# Mapping MOVES TOG to Chemical Mechanism Species for Air Quality Modeling

Harvey Michaels

FACA MOVES Review Workgroup
July 9, 2013

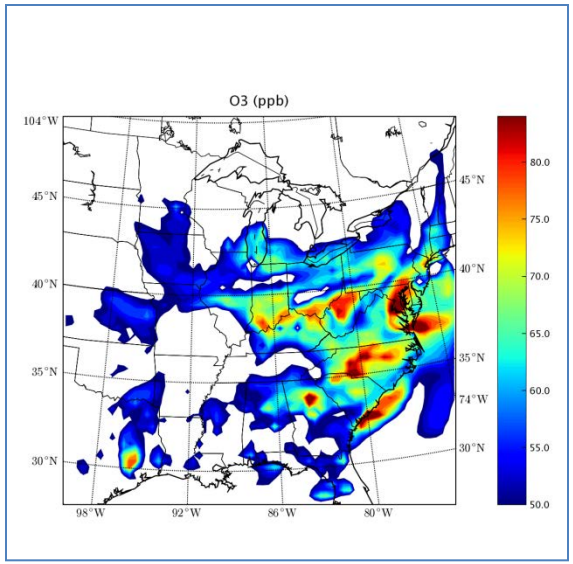
Air Quality & Modeling Center
Assessment and Standards Division
U.S. EPA Office of Transportation & Air Quality

# MOVES Output is Used for Air Quality Modeling

MOVES emission factors

SMOKE

Gridded, hourly emissions ready for air quality model




AQ Model

Source: Zubrow & Baek
MOVES Workshop, June 2011

# What are “Chemical Mechanism Species” for AQ Models?

- To make the chemistry of air quality models computationally feasible, the thousands of actual hydrocarbons are mapped to a relatively few “chemical mechanism” (CM) species.
  - Some CM species are real species (e.g., ethanol)
  - Other are artificial constructs, sometimes referred to as lumped or surrogate species. For example, in CB05, acrolein is mapped 2/3 by weight to ALDX2 and 1/3 to OLE.
- CM species are specific to a particular chemical mechanism (e.g., CB05, SAPRC-07)

# Mapping TOG to CM Species

- The mapping of pure species to CM species is not the problem.
- The problem is mapping TOG to CM species.
- The mapping depends on the composition of the TOG.
- The composition of the TOG depends on fuel, emission process, and technology.
  - Light duty gasoline:  Pre-Tier 2 vs. Tier 2
  - Heavy-duty diesel: pre-2007 and 2007+

# How do you map TOG to CM species?

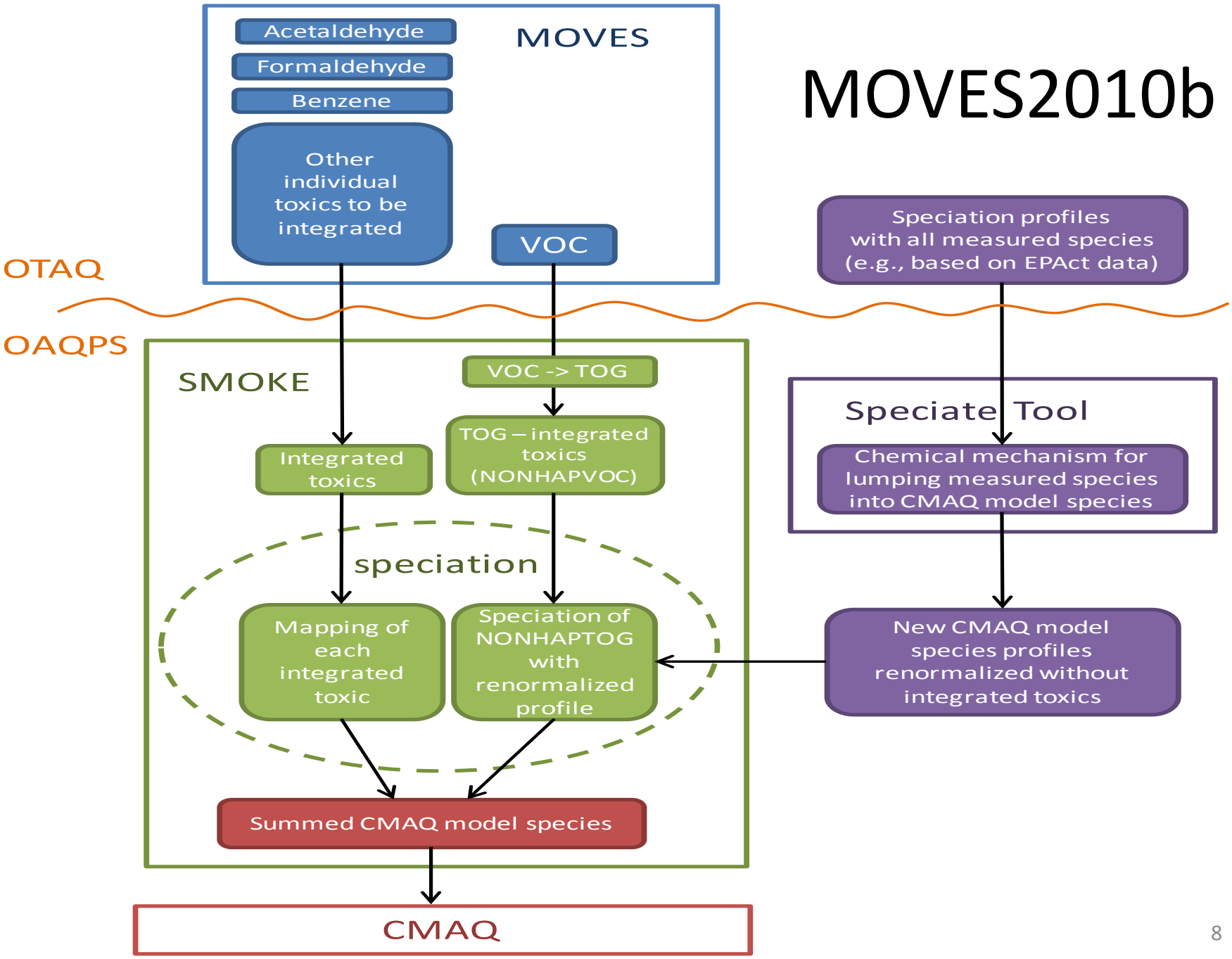
- A separate “real speciation profile” is associated with the TOG from each fuel, technology, and process.
- Each real speciation profile is used to create a “CM speciation profile” that maps TOG from each fuel-technology-process combination to the CM species needed by the chemical mechanism of the air quality model.

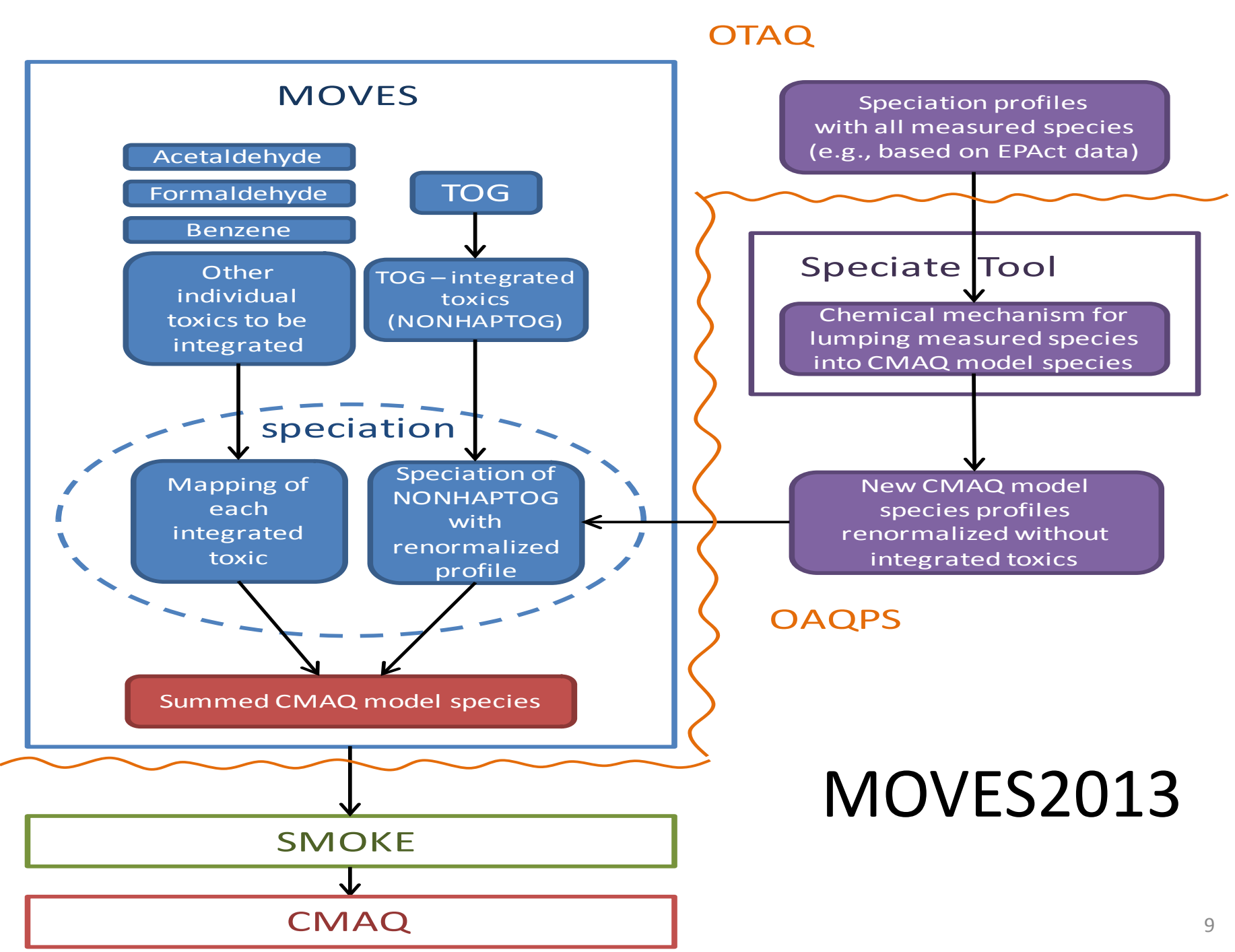
# What is the change in MOVES2013?

- We will move the mapping of TOG to CM species from outside MOVES to inside MOVES.

- MOVES2010b
  - MOVES produces TOG and some of its components
  - **SMOKE** maps these MOVES outputs into the CM species needed by the air quality model.
- MOVES2013
  - MOVES produces TOG and some of its components
  - **MOVES** maps these MOVES outputs into the CM species needed by the air quality model.

# MOVES2010b


MOVES
Acetaldehyde
Formaldehyde
Benzene
Other individual toxics to be integrated
VOC
OTAQ
OAQPS
Speciation profiles with all measured species (e.g., based on EPAct data)
SMOKE
VOC -> TOG
TOG – integrated toxics (NONHAPVOC)
Integrated toxics
Speciate Tool
Chemical mechanism for lumping measured species into CMAQ model species
speciation
Mapping of each integrated toxic
Speciation of NONHAPTOG with renormalized profile
New CMAQ model species profiles renormalized without integrated toxics
Summed CMAQ model species
CMAQ


OTAQ
MOVES
Acetaldehyde
Formaldehyde
Benzene
Other individual toxics to be integrated
TOG
TOG – integrated toxics (NONHAPTOG)
speciation
Mapping of each integrated toxic
Speciation of NONHAPTOG with renormalized profile
Summed CMAQ model species
SMOKE
CMAQ
Speciation profiles with all measured species (e.g., based on EPAct data)
Speciate Tool
Chemical mechanism for lumping measured species into CMAQ model species
New CMAQ model species profiles renormalized without integrated toxics
OAQPS
MOVES2013

# Problems with the current method

- Since speciation profiles depend on technology and fuels, they vary depending of the mix of model years and also on the location.
- Users create combined speciation profiles that approximate the mix of technologies and fuels

# Internal Mapping in MOVES2013 solves these problems

- Since MOVES knows the MY, technology, and fuels for every emission factor, it applies the correct speciation profile internally.
- External approximations are not needed.
- Approximate, combined speciation profiles do not need to be constructed.
- MOVES emission factors may be aggregated without concern that the detail needed to apply speciation profiles will be lost.
- Simpler and less error-prone emissions processing in SMOKE.

# “Integration” of MOVES’s Pure Species

- MOVES’s pure species are those it produces directly
- Those we intend to integrate are listed on the following slide.
- “Integration” means taking advantage of MOVES accuracy in estimating those species.

| MOVES pollutantID | pollutantName |
|---|---|
| 5 | Methane (CH4) |
| 20 | Benzene |
| 21 | Ethanol |
| 22 | MTBE |
| 24 | 1,3-Butadiene |
| 25 | Formaldehyde |
| 26 | Acetaldehyde |
| 27 | Acrolein |
| 40 | 2,2,4-Trimethylpentane |
| 41 | Ethyl Benzene |
| 42 | Hexane |
| 43 | Propionaldehyde |
| 44 | Styrene |
| 45 | Toluene |
| 46 | Xylene |
| 185 | Naphthalene gas |

# Integration Procedure

- Choose the pure species that you want to integrate.
- Map each pure species to CM species
- Remove each pure species from each of the TOG real speciation profiles and renormalize.
- Residual TOG = TOG – integrated species
- Run the residual TOG through the speciation tool.
- Repeat for each TOG speciation profile

# Summary

- Speciation does not change regular MOVES output.
- Able to provide CM species for multiple mechanisms.
- Able to work with multiple integrated species sets
- Table driven

# Appendices

# OTAQ's Current TOG Speciation Profiles

| Profile | Description |
|---|---|
| 1001 | CNG Exhaust |
| 4547 | Diesel Headspace |
| 8750 | Pre-Tier 2 E0 exhaust |
| 8751 | Pre-Tier 2 E10 exhaust |
| 8752 | Pre-Tier 2 E85 exhaust |
| 8753 | E0 Evap |
| 8754 | E10 Evap |
| 8755 | E85 Evap |
| 8756 | Tier 2 E0 Exhaust |
| 8757 | Tier 2 E10 Exhaust |
| 8758 | Tier 2 E15 Exhaust |
| 8766 | E0 evap permeation |
| 8769 | E10 evap permeation |
| 8770 | E15 evap permeation |
| 8774 | Pre-2007 MY HDD exhaust |
| 8775 | 2007+ MY HDD exhaust |
| 8855 | Tier 2 E85 Exhaust |
| 8869 | E0 Headspace |
| 8870 | E10 Headspace |
| 8871 | E15 Headspace |
| 8872 | E15 Evap |

# Example: Measurement data of speciation profile 8754 (E10 Evap)

| Species | Weight % | Species | Weight % | Species | Weight % |
|---|---|---|---|---|---|
| N-butane | 15.28123 | Methyl t-butyl ether (MTBE) | 0.32299 | Cis-1,3-dimethylcyclopentane | 0.01536 |
| Toluene | 14.52534 | Cis-2-pentene | 0.26655 | Trans-2-butene | 0.01496 |
| Ethyl alcohol | 12.05397 | 1-Methyl-4-ethylbenzene | 0.25152 | Cis-2-hexene | 0.00837 |
| Isopentane (2-Methylbutane) | 8.68314 | 1,3,5-trimethylbenzene | 0.20641 | 2,2-dimethylpropane | 0.00610 |
| N-pentane | 5.77987 | 1-pentene | 0.18041 | 1-nonene | 0.00503 |
| 2-methylpentane (isohexane) | 4.76063 | 2,2,5-trimethylhexane | 0.10195 | Trans-3-hexene | 0.00463 |
| M & p-xylene | 4.71071 | N-propylbenzene | 0.10093 | 4-methyl-1-pentene | 0.00362 |
| 2,2,4-trimethylpentane | 3.39812 | N-octane | 0.09355 | 2-methyl-2-hexene | 0.00358 |
| Benzene | 3.22889 | 1,2-diethylbenzene (ortho) | 0.08790 | 1-hexene | 0.00283 |
| N-hexane | 2.57000 | 2,3-dimethylhexane | 0.08696 | 4-methylheptane | 0.00249 |
| 2,3,4-trimethylpentane | 2.17414 | 3-methylheptane | 0.08234 | 3,3-dimethylhexane | 0.00184 |
| 3-methylpentane | 2.07707 | 1,2,3-trimethylbenzene | 0.07438 | 1-octene | 0.00184 |
| 2,3-dimethylpentane | 1.94405 | Methylcyclohexane | 0.06724 | 3,3-dimethylpentane | 0.00163 |
| O-xylene | 1.79764 | N-dodecane | 0.05522 | Trans-3-heptene | 0.00148 |
| Ethylbenzene | 1.74398 | 3,5-dimethylheptane | 0.04573 | Trans-2-heptene | 0.00140 |
| 2,3-dimethylbutane | 1.53902 | 2,5-dimethylhexane | 0.04538 | Isoprene (2-methyl-1,3-butadiene) | 0.00132 |
| 2,4-dimethylpentane | 1.24435 | N-butylbenzene | 0.04403 | 2,2-dimethylpentane | 0.00132 |
| 1-Methyl-3-ethylbenzene (3-Ethyltoluene) | 1.08770 | 2-methylheptane | 0.04300 | Cis-2-heptene | 0.00126 |
| 2,2-dimethylbutane | 1.03006 | Cis-2-butene | 0.03893 | 2,4,4-trimethyl-1-pentene | 0.00110 |
| 2-methyl-2-butene | 0.93867 | 3-methyl-trans-2-pentene | 0.03461 | Trans-4-octene | 0.00103 |
| 1,2,4-trimethylbenzene (1,3,4-trimethylbenzene) | 0.93781 | 4-methyl-trans-2-pentene | 0.03084 | 1-butene | 0.00084 |
| Isobutane | 0.91797 | 3-methyl-1-butene | 0.03022 | Cis-1,3-dimethylcyclohexane | 0.00082 |
| Trans-2-pentene | 0.83594 | 1-ethyltertbutylether | 0.02959 | 2,2,3-trimethylbutane | 0.00074 |
| Methylcyclopentane | 0.57393 | Cyclohexane | 0.02716 | Cyclohexene | 0.00073 |
| 3-methylcyclopentene | 0.56980 | Cyclopentene | 0.02638 | 1,3-cyclopentadiene | 0.00068 |
| N-heptane | 0.55577 | Trans-2-hexene | 0.02571 | 4-methyloctane | 0.00068 |
| 2-methyl-1-butene | 0.47804 | 2,4-dimethyloctane | 0.02353 | Isobutylene (isobutene) | 0.00066 |
| 3-methylhexane | 0.44654 | Trans-1,2-dimethylcyclopentane | 0.02319 | 3-Ethylpentene | 0.00066 |
| 2-methylhexane | 0.42919 | 1-Methyl-2-ethylbenzene | 0.02192 | 2,2-dimethylhexane | 0.00064 |
| Propane | 0.41839 | 2-methyl-2-pentene | 0.02001 | 3-methyloctane | 0.00053 |
| 2,4-dimethylhexane | 0.33404 | 1,4-diethylbenzene (para) | 0.01736 | 3,3-dimethyl-1-butene | 0.00042 |
| Cyclopentane | 0.32339 | 2-methyl-1-pentene | 0.01568 | Trans-2-octene | 0.00040 |

# Example: CM Species for Speciation Profile 8754 (E10 evap)

| CB05 Species | Mass fraction | Divisor (converts to moles) |
|---|---|---|
| ALD2 | 6.52E-03 | 28.0532 |
| ALDX | 1.63E-04 | 34.0583 |
| FORM | 1.63E-03 | 14.0266 |
| IOLE | 0.023 | 55.7057 |
| ISOP | 2.18E-05 | 68.117 |
| OLE | 1.47E-03 | 28.0505 |
| PAR | 0.8413 | 14.4007 |
| TOL | 1.81E-03 | 93.6146 |
| UNR | 6.62E-03 | 14.5616 |
| XYL | 0.1174 | 106.3957 |

# Math

- Residual TOG = TOG – integrated species
- IntermediateCMSpecies(gram-moles) = MOVES pollutant (grams) * speciationMassFraction/ speciationDivisor

  where “MOVES pollutant” refers to residual TOG and the integrated species

- CMSpeciesSum(gram-moles) = SUM(IntermediateCMSpecies(gram-moles)) eq2

# Speciation of MOVES HAPs

| Pollutant Name | CMspecies | MassFraction | Divisor |
|---|---|---|---|
| Methane | CH4 | 1 | 16.04 |
| Benzene | PAR | 0.1667 | 13.0186 |
| Benzene | UNR | 0.8333 | 13.0186 |
| Ethanol | ETOH | 1 | 45.5934 |
| MTBE | PAR | 0.8 | 17.6296 |
| MTBE | UNR | 0.2 | 17.6296 |
| 1,3-Butadiene | OLE | 1 | 27.0452 |
| Formaldehyde | FORM | 1 | 30.026 |
| Acetaldehyde | ALD2 | 1 | 44.0526 |
| Acrolein | ALDX | 0.6667 | 37.3755 |
| Acrolein | OLE | 0.3333 | 37.3755 |
| 2,2,4-Trimethylpentane | PAR | 0.875 | 14.2786 |
| 2,2,4-Trimethylpentane | UNR | 0.125 | 14.2786 |
| Ethyl Benzene | PAR | 0.125 | 13.2706 |
| Ethyl Benzene | TOL | 0.875 | 92.8944 |
| Hexane | PAR | 1 | 14.3626 |
| Propionaldehyde | ALDX | 0.6667 | 38.7194 |
| Propionaldehyde | PAR | 0.3333 | 19.3597 |
| Styrene | OLE | 0.125 | 26.0373 |
| Styrene | TOL | 0.875 | 91.1305 |
| Toluene | TOL | 1 | 92.1384 |
| Xylene | XYL | 1 | 106.165 |
| Naphthalene gas | PAR | 0.2 | 12.8171 |
| Naphthalene gas | XYL | 0.8 | 102.536 |