THE U.S. EPA COMMUNITY MULTISCALE AIR QUALITY (CMAQ) MODELING SYSTEM – GAS-PHASE CHEMISTRY

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Gas-Phase Chemical Kinetics

- Mechanisms in CMAQ model
  - RADM2
  - CB4
  - SAPRC99
- Solvers in CMAQ model
  - SMVGEAR
  - QSSA
  - MEBI
  - EBI

RADM2

- From Regional Acid Deposition Model
- Stockwell et al. (1990)
- Lumped-species mechanism
  - Uses reactivity weighting of organic compounds
  - 57 species (incl. 21 photolytic)
  - 158 reactions
- Updates
  - CH4 = 1.85 ppm (constant)
  - Negative coefficients eliminated from CSL + OH reaction (legacy rxn)

CB4

- Carbon-Bond, Version 4
- Gery et al. (1989)
- Lumped-structure mechanism
  - Uses bond structures in organics
  - 36 species (incl. 12 photolytic)
  - 93 reactions
- Updates
  - CH4 = 1.85 ppm (constant)
  - PAN rate constants updated (early 1990's)
  - Added XO2+HO2 termination reaction (early 1990's)

- Added SO2 chemistry
- Temperature- and *pressure*-dependent rate constant expressions

SAPRC99

- From Statewide Air Pollution Research Center – UC-Riverside
- Carter (2000)
- Lumped-species mechanism
  - Uses reactivity weighting of organic compounds
  - 72 species (incl. 30 photolytic)
  - 214 reactions
- Updates
  - CH4 = 1.85 ppm (constant)
  - Added OH reactions with formic, acetic, and higher organic acids

Isoprene Extensions

- Based on Carter (1996)
- 2 versions:
  - 1-product
    - ISOP oxidation → ISOPROD
  - 4-product
    - ISOP oxidation → METHACRO, MA_PAN (PAN analogue from METHACRO), MVK, ISOPROD (other products)
- RADM2- 1- and 4-product versions
- CB4- 1-product version
- SAPRC99- 4-product version

Aerosol Extensions

- Heterogeneous rxn: $N_2O_5 \rightarrow HNO_3$
  - Method of Dentener and Crutzen (1993)
  - Rate is function of gas-phase N_2O_5 diffusion, aerosol particle radius, aerosol sfc area, reaction probability
    - Reaction probability based on Riemer (2003); function of aerosol composition
      - Varies from 0.02-0.002
- Heterogeneous rxn used when modeling gases and aerosols; gas-phase rxn turned off
- Gas-phase rxn turned on when modeling gas-phase only

- SOA produced from gas-phase alkanes, aromatics, cresols, and terpenes
  - SOA production from olefins omitted because of high vapor pressures of semivolatiles
    - SOA from olefins estimated at <5-10% of anthropogenic SOA)
- Partitioning model based on Schell et al. (2001)
- Gas-phase yields are based on:
  - Odum (1997) for aromatics
  - Griffin et al. (1999) for terpenes
  - Strader et al. (1999) for alkanes and cresols

Photolysis Rates

- Clear-sky photolysis rates calculated in preprocessor (JPROC)
  - 2-stream Delta-Eddington RT model calculates actinic flux
  - Table look-up, based on latitude, height, date/time
- Cloud attenuation/enhancement as in RADM
- Fast TUV code (Madronich) now being incorporated for on-line photolysis rate calculations
  - Met/chem feedbacks through aerosols

SMVGEAR

- Sparse Matrix Vectorized Gear solver
  - Generalized solver
  - Most accurate solution to stiff ODE systems
  - Jacobson and Turco (1994)
- Sparse matrix techniques make for efficient code on vector and non-vector computers
- Error tolerances are user-specified
  - Relative error: 0.001
  - Absolute error: 10^{-9} ppm

QSSA

- Quasi-steady state approximation
- Low-order, generalized solver
- Based on solver in Regional Oxidant Model
- Accuracy controlled by setting limits on chemistry time step
  - Upper limit now set at 1 min in CMAQ
- Issues of solution accuracy have been seen in some applications

MEBI and EBI

- Euler Backward and Modified Euler Backward Iterative schemes (after Hertel, 1993; Huang and Chang, 2001)
- Functional iteration used to obtain solution to implicit Euler backward approximation
- Fast and accurate
- Not a generalized method

- For speed, coupled species groupings are solved together
  - NO, NO2, O3, O(3P)
  - OH, HO2, HONO, HNO4
  - NO3, N2O5
  - PAN, C2O3
- EBI
  - Fastest; most “hard-wired” to a mechanism
  - Analytical expressions used to solve 4 groups
  - Implemented for CB4; SAPRC99 being tested now

- MEBI
  - Somewhat slower than EBI, but still faster than SMVGEAR or QSSA
  - Somewhat less hard-wired than EBI, but still not a generalized solver
  - Uses Newton-Raphson numerical solutions for first 2 species groups; analytical expressions for second 2 groups
  - Implemented for CB4; RADM2; SAPRC99

CMAQ Solver Performance Comparison (for SAPRC99)

CONUS 32 Km / Jun 30 - Jul 5, 1999 / No AE or CLDS / (178 x 124 x 21 cells)

Linux P3/1.4 GHz using 2 CPUs

Solver	Average CPU time / day (hrs)	Mean Rel. Abs. Differences, % (C >1.0E-06 ppm)			
		O3	NO	NO2	HNO3
SMVGEAR	16.7				
QSSA	8.6	1.15	4.72	6.25	2.88
MEBI	5.1	0.12	3.13	0.99	0.45
EBI	4.0	0.02	0.36	0.54	0.22
EBI (nrt)	3.5	0.04	0.94	0.91	0.31

versus SMVGEAR versus MEBI nrt=no radical transport

Future Work

- Replace CB4 with CB4-2002
  - Implementation and testing- 2004
  - In public CMAQ release- 2005
- Drop RADM2 from CMAQ
  - Work with Stockwell to include RACM
- Upgrades to SAPRC from Carter
- Morphecule-type mechanism
  - Carries detailed chemical information with fewer numerical solutions
  - Major implications for emissions processing

- More simplified chemistry for engineering approach?
- EBI solver for all mechanisms
- Combined gas- and aqueous phase chemistry module
- On-line radiation and photolysis calculations
  - Feedback to meteorology through aerosols and radiation
  - Working with WRF-Chem online model