# DEVELOPMENT OF CHEMICAL SPECIATION DATABASE AND SOFTWARE FOR PROCESSING VOC EMISSIONS

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- 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:

| Code | Description | For assignment to: | Categories |
|---|---|---|---|
| 1 | Single compound | Model species | 1387 |
| 2 | Isomeric mixture | Compounds | 367 |
| 3 | Complex mixture | Compounds | 187 |
| 4 | Poorly defined | Unassigned mass | 32 |
| | | Total: | 1973 |

# ASSIGNMENTS MADE TO SINGLE COMPOUNDS

| Assignment Type | Fraction Ass'd | |
|---|---|---|
| | Cmpds | Mass[1] |
| Atomic formula and molecular weight | All | All |
| EPA's VOC exempt status | All | All |
| CAS number | 0.92 | 0.997 |
| SAPRC-99 Detailed Model Species[2] (666)[3] | 0.75 | 0.9995 |
| Emissions Groups[2] (used to make lumped SAPRC-99 and RADM-2 assignments) (64)[3] | 0.91 | ~1 |
| Carbon Bond 4 Species[2] (11)[3] | 0.94 | ~1 |
| Compounds judged to be non-volatile | 0.04 | 0.003 |

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) | Lumped SAPRC-99 | RADM-2 |
|---|---|---|
| Alkanes ($k_{OH}$= 1-2 x $10^4$ $ppm^{-1}$ $min^{-1}$) | ALK5 | 0.945 HC8 |
| Ethanol | ALK3 | 1.198 HC3 |
| Aromatic aldehydes | BALD | NR |

- 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:<br>$C_{12}$ alkyl benzenes | 1/3 heptyl benzene<br>1/3 1-butyl-3-ethyl benzene<br>1/3 1-methyl-2,4-dipropyl benzene |
| Complex Mixtures:<br>Distillates, naphtha, mineral spirits | Composite petroleum distillate profile derived by Censullo, et al, 1996 |
| $C_{19}$ compounds (diesel exh.) | Nonvolatile |
| “Fragrances” | Not assigned |
| Poorly defined category:<br>CB4 paraffin bond (PAR) | Not assigned |

- 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
    - Provided by Gipson, 11/01
    - Most but not all judged to be same as Speciate profiles
  - Texas database
    - Provided by Yarwood (Environ) in July, 2002.
    - Does not include newer profiles developed for TCAQ
    - All but 5 are same as Speciate or EPA profiles
  - California ARB database
    - Downloaded from CARB web site. Dated 3/19/03
    - 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

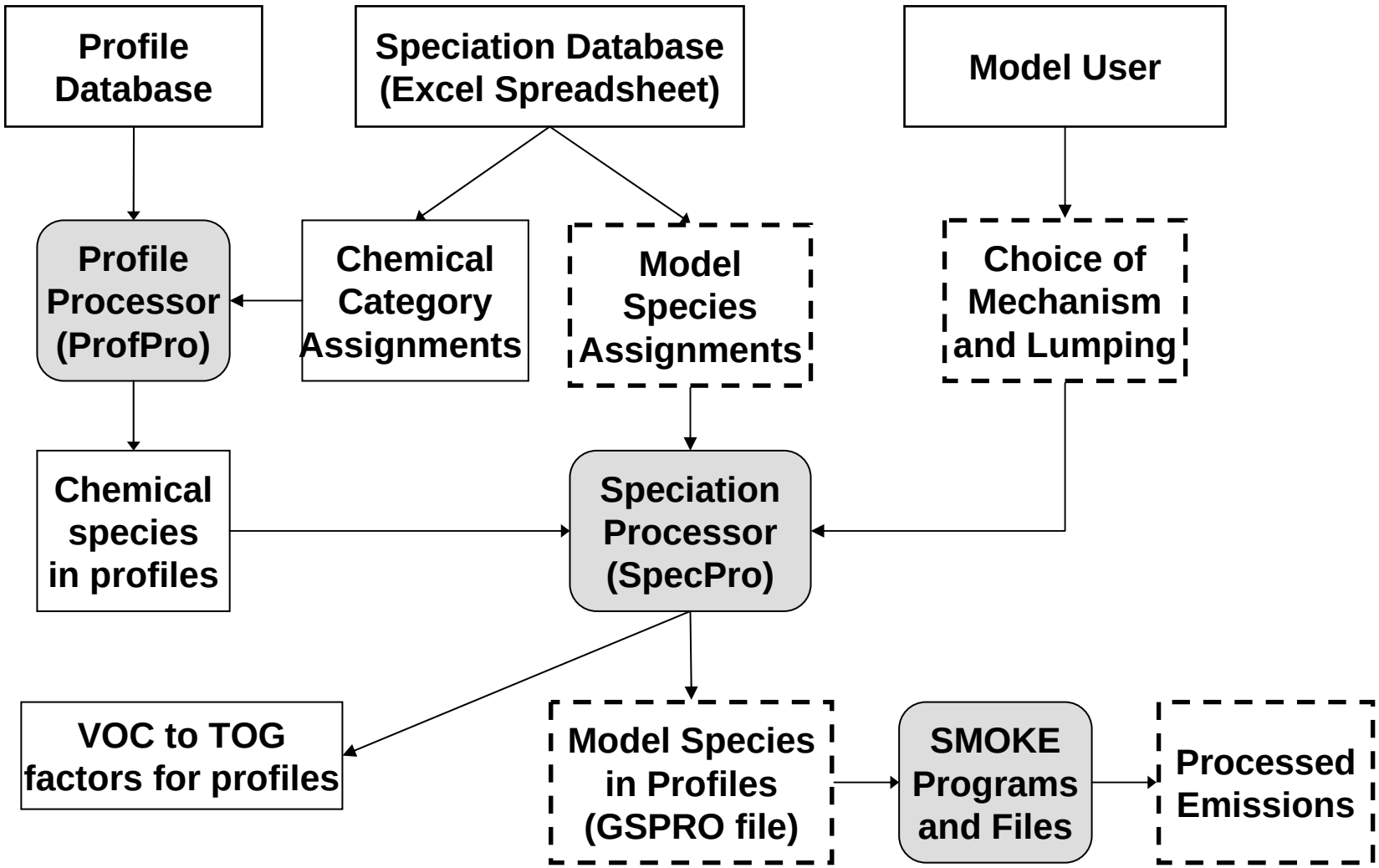
# CURRENT IMPLEMENTATION OF DATABASES

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

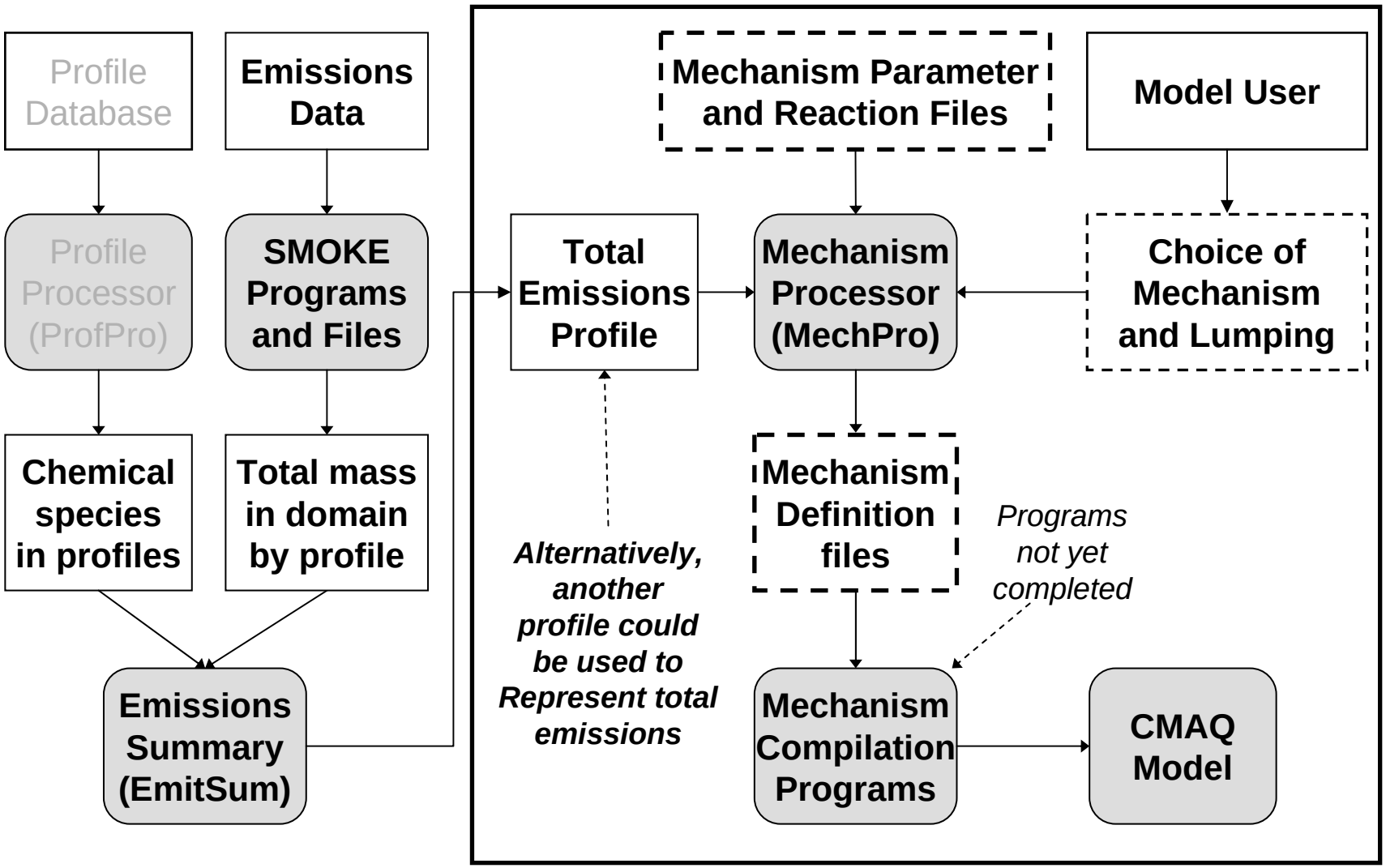
# SPECIATION PROCESSING PROGRAMS



# 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



# 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**

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  - Gerry Gipson, EPA
  - Greg Yarwood, Environ
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