DEVELOPMENT OF CHEMICAL SPECIATION DATABASE AND SOFTWARE FOR PROCESSING VOC EMISSIONS

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June 9, 2004

• Problems with current VOC speciation databases and software
• Project Objectives and Approach
• Speciation Database Development
• Speciation Processing Software for SMOKE
• Current Status and Additional Work Needed
BACKGROUND

- VOC emissions consist of many hundreds of chemical compounds with widely varying atmospheric reactivities.
- These are represented in models by a much smaller number of model species, depending on the chemical mechanism used.
- The most appropriate mechanism and set of model species depends on the model application.
- Most models use highly condensed mechanisms that are not appropriate for VOC reactivity or toxics assessment applications.
- Emissions processing is a major obstacle to implementing new or more detailed mechanisms into airshed models.
  - Emissions and mechanism processing software have limitations that make changing mechanisms difficult.
  - Difficult to make assignments for the hundreds of chemical using the current categorization systems.
PROBLEMS WITH CURRENT SPECIATION PROFILE DATABASES

• Different profile databases use different chemical categorization systems. For example
  - EPA and California SAROAD codes are incompatible
  - EPA’s SPECIATE database uses different categories

• Many chemical categories are redundant, poorly defined, or refer to mixtures of uncertain composition. This means:
  - Assigning model species requires assumptions about compositions of the uncertain mixture categories
  - Inconsistent or inappropriate mechanism assignments occur

• Model species assignment files exist for only a few condensed mechanisms (CB4, RADM-2, lumped SAPRC) that are not suitable for many toxics or VOC reactivity applications

• Data bases are not set up for easy modifications of mechanisms
PROBLEMS WITH CURRENT SPECIATION SOFTWARE

• Re-processing emissions for new or modified mechanisms is very computer and labor intensive

• Emissions processing systems do not include documented software to easily update mechanism assignment files when:
  - speciation profiles change or are updated
  - mechanisms or model species assignments are changed
  - selected compounds are to be represented explicitly

• The capabilities of the detailed SAPRC mechanisms for VOC reactivity assessment is not supported. These include:
  - Adjusting parameters in mechanism to best represent detailed compositions of VOC emissions
  - Change how VOCs are lumped and compute the mechanisms for the new lumped or explicit species
PROJECT OBJECTIVES AND APPROACH

OBJECTIVES

• **Specific Objective**: Implement capabilities of the SAPRC-99 detailed mechanism into the SMOKE emissions system

• **Broader Objective**: Improve speciation database and software for easier and consistent implementation of all mechanisms

APPROACH

• Develop an improved emissions speciation database with consistent assignments for SAPRC-99, CB4 and RADM-2

• Develop software to implement speciation database and assignments in SMOKE

• Test programs to demonstrate application to VOC reactivity assessment
### SPECIATION DATABASE DEVELOPMENT

- Chemical categories used to specify chemical compositions of profiles in various databases combined into a single database
  - U.S. EPA, California, and Texas modeling databases
  - EPA’s Speciate 3.2 database
  - Categories used in the SAPRC-99 detailed mechanism
- Duplicate categories removed.
- Categories classified as follows:

<table>
<thead>
<tr>
<th>Code</th>
<th>Description</th>
<th>For assignment to</th>
<th>Categories</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Single compound</td>
<td>Model species</td>
<td>1387</td>
</tr>
<tr>
<td>2</td>
<td>Isomeric mixture</td>
<td>Compounds</td>
<td>367</td>
</tr>
<tr>
<td>3</td>
<td>Complex mixture</td>
<td>Compounds</td>
<td>187</td>
</tr>
<tr>
<td>4</td>
<td>Poorly defined</td>
<td>Unassigned mass</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td><strong>Total:</strong></td>
<td></td>
<td><strong>1973</strong></td>
</tr>
</tbody>
</table>
## ASSIGNMENTS MADE TO SINGLE COMPOUNDS

<table>
<thead>
<tr>
<th>Assignment Type</th>
<th>Fraction Ass’d Cmpds</th>
<th>Mass¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic formula and molecular weight</td>
<td>All</td>
<td>All</td>
</tr>
<tr>
<td>EPA’s VOC exempt status</td>
<td>All</td>
<td>All</td>
</tr>
<tr>
<td>CAS number</td>
<td>0.92</td>
<td>0.997</td>
</tr>
<tr>
<td>SAPRC-99 Detailed Model Species² (666)³</td>
<td>0.75</td>
<td>0.9995</td>
</tr>
<tr>
<td>Emissions Groups² (used to make lumped SAPRC-99 and RADM-2 assignments) (64)³</td>
<td>0.91</td>
<td>~1</td>
</tr>
<tr>
<td>Carbon Bond 4 Species² (11)³</td>
<td>0.94</td>
<td>~1</td>
</tr>
<tr>
<td>Compounds judged to be non-volatile</td>
<td>0.04</td>
<td>0.003</td>
</tr>
</tbody>
</table>

1. Fraction of mass in all Speciate 3.2 profiles, each weighted equally
2. Assignment fractions exclude compounds judged to be non-volatile
3. Number of model species or groups

TYPES OF MODEL SPECIES

- SAPRC-99 Detailed model species: individual compounds or groups of compounds assumed to have similar reactivities, for which reactivity values have can be calculated.

- Emissions groups: Groups of compounds expected to be lumped together in “lumped molecule” mechanisms.
  - Originally developed for emissions processing for RADM-2, and extended to lumped SAPRC-99 and RACM

Examples of Emissions Groups (of 64)

<table>
<thead>
<tr>
<th>Emissions Groups</th>
<th>Lumped SAPRC-99</th>
<th>RADM-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkanes ( k_{OH} = 1-2 \times 10^4 \text{ ppm}^{-1} \text{ min}^{-1} )</td>
<td>ALK5</td>
<td>0.945 HC8</td>
</tr>
<tr>
<td>Ethanol</td>
<td>ALK3</td>
<td>1.198 HC3</td>
</tr>
<tr>
<td>Aromatic aldehydes</td>
<td>BALD</td>
<td>NR</td>
</tr>
</tbody>
</table>

- Carbon Bond species: Used to represent parts of molecules that are assumed to react independently in Carbon Bond 4
ASSIGNMENTS MADE TO MIXTURES

- As many mixtures as possible were assigned to distributions of individual compounds or designated “nonvolatile”.

**Examples:**

| Simple mixture: | 1/3 heptyl benzene |
|                | 1/3 1-butyl-3-ethyl benzene |
|                | 1/3 1-methyl-2,4-dipropyl benzene |

| Complex Mixtures: | Composite petroleum distillate profile derived by Censullo, et al, 1996 |
| Distillates, naphtha, mineral spirits |

| C_{19} compounds (diesel exh.) | Nonvolatile |
| “Fragrances” | Not assigned |

| Poorly defined category: | Not assigned |
| CB4 paraffin bond (PAR) |

- All “Simple Mixtures” and 60% of the “Complex Mixtures” were assigned. (92% of the mass in sum of all Speciate 3.2 profiles)
TREATMENT OF NONVOLATILE COMPOUNDS

• Although VOC (or TOG) profiles should not contain non-volatile compounds, profiles contain compounds or mixtures such as:
  - eicosane ($C_{20}H_{42}$)
  - n-hexadecanoic acid ($C_{16}H_{32}O_2$)
  - benzo(a)pyrene ($C_{20}H_{12}$)
  - 2-propenoic acid, butyl ester, polymer with ethenyl acetate

• These are judged to be non-volatile and therefore not appropriately represented by gas-phase model species

• If these judgments are correct, these need to be either
  - moved to the PM profiles and the VOC mass reduced
  - Processed as PM species

• In the meanwhile, the alternatives are to:
  - represent the nonvolatiles as if they were inert volatiles, or
  - exclude nonvolatiles from emitted volatile mass
PROFILE DATABASE

- Profiles from various sources combined into a single database
  - EPA’s Speciate 3.2 database
  - EPA’s Models-3 emissions database
    o Provided by Gipson, 11/01
    o Most but not all judged to be same as Speciate profiles
  - Texas database
    o Provided by Yarwood (Environ) in July, 2002.
    o Does not include newer profiles developed for TCAQ
    o All but 5 are same as Speciate or EPA profiles
  - California ARB database
    o Downloaded from CARB web site. Dated 3/19/03
    o Most are different from Speciate or EPA profiles
- Profiles judged to be same as others flagged as such
- All chemical categories in these databases assigned master speciation database categories for mechanism processing
SPECIAL PROFILES ALSO INCLUDED IN THE PROFILE DATABASE

USEFUL FOR ASSIGNING MODEL SPECIES TO EMISSIONS:

• “Representative Unknown #1”
  - Example of a type of profile that might be used to represent unknown mass when assigning model species to emissions
  - Consists of the mixture of all nC>6, Mwt>120 compounds in the Speciate 3.2 all-profile average

• “Representative Unassigned #1”
  - Example of a type of profile that might be used to represent compounds not assigned to model species
  - Molecule-weighed average of all compounds represented by SAPRC-99 mechanism in each SAPRC-99 chemical class.
SPECIAL PROFILES ALSO INCLUDED IN THE PROFILE DATABASE

USEFUL FOR DERIVING MECHANISM PARAMETERS

• “ARB 1994 Base ROG”
  - Derived from morning urban ambient air measurements
  - Used to represent base case emissions from all sources in scenarios used to derive “Carter” reactivity scales
  - Used to derive mechanistic parameters for the “fixed parameter” lumped SAPRC-99 mechanism in CMAQ

• “EPA Models-3 1998 Base ROG”
  - Derived from total anthropogenic emissions data in a 1998 EPA Models-3 emissions database
  - Included with SAPRC-99 mechanism files as an option for deriving mechanistic parameters based on emissions data
CURRENT IMPLEMENTATION OF DATABASES

• SPECIATION DATABASE
  - Implemented in Excel spreadsheet file with assignments of:
    o Existing profile speciation categories to master categories
    o Mixture categories to compounds
    o Compounds to model species
    o Characteristics of model species for various mechanisms
  - Macros written for following functions:
    o Compile mixture and mechanism assignments
    o Output assignments in ASCII files for use by speciation software for SMOKE

• PROFILE DATABASE
  - Implemented in an Excel spreadsheet with
    o Available documentation information for profiles
    o Profile compositions (using native categories)
  - Macro to output ASCII files with profile compositions and documentation for use by speciation software
SPECIATION PROCESSING PROGRAMS

- Profile Processor (**ProfPro**)
  - Converts profile composition data using native chemical categories to compositions of individual compounds
  - Needs only be run once for each profile unless assignments or profile compositions changes

- Speciation Processor (**SpecPro**)
  - Produces model species assignments for profiles (SMOKE GSPRO file) given profile compositions and mechanism lumping assignments
  - Allows users to specify alternative lumping or explicit representation of selected compounds
  - Gives users options for how to represent unknown or unassigned mass
  - Optionally outputs VOC to TOG factors for the profiles (mechanism independent)
MECHANISM PROCESSING PROGRAMS

• Mechanism Processor (MechPro)
  - Prepare mechanism files for CMAQ for adjusted parameter mechanisms given lumping and total emissions profile
  - Can also prepare mechanism files with new model species given reactions or mechanism parameters and lumping
  - Needed to implement full capabilities of SAPRC-99

• Emissions Summary program (EmitSum)
  - Prepares total emissions profile given total mass emissions of all profiles into modeling domain and profile compositions
  - Output used as input to MechPro to derive SAPRC-99 parameters that best fit emissions data for this domain

• CMAQ mechanism compiler (under preparation)
  - Compiles MechPro output into mechanism-dependent source files to be linked into CMAQ software
MECHANISM PROCESSING PROGRAMS

Profile Database → Profile Processor (ProfPro) → SMOKE Programs and Files → Chemical species in profiles → Emissions Summary (EmitSum)

Emissions Data → Total mass in domain by profile

Mechanism Parameter and Reaction Files → Mechanism Processor (MechPro) → Total Emissions Profile

Alternatively, another profile could be used to Represent total emissions

Mechanism Definition files → Mechanism Compilation Programs → CMAQ Model

Model User → Choice of Mechanism and Lumping

CURRENT STATUS

• The speciation and profile database development that can be carried out for current project is essentially complete

• Software development still underway
  - ProfPro, SpecPro, EmitSum, and MechPro run on PC systems but need to be integrated into SMOKE
  - Programs to compile MechPro output into CMAQ still in preparation
  - Programs still need to be tested and debugged

• CMAQ model simulation demonstrating applicability to reactivity assessment still need to be conducted

• Database spreadsheets, software and example input and output files are available at http://www.cert.ucr.edu/~carter/emitdb

• Databases have been incorporated into a PostgreSQL database programmed for online access
ADDITIONAL WORK NEEDED

• Success requires that the database be **used**. It also needs to be **updated** in to include new profiles and mechanisms.

• Assignments in database need to be reviewed and improved:
  - Volatility assignments – need objective basis
  - Mixture assignments – many are arbitrary guesses
  - CB4 assignments not all on consistent basis
  - Other mechanism assignments – may be mistakes

• Need to think about to represent unknown mass and unassigned compounds

• Assignments should be placed in “true” database and made available on web. (On-line PostgreSQL database a start)

• Need central clearing house and standards for profiles

• **Need to extend speciation database needs to PM profiles**
ACKNOWLEDGEMENTS

• Funding sources
  - University of Houston (project for Dr. Anthony Haymet): initial speciation database development
  - Subcontract to the UNC Carolina Environmental Programs for a project for the American Chemistry Council: completion of database, software development, and implementation

• Collaborators on UNC/ACC project
  - Mark Houhoux (now at EPA) -- work plan development
  - Jeff Vukovich (UNC) -- SMOKE implementation and testing
  - Chao-Jung Chien (UCR) -- CMAQ mechanism compiling

• Assistance and helpful discussions in data compilation
  - Paul Allen, CARB
  - Gerry Gipson, EPA
  - Ron Ryan, EPA
  - Greg Yarwood, Environ

• Programming for on-line PostgreSQL database
  - David Boss (personal initiative)