Supplement of

Regional evaluation of the performance of the global CAMS chemical modeling system over the United States (IFS cycle 47r1)

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Table S1: Updates to the C$_3$H$_8$ oxidation scheme in CBA as compared to Huijnen et al. (2019). [1] Stavrakou et al. (2010), [2] Lamarque et al. (2012), [3] Myriokefalitakis et al. (2020), [4] spectral absorption data from http://iupac.pole-ether.fr (last access: 21 Sept 2021), [5] Quantum Yields as for 298K.

| Reaction | Rate expression | Reference |
|----------|----------------|-----------|
| OH + ISOP $\rightarrow$ 0.65 ISOPBO$_2$ + 0.35 ISOPDO$_2$ | $2.7 \times 10^{-12} \times \exp(390/T)$ | [1] |
| ISOPBO$_2$ $\rightarrow$ HPALD1 + HO$_2$ | $4.1 \times 10^8 \times \exp(-7700/T)$ | [1],[3] |
| ISOPBO$_2$ $\rightarrow$ ISPD + CH$_2$O + HO$_2$ | $2.08 \times 10^{11} \times \exp(-8993/T)$ | [1] |
| ISOPDO$_2$ $\rightarrow$ HPALD2 + HO$_2$ | $4.1 \times 10^8 \times \exp(-7700/T)$ | [1],[3] |
| ISOPDO$_2$ $\rightarrow$ ISPD + CH$_2$O + HO$_2$ | $2.08 \times 10^{11} \times \exp(-8993/T)$ | [1] |
| ISOPBO$_2$ + HO$_2$ $\rightarrow$ ISOPOOH | $2.05 \times 10^{-13} \times \exp(1300/T)$ | [2] |
| ISOPBO$_2$ + NO $\rightarrow$ 0.08 ORGNTR + 0.92 NO$_2$ + HO$_2$ + 0.51 CH$_2$O + 0.55 ISPD + 0.37 HPALD1 | $4.4 \times 10^{-12} \times \exp(180/T)$ | [2] |
| ISOPDO$_2$ + HO$_2$ $\rightarrow$ ISOPOOH | $2.05 \times 10^{-13} \times \exp(1300/T)$ | [2] |
| ISOPDO$_2$ + NO $\rightarrow$ 0.08 ORGNTR + 0.92 NO$_2$ + HO$_2$ + 0.51 CH$_2$O + 0.55 ISPD + 0.37 HPALD2 | $4.4 \times 10^{-12} \times \exp(180/T)$ | [2] |
| OH + ISOPPOOH $\rightarrow$ 0.1 XO$_2$ + 0.4 CH$_3$COCHO + 0.3 CHOCHO + 0.12 ISOPBO$_2$ + 0.08 ISOPDO$_2$ | $1.52 \times 10^{-11} \times \exp(200/T)$ | [1] |
| ISOPOOH + hv $\rightarrow$ 0.69 ISPD + 0.69 HCHO + HO$_2$ | Explicit | [4] |
| OH + HPALD1 $\rightarrow$ 0.65 XO$_2$ + 0.25 CHOCHO + 0.1 CH$_3$COCHO | $1.86 \times 10^{-11} \times \exp(175/T)$ | [2] |
| HPALD1 + hv $\rightarrow$ OH + HO$_2$ + 0.5 HYAC + 0.5 CH$_3$COCHO + 0.5 GLYALD + HCHO | Explicit | [4] |
| OH + HPALD2 $\rightarrow$ 0.65 XO$_2$ + 0.25 CHOCHO + 0.1 CH$_3$COCHO | $1.86 \times 10^{-11} \times \exp(175/T)$ | [1] |
| HPALD2 + hv $\rightarrow$ HO$_2$ + OH + 0.5 HYAC + 0.5 CHOCHO + 0.5 GLYALD + HCHO | Explicit | [4] |
| OH + CHOCHO $\rightarrow$ 0.63 HO$_2$ + 1.26 CO + C$_2$O$_3$ | $3.1 \times 10^{-12} \times \exp(340/T)$ | [1] |
| CHOCHO + hv $\rightarrow$ 2 CO + 2 HO$_2$ | Explicit | [4],[5] |
| CHOCHO + hv $\rightarrow$ HCHO + CO | Explicit | [4],[5] |
| OH + GLYALD $\rightarrow$ 0.25 OH + 0.75 HO$_2$ + 0.17 CHOCHO + 0.17 HCOOH + 0.67 HCHO + 0.5 CO | $8.0 \times 10^{-12}$ | [1] |
| GLYALD + hv $\rightarrow$ 2 HO$_2$ + CO + HCHO | Explicit | [4] |
| OH + HYAC $\rightarrow$ 0.1 OH + 0.825 HO$_2$ + 0.75 CH$_3$COCHO + 0.125 HCOOH + 0.125 CH$_3$O$_2$ + 0.125 CH$_3$COOH + 0.05 CO | $2.0 \times 10^{-12} \times \exp(320/T)$ | [1] |
| HYAC + hv $\rightarrow$ C$_2$O$_3$ + HO$_2$ + HCHO | As J(CH$_3$COCH$_3$) | [1] |
Table S2: Updates to the oxidation of TOL and XYL as implemented in the IFS(CBA) chemistry as compared to Huijnen et al. (2019). The reaction scheme is adapted from Karl et al. (2009), with modification to the product distribution for loss of AROO$_2$ following Myriokefalitakis et al. (2020). (*) This indicates the final rate applied accounts for the ortho-, meta- and para-isomers of the cyclic aromatics.

| Reaction | Rate expression |
|----------|----------------|
| OH + TOL → 5PAR + AROO$_2$ | 5.96 x 10$^{-12}$ |
| O$_3$ + TOL → 5PAR + AROO$_2$ | 2.34 x 10$^{-17}$ x exp(-6694/T) |
| NO$_3$ + TOL → ORGNTR + PAR | 6.8 x 10$^{-17}$ |
| OH + XYL → 5PAR + AROO$_2$ | avg of (1.3 x 10$^{-11}$, 2.36 x 10$^{-11}$, 1.43 x 10$^{-11}$)* |
| O$_3$ + XYL → 5PAR + AROO$_2$ | avg of (5.37 x 10$^{-13}$ x exp(-6039/T), 1.91 x 10$^{-13}$ x exp(-5586/T), 2.4 x 10$^{-13}$ x exp(-5586/T)) |
| NO$_3$ + XYL → CH$_3$COCHO + PAR | avg of (3.6 x 10$^{-16}$, 2.33 x 10$^{-16}$, 4.5 x 10$^{-16}$)* |
| NO + AROO$_2$ → NO$_2$ + CHOCHO + 0.33 CH$_3$COCHO | 4.2 x 10$^{-12}$ x exp(180/T) |
| XO$_2$ + AROO$_2$ | 1.7 x 10$^{-14}$ x exp(1300/T) |
| HO$_2$ + AROO$_2$ → ROOH + CHOCHO | 3.5 x 10$^{-13}$ x exp(1000/T) |
| AROO$_2$ + AROO$_2$ | 1.7 x 10$^{-14}$ x exp(1300/T) |

Table S3: Details related to the inclusion of HCN and CH$_3$CN in IFS(CBA), with rate expressions coming from Atkinson et al. (2004).

| Reaction | Rate expression | Comments |
|----------|----------------|----------|
| OH + HCN → | 1.2 x 10$^{-13}$ x exp(-400/T) | No products defined |
| OH + CH$_3$CN → 0.3HCN | 8.1 x 10$^{-13}$ x exp(-1080/T) | Products not completely defined |
Figure S1. The horizontal seasonal mean for tropospheric OH below 1km over the US domain for JJA 2014 (top) and DJF (2014/2015).

Figure S2. The horizontal seasonal mean for tropospheric NO below 1km over the US domain for JJA 2014 (top) and DJF (2014/2015).
**Figure S3.** Comparisons of lower tropospheric NO profiles for 2014/2015 against composites of aircraft measurements for the regional domains shown in Figure 1. Campaigns shown (top left to bottom right) are DISCOVER-AQ, FRAPPE, WINTER and SONGNEX.

**Figure S4.** The horizontal seasonal mean for tropospheric HNO$_3$ below 1km over the US domain for JJA 2014 (top) and DJF (2014/2015).
Figure S5. Comparisons of lower tropospheric HNO$_3$ profiles for 2014/2015 against composites of aircraft measurements for the regional domains shown in Figure 1. Campaigns shown (top left to bottom right) are DISCOVER-AQ, FRAPPE, WINTER and SONGNEX.

Figure S6. The horizontal seasonal mean for tropospheric PAN below 850 hPa over the US domain for JJA 2014 (top) and DJF (2014/2015).
Figure S7. Comparisons of lower tropospheric PAN profiles for 2014/2015 against composites of aircraft measurements for the regional domains shown in Figure 1. Campaigns shown (top left to bottom right) are DISCOVER-AQ, FRAPPE, WINTER and SONGNEX.

Figure S8. Seasonal zonal mean distributions of PAN profiles for 2014/2015 over the US domain.
Figure S9. Comparisons of the [HNO₃]/[N₂O₅] ratio between nighttime observations and those simulated in the IFS, with the associated correlation coefficients being given in each panel.

| Month/region | nobs | mean observations | IFS(CBA) | IFS(MOC) | IFS(MOZ) | CAMSRA |
|--------------|------|-------------------|----------|----------|----------|---------|
| 05.2014 /ND | 2558 | 59.4 ± 32.4       | -15.3 ± 16.9 | -14.3 ± 16.9 | -13.2 ± 17.0 | -9.5 ± 17.2 |
| 06.2014 /NM | 478  | 60.5 ± 3.5        | 11.4 ± 7.8  | 10.8 ± 7.8  | 8.8 ± 7.8  | 6.8 ± 8.1  |
| *07.2014/Col| 450  | 62.7 ± 6.3        | -7.3 ± 7.0  | -5.7 ± 7.9  | -5.2 ± 7.2  | -16.6 ± 7.4 |
| 07.2014/Col | 2838 | 61.8 ± 9.9        | -5.3 ± 2.2  | 0.5 ± 2.6   | -4.5 ± 2.4  | -11.1 ± 2.3 |
| *08.2014/Col| 354  | 62.0 ± 8.4        | -4.6 ± 6.7  | 0.0 ± 7.2   | -5.0 ± 6.8  | -16.2 ± 7.6 |
| 08.2014/Col | 1024 | 63.2 ± 9.5        | 2.2 ± 4.1   | 6.0 ± 4.0   | 0.1 ± 4.0   | -7.9 ± 3.9  |
| 02.2015/EC  | 1054 | 37.7 ± 2.7        | 1.2 ± 2.9   | 4.9 ± 2.9   | 11.8 ± 3.0  | 0.7 ± 3.4   |
| 03.2015/EC  | 477  | 45.5 ± 4.3        | -1.7 ± 3.8  | 2.5 ± 3.8   | 9.8 ± 3.9   | 0.5 ± 4.2   |
| 03.2015/Col | 3434 | 49.4 ± 3.7        | 0.6 ± 1.3   | 3.9 ± 1.6   | 4.7 ± 1.6   | 2.5 ± 1.3   |
| 04.2015/ND  | 4018 | 51.2 ± 7.7        | 0.5 ± 0.6   | 2.0 ± 0.6   | 5.8 ± 0.6   | 6.7 ± 0.8   |
| 04.2015/Col | 2560 | 53.3 ± 3.6        | -0.9 ± 1.8  | 6.8 ± 1.5   | 6.6 ± 1.7   | -0.8 ± 1.6  |
| 04.2015/Texas| 1869 | 44.0 ± 11.9       | 5.5 ± 2.6   | 5.3 ± 2.6   | 5.1 ± 2.6   | 5.3 ± 2.6   |

Table S4. Mean biases and standard deviations from the mean of tropospheric O₃ for the lower troposphere using all valid points aggregated over the selected days for each of the aircraft campaigns presented in Table 9. Only points below 815 hPa (Colorado) or 900 hPa (EC,ND,Texas) are included thus limiting the sample size but minimizing transport effects. Each mean bias is calculated as the difference between the IFS mini-ensemble member minus observational value from the respective aircraft campaign. In addition, the number of observations (‘n. obs’) and observational mean, and its standard deviation, are given.
| Month/region | nobs | mean observations | IFS(CBA) | IFS(MOC) | IFS(MOZ) | CAMSRA |
|-------------|------|------------------|----------|----------|----------|--------|
| 05.2014 /ND | 2558 | 125.5 ± 6.4 | -3.6 ± 3.9 | -11.1 ± 3.9 | -31.9 ± 3.8 | 2.4 ± 4.1 |
| 06.2014 /NM | 478  | 145.2 ± 34.3 | -41.6 ± 13.6 | -50.8 ± 13.5 | -62.1 ± 13.6 | -34.9 ± 13.6 |
| *07.2014/ Col | 437  | 131.3 ± 6.6 | 22.2 ± 27.2 | 5.5 ± 26.6 | 6.1 ± 26.6 | 15.8 ± 32.7 |
| *08.2014/ Col | 366  | 125.3 ± 12.0 | 15.2 ± 33.9 | 1.5 ± 40.0 | -0.4 ± 34.1 | 15.4 ± 42.2 |
| 08.2014/Col | 1081 | 118.1 ± 26.9 | 4.1 ± 7.8 | -9.2 ± 7.6 | -11.1 ± 7.6 | -9.3 ± 7.5 |
| 02.2015/EC | 1047 | 158.4 ± 10.0 | -12.0 ± 13.9 | -21.0 ± 13.9 | -36.5 ± 13.8 | -11.7 ± 14.6 |
| 03.2015/EC | 487  | 147.5 ± 11.5 | -10.8 ± 11.7 | -20.1 ± 11.7 | -38.0 ± 11.8 | -8.5 ± 12.1 |
| 03.2015/Col | 3291 | 135.4 ± 20.6 | -10.9 ± 7.3 | -21.8 ± 7.2 | -38.1 ± 7.2 | -7.5 ± 8.2 |
| 04.2015/ND | 3742 | 127.9 ± 17.5 | -5.1 ± 0.7 | -16.8 ± 0.4 | -36.2 ± 0.1 | -2.1 ± 0.8 |
| 04.2015/Col | 2459 | 173.1 ± 47.3 | -10.9 ± 21.2 | -22.8 ± 20.7 | -39.9 ± 20.1 | -10.6 ± 15.1 |
| 04.2015/Texas | 1793 | 133.0 ± 11.0 | -4.8 ± 1.8 | -18.0 ± 1.7 | -29.2 ± 1.5 | 1.5 ± 2.8 |

70 Table S5: As for Table S4 except for tropospheric CO

| Month/region | nobs | mean observations | IFS(CBA) | IFS(MOC) | IFS(MOZ) | CAMSRA |
|-------------|------|------------------|----------|----------|----------|--------|
| *07.2014/ Col | 452  | 2462 ± 572 | -359 ± 829 | -564 ± 849 | -345 ± 802 | 324 ± 1096 |
| 07.2014/ Col | 2894 | 1764 ± 109 | -33 ± 291 | -350 ± 299 | 8 ± 306 | 91 ± 314 |
| *08.2014/Col | 367  | 1971 ± 464 | -249 ± 592 | -380 ± 594 | -209 ± 558 | 254 ± 799 |
| 08.2014/Col | 1038 | 2125 ± 1041 | -816 ± 303 | -931 ± 302 | -752 ± 304 | -857 ± 296 |
| 02.2015/EC | 837  | 458 ± 239 | -199 ± 157 | -128 ± 159 | -158 ± 156 | -318 ± 169 |
| 03.2015/EC | 638  | 506 ± 186 | -211 ± 170 | -127 ± 186 | -126 ± 167 | -320 ± 172 |
| 03.2015/Col | 3345 | 800 ± 140 | -306 ± 150 | -243 ± 149 | -163 ± 149 | -371 ± 145 |
| 04.2015/Col | 2579 | 1055 ± 384 | -313 ± 362 | -220 ± 355 | -150 ± 361 | -578 ± 363 |
| 04.2015/Texas | 1659 | 874 ± 530 | 136 ± 77 | -2 ± 63 | 182 ± 65 | -35 ± 65 |

Table S6. As for Table S4 except for tropospheric CH$_2$O.
### Table S7.

As for Table S4 except for tropospheric NO$_2$ with mean biases and associated standard deviations are given in ppt.

| Month/region | nobs | mean observations | IFS(CBA) | IFS(MOC) | IFS(MOZ) | CAMSRA |
|--------------|------|-------------------|----------|----------|----------|--------|
| *07.2014/ Col | 469  | 2284 ± 955        | 488 ± 1913 | -64 ± 1838 | -6 ± 1808 | 865 ± 2216 |
| 07.2014/ Col  | 2329 | 915 ± 776         | -218 ± 642 | -358 ± 641 | -383 ± 641 | -330 ± 666 |
| *08.2014/Col  | 359  | 2071 ± 603        | 141 ± 2086 | 33 ± 2120 | -22 ± 2108 | 793 ± 2496 |
| 08.2014/Col   | 907  | 1732 ± 1766       | -965 ± 661 | -1048 ± 655 | -1097 ± 652 | -1216 ± 659 |
| 02.2015/EC    | 973  | 2535 ± 812        | -276 ± 1128 | -374 ± 1139 | -299 ± 1120 | -896 ± 1108 |
| 03.2015/EC    | 470  | 1446 ± 879        | -300 ± 1170 | -240 ± 1125 | -406 ± 1089 | -717 ± 1045 |
| 03.2015/Col   | 3345 | 788 ± 236         | -164 ± 501 | -230 ± 507 | -254 ± 502 | -129 ± 501 |
| 04.2015/ND    | 3962 | 163 ± 167         | -70 ± 194  | -77 ± 194  | -69 ± 194  | -61 ± 196  |
| 04.2015/Col   | 2297 | 2293 ± 834        | 1408 ± 834 | 404 ± 651  | 125 ± 650  | 2293 ± 640 |
| 04.2015/Texas | 1799 | 389 ± 287         | 195 ± 271  | 202 ± 269  | 158 ± 267  | 161 ± 266  |

### Table S8.

As for Table S4 except for tropospheric NO with mean biases and associated standard deviations are given in ppt.
| Month/region | nobs | mean observations | IFS(CBA) | IFS(MOC) | IFS(MOZ) | CAMSRA |
|--------------|------|-------------------|----------|----------|----------|--------|
| *07.2014/ Col | 251  | 1058 ± 414        | 75 ± 373 | 428 ± 450 | 513 ± 474 | -21 ± 302 |
| 07.2014/ Col  | 11962| 1991 ± 466        | -745 ± 1083 | -208 ± 1229 | -180 ± 1252 | -793 ± 986 |
| *08.2014/Col  | 262  | 1122 ± 425        | 482 ± 403 | 878 ± 493 | 960 ± 484 | -156 ± 295 |
| 08.2014/Col   | 12541| 2061 ± 361        | -561 ± 756 | -182 ± 758 | -175 ± 745 | -1072 ± 765 |
| 02.2015/EC    | 752  | 174 ± 95          | 97 ± 150 | 441 ± 275 | 328 ± 264 | 89 ± 164  |
| 03.2015/EC    | 487  | 509 ± 246         | 55 ± 564 | 64 ± 544 | 272 ± 673 | 309 ± 518 |
| 03.2015/Col   | 3356 | 618 ± 542         | -559 ± 202 | -493 ± 189 | -494 ± 191 | -64 ± 201 |
| 04.2015/ND    | 3230 | 88 ± 67           | -47 ± 33 | -49 ± 34 | -38 ± 33 | -3 ± 34 |
| 04.2015/Col   | 2481 | 657 ± 460         | -562 ± 179 | -474 ± 184 | -450 ± 186 | 56 ± 251 |
| 04.2015/Texas | 1746 | 320 ± 211         | -279 ± 48 | -279 ± 50 | -261 ± 51 | -70 ± 57 |

**Table S9.** As for Table S1 except for tropospheric HNO$_3$ with mean biases and associated standard deviations are given in ppt