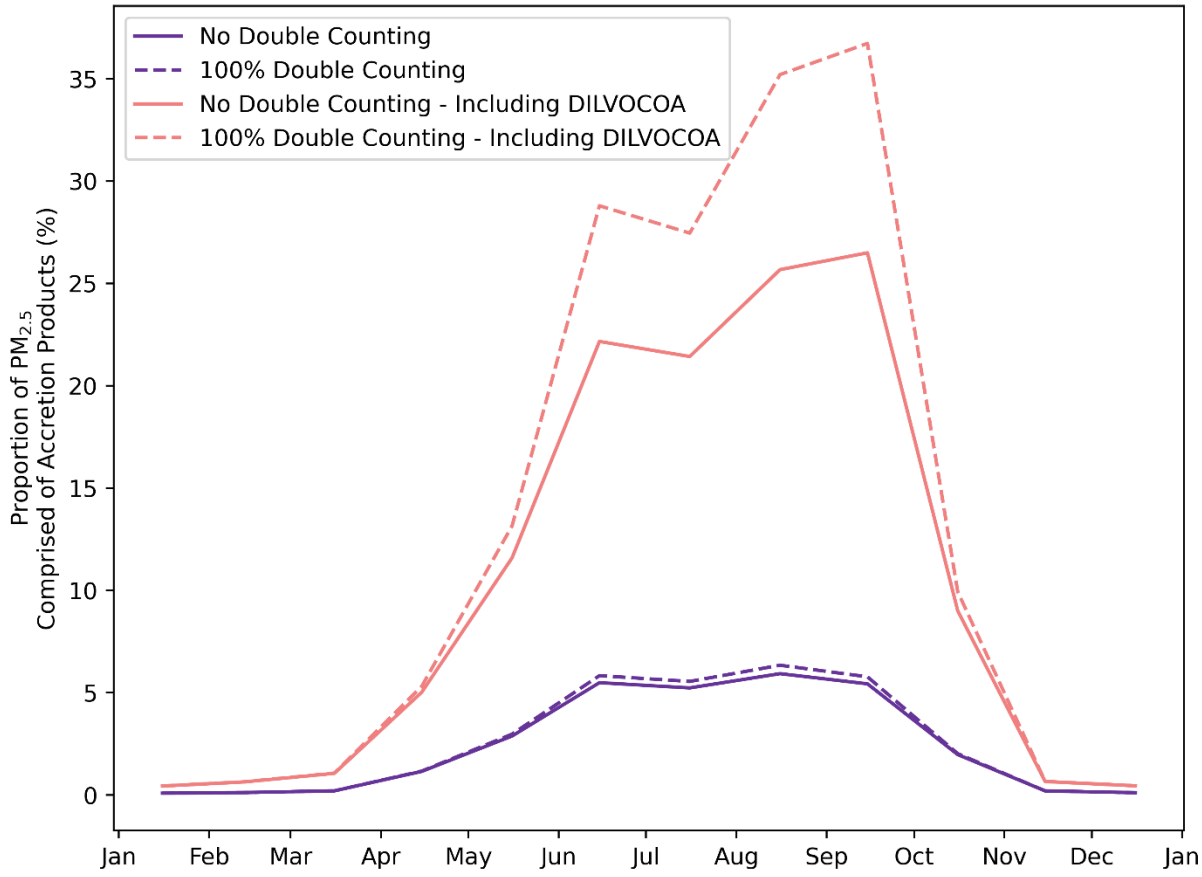


*Figure S8. Proportion of $PM_{2.5}$ comprised of $RO_2$ accretion products, calculated using monthly average surface concentrations throughout 2013 in the south-eastern united states between latitude- longitude coordinates of (31.0, -90.0) and (37.0, -82.0).*

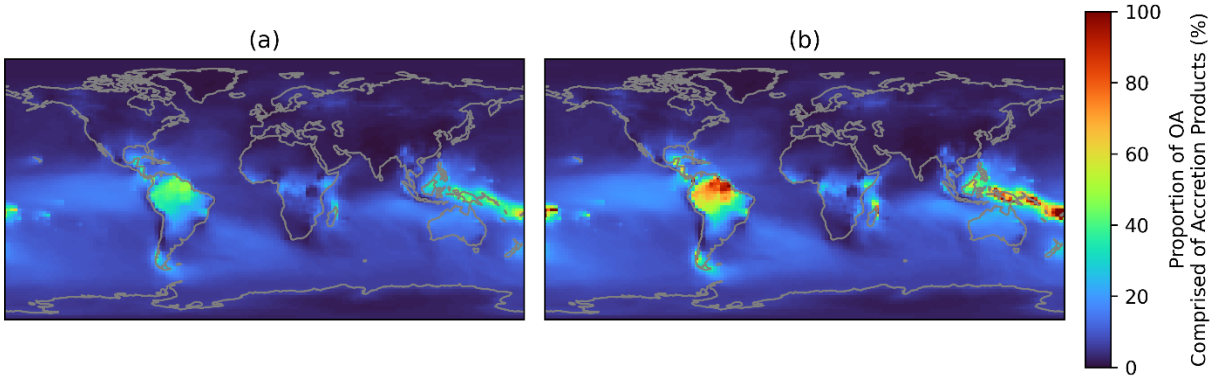


*Figure S9. Proportion of organic aerosol (OA) comprised of $RO_2$ accretion products, calculated using annual average surface concentrations. (a) Simulated accretion product concentrations divided by the simulated OA mass concentration. (b) Assumes 100% double counting of accretion products by subtracting the accretion product concentrations from the OA denominator.*

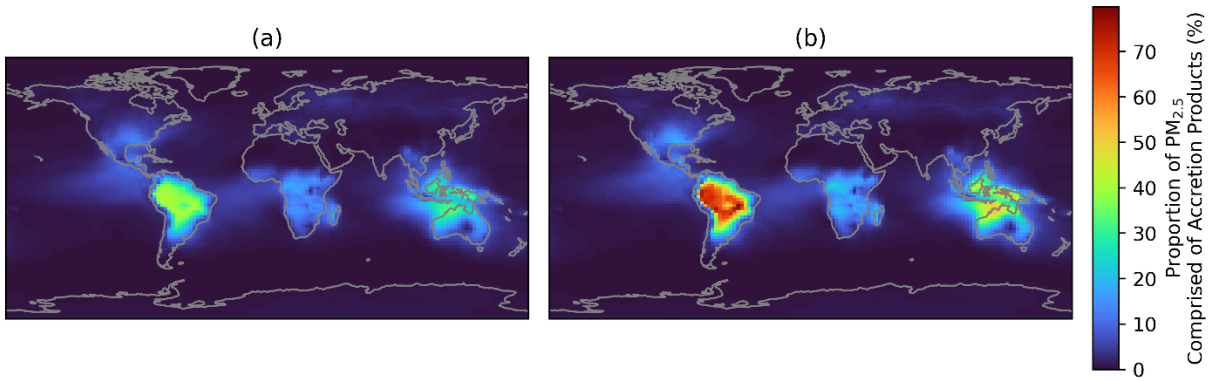


*Figure S10. Proportion of $PM_{2.5}$ comprised of $RO_2$ accretion products, including the products of secondary oxidation of accretion products, DILVOC, calculated using annual average surface concentrations. (a) Simulated accretion product and DILVOC concentrations divided by the simulated $PM_{2.5}$ mass concentration. (b) Assumes 100% double counting by subtracting the accretion product and DILVOC concentrations from the $PM_{2.5}$ denominator.*

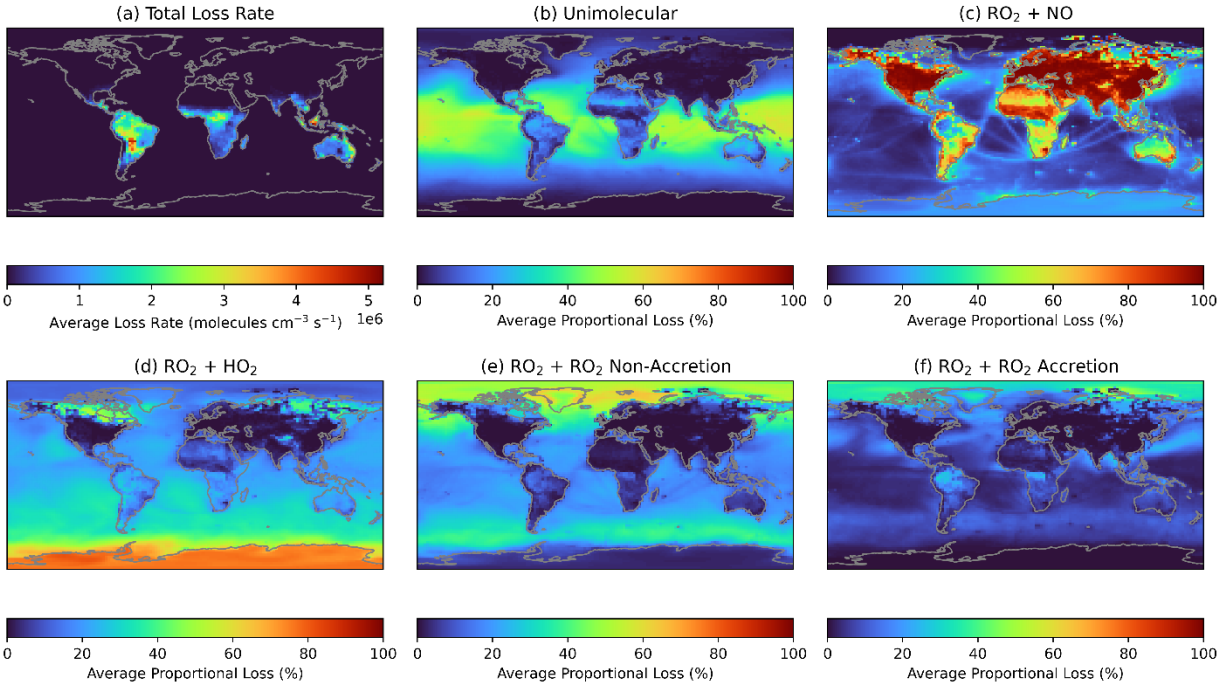


*Figure S11. (a) Average total loss rate of the primary isoprene $RO_2$, IHOO1, during December of the GEOS-Chem simulation. (b-f) Average fractional loss of IHOO1 to each loss pathway.*

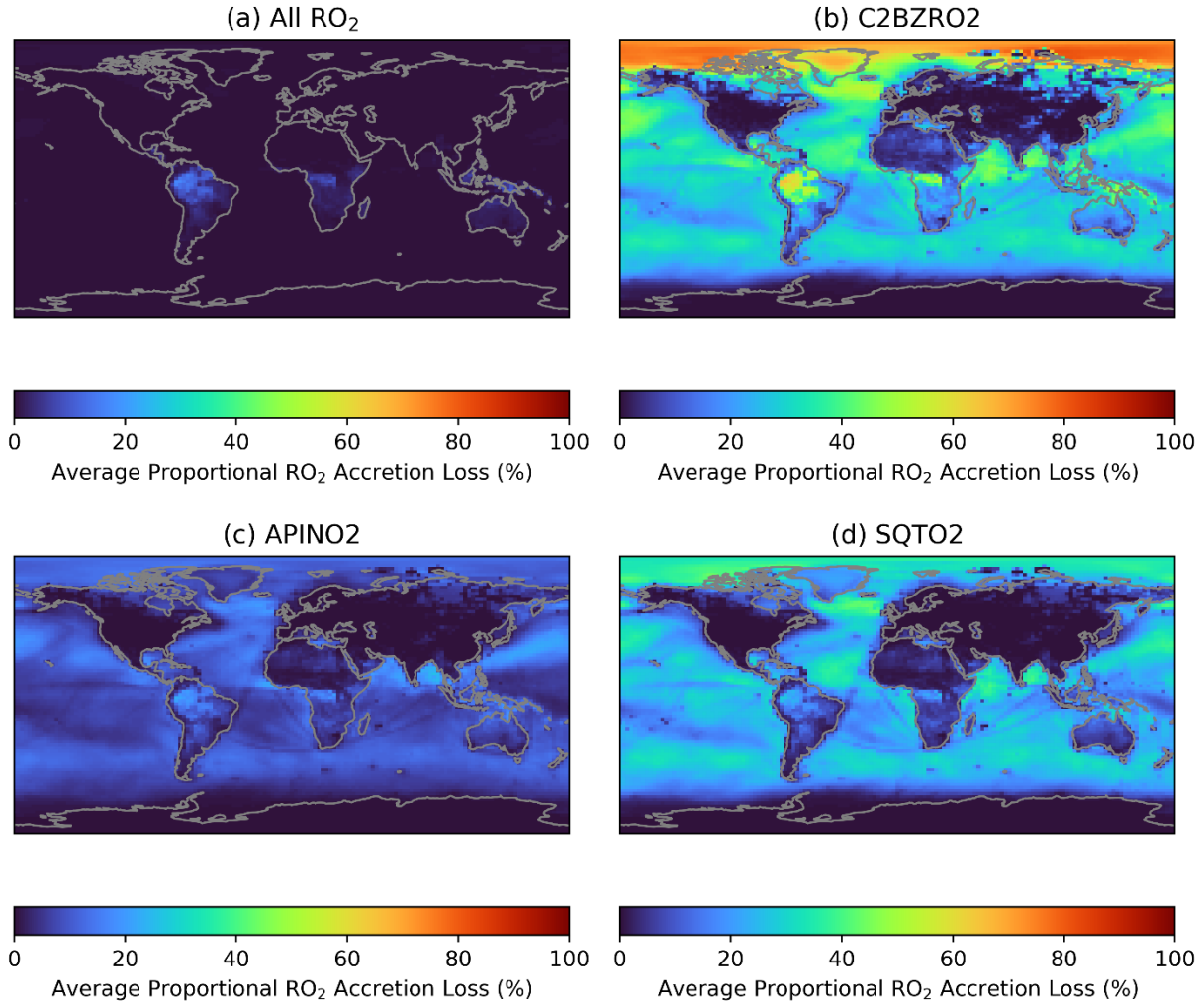


*Figure S12. Proportional loss of $RO_2$ to accretion reactions during December of the GEOS-Chem simulation. (a) average for all $RO_2$, (b) primary $RO_2$ from styrene oxidation (C2BZRO2), (c) primary α-pinene $RO_2$ (APINO2), (d) primary sesquiterpene $RO_2$ (SQTO2).*