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WRF-Chem Chemistry Option T1-MOZCART (chem_opt = 114)

With WRF-Chem Version V4.0 a new chemistry option has been added: T1_MOZCART.

T1_MOZCART presents an update to the MOZART-4 chemical gas phase mechanism in chem_opt 112 (MOZCART; Emmons et al., 2010). The updates from the gas phase chemistry in MOZART-4 to T1 are described in more detail in the "Scientific Background" Section and in Emmons et al. ("*The expanded MOZART tropospheric chemistry mechanism T1: updated representation of ozone and secondary organic aerosol precursors*", in preparation). T1_MOZCART has 142 gas phase species compared to 81 gas phase species in MOZCART.

Similar to MOZCART, T1-MOZCART is linked to the GOCART aerosol scheme. The T1 mechanism is also included in the global CAM-Chem model and any future updates and changes to T1 will be transferred to both models, CAM-Chem and WRF-Chem.

The previous version 4 of the MOZART tropospheric gas phase chemistry mechanism (Emmons et al., 2010) is implemented in the WRF-Chem chemistry options MOZART (chem_opt = 111; note that this option will no longer be supported) and MOZCART (chem_opt = 112). Preliminary versions of the T1 mechanism were used in Knote et al. (2014) as part of the WRF-Chem MOZART-MOSAIC schemes (chem_opt = 201 and 202).

If you have questions about any of the MOZART chemical options please use the NCAR/ACOM WRF-Chem Discussion Forum: https://www2.acom.ucar.edu/wrf-chem/discussion-forum. Note that chem_opt = 111 (MOZART) is no longer supported.

Running WRF-Chem with MOZCART_T1

MOZCART_T1 is included through KPP and is chem_opt = 114. An example namelist.input is provided below. The NCAR/ACOM WRF-Chem preprocessing tools have been updated for examples with MOZCART_T1 and can be downloaded from the NCAR/ACOM WRF-Chem Webpage, https://www2.acom.ucar.edu/wrf-chem/wrf-chem-tools-community.

Setting up WRF-Chem with T1_MOZCART

- Anthropogenic emission species for T1 as defined in registry.chem. Species that differ from MOZCART are highlighted in bold.

mozc_t1_em emiss_opt==11
e_co,e_no,e_no2,e_bigalk,e_bigene,e_c2h4,e_c2h5oh,e_c2h6,e_c3h6,e_c3h8,e_ch2o,e_ch3cho,
e_ch3coch3,e_ch3oh,e_mek,e_so2,**e_toluene**,e_nh3,e_isop,**e_hcooh,e_ch3cn,e_ch3cooh,e_hcn,**
e_apin,e_mvk,e_mgly,e_benzene,e_xylene,e_sulf,e_c2h2,e_pm_10,e_pm_25,e_bc,e_oc

- Biomass burning emission species for T1 as defined in registry.chem (if run with online plumerise). Species that differ from MOZCART are highlighted in bold.

biomassb_t1_mozcart biomass_burn_opt==4 -
ebu_in_co,ebu_in_no,ebu_in_bigalk,ebu_in_bigene,ebu_in_c2h4,ebu_in_c2h5oh,ebu_in_c2h6,
ebu_in_c3h6,ebu_in_c3h8,ebu_in_ch2o,ebu_in_ch3cho,ebu_in_ch3coch3,ebu_in_ch3oh,
ebu_in_mek,ebu_in_so2,**ebu_in_toluene**,ebu_in_nh3,ebu_in_no2,**ebu_in_mgly,ebu_in_ch3cooh,**
ebu_in_cres,ebu_in_glyald,ebu_in_acetol,ebu_in_isop,ebu_in_macr,ebu_in_mvk,ebu_in_pm25,
ebu_in_pm10,ebu_in_oc,ebu_in_bc,**ebu_in_apin,ebu_in_ch3cn,ebu_in_hcn,ebu_in_hcooh,**
ebu_in_c2h2,ebu_in_dms,ebu_in_hpald,ebu_in_xylenes, ebu_in_benzene

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Notes:

The lumped toluene species in MOZCART has been split into toluene, benzene and xylenes.
apin represents alpha-pinenes and can be mapped to anthropogenic $C_{10}H_{16}$ emissions

- Example &chem namelist.input entries for MOZCART_T1 with MEGAN biogenic emissions, FINN fire emissions with online plumerise, and chemical boundary conditions

```
&chem
chem_opt                = 114
emiss_inpt_opt          = 102
emiss_opt               = 11
emiss_opt_vol           = 0
chem_in_opt             = 1
gas_drydep_opt          = 1
aer_drydep_opt          = 1
bio_emiss_opt           = 3
ne_area                 = 210,
gas_bc_opt              = 1,
gas_ic_opt              = 1,
aer_bc_opt              = 1
aer_ic_opt              = 1
gaschem_onoff           = 1
wetscav_onoff           = 1
conv_tr_wetscav         = 1
biomass_burn_opt        = 4
plumerisefire_frq       = 30
scale_fire_emiss        = .true.
have_bcs_chem           = .true.
/
```

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Scientific Background

The current expansion of the MOZART-4 tropospheric chemistry to T1-MOZART is motivated by improved understanding of VOC oxidation processes through laboratory measurements, as well as a need to better represent precursors of secondary organic aerosols. New field measurements of an increasing number of isoprene oxidation products, as well as individual aromatic and terpene hydrocarbons, allow for more precise model evaluation.

Updates from MOZART-4 to T1-MOZCART

The updates from the MOZART-4 chemical scheme to T1-MOZCART include an expansion of the isoprene oxidation scheme, splitting lumped aromatics and terpenes to individual species, and a more detailed representation of organic nitrates. The number of gas phase species has been increased from 81 in MOZART-4 to 142 in T1 and the number of gas phase reactions from 142 to 344, respectively.

The T1 mechanism includes:

- Two 'lumped' peroxy radicals (one beta, one gamma) from OH + isoprene
- One peroxy radical from NO_3 + isoprene, with subsequent parameterized chemistry
- Obviously, MVK / MACR, their chemistry, and that of their products
- First generation HYAC/ MGLY/ GLYOXAL/ GLYALD formation
- "Lumped" isoprene nitrate formation and chemistry
- Parameterized peroxy radical isomerization
- One "lumped" ISOPOOH, but with multiple product channels to account for partial IEPOX formation
- IEPOX & HPALD formation and destruction

The original lumped aromatic in MOZART-4 (called "TOLUENE") has been replaced by the specific aromatic species BENZENE, TOLUENE and XYLENES (lumped isomers), as described in Knote et al. (2014).

MOZART-4 has a single lumped terpene species ("C10H16") with a very simple oxidation scheme with rates based on alpha-pinene. In T1 this lumped species is replaced by four monoterpenes and one sesquiterpene and the oxidation scheme has been expanded. The primary degradation rates for these new species are based on alpha-pinene (APIN), beta-pinene (BPIN), limonene (LIMON), myrcene (MYRC) and beta-caryophyllene (BCARY), but each species includes a number of similar terpenes in their emissions, so as to better represent the total carbon emissions. These five species, however, create common lumped oxidation products in our mechanism (TERPROD1, etc.) for computational efficiency.

The biogenic compound MBO (2-methyl-3-buten-2-ol) and its oxidation products are also included as described in Knote et al. (2014).

The MOZART-4 mechanism included just a few lumped organic nitrate compounds (ONIT, ONITR, ISOPNO3) created from a wide variety of precursors. T1 adds a number of organic nitrate species. The oxidation of the lumped large alkane ("BIGALK", butanes and larger) now creates an alkyl nitrate, ALKNIT. Propene is oxidized (by NO3) producing nitrooxyacetone (NOA). The lumped large alkene ("BIGENE", butenes and larger), along with other species (e.g., MACR, MBO …), creates a lumped species HONITR that represents an eclectic mix of hydroxyl- and carbonyl-nitrates.

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The two isoprene peroxy radicals formed from isoprene + OH create 1,2- and 1,4-hydroxynitrate, ISOPNITA and ISOPNITB, which react with OH forming NOA and HONITR.

ISOP+NO3 forms ISOPNO3, which then oxidizes to ISOPNOOH (nitroxy-hydroperoxide) and NC4CHO (nitrooxy-aldehyde), which then break down to NOA, ISOPOOH, GLYALD, GLYOXAL, BIGALD3.

The terpene oxidation mechanism now creates a hydroxynitrate TERPNIT, and a nitrooxy-hydroperoxide NTERPOOH; both react with OH and photolyze releasing NO_2.

Heterogeneous uptake of several species including the new organic nitrates on aerosols is included.

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References

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Changes in ozone between T1_MOZART and MOZCART

Below we provide an example of the changes that might be expected from the update to the T1 mechanisms. Note that this is only one example; the results may differ when simulating other regions or times.

Simulations:

- Single domain, 12 km x 12 km over the Western U.S.
- Initial start 2014-08-12 06 UTC
- Meteorological IC and BC from ECMWF, Chemical IC and BC from global-scale, MOZART-4 chemistry transport model.
- No feedback of chemistry on meteorology
- Emissions: EPA NEI 2011 anthropogenic; FINN v1.5 fires; MEGAN online biogenic
- Results are shown for 2014-08-12 22 UTC (local afternoon), surface concentrations

The biggest changes between T1_MOZCART and MOZCART and MOZART-MOZAIC_4bin are due to the inclusion of heterogeneous reactions on aerosols in T1.

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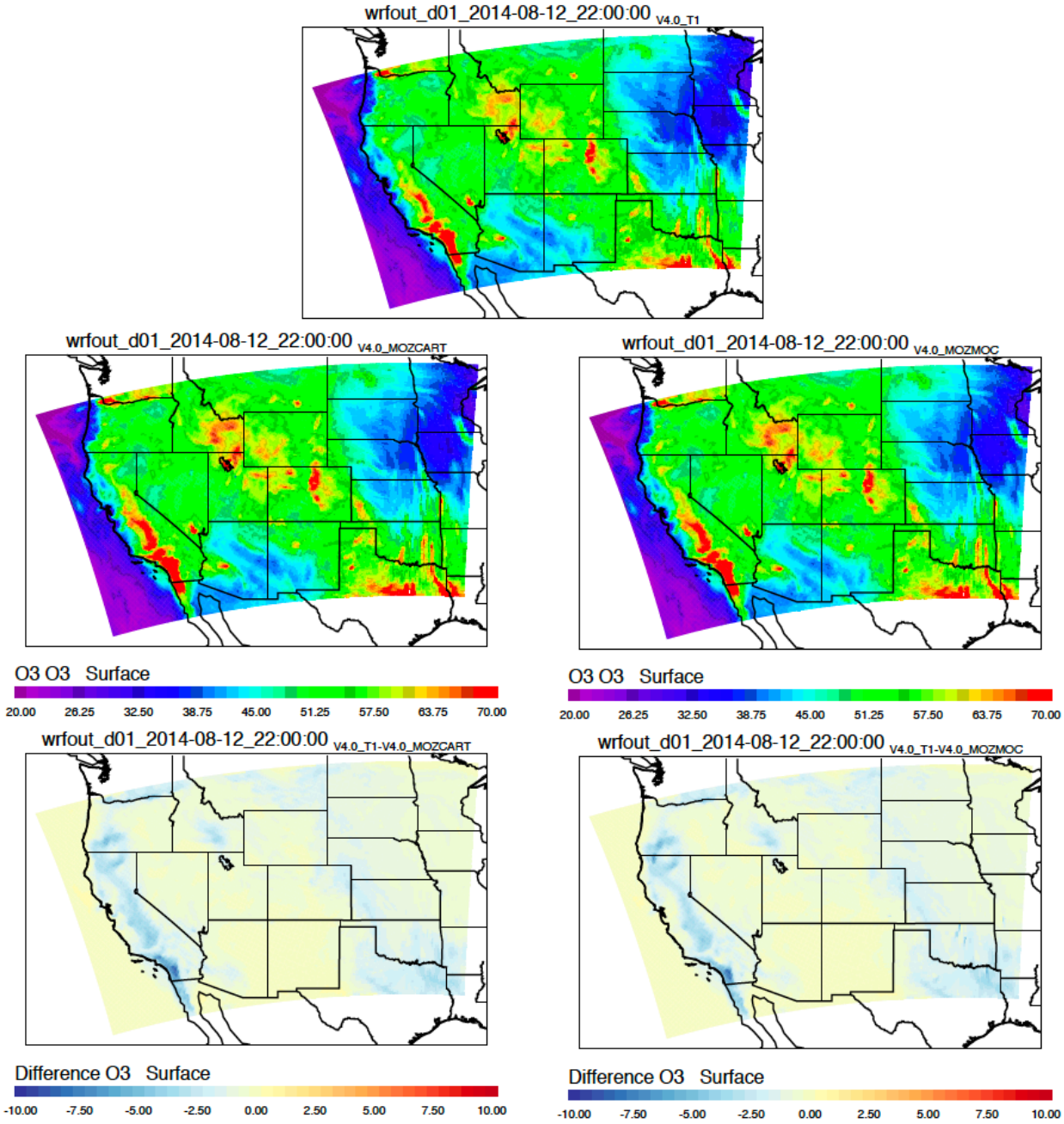

Top row: Surface Ozone (ppb) in T1_MOZCART

Middle row: Surface Ozone (ppb) in MOZCART (left) and MOZART-MOZAIC-4bin (right)

Bottom row: Difference in Surface Ozone (ppb) for T1_MOZCART-MOZCART (left) and T1_MOZCART- MOZART-MOZAIC-4bin (right)