Implementation and evaluation of PM2.5 source contribution analysis in a photochemical model

Roger Kwok[1], Sergey Napelenok[1], Kirk Baker[2]

1. ORD/NERL/AMAD, U.S. EPA, Research Triangle Park, NC
2. OAQPS, U.S. EPA, Research Triangle Park, NC

October 17, 2012

11th Annual CMAS Conference, Oct 15-17, 2012

What Necessitates the Study

- **Culpability assessments**
- The NOX Sip Call and Transport Rule regulate interstate transport of emissions under authority of the Clean Air Act Section 110a2di
  - Prohibiting any source or other type of emissions activity within the State from emitting any air pollutant in amounts which will … contribute significantly to nonattainment in, or interfere with maintenance by, any other State with respect to any such national primary or secondary ambient air quality standard
- Total county level contribution estimates to ozone or PM2.5 for the purposes of selecting counties for inclusion or exclusion from a nonattainment area
- These regulatory needs require a total culpability assessment

What is source apportionment?

- Provides information similar to receptor based source apportionment techniques such as Chemical Mass Balance and Positive Matrix Factorization where ambient concentrations are apportioned to source categories using source “fingerprints”
- Receptor (observation) based approaches are limited by the amount of ambient measurements, the availability of distinct source fingerprints (many sources have similar fingerprints), and chemical transformations between source and receptor
- Source-oriented approaches in photochemical models do not have any limitations in terms of differentiating sources, but do have the same challenge of tracking source contribution through chemical and physical processes

Existing Source Apportionment Algorithms

Algorithm	Remarks
1. SOEM	UC Davis; tracks PMs; accurate but computationally prohibitive
2. PSAT/OSAT	In CAMx
3. PPTM/OPTM	In CMAQ 4.6
4. TSSA	In CMAQ 4.5
5. Carbon tracking	CMAQ 4.7+; public release; tracks primary OC and EC

1. Mysliwiec and Kleeman: ES&T 2002, 36, 5376-5384.
2. Wagstrom et al: AE 2008, 42, 5650-5659.
3. USEPA: Peer Review of Source Apportionment Tools in CAMx and CMAQ. EP-D-07-102
4. Wang et al: JGR 2009, 114, doi:10.1029/2008JD010846
5. Bhave et al: ES&T 2007, 41, 1577-1583.

Integrated Source Apportionment Method (ISAM)

Host Model CMAQ 4.7.1

What sources to track:

- Emission categories and/or
- originating regions, and
- Initial and boundary concentrations

What species to track in ambient concentrations, dry/wet depositions:

- OC and EC
- PM ammonium + precursor NH3
- PM sulfate + precursor SO2
- PM nitrate + precursor NOx

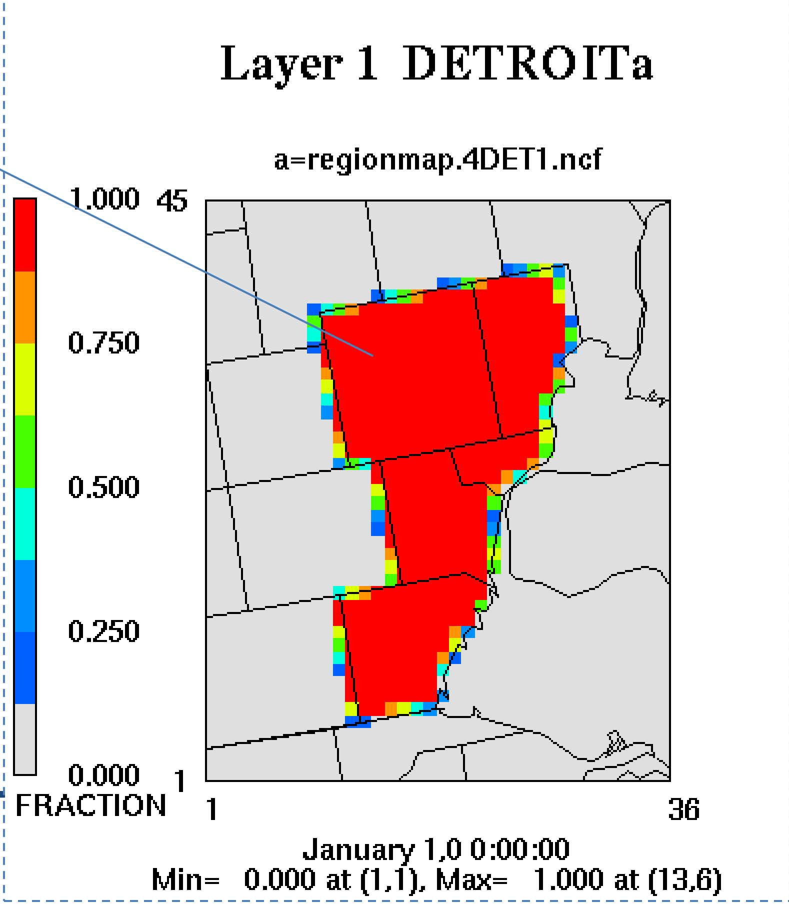
Definition of Tag Classes

Tag Classes	Species in EMISfile	Species in IC/BC, CGRID, DRYDEP, WETDEP and appearing in tags
EC	PEC	AECI, AECJ
OC	POC	AORGPAI, AORGPAJ
SULFATE	SO2, SULF, PSO4	SO2, SULF, ASO4I, ASO4J
NITRATE	PNO3, NO2, NO, HONO	ANO3I, ANO3J, HNO3, NTR, NO2, NO, NO3, HONO, N2O5, PNA, PAN, PANX
AMMONIUM	NH3	NH3, ANH4I, ANH4J

Input Requirements of Source Apportionment

- Example input control file

```
TAG NAME        |PIPM_DT
TAG CLASSES     |EC OC SULFATE NITRATE AMMONIUM NOX
REGION(S)       |DETROIT
FILENAME(S)     |SG02
STACK FILE(S)   |SGSTACK02
      :
      :
TAG NAME        |AGRI_EV
TAG CLASSES     |AMMONIUM
REGION(S)       |EVERYWHERE
FILENAME(S)     |SG05
STACK FILE(S)   |SGSTACK05
```



Evaluation --- with respect to zero-out runs

- Checking for correctness in apportioning tags C_{tag} is problematic because of nonlinearity in science processes (e.g. in-cloud and gas chemistry, aerosol dynamics, see later)

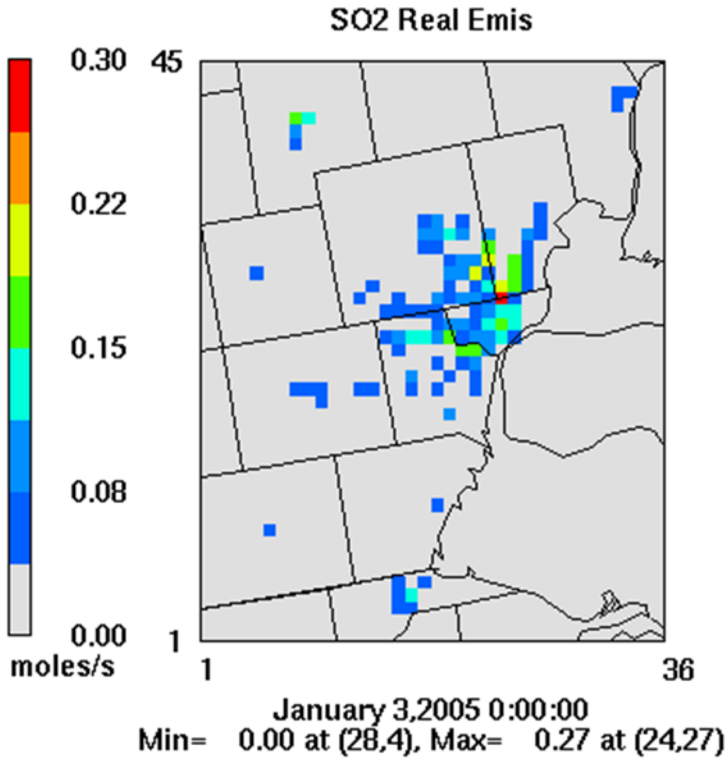
- One approach for evaluation is a comparison of tags with brute force zero out

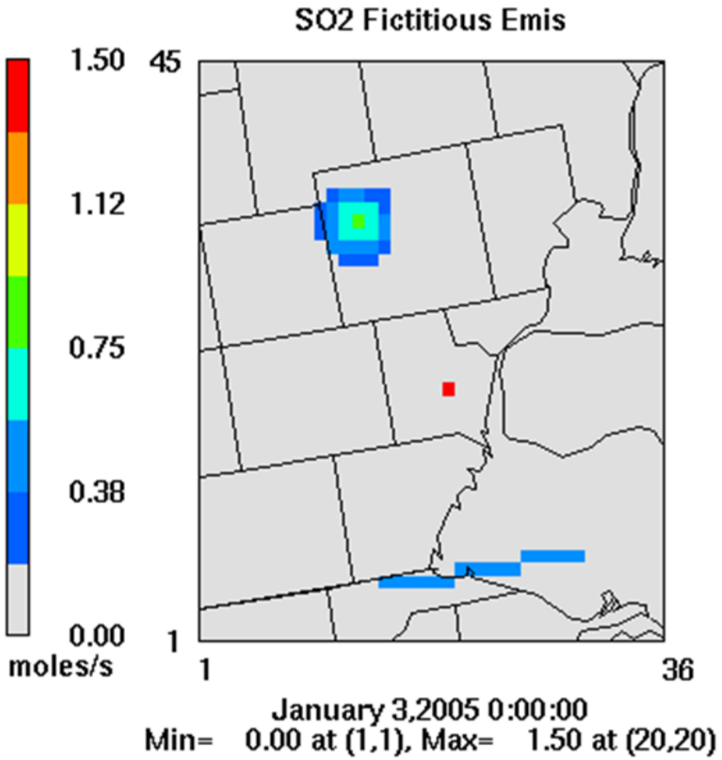
  $C_{0out} = C(E_{total}) - C(E_{total} - E_{ideal})$

- Comparing C_{tag} with C_{0out}, expect them to be
  - closest for chemically inert species (EC, OC) and primary species (SO2, NOx, NH3)
  - still similar for species NH4, SO4
  - noticeably different for secondary nitrogen species

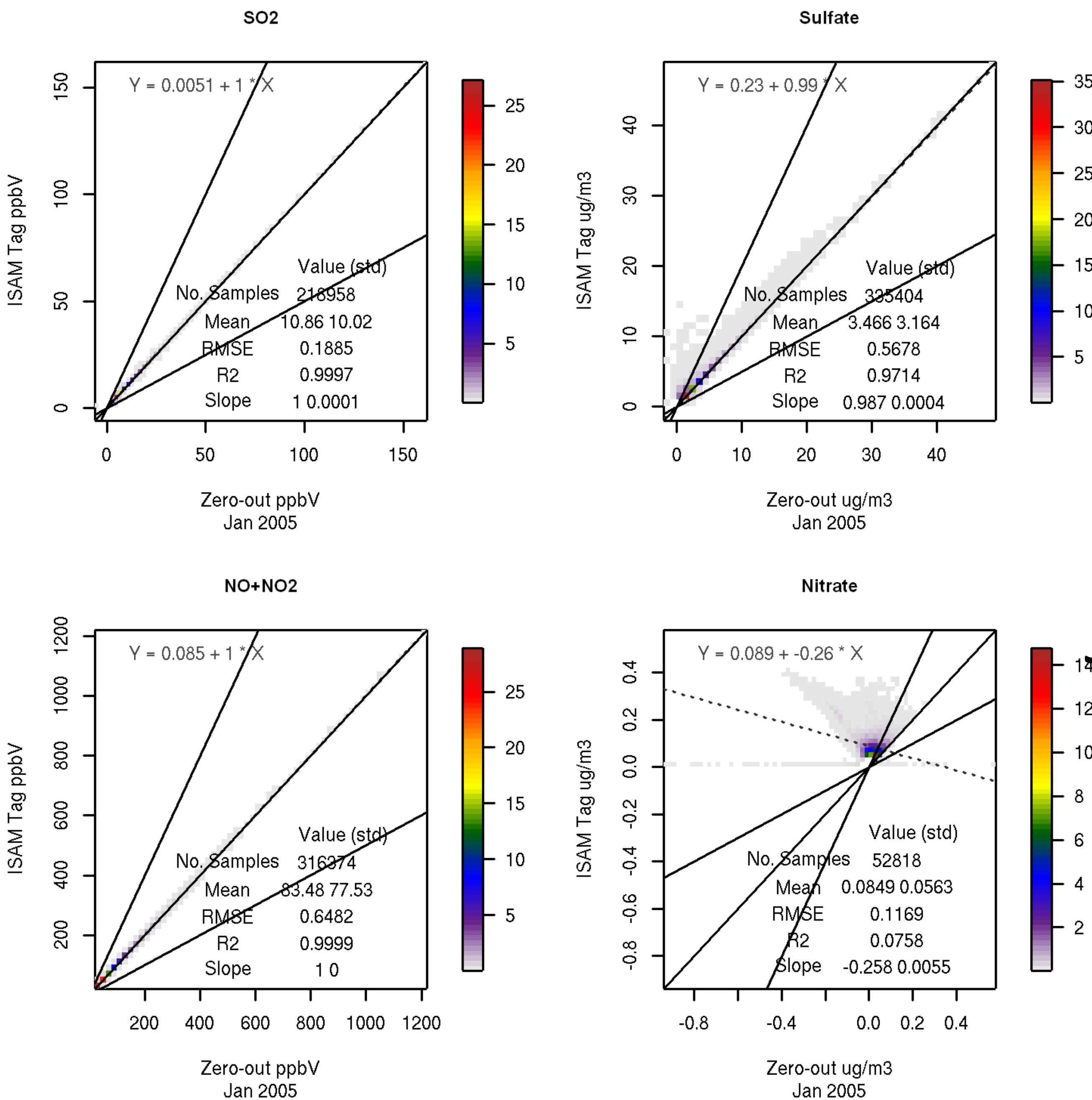
Test Case Emissions (Red to be tracked by ISAM)

$E_{total} = E_{baseline} + E_{ideal}$

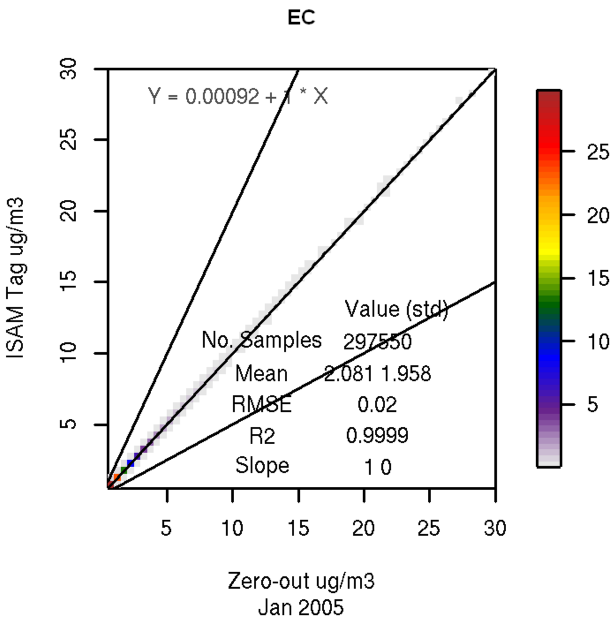


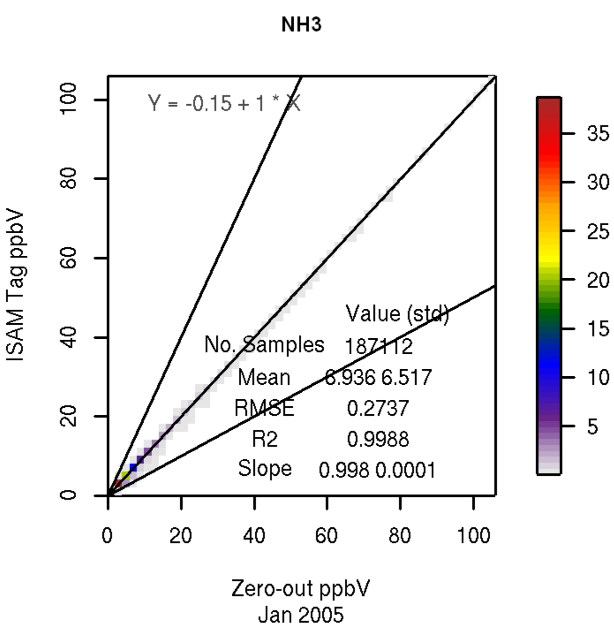


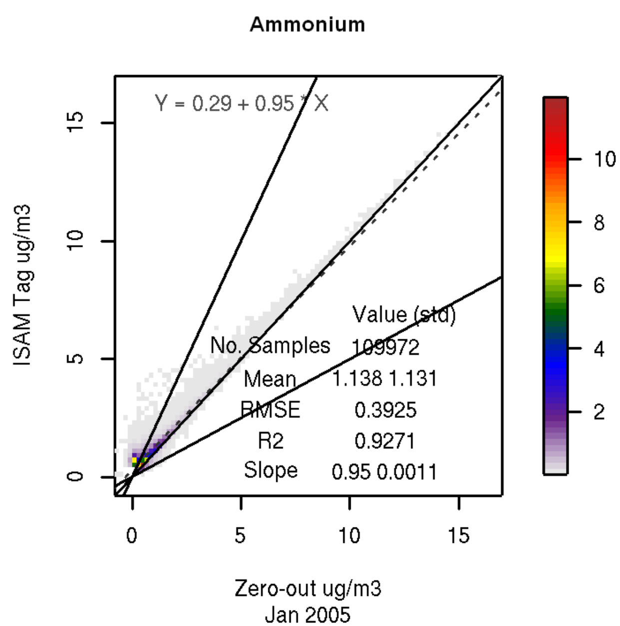
ISAM-0out Scattered Density Plots of Conc - January 2005



ISAM-0out Scattered Density Plots of Conc - January 2005

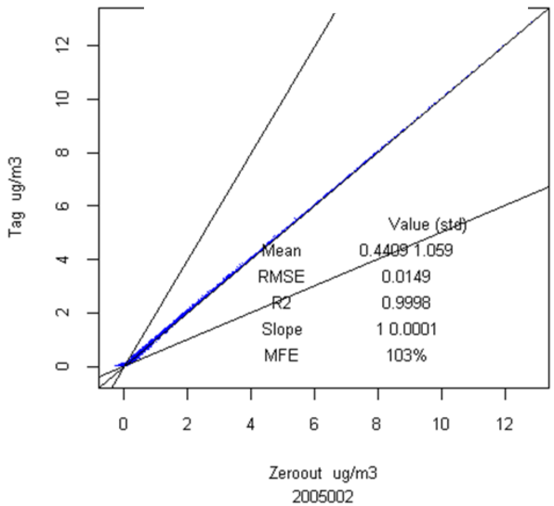




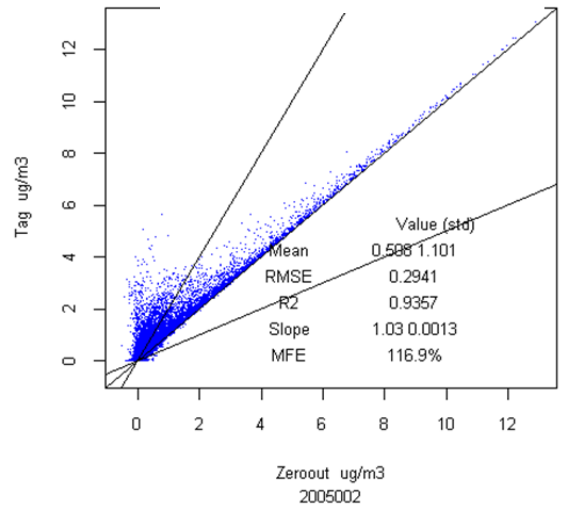


Process-level Analysis -- Sulfate

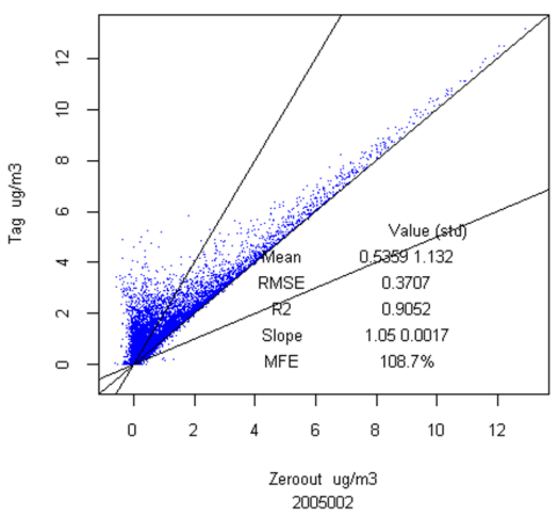
Phys+Gas ON;
Cld+Aer OFF



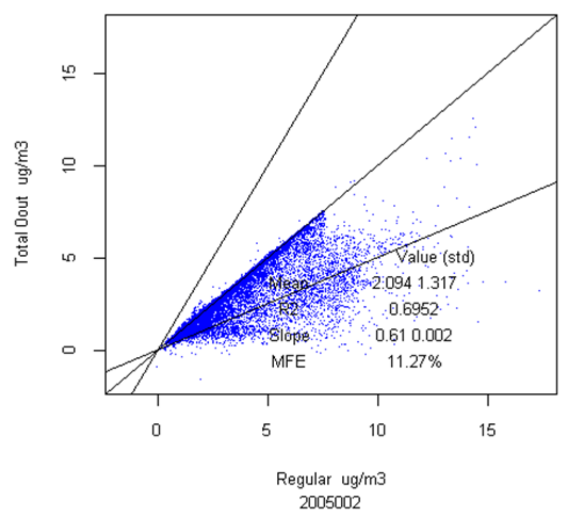
Phys+Cld ON;
Gas+Aer OFF



Full Process ON



Total 0out vs Bulk Conc



Message:

1. ISAM/zeroout discrepancy mostly attributed to in-cloud chemistry

2. ISAM/zeroout discrepancy has nothing to do with ISAM; the zero-out total mass is always different from the bulk mass

Process-level Analysis --- Nitrate

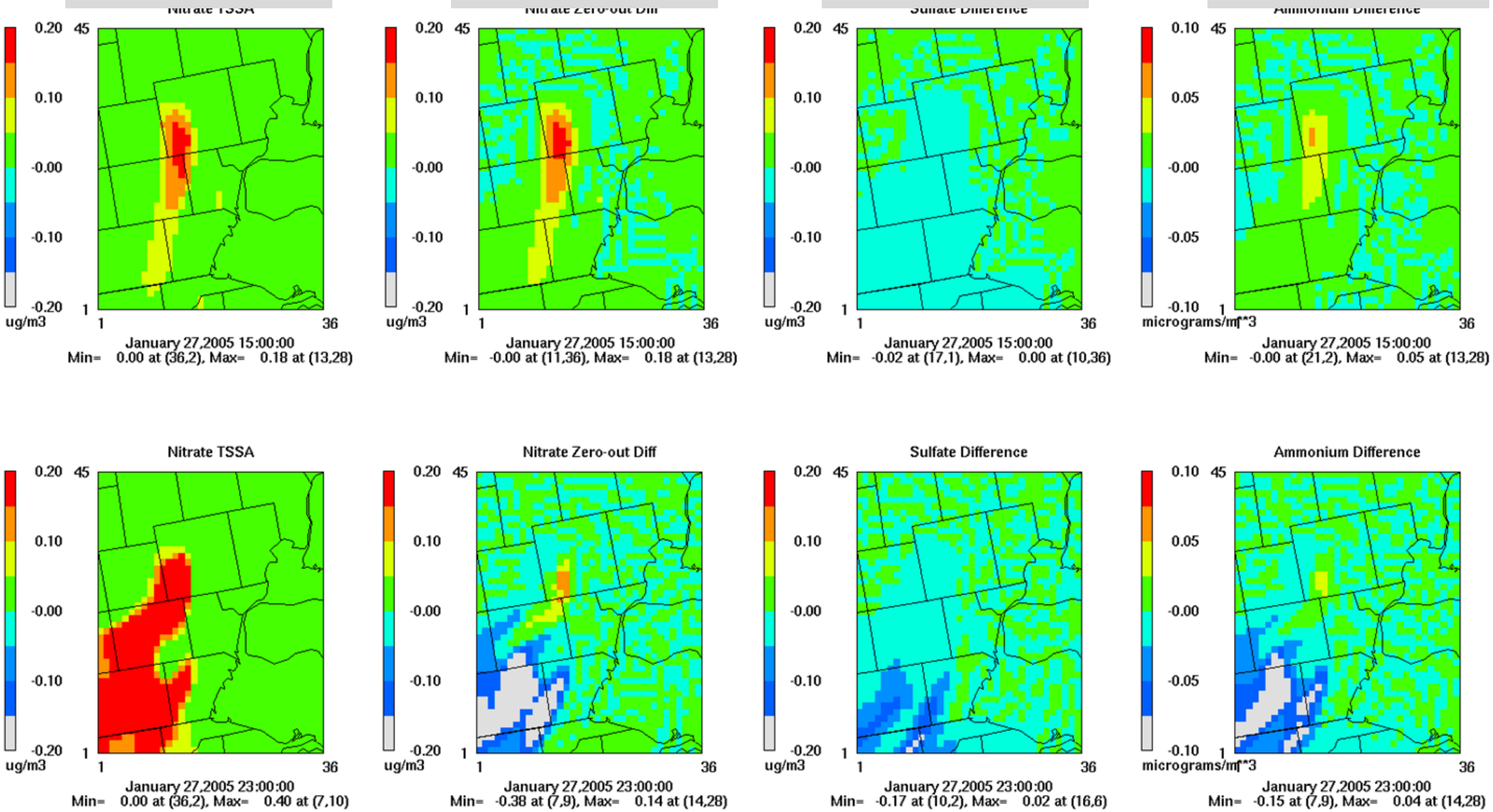
$C_{0,speciesJ} = C(E_{total}) - C(E_{total} - E_{speciesK})$

speciesJ = speciesK | speciesJ ≠ speciesK | speciesJ ≠ speciesK

ISAM nitrate | 0out nitrate | SO4 Diffrnce | NH4 Diffrnce

High ISAM-zeroout Correlation

Low ISAM-zeroout Correlation



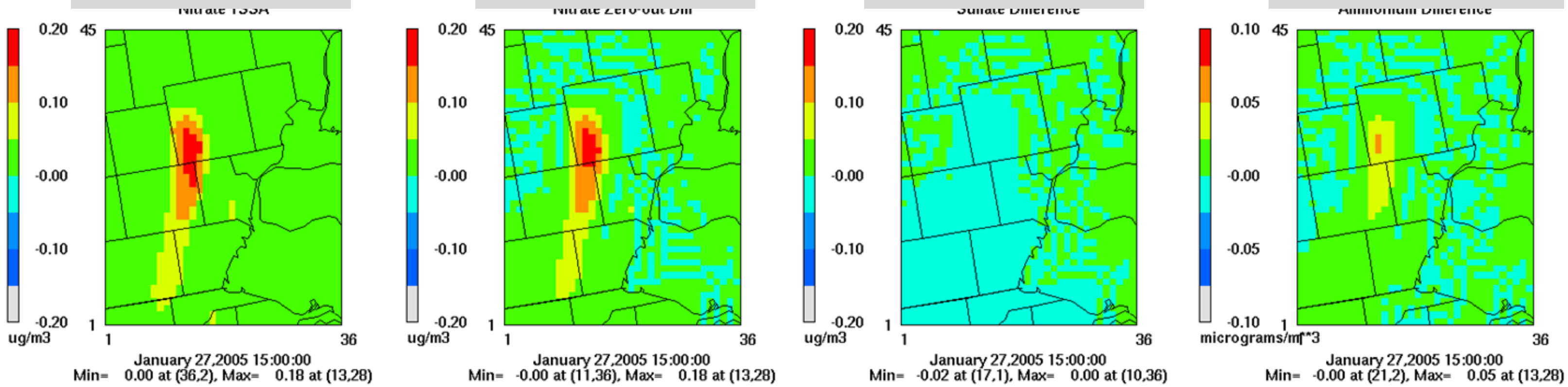
Process-level Analysis --- Nitrate

$C_{0,speciesJ} = C(E_{total}) - C(E_{total} - E_{speciesK})$

speciesJ = speciesK | speciesJ ≠ speciesK | speciesJ ≠ speciesK

ISAM nitrate | 0out nitrate | SO4 Diffrnce | NH4 Diffrnce

High ISAM-zeroout Correlation



Sulfate regimes depend on sulfate and NH_3; independent of HNO_3;

NH3 first neutralizes sulfate to form $(NH_4)_2SO_4$;

Remaining NH_3 then combines with HNO_3 to form NH_4NO_3.

Small SO4 diff => same SO4 regime => nitrate formation unaffected

Process-level Analysis --- Nitrate

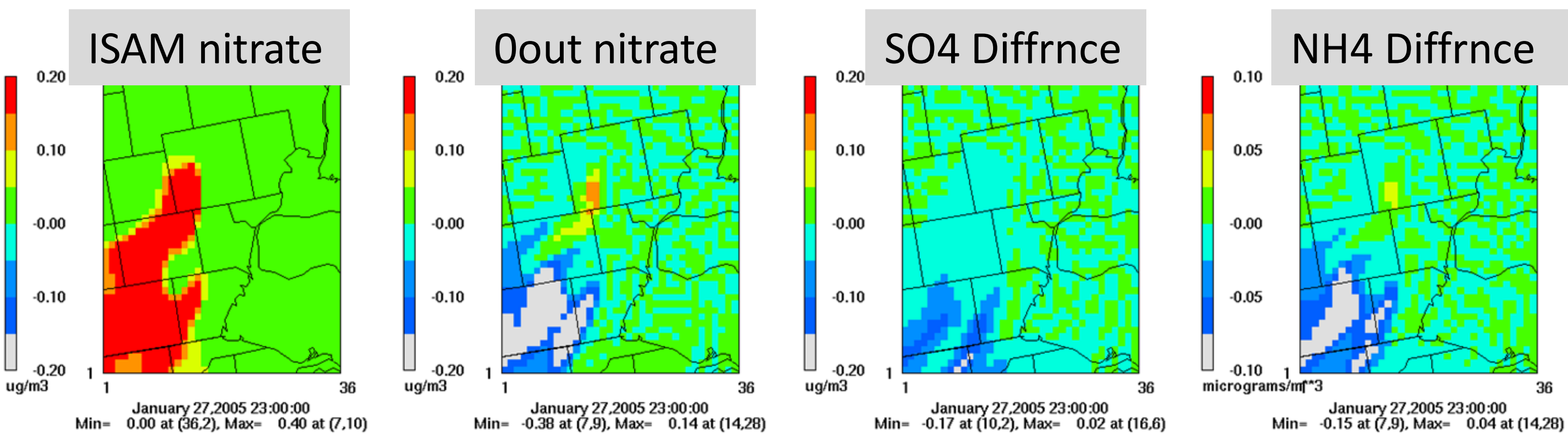
Sulfate regimes depend on sulfate and NH_3; independent of HNO_3;

NH3 first neutralizes sulfate to form $(NH_4)_2SO_4$;

Remaining NH_3 then combines with HNO_3 to form NH_4NO_3;

Clear SO4 diff => change in SO4 regimes => NO3 formation affected => ISAM/zeroout discrepancy

Low ISAM-zeroout Correlation

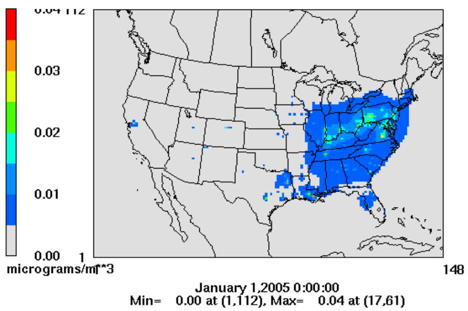


CONUS 2005 Application

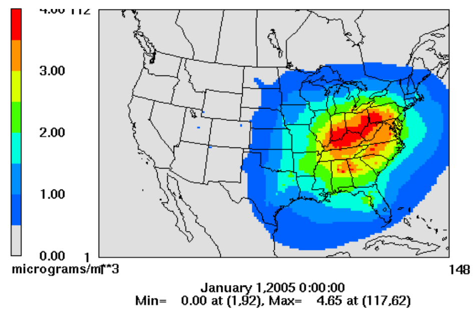
- Intended to illustrate capability of the tool and provide a “sanity check” of the results
- Tracking well known emissions sector and pollutant combinations
- Included contributions from lateral boundary conditions
- Annual 36 km simulation

CONUS Application 2005

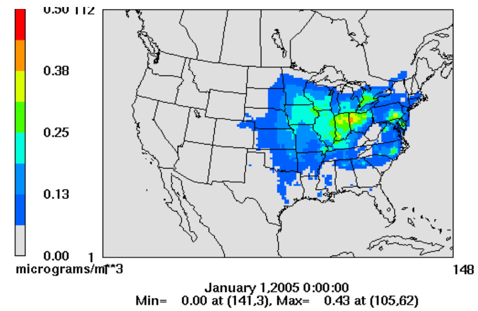
EC Electric Gen Units



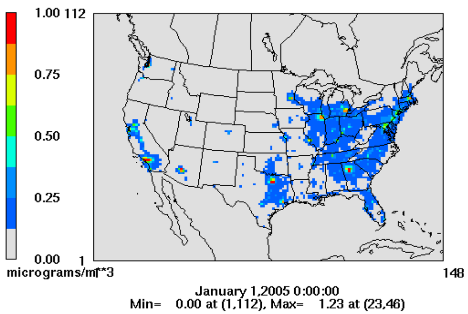
SO4 Electric Gen Units



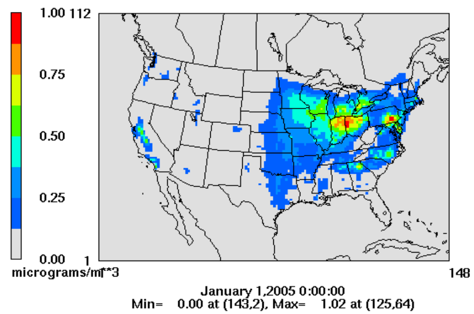
NO3 Electric Gen Units



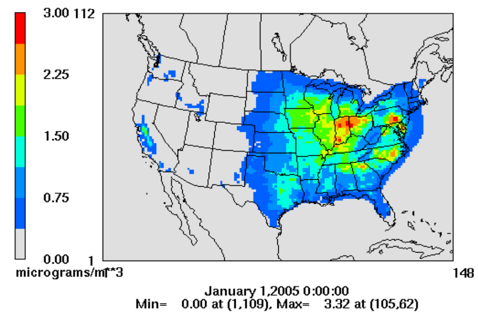
EC On-road



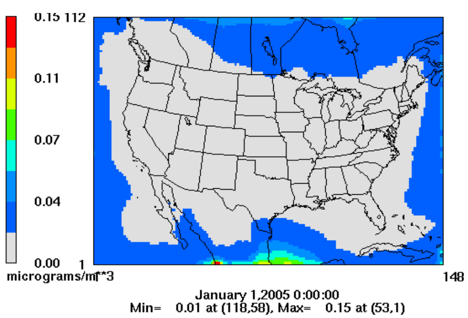
NO3 On-road



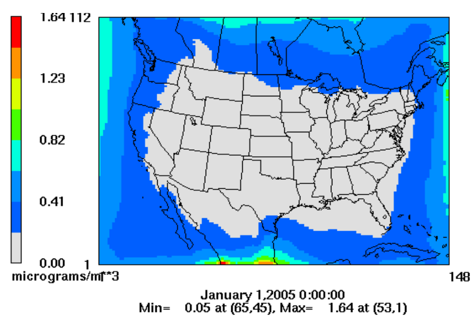
NH4 Agriculture



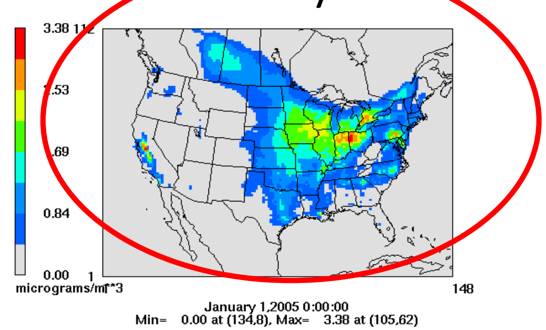
EC Boundary Condition



SO4 Boundary Condition

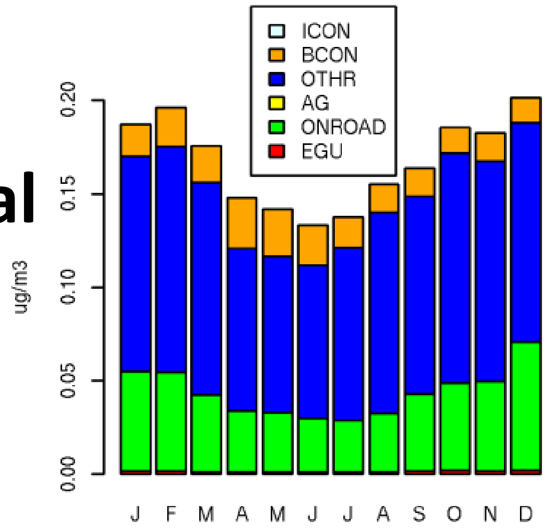


NO3 Boundary Condition

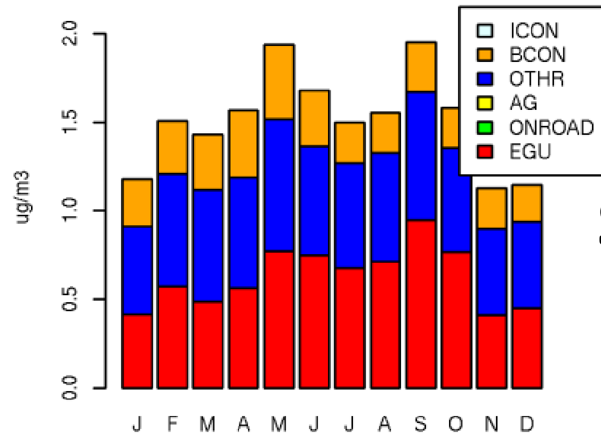


CONUS Application 2005

Elemental Carbon



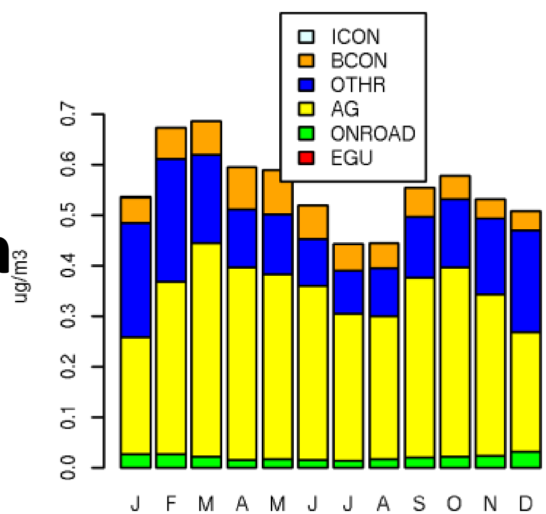
Contributing Sectors of 2005 CONUS AEC



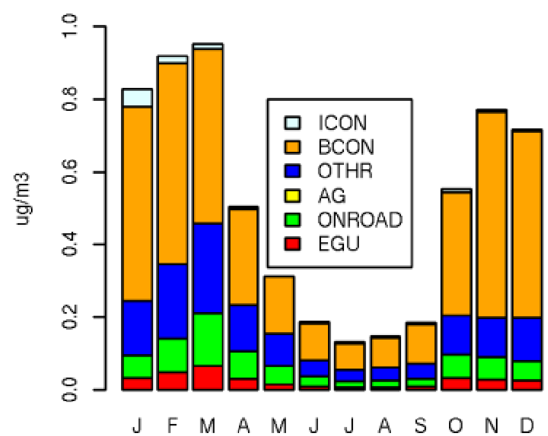
Contributing Sectors of 2005 CONUS ASO4

Sulfate

Ammonium



Contributing Sectors of 2005 CONUS ANH4



Contributing Sectors of 2005 CONUS ANO3

Nitrate

Conclusions

- ISAM compares well with zero-out for near-linear systems (EC, OC, SO_2, NH_3, NO_x)

- ISAM compares less well for nonlinear systems:

  (a) Sulfate mainly due to in-cloud chemistry

  (b) Nitrate and ammonium due to change of mass balance between total nitrate (HNO_3+NO_3), total ammonium (NH_3+NH_4) and sulfate during aerosol thermo-dynamic equilibrium

- For nonlinear systems, zero-out approach is not a good reference to evaluate ISAM because difference in emissions alters chemical and ionic balances which do not occur in ISAM

- ISAM/zero-out compared for dry and wet deposition as well

Ongoing work on ISAM

- Migration of ISAM to CMAQ 5+
- Documentation
- Additional capabilities of apportioning ozone and PM2.5 ions
- Improvement on dry deposition attribution by recalculating deposition velocities of species from individual source groups
- Inclusion of an option to discern sulfate regimes when apportioning ammonium and nitrate

Acknowledgment

The project participants would like to recognize the contributions of Zion Wang, Gail Tonnesen, Kristen Foley, and David Wong to this project.