## Conditions of the Simulations

Location: 44.4N, 73.9W, z = 1.5 km, Whiteface Mountain (WFM) summit
Start time: 1730 (5:30 pm) local time September 17, 2016
End time:  1500 (3 pm) local time September 18, 2016
Note that the date is for photolysis reaction rates.

*State variables:*
Temperature: 286K
Pressure: 847 hPa
Air density: 1.032 kg/m$^3$  (actually dry air density, water vapor not included)
Water vapor: $16.19 \times 10^{-3}$ mol/mol = 10.068 g/kg
For clear air relative humidity, use water vapor = 9.06 g/kg to get RH = 90%.

Simulation 1: Clear Sky Only
Simulation 2: Cloud Water = 0.78 g/kg (Table 1),  pH = 4.5
Simulation 3: Cloud Water = 0.78 g/kg,  pH varies as calculated by model
Simulation 4: Cloud Water varies following WFM measurements (Table 2) ; pH varies
See Tables 1 and 2 for prescribed cloud water amounts.

For all cloud water simulations, set drop size to *10 micron radius*

*Trace Gases*
Initial concentrations are provided in Table 3.

*Aerosols*
Table 4 lists WRF-Chem results for several aerosol species in 4 size bins. The total PM2.5 composition is used to initialize the box model simulations. These concentrations are repeated here, but are in nmol/mol-air units.

| Aerosol Species | Concentration | Volume mixing ratio |
|---|---|---|
| Sulfate, <2.5 um diameter | 1.5774 ug/kg | 0.476 ppbv |
| Ammonium, <2.5 um diameter | 0.1005 ug/kg | 0.16175 ppbv |
| Organic carbon, <2.5 um diameter | 0.5196 ug/kg | 0.62664 ppbv |

For these concentrations, use sulfate and ammonium as the activated aerosol in the cloud drops. Therefore, for qc = 0.78 g/kg, the aqueous concentrations are $[SO_4^{2-}]$ = 21.066μM, $[NH_4^+]$ = 7.16μM, giving $[H^+]$=13.91μM and pH=4.86.

*Photolysis Rates*
Clear sky (no cloud, but some aerosol) photolysis rates were calculated from Troposphere UltraViolet and Visible (TUV) radiation model version 5.3
https://www2.acom.ucar.edu/modeling/tropospheric-ultraviolet-and-visible-tuv-radiation-model for conditions listed in Table 5.
The diurnally-varying photolysis rates for several trace gases are given in the file CLEARSKY_JVALUES_18Sept.txt.

*Output*

Please provide time series concentrations of the following species and parameters.

<u>Gas and aqueous-phase concentrations</u>

- O3, NOx (or NO and NO2 separately), HNO3, NO3, N2O5, PAN, other organic nitrates (total)
- OH, HO2, CH3OO, H2O2, CH3OOH, isoprene, glyoxal, methyl glyoxal, SO2
- organic aldehydes (C1-C3 aldehydes given individually, lump C4 and higher aldehydes)
- organic acids (C1-C3 acids given individually, lump C4 and higher acids)
- use **ppbv** (or mol/mol) for gas phase and **Molar** for aqueous phase

- Aqueous-phase nitrate and sulfate concentrations (Molar) and pH

Please provide a description of gas and aqueous chemical mechanism and method used to solve it.

Table 1. Cloud water for Simulations 2 and 3

| Time (LT) | Cloud Water (g/kg) |
|-----------|--------------------|
| 17:30:00 | 0.00 |
| 17:59:58 | 0.00 |
| 17:59:59 | 0.01 |
| 18:00:00 | 0.78 |
| 38:00:00 | 0.78 |
| 38:00:01 | 0.01 |
| 38:00:02 | 0.00 |
| 39:00:00 | 0.00 |

38:00 = 1400 LT on next day

Table 2. Cloud water for Simulation 4

| Time (LT) | Cloud Water (g/kg) |
|-----------|--------------------|
| 17:30:00 | 0.00 |
| 17:59:58 | 0.00 |
| 17:59:59 | 0.01 |
| 18:00:00 | 0.636 |
| 18:30:00 | 0.765 |
| 19:30:00 | 0.760 |
| 20:30:00 | 0.753 |
| 21:30:00 | 0.959 |
| 22:30:00 | 0.998 |
| 23:30:00 | 1.021 |

| | |
|---|---|
| 24:30:00 | 0.998 |
| 25:30:00 | 1.010 |
| 26:30:00 | 1.043 |
| 27:30:00 | 0.934 |
| 28:30:00 | 0.720 |
| 29:30:00 | 0.801 |
| 30:30:00 | 0.851 |
| 31:30:00 | 0.827 |
| 32:30:00 | 0.771 |
| 33:30:00 | 0.799 |
| 34:30:00 | 0.718 |
| 35:30:00 | 0.629 |
| 36:30:00 | 0.240 |
| 37:30:00 | 0.037 |
| 38:00:00 | 0.017 |
| 38:00:01 | 0.01 |
| 38:00:02 | 0.00 |
| 39:00:00 | 0.00 |

Table 3. Species formula, name, molecular weight, and initial mixing ratio.

| Species Formula | Species Name | MW (g/mol) | Initial Mixing Ratio (mol/mol) |
|---|---|---|---|
| $H_2O$ | water vapor | 18 | 1.619E-02 |
| $H_2$ | hydrogen | 2 | 5.50E-07 |
| $O_3$ | ozone | 48 | 3.895E-08 |
| $H_2O_2$ | hydrogen peroxide | 34 | 1.202E-09 |
| HO | hydroxyl radical | 17 | 3.056E-15 |
| $HO_2$ | hydroperoxyl radical | 33 | 9.074E-12 |
| $CH_3OO$ | methylperoxy radical | 47 | 1.398E-12 |
| $CH_3OOH$ | methyl hydrogen peroxide | 48 | 2.11E-10 |
| $CH_2O$ | formaldehyde | 30 | 2.519E-09 |
| HCOOH | formic acid | 46 | 2.239E-12 |
| NO | nitric oxide | 30 | 42.90E-12 |
| $NO_2$ | nitrogen dioxide | 46 | 1.79E-10 |
| $HNO_3$ | nitric acid | 63 | 3.97E-10 |
| $N_2O_5$ | dinitrogen pentoxide | 108 | 4.806E-13 |
| $NO_3$ | nitrate radical | 62 | 3.502E-13 |
| $C_5H_8$ | isoprene | 68 | 1.031E-09 |
| $C_2H_6$ | ethane | 30 | 0.846E-09 |
| $C_3H_6$ | propene | 42 | 0.118E-09 |
| $C_{10}H_{16}$ | lumped monoterpenes | 136 | 4.07E-11 |

| | | | |
|---|---|---|---|
| big alkane | lumped alkanes with C > 3 | 58 | 0.142E-09 |
| C2H4 | ethene | 28 | 0.469E-09 |
| CH3CO(OO) | acetylperoxy radical | 75 | 3.461E-13 |
| CH2=C(CH3)CO(OO) | MCO3, peroxy radical from MACR * | 101 | 0.558E-13 |
| HNO4 | pernitric acid | 79 | 8.835E-12 |
| CH3CH2(OO) | ethylperoxy radical | 61 | 7.144E-15 |
| isop-OO | peroxy radical from isoprene | 117 | 4.181E-12 |
| CH3CH(OO.)CH2(OH) | peroxy radical from propane | 91 | 1.414E-13 |
| mvk-OO | peroxy radical from MVK, MACR * | 119 | 1.678E-13 |
| PAN | peroxy acetyl nitrate | 121 | 5.86E-10 |
| MPAN | methacryloyl peroxynitrate | 147 | 7.20E-11 |
| MACR | methacrolein | 70 | 2.82E-10 |
| MVK | methyl vinyl ketone | 70 | 1.13E-10 |
| CH3CHO | acetaldehyde | 44 | 4.091E-10 |
| CH3CH(OOH)CH2(OH) | peroxide from C3H6 | 92 | 2.076E-12 |
| CH3CO(OOH) | peracetic acid | 76 | 2.401E-10 |
| CHOCHO | glyoxal | 58 | 0.218E-09 |
| CH3CH2(OOH) | ethyl hydrogen peroxide | 62 | 2.423E-12 |
| CH2(OH)CHO | glycolaldehyde | 60 | 4.273E-10 |
| CH3COCHO | methyl glyoxal | 72 | 1.904E-10 |
| CH2=CHC(OO.)(CH3)CH2(ONO2) | peroxy radical from NO3+ISOP | 162 | 2.841E-14 |
| isop-ONO2 | lumped isoprene nitrate | 147 | 9.212E-11 |
| CHOCH(CH3)CH2CHO | HYDRALD, hydroxy carbonyl | 100 | 4.371E-10 |
| CH3OH | methanol | 32 | 3.403E-09 |
| terpene-OO | a-pinene peroxy radical | 185 | 2.020E-13 |
| CH3COCH3 | acetone | 58 | 1.437E-09 |
| terpene-OOH | a-pinene peroxide | 186 | 2.499E-12 |
| macr-OOH | methacrolein peroxide | 120 | 3.322E-12 |
| CH3COCH2OH | hydroxy acetone | 74 | 4.371E-10 |
| CH3COCH2(OO) | peroxy radical from acetone | 89 | 3.614E-14 |
| CH3COCH2OOH | peroxide from acetone root | 90 | 3.220E-12 |
| HOCH2C(OO)CH3CH(OH)CHO | peroxy radical from OH+HYDRALD | 133 | 5.318E-13 |
| HOCH2C(OOH)CH3CH(OH)CHO | peroxide from HYDRALD root | 134 | 8.885E-12 |
| HOCH2C(OOH)CH3CHCH2 | ISOPOOH, peroxide from isoprene | 118 | 3.183E-11 |
| SO2 | sulfur dioxide | 64 | 1.500E-10 |
| SO4 | sulfate aerosol | 96 | 0.476E-09 |
| CO2 | carbon dioxide | 44 | 396.0E-06 |
| CH4 | methane | 16 | 1850.E-09 |
| CO | carbon monoxide | 28 | 140.3E-09 |
| CH3COOH | acetic acid | 60 | 0.198E-09 |
| HOCH2COOH | glycolic acid | 76 | 1.00E-15 |

| | | | |
|---|---|---|---|
| CHOCOOH | glyoxylic acid | 74 | 1.00E-15 |
| CH3COCOOH | pyruvic acid | 88 | 1.00E-15 |
| HOOCCOOH | oxalic acid | 90 | 1.00E-15 |

*MCO3 is peroxy radical derived from abstraction reaction of OH with MACR, and mvk-OO is peroxy radical from OH addition to MVK, MACR

**Table 4.** Aerosol Species Concentrations from the MOSAIC aerosol model.

| Aerosol Species | Units | Concentration |
|---|---|---|
| Sulfate, aerosol bin 01 | ug/kg-dryair | 0.04524 |
| Sulfate, aerosol bin 02 | ug/kg-dryair | 0.76484 |
| Sulfate, aerosol bin 03 | ug/kg-dryair | 0.76733 |
| Sulfate, aerosol bin 04 | ug/kg-dryair | 0.00256 |
| | | |
| Ammonium, aerosol bin 01 | ug/kg-dryair | 0.00332 |
| Ammonium, aerosol bin 02 | ug/kg-dryair | 0.04889 |
| Ammonium, aerosol bin 03 | ug/kg-dryair | 0.04829 |
| Ammonium, aerosol bin 04 | ug/kg-dryair | 0.1604E-03 |
| | | |
| Organic carbon, aerosol bin 01 | ug/kg-dryair | 0.1333 |
| Organic carbon, aerosol bin 02 | ug/kg-dryair | 0.3156 |
| Organic carbon, aerosol bin 03 | ug/kg-dryair | 0.0707 |
| Organic carbon, aerosol bin 04 | ug/kg-dryair | 0.3588E-04 |
| | | |
| Black carbon, aerosol bin 01 | ug/kg-dryair | 0.0828 |
| Black carbon, aerosol bin 02 | ug/kg-dryair | 0.1128 |
| Black carbon, aerosol bin 03 | ug/kg-dryair | 0.0211 |
| Black carbon, aerosol bin 04 | ug/kg-dryair | 0.45625E-05 |
| *Other inorganics, aerosol bin 01 | ug/kg-dryair | 0.1631 |
| Other inorganics, aerosol bin 02 | ug/kg-dryair | 0.3426 |
| Other inorganics, aerosol bin 03 | ug/kg-dryair | 0.5669 |
| Other inorganics, aerosol bin 04 | ug/kg-dryair | 0.1367 |
| | | |
| Sulfate, <2.5 um diameter | ug/kg-dryair | 1.5774 |
| Ammonium, <2.5 um diameter | ug/kg-dryair | 0.1005 |
| Organic carbon, <2.5 um diameter | ug/kg-dryair | 0.5196 |
| Black carbon, <2.5 um diameter | ug/kg-dryair | 0.2167 |
| Other inorganics, <2.5 um diameter | ug/kg-dryair | 1.2093 |

Bin 01: 0.039-0.156 um diameter ; Bin 02: 0.156-0.625 um diameter
Bin 03: 0.625-2.5 um diameter ; Bin 04: 2.5-10. um diameter
Note, $NO_3$ < 0.0110 ug/kg-dryair, Na and Cl < 0.6873 ug/kg-dryair and could be included in sensitivity simulations.
*Other inorganics usually refers to dust, but can contain other species.  See Zaveri et al. (2008) for more information.

**Table 5.** Conditions for the TUV radiation calculation.

| | | | | | |
|---|---|---|---|---|---|
| inpfil = | WFMit0 | outfil = | WFMt0 | nstr = | 4 |
| lat = | 44.4 | lon = | -73.9 | tmzone = | -4 |
| iyear = | 2016 | imonth = | 9 | iday = | 18 |
| zstart = | 0 | zstop = | 120 | nz = | 121 |
| wstart = | 120 | wstop = | 735 | nwint = | -156 |
| tstart = | 0 | tstop = | 23.75 | nt = | 96 |
| lzenit = | F | alsurf = | 0.1 | psurf = | -999 |
| o3col = | 300 | so2col = | 0 | no2col = | 0 |
| taucld = | 0 | zbase = | 1.2 | ztop = | 2.5 |
| tauaer = | 0.235 | ssaaer = | 0.99 | alpha = | 1 |
| dirsun = | 1 | difdn = | 1 | difup = | 1 |
| zout = | 1.5 | zaird = | -9.99E+02 | ztemp = | -999 |
| lirrad = | F | laflux = | F | lmmech = | T |
| lrates = | F | isfix = | 0 | nms = | 0 |
| ljvals = | F | ijfix = | 0 | nmj = | 2 |
| iwfix = | 0 | itfix = | 0 | izfix = | 0 |