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Supporting Information for

Investigating the Understanding of Oxidation Chemistry Using 20 Years of
Airborne OH and HO₂ Observations

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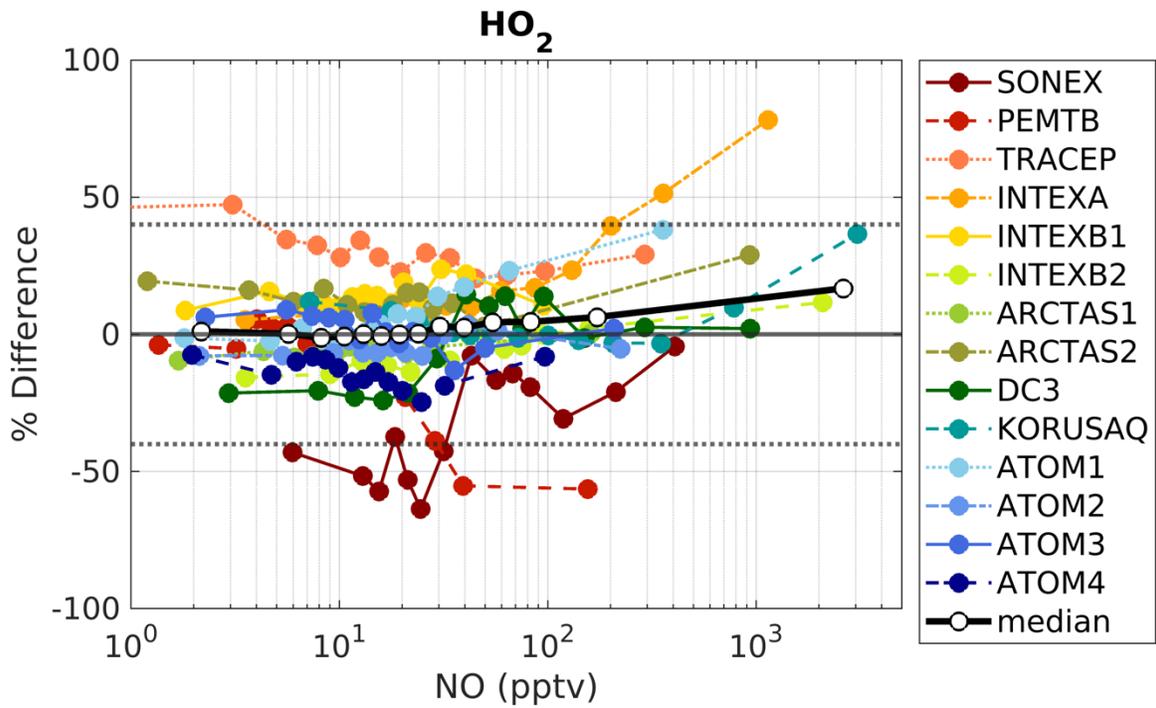


Figure S1: Dependence of HO₂ percent difference on NO. For each mission, median values for PD and NO were determined for equal numbers of one-minute data points, so that the spacing on the NO axis varies. The horizontal dashed lines at -40% and +40% indicate the combined observation and model uncertainties.

Table S1. Species used as model inputs for the missions in this study. The dark gray colored rows mark the species common to all missions and are used as inputs for the common input set MCM model runs.

| Species | SONEX | PEMT-B | TRACE-P | INTEX-A | INTEX-B1 | INTEX-B2 | ARCTAS-A | ARCTAS-B | DC3 | KORUS-AQ | ATom-1 | ATom-2 | ATom-3 | ATom-4 |
|-----------------------------------|-------|--------|---------|---------|----------|----------|----------|----------|-----|----------|--------|--------|--------|--------|
| CH ₄ | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| CO | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| H ₂ O ₂ | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| HCHO | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| NO | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| NO ₂ | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| O ₃ | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| Alcohols | | | | | | | | | | | | | | |
| C ₂ H ₅ OH | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| CH ₃ OH | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| Aldehydes | | | | | | | | | | | | | | |
| ACR | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| C ₂ H ₅ CHO | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| C ₃ H ₇ CHO | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| CH ₃ CHO | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| MACR | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| Alkanes | | | | | | | | | | | | | | |
| BUT1ENE | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| C ₂ H ₆ | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| C ₃ H ₈ | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| CHEX | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| IC ₄ H ₁₀ | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| IC ₅ H ₁₂ | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| M23C4 | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| M2PE | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| M3PE | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| NC ₁₀ H ₂₂ | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| NC ₄ H ₁₀ | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| NC ₅ H ₁₂ | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| NC ₆ H ₁₄ | • | • | • | • | • | • | • | • | • | • | • | • | • | • |

| | | | | | | | | | | | | | | |
|--------------------------------------|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| NC ₇ H ₁₆ | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| NC ₈ H ₁₈ | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| NC ₉ H ₂₀ | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| Alkenes | | | | | | | | | | | | | | |
| C ₂ H ₄ | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| C ₃ H ₆ | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| MEPROPENE | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| Alkynes | | | | | | | | | | | | | | |
| C ₂ H ₂ | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| C ₅ H ₈ | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| Aromatics | | | | | | | | | | | | | | |
| BENZENE | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| EBENZ | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| MXYL | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| OETHTOL | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| OXYL | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| PBENZ | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| PXYL | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| TM124B | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| TOLUENE | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| HCOOH | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| Chloro | | | | | | | | | | | | | | |
| CH ₂ CL ₂ | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| CH ₂ CLCH ₂ CL | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| CH ₃ CCL ₃ | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| CH ₃ CL | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| CHCL ₃ | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| TCE | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| TRICLETH | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| Ketones | | | | | | | | | | | | | | |
| CH ₃ COCH ₃ | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| MEK | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| MVK | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| Monoterpenes | | | | | | | | | | | | | | |
| APINENE | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| BPINENE | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| Nitrates | | | | | | | | | | | | | | |
| HNO ₃ | • | • | • | • | • | • | • | • | • | • | • | • | • | • |

| | | | | | | | | | | | | | | |
|--|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| C ₂ H ₅ NO ₃ | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| CH ₃ NO ₃ | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| IC ₃ H ₇ NO ₃ | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| NC ₃ H ₇ NO ₃ | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| NC ₄ H ₉ NO ₃ | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| PEANO ₃ | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| PPN | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| CH ₃ CN | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| Unclassified | | | | | | | | | | | | | | |
| CH ₃ CO ₃ H | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| CH ₃ OOH | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| DMS | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| HO ₂ NO ₂ | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| SO ₂ | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| MTBE | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| PAN | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| STYRENE | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| TM123B | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| TM135B | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
| # of obs | 32 | 31 | 44 | 48 | 41 | 51 | 62 | 60 | 48 | 66 | 61 | 61 | 61 | 61 |

Table S2. Statistics for observed and modeled OH. MCM rows are the results using the Master Chemical Mechanism. Prev rows are the results from previous analyses (SONEX through ARCTAS-B). The slope, intercept, and R^2 are from the York fit. The values in parentheses are the corresponding results using the common input set.

| Mission | Model | Slope | Intercept | R^2 | Median ratio | Median PD | # of points | Frac. within $\pm 40\%$ |
|--------------------------------|-------|-------------|---------------|-------------|--------------|-----------------|-------------|-------------------------|
| SONEX | MCM | 0.66 (0.65) | 0.02 (0.01) | 0.75 (0.75) | 0.68 (0.66) | -38.59 (-41.17) | 558 | 50.18 (47.31) |
| | Prev | 0.70 | -0.10 | 0.64 | 0.63 | -44.94 | | 40.50 |
| PEM | MCM | 0.83 (0.80) | 0.61 (0.59) | 0.56 (0.56) | 1.10 (1.05) | 9.71 (5.19) | 1410 | 78.01 (80.43) |
| | Prev | 0.74 | 0.85 | 0.60 | 1.15 | 14.06 | | 75.04 |
| Tropics-B | MCM | 1.09 (0.88) | 0.21 (0.30) | 0.56 (0.67) | 1.22 (1.03) | 20.05 (3.06) | 1354 | 62.56 (71.96) |
| | Prev | 0.68 | 0.85 | 0.59 | 1.18 | 16.71 | | 62.85 |
| INTEX-A | MCM | 0.63 (0.62) | 1.08 (0.75) | 0.50 (0.65) | 0.86 (0.76) | -14.70 (-27.17) | 3216 | 70.27 (66.70) |
| | Prev | 0.64 | 1.12 | 0.57 | 0.88 | -12.53 | | 71.80 |
| INTEX-B (P1) (N. Pacific) | MCM | 0.81 (0.76) | 0.20 (0.20) | 0.50 (0.50) | 0.93 (0.86) | -7.32 (-15.03) | 1375 | 80.95 (77.02) |
| | Prev | 0.83 | 0.19 | 0.50 | 0.95 | -5.32 | | 81.31 |
| INTEX-B (P2) (Gulf of Mex.) | MCM | 0.77 (0.56) | 0.52 (0.76) | 0.40 (0.45) | 0.97 (0.79) | -2.97 (-24.05) | 1549 | 70.37 (60.30) |
| | Prev | 0.70 | 0.66 | 0.54 | 0.95 | -5.34 | | 68.24 |
| ARCTAS-A (Arctic) | MCM | 1.34 (1.21) | -0.12 (-0.09) | 0.48 (0.49) | 1.15 (1.07) | 13.99 (7.13) | 2971 | 59.91 (60.70) |
| | Prev | 1.17 | -0.00 | 0.48 | 1.17 | 15.45 | | 59.10 |
| ARCTAS-B (W. Canada) | MCM | 1.23 (1.02) | -0.08 (-0.05) | 0.24 (0.23) | 1.18 (0.99) | 16.15 (-0.60) | 2866 | 59.07 (60.19) |
| | Prev | 1.06 | 0.19 | 0.28 | 1.22 | 19.62 | | 56.42 |
| SONEX - ARCTAS-B | MCM | 0.97 (0.83) | 0.08 (0.12) | 0.65 (0.70) | 1.02 (0.90) | 1.69 (-10.41) | 15299 | 66.43 (65.59) |
| | Prev | 0.92 | 0.15 | 0.71 | 1.03 | 2.92 | | 65.31 |
| DC3 | MCM | 0.78 (0.62) | 0.17 (0.19) | 0.65 (0.62) | 0.84 (0.69) | -17.33 (-37.24) | 3587 | 77.53 (53.02) |
| | MCM | 0.89 (0.57) | 0.44 (0.88) | 0.63 (0.64) | 1.02 (0.74) | 1.70 (-29.51) | 5392 | 82.29 (58.92) |
| ATom-1 | MCM | 1.34 (1.27) | -0.18 (-0.10) | 0.54 (0.56) | 1.27 (1.23) | 23.92 (20.87) | 2330 | 62.27 (62.68) |
| | MCM | 1.08 (1.10) | -0.04 (-0.06) | 0.65 (0.69) | 1.05 (1.06) | 5.29 (6.26) | 2003 | 78.48 (79.59) |
| ATom-3 | MCM | 1.06 (1.01) | -0.00 (0.03) | 0.35 (0.29) | 1.06 (1.02) | 5.71 (2.15) | 2383 | 73.69 (70.35) |
| | MCM | 1.01 (0.94) | 0.04 (0.08) | 0.61 (0.59) | 1.03 (0.98) | 2.88 (-1.98) | 1399 | 76.13 (71.69) |
| ALL | MCM | 0.97 (0.80) | 0.07 (0.15) | 0.64 (0.65) | 1.01 (0.88) | 1.12 (-12.67) | 32393 | 71.70 (64.37) |

Table S3. Statistics for observed and modeled HO_2 . *MCM* rows are the results using the Master Chemical Mechanism. *Prev* rows are the results from previous analyses (SONEX through ARCTAS-B). The slope, intercept, and R^2 are from the York fit. The values in parentheses are the corresponding results using the common input set.

| Mission | Model | Slope | Intercept | R^2 | Median ratio | Median PD | # of points | Frac. within $\pm 40\%$ |
|--------------------------------|--------------|--------------|------------------|-------------|---------------------|------------------|--------------------|---|
| SONEX | MCM | 0.48 (0.47) | 1.08 (1.09) | 0.83 (0.83) | 0.72 (0.71) | -32.96 (-34.16) | 558 | 60.04 (57.35) |
| | Prev | 0.42 | 1.20 | 0.76 | 0.65 | -41.80 | | 43.01 |
| PEM | MCM | 1.25 (1.21) | -4.50 (-4.40) | 0.84 (0.85) | 0.93 (0.91) | -6.81 (-9.85) | 1410 | 81.56 (80.43) |
| | Prev | 1.04 | -0.58 | 0.82 | 1.02 | 2.38 | | 93.26 |
| Tropics-B | MCM | 1.44 (1.21) | -0.97 (0.27) | 0.76 (0.81) | 1.35 (1.23) | 29.61 (20.61) | 1354 | 69.35 (84.25) |
| | Prev | 0.81 | 6.28 | 0.58 | 1.36 | 30.26 | | 67.06 |
| INTEX-A | MCM | 0.96 (0.88) | 3.60 (3.85) | 0.48 (0.76) | 1.20 (1.12) | 18.46 (11.09) | 3216 | 69.15 (77.16) |
| | Prev | 0.98 | 4.14 | 0.64 | 1.26 | 22.71 | | 68.03 |
| INTEX-B (P1) (N. Pacific) | MCM | 1.15 (1.05) | -0.20 (0.12) | 0.61 (0.64) | 1.15 (1.09) | 14.11 (8.42) | 1375 | 86.04 (90.47) |
| | Prev | 1.12 | -0.71 | 0.64 | 1.09 | 8.20 | | 90.04 |
| INTEX-B (P2) (Gulf of Mex.) | MCM | 0.99 (0.87) | -0.99 (-0.21) | 0.77 (0.77) | 0.94 (0.88) | -5.96 (-13.15) | 1549 | 87.60 (82.76) |
| | Prev | 0.97 | -0.79 | 0.78 | 0.94 | -5.97 | | 86.83 |
| ARCTAS-A (Arctic) | MCM | 0.92 (0.89) | 0.09 (0.12) | 0.77 (0.78) | 0.95 (0.92) | -5.07 (-8.18) | 2971 | 90.54 (88.62) |
| | Prev | 0.92 | 0.40 | 0.80 | 0.99 | -1.01 | | 94.08 |
| ARCTAS-B (W. Canada) | MCM | 1.44 (1.59) | -4.06 (-6.07) | 0.66 (0.73) | 1.14 (1.16) | 12.81 (15.03) | 2866 | 80.50 (77.98) |
| | Prev | 1.45 | -3.05 | 0.61 | 1.18 | 16.50 | | 74.88 |
| SONEX - ARCTAS-B | MCM | 1.12 (1.06) | -0.56 (-0.41) | 0.68 (0.77) | 1.07 (1.02) | 6.36 (2.40) | 15299 | 79.65 (81.54) |
| | Prev | 1.08 | 0.13 | 0.69 | 1.10 | 9.16 | | 79.58 |
| DC3 | MCM | 1.01 (0.80) | -0.76 (0.89) | 0.56 (0.81) | 0.92 (0.87) | -8.17 (-13.65) | 3587 | 77.67 (81.29) |
| KORUS-AQ | MCM | 0.95 (0.80) | 1.28 (2.43) | 0.69 (0.68) | 1.04 (0.92) | 3.50 (-7.86) | 5392 | 84.77 (76.13) |
| ATom-1 | MCM | 1.12 (1.13) | -0.81 (-0.60) | 0.37 (0.74) | 1.06 (1.09) | 6.07 (8.34) | 2330 | 79.14 (83.10) |
| ATom-2 | MCM | 1.09 (1.19) | -1.58 (-2.11) | 0.50 (0.83) | 0.96 (0.99) | -4.42 (-0.70) | 2003 | 84.17 (92.27) |
| ATom-3 | MCM | 1.27 (1.13) | -2.00 (-1.28) | 0.64 (0.69) | 1.01 (0.97) | 0.58 (-2.82) | 2383 | 74.53 (76.12) |
| ATom-4 | MCM | 1.08 (1.00) | -2.03 (-1.64) | 0.76 (0.77) | 0.87 (0.84) | -14.11 (-17.67) | 1399 | 83.70 (82.84) |
| ALL | MCM | 1.07 (0.96) | -0.46 (0.16) | 0.63 (0.73) | 1.03 (0.98) | 2.56 (-1.90) | 32393 | 80.32 (81.04) |