Additional model documentation

Equations

To compute the NOx recycling efficiency () and RONO2 lifetime ( we use Eq (1) and Eq (2):

(1)

(2)

where P (NOx) and Loss (NOx) refer to the re-released NOx due to oxidation and photolysis of RONO2, and loss of NOx due to the production of RONO2, respectively. Loss (RONO2) is loss rate of RONO2. This lifetime does not include reactions that convert one nitrate into a different nitrate. In contrast, to calculate the lifetime of specific individual molecules we consider all reactions.

A simplified scheme, as an example, provides more detail on the approach used.

|  |  |  |
| --- | --- | --- |
| Reactants | Products | Species to track rates |
| BVOC + OH | RO2 |  |
| RO2 + NO | α AN1 + (1- α) NO2 | + α LNOX |
| AN1 + OH/O3/hv | γ ΑΝ2 + (1- γ) NO2 | + (1- γ) PNOX1 +LAN1 |
| AN2 + OH/hv | NO2 | + PNOX2 + LAN2 |

LAN1, LAN2, LNOX are used to track insatantanous loss of first- and second-generation RONO2 (AN1 and AN2) and NOx at each time step. PNOX1and PNOX2 track instantaneous re-released NOx due to loss of first- and second-generation RONO2. Thus, NOx recycling efficiency and lifetime of first- and total RONO2 at each time step are calculated as:

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Reactants | Products | Rate | References | Status |
| ISOP+HO2 | 0.628 ISHPA+0.272 ISHPB+0.037 ISHPD+0.063 HO+0.063 HO2+0.063 HCHO+0.025 MACR+0.038 MVK | 2.06D-13 exp(1300/T) | (Liu et al., 2013; St. Clair et al., 2015) | Modified |
| ISHPA+HO | 0.75 ISOP+0.25 HC5 +0.125 HO+0.125 H2O | 6.13D-12exp(200/T) |  | Added |
| ISHPB+HO | 0.480 ISOP+0.520 HC5+0.26 HO+0.26 H2O | 4.14D-12exp(200/T) |  | Modified |
| ISHPD+HO | 0.250 ISOP+0.750 HC5+0.375 HO+0.375 H2O | 5.11D-12exp(200/T) |  | Added |
| ISHPA+HO | 0.578 IEPOXA+0.272 IEPOXB+0.850 HO+0.150 HC5P | 1.7D-11exp(390/T) |  | Added |
| ISHPB+HO | 0.68 IEPOXA+0.32 IEPOXB+1.00 HO | 2.97D-11exp(390/T) |  | Modified |
| ISHPD+HO | 0.50 IEPOXD+0.50 HC5P+0.50 HO | 2.92D-11exp(390/T) |  | Added |
| IEPOXA+HO | IEPOXOO | 3.73D-11exp(-400/T) |  | Added |
| IEPOXB+HO | IEPOXOO | 5.79D-11exp(-400/T) |  | Modified |
| IEPOXD+HO | IEPOXOO | 3.20D-11exp(-400/T) |  | Added |
| ISOP+NO | 0.4 MVK+0.26 MACR+0.883 NO2+0.0117 ISOPND+0.1053 ISOPNB+0 .66 HCHO+0.143 UHC+0.08 DIBOO+0.803 HO2 | 2.7D-12exp(360/T) |  | Modified |
| ISOPNB+O3 | 0.541 HCHO+0.506 CO+0.526 HO+0.327 NO2+0.179 HAC+0.102 H2O2+0.349 MACRN+0.112 IMONIT+0.128 CO2+0.327 HO2+0.068 ORA1+0.212 MVKN+0.14 8 MGLY | 3.7D-19 |  | Modified |
| ISOPND+O3 | 0.266 PROPNN+0.017 ORA2+0.249 GLYC+0.075 H2O2+0.89 HO+0.445 HO2+0.214 CO+0.214 HCHO+0.445 NO2+0.271 ETHLN+0.018 IMONIT+0.445 MGLY+0 .289 HAC+0.231 GLY | 2.9D-17 |  | Modified |
| ISOPNB+HO | 0.88 ISOPNBO2+0.12 IEPOXA+0.12 NO2 | 2.4D-12exp(745/T) |  | Modified |
| ISOPND+HO | ISOPNDO2 | 1.2D-11exp(652/T) |  | Modified |
| ISOPNDO2+NO | 0.15 PROPNN+0.44 HAC+0.07 MVKN+0.13 ETHLN+0.31 ORA1+0 .31 NO3+0.72 HCHO+0.15 GLYC+1.34 NO2+0.35 HO2+0.34 HKET | 2.4D-12exp(360/T) |  | Modified |
| ISOPNBO2+NO | 0.29 GLYC+0.29 HAC+0.71 HCHO+0.71 HO2+0.461 MACRN+0.249 MVKN+1.29 NO2 | 2.4D-12exp(360/T) |  | Modified |
| MVK+HO | MVKP | 2.60D-12exp(610/T) |  | Modified |
| MVKP+NO | 0.716 GLYC+0.716 ACO3+0.249 MGLY+0.249 HCHO+0.249 HO2+0.035 MVKN+0.965 NO2 | 2.7D-12exp(350/T) |  | Modified |
| MVKP+HO2 | 0.38 VRP+0.37 GLYC+0.37 ACO3+0.62 HO+0.13 KET+0.25 HO2+0.12 MGLY+0.12 HCHO | 1.82D-13exp(1300/T) |  | Modified |
| ISO+NO3 | INO2 | 3.15D-12exp(-450/T) | MCM v3.3.1 | Modified |
| INO2+NO3 | 0.54 ICN+0.42 MVK+0.04 MACR+1.46 NO2+0.54 HO2+0.46 HCHO | 2.30D-12 |  | Added |
| INO2+INO2 | 0.39 INO+0.728 ICN+0.10 MACR+0.616 IHND+0.154 IHNB | 5.2D-12 |  | Added |
| INO{+O2} | 0.88 ICN+0.88 HO2+0.12 NO2+0.12 HCHO+0.12 MACR | 2.5D-14exp(-300/T) |  | Added |
| ICN+NO3 | NH4CO3+HNO3 | 6.3D-12exp(-1860/T) | MCM v3.3.1 | Added |
| NH4CO3+NO | PROPNN+CO+HO2+NO2 | 7.5D-12exp(-690/T) | MCM v3.3.1 | Added |
| NH4CO3+NH4CO3 | 0.3 R4N+0.7 PROPNN +0.7 HO2+0.7 CO | 1.0D-11 | MCM v3.3.1 | Added |
| ICN+HO | 0.52 R4NO+ CO+0.52 HO2+0.48 R4N+0.48 HO | 4.1D-11 | MCM v3.3.1  & Schwantes(2015) | Added |
| IHND+HO | 0.92 IDHNO2D+0.08 IEPOXD+0.08 NO2 | 1.1D-10 |  | Added |
| IHNB+HO | IDHNO2B | 4.2D-11 |  | Added |
| IDHNO2D+NO3 | HO2+NO2+0.12 HAC+0.12 ETHLN+0.8 GLYC+0.80 PROPNN+0.08 R4N+0.08 HCHO | 2.3D-12 |  | Added |
| IDHNO2B+NO3 | HO2+NO2+0.76 HAC+0.76 ETHLN+0.23 R4N+0.23 HCHO | 2.3D-12 |  | Added |
| INO2+HO2 | 0.22 MVK+0.015 MACR+0.235 NO2+0.235 HO+0.235 HCHO+0.54 INPD+0.23 INPB | 2.06D-13exp(1300/T) |  | Added |
| INPD+HO | HO2+INO2 | 6.9D-12 |  | Added |
| INPB+HO | HO2+INO2 | 6.9D-12 |  | Added |
| INPD+HO | 0.37 INHED+0.37 HO+0.63 INPHO2D | 1.1D-10 |  | Added |
| INPB+HO | 0.78 INHEB+0.78 HO+0.22 INPHO2B | 4.2D-11 |  | Added |
| INPHO2B+NO3 | NO2+HO2+HCHO+R4NO | 2.3D-12 |  | Added |
| INPHO2D+NO3 | NO2+HO2+0.92 PROPNN+0.92 GLY+0.08 HAC+0.08 ETHLN | 2.3D-12 |  | Added |
| INHED+HO | 0.27 HAC+0.73 CO+0.27 NO2+0.27 HCHO+0.27 PROPNN+0.27 GLY+0.46 R4N | 8.4D-12 |  | Added |
| INHEB+HO | 0.30 PROPNN+0.30 GLY+0.31 GLYC+0.31 MGLY+0.09 HAC+0.43 NO2+0.39 HCHO+0.01 ETHLN+0.01 HAC+0.12 KET+0.26 R4N | 1.25D-11 |  | Added |
| R4N+HO | PROPNN+HO2+CO | 1.7D-11 |  | Added |
| R4NO+HO | PROPNN+HO+CO | 1.7D-11 |  | Added |
| INPD+hv | INO+HO | j(Pj\_ch3o2h) | MCM v3.3.1  Schwantes et al. (2015) | Added |
| INPB+hv | INO+HO | j(Pj\_ch3o2h) | MCM v3.3.1  Schwantes et al. (2015) | Added |
| ICN+hv | PROPNN+CO+CO+HO2+HO2 | 10\*j(Pj\_noa) |  | Added |
| R4N+hv | NO2+ACO3+0.5 ETHP+0.5 MO2 | j(Pj\_ch3coc2h5) | MCM v3.3.1  Schwantes et al. (2015) | Added |
| R4NO+hv | HO+MGLY+HCHO+NO2 | j(Pj\_ch3coc2h5) | MCM v3.3.1  Schwantes et al. (2015) | Added |
| IHND+hv | HO2+NO2+UHC+DIBOO | j(Pj\_onit1) | Same as ISOPND | Added |
| IHNB+hv | HO2+NO2+UHC+DIBOO | j(Pj\_onitOH3) | Same as ISOPNB | Added |
| PROPNN+hv | NO2+ACO3+HCHO | 10\*j(Pj\_noa) | Müller et al. (2014) | Modified |
| ETHLN+hv | HO2+CO+HCHO+NO2 | 10\*j(Pj\_noa) | (Müller et al., 2014) | Modified |
| MACRN+hv | NO2+CO+HAC+HO2 | 10\*j(Pj\_ibutald) | (Müller et al., 2014) | Modified |
| MVKN+hv | GLYC+NO2+ACO3 | 10\*j(Pj\_noa) | (Müller et al., 2014) | Modified |
| API+NO3 | 0.10 TOLNN+0.90 TOLND | 8.33D-13exp(490/T) | MCM v3.3.1 | Modified |
| UTONIT+NO3 | HONIT | 3.15D-13exp(-448/T) |  | Added |
| UTONIN+NO3 | HONIT | 3.15D-13exp(-448/T) |  | Added |
| TONIN+NO3 | HONIT | 3.15D-13exp(-448/T) |  | Added |
| TONIT+NO3 | HONIT | 3.15D-13exp(-448/T) |  | Added |
| TONIH+NO3 | HONIT | 3.15D-13exp(-448/T) |  | Added |

Table S1: Isoprene and Monoterpene reactions added to/revised from RACM2\_Berkeley.

|  |  |  |  |
| --- | --- | --- | --- |
| Species | Description | Species | Description |
| ISHPA | (1,2) hydroxy hydro peroxides | INO2 | Isoprene nitrooxy peroxy radical |
| ISHPB | (4,3) hydroxy hydro peroxides | ICN | C5 carbonyl nitrate |
| ISHPD | delta (1,4 and 4,1) hydroxy hydro peroxides | INO | C5 nitrooxyalkoxy radical |
| IEPOXA | trans-β isoprene-derived dihydroxy  epoxide | IHND | C5 hydroxy nitrate – β isomer |
| IEPOXB | cis-β isoprene-derived dihydroxy  epoxide | IHNB | C5 hydroxy nitrate – δ isomer |
| IEPOXD | delta isoprene-derived dihydroxy  epoxide | NH4CO3 | Radical from ICN |
| R4N | C4 carbonyl hydroxynitrate | INPB | C5 nitrooxy hydroperoxide – β isome |
| R4NO | C4 nitrooxycarbonyl hydroperoxide | INPHO2B | C5 nitrooxy hydroperoxy hydroxy peroxy radical (From β isomers) |
| IDHNO2D | C5 dihydroxy nitrooxyperoxy radical – δ isomer | INPHO2D | C5 nitrooxy hydroperoxy hydroxy peroxy radical (From δ isomers) |
| IDHNO2B | C5 dihydroxy nitrooxyperoxy radical– β isomer | INHED | C5 nitrooxy hydroxy epoxide – δ isomer |
| INPD | C5 nitrooxy hydroperoxide – δ isomer | INHEB | C5 nitrooxy hydroxy epoxide – β isomer |

Table S2: New chemical species that are introduced in RACM2\_Berkeley2 mechanism.

|  |  |  |
| --- | --- | --- |
| Species | H\* (M atm-1) | f0 |
| ISOPND, ISOPNB, IMONIT,  MACRN,  MVKN, INPD, INPB, ICN, R4N, R4NO, IHND, IHNB, TONIT, UTONIT, TONIN, UTONIN, TONIH | 2.00E+06 | 1 |
| PROPNN | 5.0E+5 | 1 |
| ISHPA, ISHPB, ISHPD | 1.0E+14 | 0 |
| IEPOXA, IEPOXB, IEPOXD, INHEB, INHED | 8.0E+7 | 1 |
| GLYC | 2.00E+7 | 1 |
| HAC | 1.4E+6 | 1 |
| H2O2 | 5.0E+7 | 1 |

Table S3: Changes to dry deposition parameters for isoprene chemistry species and organic nitrate species as recommended by Nguyen et al. (2015). H\* is the Henry’s law coefficient and f0 is the reactivity factor as defined in Wesely (1989).

# Figure captions

Figure S1: The concentration of tertiary organic nitrates versus their loss rates through deposition and hydrolysis during SOAS. Slopes of the linear fit give the lifetimes against deposition and hydrolysis of tertiary organic nitrates.

Figure S2: Median diurnal cycles of observed and simulated NO and OH concentrations at Centreville (CTR) during the 2013 SOAS campaign. The vertical bars show the interquartile range of the hourly data. The panel includes mean of the simulated and observed concentrations.

Figure S3: The (a) simulated and (b) observed concentration of C5 hydroxy nitrate, MVKN+MACRN, C5 nitrooxy hydroperoxide [first panel], Propanone nitrate (PROPNN), Ethanal nitrate (ETHLN), C5 carbonyl nitrate (ICN) [second panel], and terpene hydroxynitrates, terpene nitrooxy hydroperoxide, and anthropogenic organic nitrates (Others) [3rd panel] in June 2013 during the SOAS field campaign. At the figure (b) on 3rd panel, observed ethyl Nitrate + propyl Nitrate is shown.

Figure S4: Median diurnal cycles of observed and simulated CH2O, isoprene and monoterpenes at Centreville during the 2013 SOAS campaign. The vertical bars show the interquartile range of the hourly data. The panel includes mean of the simulated and observed values.

Figure S5: Fraction of isoprene nitrates from OH and NO3 oxidations to total isoprene nitrate production at boundary layer at the CTR site during SOAS.

Figure S6: The concentrations of organic nitrates versus their loss rates (black) and production rates (blue) at 12:00-16:00 during SOAS. Slopes of the linear fit give lifetime of organic nitrates.

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