Expanded Chemical Tagging

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Outline

- Tropospheric ozone production
- Our goal: VOC tagging in CAM-Chem
- Established chemical tagging in CAM-Chem
- Extension: multiple simultaneous NO_x/O_3 tags
  - Preliminary results
- Outlook

Tropospheric ozone production

- Oxidation of VOC in the presence of NO_x leads to production of ozone
  - $RH + OH \rightarrow RO_2$
  - $RO_2 + \mathbf{NO} \rightarrow \mathbf{NO_2} + R'CHO + HO_2$
  - $HO_2 + \mathbf{NO} \rightarrow \mathbf{NO_2} + OH$
  - $\mathbf{NO_2} + h\nu \rightarrow NO + \mathbf{O}$
  - $\mathbf{O} + O_2 \rightarrow \mathbf{O_3}$
- NO_x and O_3 can take part in rapid “null cycles”
  - $NO + O_3 \rightarrow NO_2$
  - $NO_2 + h\nu \rightarrow \ldots \rightarrow NO + O_3$
- Often more useful to consider “odd oxygen”
  - $[O_x] = [O_3] + [NO_2] + [O]$

Tagging VOCs: an example

Methane

$CH_4 + OH \rightarrow CH_3O_2$

$CH_3O_2 + NO \rightarrow HCHO + HO_2 + NO_2$

Methanol

$CH_3OH + OH \rightarrow HCHO + HO_2$

Formaldehyde

$HCHO + hv \rightarrow CO + 2\ HO_2$

Tagging VOCs: an example

Methane

$CH_4 + OH \rightarrow CH_3O_2\_CH_4$

$CH_3O_2 + NO \rightarrow HCHO + HO_2 + NO_2$

Methanol

$CH_3OH + OH \rightarrow HCHO + HO_2$

Formaldehyde

$HCHO + hv \rightarrow CO + 2\ HO_2$

Tagging VOCs: an example

Methane

$CH_4 + OH \rightarrow CH_3O_2\_CH_4$

$CH_3O_2\_CH_4 + NO \rightarrow HCHO\_CH_4 + HO_2 + NO_2$

Methanol

$CH_3OH + OH \rightarrow HCHO + HO_2$

Formaldehyde

$HCHO + hv \rightarrow CO + 2\ HO_2$

Tagging VOCs: an example

Methane

$CH_4 + OH \rightarrow CH_3O_2\_CH_4$

$CH_3O_2\_CH_4 + NO \rightarrow HCHO\_CH_4 + HO_2 + NO_2$

Methanol

$CH_3OH + OH \rightarrow HCHO\_CH_3OH + HO_2$

Formaldehyde

$HCHO + hv \rightarrow CO + 2\ HO_2$

Tagging VOCs: an example

Methane

CH_4 + OH -> $CH_3O_2\_CH_4$

$CH_3O_2\_CH_4$ + NO -> $HCHO\_CH_4$ + HO_2 + NO_2

Methanol

CH_3OH + OH -> $HCHO\_CH_3OH$ + HO_2

Formaldehyde

HCHO + hv -> CO_HCHO + 2 HO_2

$HCHO\_CH_4$ + hv -> CO_CH_4 + 2 HO_2

$HCHO\_CH_3OH$ + hv -> CO_CH_3OH + 2 HO_2

VOC tagging

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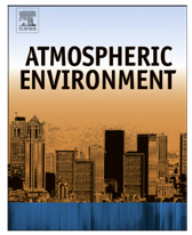

Multi-day ozone production potential of volatile organic compounds calculated with a tagging approach

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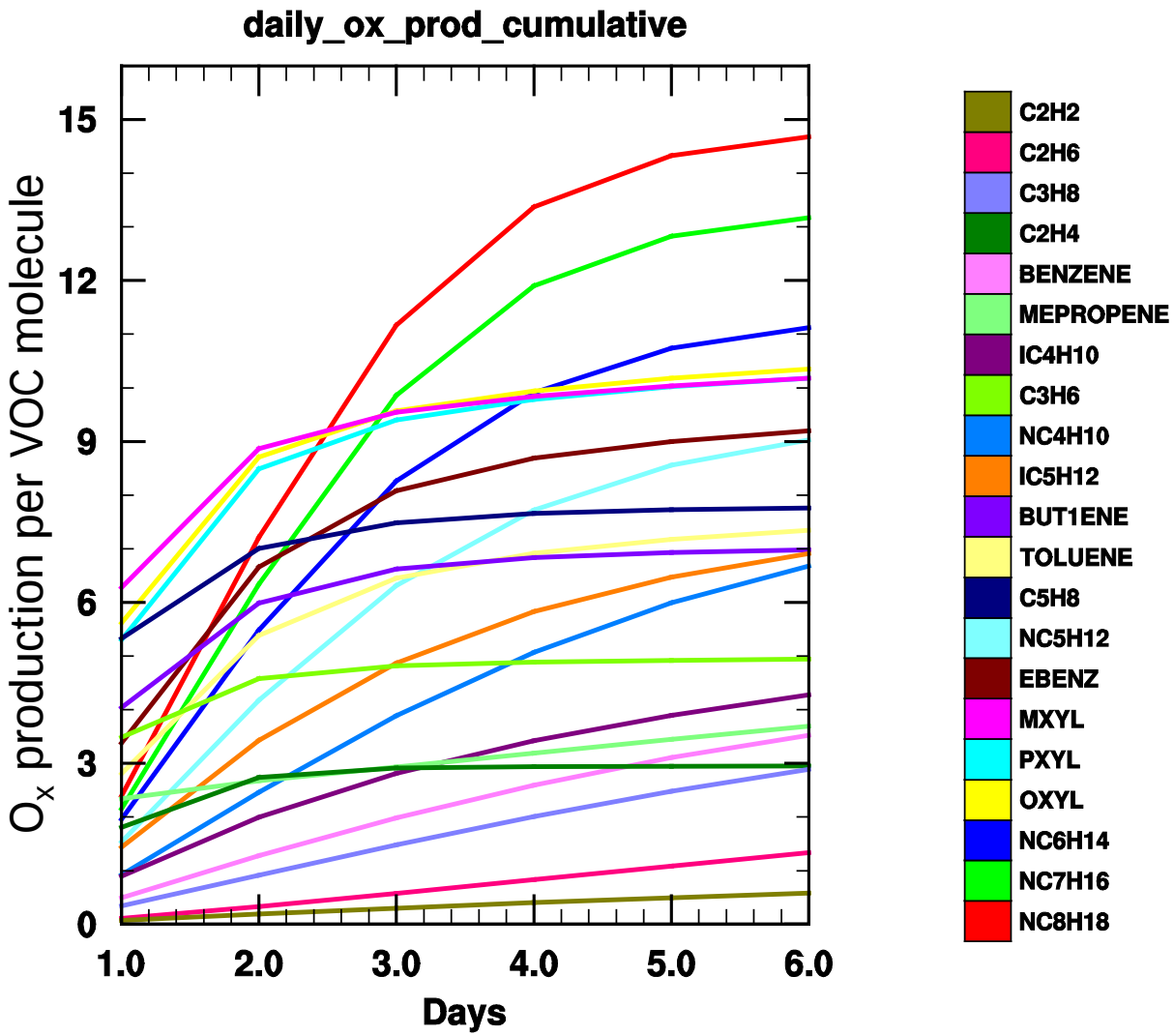
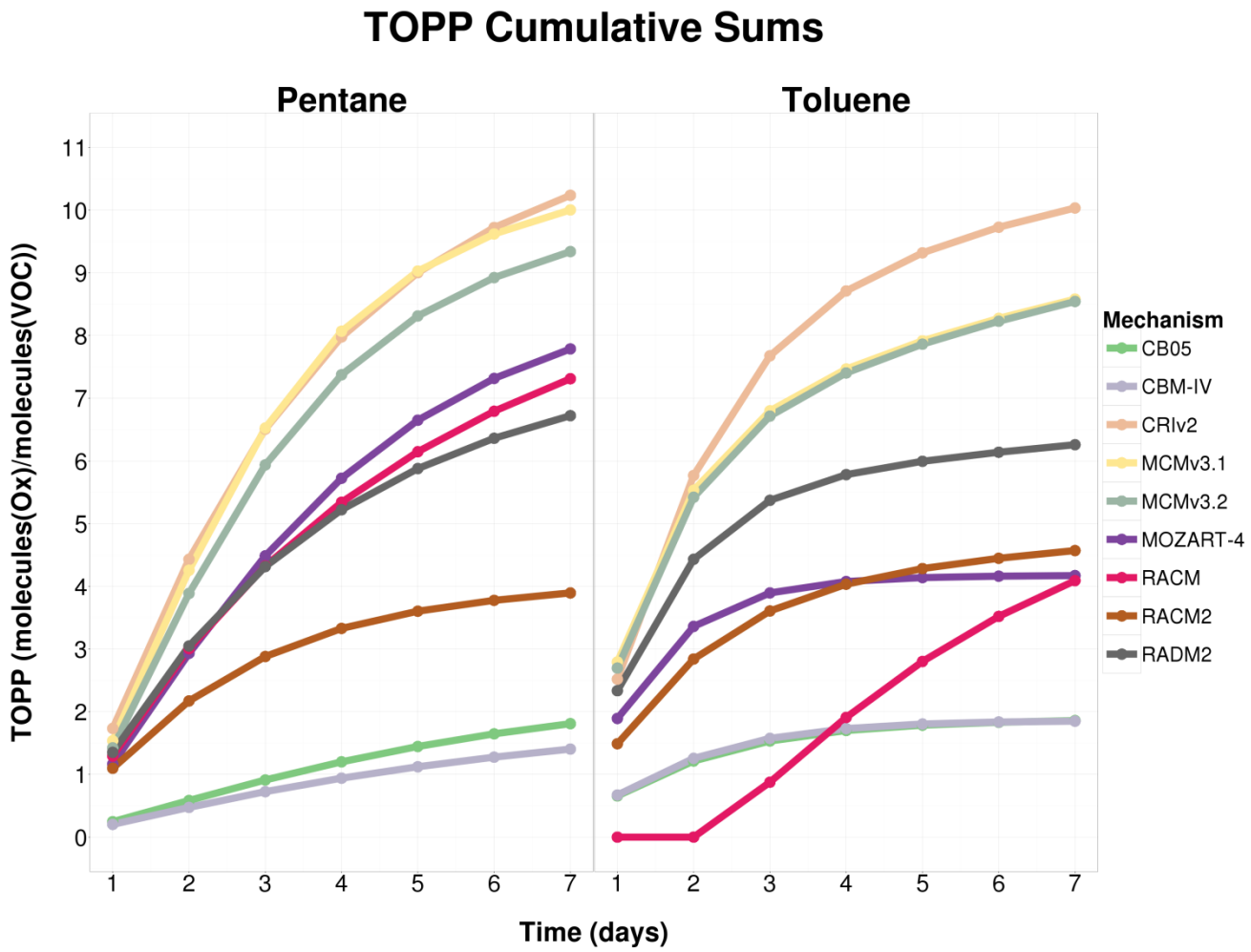
Cumulative ozone production potential



Chemical mechanism comparison



Established tagging in CAM-Chem: NO_x-based

- One tag allowed per model run
  - Tagging multiple NO_x sources requires multiple runs
- Tagged source duplicated as emissions of “XNO”
  - $XNO + RO_2 \rightarrow XNO_2$
  - $XNO_2 + hv \rightarrow ... \rightarrow O_3A$
- Tag is followed through all other reactions involving NO_x
- What happens with the “null cycle”
  - $O_3 + NO \rightarrow NO_2$
  - Which tag does NO_2 get?
  - It gets the tag from NO
  - The null cycle replaces O_3 tags

Established tagging in CAM-Chem: NO_x-based

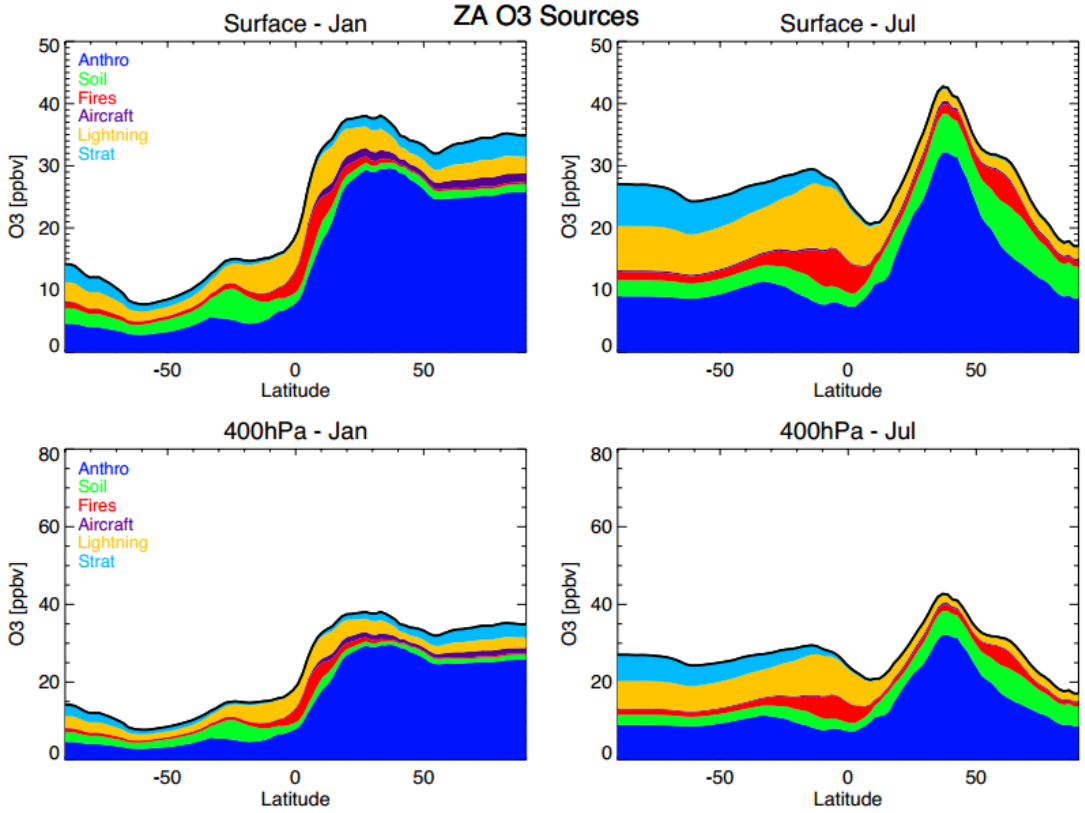


Fig. 6. Zonal average of tagged ozone source contributions at the surface and at 400 hPa, for January and July of 2008. Stratospheric contribution is determined as the difference between total ozone and tagged ozone from all tropospheric sources combined.

Emmons et al. (2012)

Extended tagging in CAM-Chem: NO_x-based

- Allow for multiple tags in a single model run
- Tagged sources emitted as NO_XXX
  - NO_TAG + RO_2 -> NO_2_TAG
  - NO_FOO + RO_2 -> NO_2_FOO
  - NO_BAR + RO_2 -> NO_2_BAR
- Null cycle
  - O_3 + NO -> NO_2
  - Possibility for NO_2 to inherit from **either** O_3 or NO_2

Implementation

- Predominantly a text processing problem
  - Perl scripts
- Preprocessing of the chemical mechanism file
  - Specify a list of tags to apply (eg. “TAG”, “FOO”, “BAR”)
  - Rewrite the mechanism file
    - XNO -> NO_TAG, NO_FOO, NO_BAR
    - Each tagged reaction is repeated for each additional tag

Implementation

- Preprocessing the model source files
  - Everywhere with existing tagging code:
    - Deposition
    - Reaction rates
    - Chemical solver
    - Heterogeneous chemistry
    - Aircraft and lightning emissions
    - Upper boundary

Implementation

- Original code:

```
if( jno2a_ndx > 0 .and. jno2_ndx > 0 ) then
      photos(:,:,jno2a_ndx) = photos(:,:,jno2_ndx)
end if
```

- Manually modified “template” code:

```
! BEGIN TAGGING CODE
if( jno2_tag_ndx > 0 .and. jno2_ndx > 0 ) then
      photos(:,:,jno2_tag_ndx) = photos(:,:,jno2_ndx)
end if
! END TAGGING CODE
```

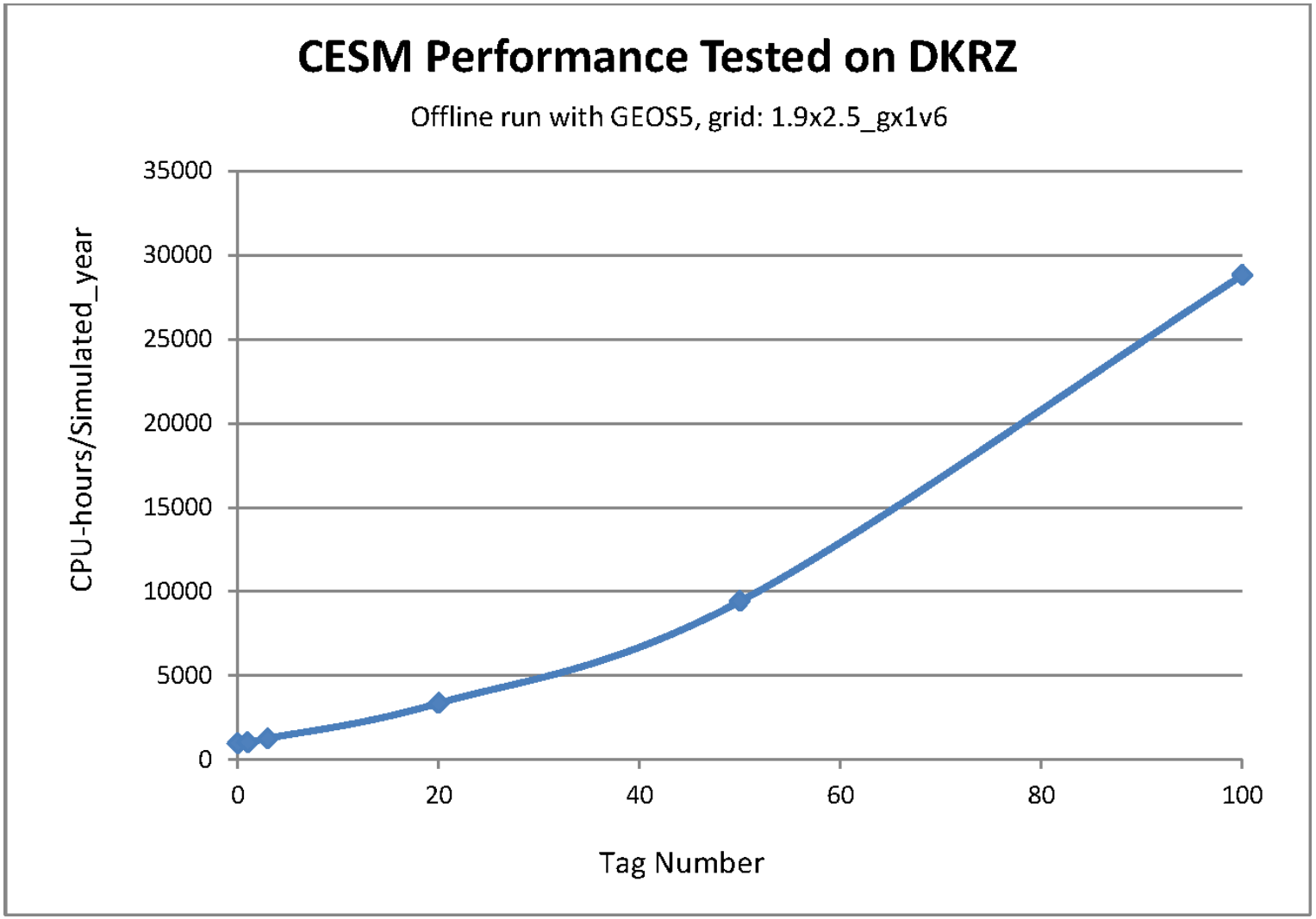
- Template code is then automatically processed to produce compiler-ready code...

Implementation

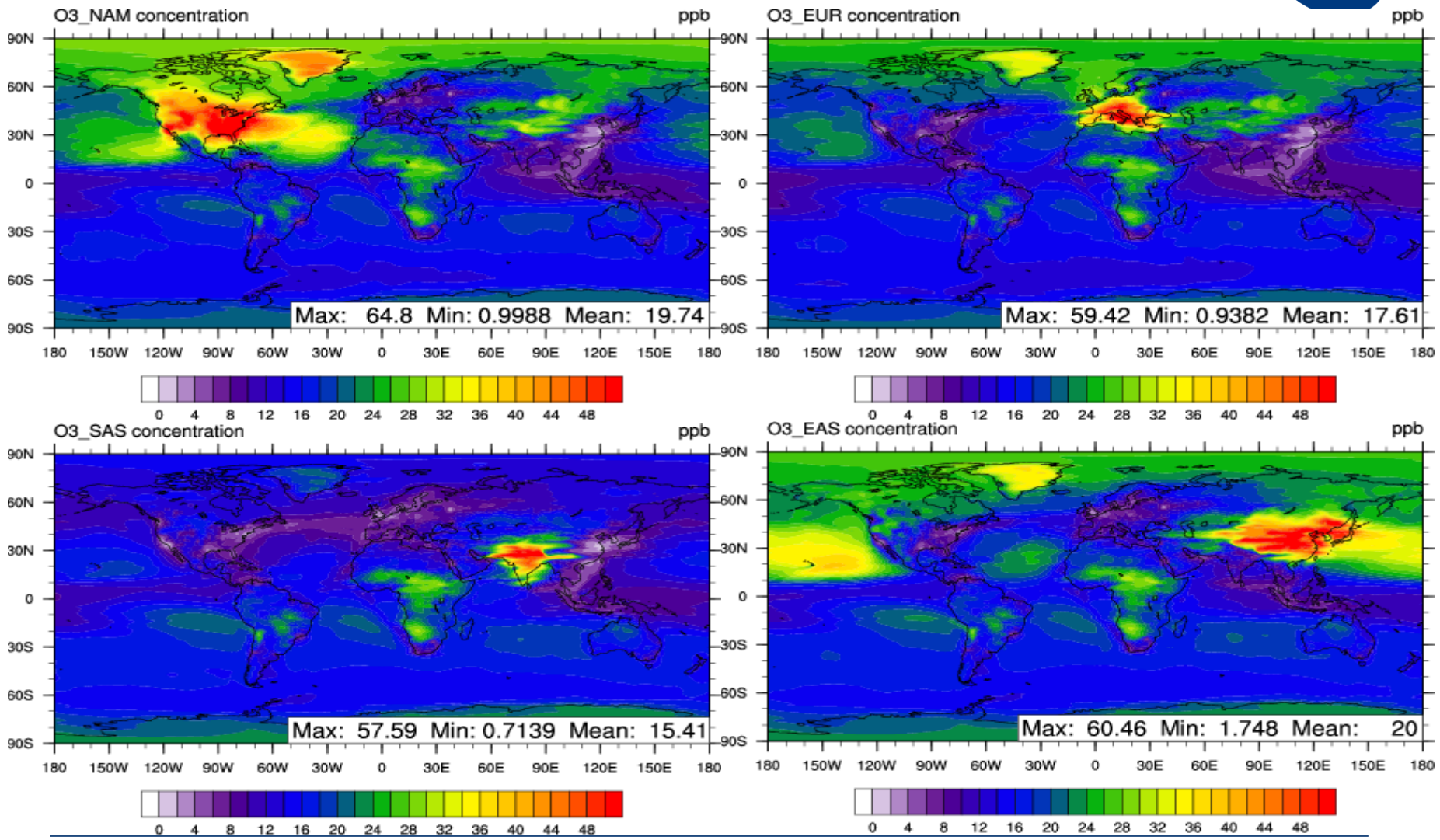
```
! BEGIN TAGGING CODE
if( jno2_tag_ndx > 0 .and. jno2_ndx > 0 ) then
      photos(:,:,jno2_tag_ndx) = photos(:,:,jno2_ndx)
end if
if( jno2_foo_ndx > 0 .and. jno2_ndx > 0 ) then
      photos(:,:,jno2_foo_ndx) = photos(:,:,jno2_ndx)
end if
if( jno2_bar_ndx > 0 .and. jno2_ndx > 0 ) then
      photos(:,:,jno2_bar_ndx) = photos(:,:,jno2_ndx)
end if
! END TAGGING CODE
```

Implementation

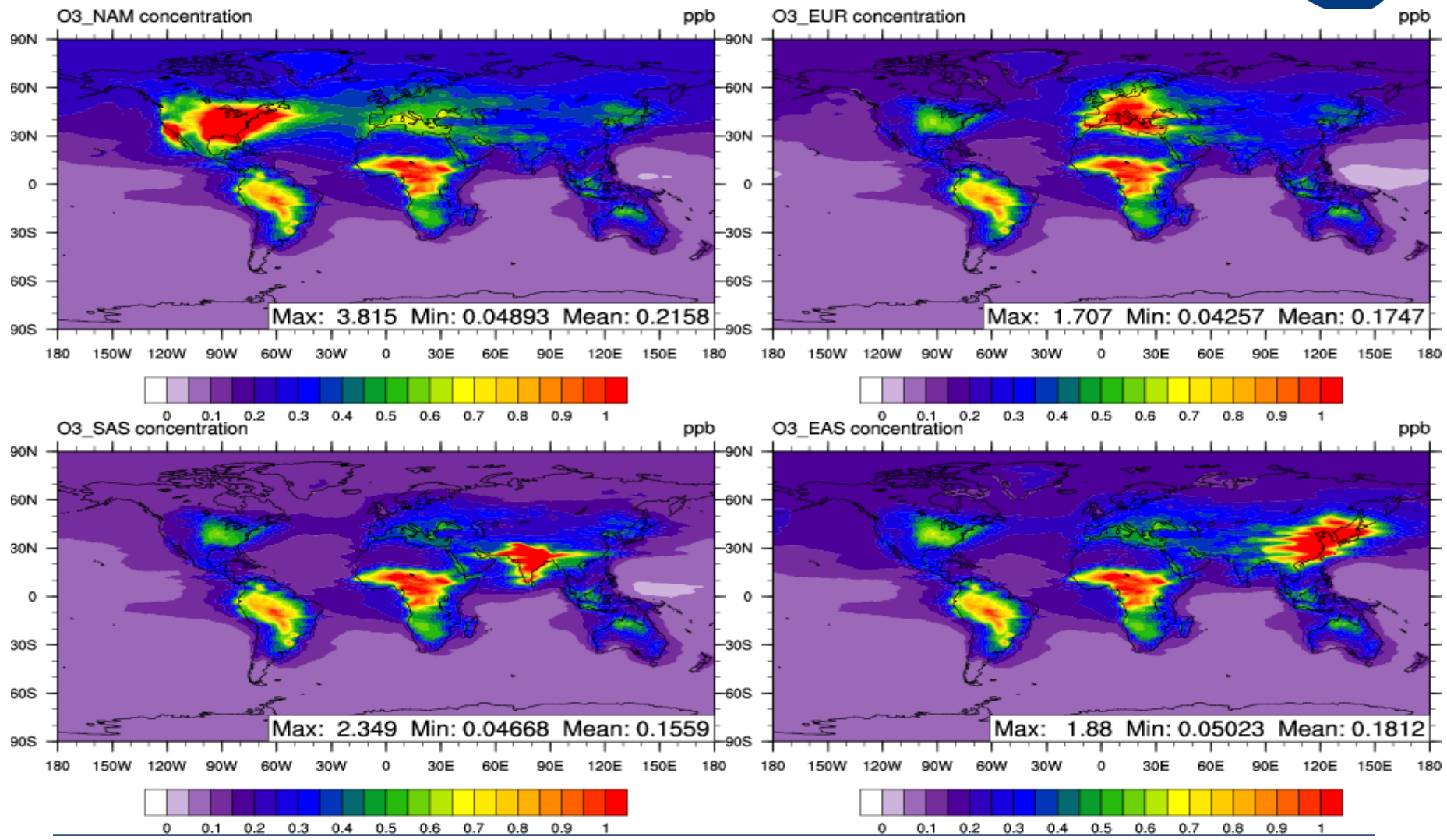
- Increase hard-coded limits in the chemical pre-processor
- Need to use implicit solution class for tagged species
  - And their “untagged” equivalents
- Modify namelist variables
  - Eg. Add tagged species to list of dry-deposited species
- Generate emission files
  - Eg. Tagged species emitted from the HTAP regions


CESM Performance Tested on DKRZ
Offline run with GEOS5, grid: 1.9x2.5_gx1v6
CPU-hours/Simulated_year
35000
30000
25000
20000
15000
10000
5000
0
0
20
40
60
80
100
Tag Number

Preliminary results: O_3 tag altered by null cycle



Preliminary results: O_3 tag unchanged by null cycle

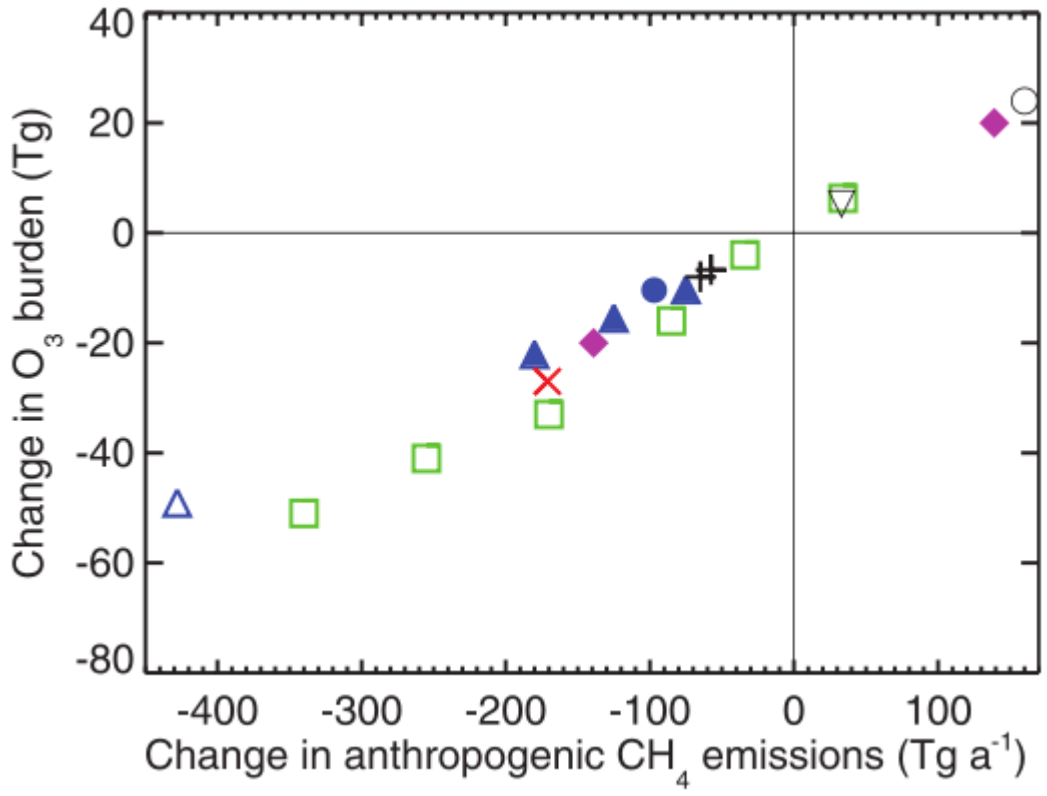


Next steps

- Sum of tagged O_3 does not equal the “untagged” O_3 burden
  - Debugging required
- Implementation of VOC tagging
  - Mechanism already tagged in box model
  - Integration with CAM-Chem (hopefully) mostly analogous to NO_x tagging
- Application of both tagging schemes to HTAP simulations
- Comparison of different chemical mechanisms in CAM-Chem
- ...?

Extra slides

VOC sensitivity of tropospheric ozone



Fiore et al. (2008)

Tuning the NO_x source

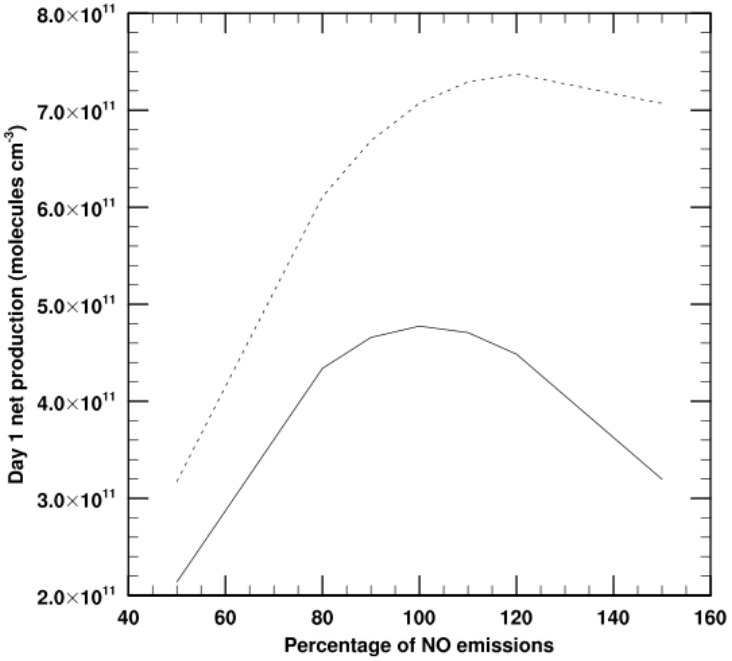


Figure S1: Sensitivity of net production of O_3 (solid line) and O_x (dotted line) during day 1 of the Los Angeles model simulation to changes in NO emissions (as a percentage of the emissions required to balance the source of radicals in the model simulation). At 100%, the mixing ratios of NO and NO_2 are 0.8 and 5 nmol mol^{-1}, respectively.

Butler et al. (2011) Supplement