September 27, 2016

MEMORANDUM

To: Alison Eyth and Madeleine Strum, OAQPS, EPA
From: Michele Jimenez, Greg Yarwood, Tejas Shah, and Bonyoung Koo, Ramboll Environ
Subject: Speciation Tool version 4.0 updates

Purpose

Ramboll Environ recently updated the Speciation Tool to version 4.0. The updates include adding support for the CAMx $PM_{2.5}$ speciation and Volatility Basis Set (VBS) schemes. The implementation details are discussed below.

Implementation of CAMx $PM_{2.5}$ Speciation

The AE6 aerosol mechanism was developed specifically for CMAQ. In order to support the CAMx PM speciation scheme (scheme CAMx CF), the Speciation Tool was enhanced to calculate the PM model species required by CAMx from the AE6 definition. Table 1 shows the relationship between CAMx CF scheme model species and the AE6 compounds.

Table 1. $PM_{2.5}$ components from CMAQ AE6 to CAMx CF.

CMAQ AE6 compounds	CAMx CF
PAL	sum >> FPRM
PCA	
PFE	
PK	
PMG	
PMN	
PMOTHR	
PSI	
PTI	
PNCOM	sum >> POA
POC	
PEC	PEC
PNA	NA
PH2O	PH2O
PNH4	PNH4
PNO3	PNO3
PSO4	PSO4
PCL	PCL
POC	POC*

* Note that POC is accounted for under the CAMx POA compound. Although CAMx ignores POC, it is still included as a separate compound to assist with model performance evaluation.

An additional input file was provided to specify dust profiles for renaming FPRM model species to FCRS (fine dust particles). The file "camx_fcrs.profile.lst" is imported to the shared table "tbl_camx_fcrs".

Implementation of VBS in the Speciation Tool

VBS schemes for modeling organic aerosol (OA) in CAMx and CMAQ are based on the 1.5 dimensional (1.5D) VBS implementation[1]. The Speciation Tool was enhanced to support the VBS schemes in these models. The Speciation Tool update includes computing semi-volatile OC (SVOC) species fractions (split factors) from primary OA species (POA= POC plus PNCOM), as well as intermediate volatility organic compound (IVOC) species from total non-methane organic compounds (TNMOC). Both the VOC and $PM_{2.5}$ modules of the Speciation Tool were modified to support the VBS schemes. In addition, the modules that define tables, import controls, import data files, and generate the output files were enhanced to support these new schemes.

Adding SVOC to $PM_{2.5}$ Split Factors

The VBS schemes include three distinct sets of SVOC model species to represent emissions from cooking meat (charbroiling), biomass-burning and other anthropogenic sources. Each SVOC model species set has five model species with different saturation pressure ranging from zero (non-volatile) to 1000 µg/m^3 (most volatile).

The Speciation Tool needs new input data to support generating SVOC model species, specifically assignment of each profile code to one of the three emission categories (cooking induced, biomass-burning, other anthropogenic), and SVOC species fractions for each saturation concentration bin. Table 2 provides examples of the input data required for SVOC generation. The Speciation Tool distribution includes this information in "vbs_ivoc.profile.30aug2016.csv" which is imported to "tbl_vbs_svoc_factors".

Table 2. Example SVOC model species assignments for three profile codes.

Profile Code	Profile Description	Emission Category		Saturation Concentration Bin (µg/m3)				
			CAMx CMAQ	0	1	10	100	1000
			Model Species	bin_0	bin_1	bin_2	bin_3	bin_4
91106	Diesel engines	Anthropogenic	PAP*i* P_PVB*i*	0.03	0.25	0.37	0.24	0.11
91102	Wildfires	Biomass Burning	PFP*i* P_FVB*i*	0.2	0.1	0.1	0.2	0.4
91116	Charbroiling	Cooking-induced	PCP*i* P_CVB*i*	0.35	0.35	0.1	0.1	0.1

[1] Koo, B., Knipping, E., & Yarwood, G. (2014). 1.5-Dimensional volatility basis set approach for modeling organic aerosol in CAMx and CMAQ.Atmospheric Environment, 95, 158-164.

The data fields shown in Table 2 must be assigned for every $PM_{2.5}$ profile. If a profile assignment is missing from the SVOC fractions file then the run will stop with an informative message. If the sum of the fractions is not equal to one, which would result in a loss of mass, the run will stop with an informative message. No default assumptions are made within the Speciation Tool.

Speciation Tool Input and Control Parameters for VBS SVOC

The Speciation Tool control file requires the following keyword parameters (and options) for a VBS SVOC run.

Control file keyword parameters:

AQM (CAMX or CMAQ)
OUTPUT (PM)
MECH_BASIS (AE6)
RUN_TYPE (VBS)

Speciation Tool Processing Steps for VBS SVOC

A. Verify SVOC Input Data
   1. Check that input file name is specified.
   2. Verify file exists.
   3. Read and store data in table.
   4. Verify fractions sum to one. If not, exit with message.
   5. Verify every profile has SVOC fraction assignments. If an assignment is missing stop run with message.

Items 1 – 3 occur during database initialization, items 4 – 5 happen while setting up temporary tables for developing output profiles.

B. Calculation

CAMx

1. For each $PM_{2.5}$ profile
   Select POA split factor
   For volatility bins 0 - 4
   Append SVOC compound *i* with
   split fraction = POA split factor * SVOC table volatility bin i fraction
2. Delete POA

CMAQ

1. For each $PM_{2.5}$ profile
   Select and sum PNCOM and POC split factors
   For volatility bins 0 - 4
   Append SVOC compound *i* with
   split fraction = (PNCOM and POA split factor sum)
   * SVOC table volatility bin i fraction

2. Delete PNCOM
3. Delete POC

Adding IVOC to VOC Split Factors

IVOC represents VOC with volatility ranging from 10^3 to 10^6 µg/m^3. Three IVOC model species are used to represent the source categories gasoline engine exhaust, diesel engine exhaust, and biomass-burning. When IVOC is added to a profile the VOC model species must be reduced so that TNMOC is conserved[2]. The IVOC fraction (i.e., IVOC/TNMOC) may vary by source category.

The Speciation Tool requires a new input data to support generating IVOC model species, specifically the source category type of each profile code (which is reflected in the model species name) and the IVOC fraction of TNMOC. Table 3 provides several examples of the input data required for IVOC generation. The Speciation Tool distribution package includes this data in "vbs_svoc.profile.26sep2016.csv" which is imported to table "tbl_vbs_ivoc_nmogfactors".

Table 3. Example IVOC assignments for three profile codes

Profile Code	Profile Description	Emission Category	Model Species		IVOC/NMOG
			CAMx	CMAQ	
5345	Gasoline Exhaust - E10 splash blend gasoline	Gasoline Engines	IVOG	IVOC_G	0.25
8774	Diesel Exhaust Emissions from Pre-2007 Model Year Heavy-Duty Diesel Trucks	Diesel Engines	IVOD	IVOC_D	0.20
8743	Composite Profile - Forest Fires	Biomass Burning	IVOB	IVOC_F	0.20
5650	Residential Wood Combustion	Wood Burning	IVOB	IVOC_F	0.07

Speciation Tool Input and Control Parameters for VBS IVOC

The Speciation Tool control file requires the following keyword parameters (and options) for a VBS SVOC run.

Control file keyword parameters:

AQM (CAMX or CMAQ)
RUN_TYPE (VBS)
OUTPUT (VOC)
MECH_BASIS (CB6 or other VOC based mechanism)

Speciation Tool Processing Steps for VBS IVOC

A. Input Data
   1. Check that input file is specified
   2. Verify file exists

[2] Jathar, S. H., Gordon, T. D., Hennigan, C. J., Pye, H. O. T., Adams, P. J., Donahue, N. M., and Robinson, A. L.: Unspeciated organic emissions from combustion sources and their influence on the secondary organic aerosol budget in the United States, submitted to Proc. Natl. Acad. Sci., 2013.

3. Read and store data in table

Items 1 – 3 occur during data base initialization.

B. The IVOC calculation is based on non-methane organic gas (NMOG).
   1. For each profile
      sNMOGwtpct = Sum weight percent for non-methane species
      Insert IVOC compound based on profile id
      Compute IVOC weight percent = sNMOGwtpct * NMOG fraction from Table 3
      Adjust profile non-methane components = (1 – sNMOGwtpct)
      * component weight percent
   2. Compute VOC split factors. Molecular weights are required for this calculation and are provided in the file "ivoc_species.csv" which is imported to table "tbl_vbs_ivoc_species". The following will be used for the IVOC compounds[3] :
      IVOG = 184
      IVOD = 212
      IVOB = 212

VBS Example Calculations

SVOC

The following is an example of SVOC calculation for speciation profile 91122, Onroad Gasoline Exhaust – Composite.

Table 4. SPECIATE 4.4 profile definition for profile 91122, On-road Gasoline Exhaust.

SPECIES_ID	WEIGHT_PER	NAME	SYMBOL
292	0.147	Aluminum	Al
296	0.019	Antimony	Sb
298	0.001	Arsenic	As
300	0.059	Barium	Ba
328	0.007	Cadmium	Cd
329	0.288	Calcium	Ca
347	0.005	Chromium	Cr
379	0.001	Cobalt	Co
380	0.021	Copper	Cu
468	0.001	Gallium	Ga
487	0.004	Indium	In
488	0.404	Iron	Fe
519	0.033	Lanthanum	La
520	0.048	Lead	Pb
525	0.053	Magnesium	Mg
526	0.004	Manganese	Mn

[3] Jathar, S. H., Gordon, T. D., Hennigan, C. J., Pye, H. O. T., Adams, P. J., Donahue, N. M., and Robinson, A. L.: Unspeciated organic emissions from combustion sources and their influence on the secondary organic aerosol budget in the United States, submitted to Proc. Natl. Acad. Sci., 2013.

SPECIES_ID	WEIGHT_PER	NAME	SYMBOL
528	0.001	Mercury	Hg
586	0.002	Molybdenum	Mo
612	0.006	Nickel	Ni
613	0.151	Nitrate	NO3-
626	54.926	Organic carbon	OC
649	0.006	Palladium	Pd
666	0.173	Phosphorus	P
669	0.018	Potassium	K
689	0.000	Rubidium	Rb
693	0.001	Selenium	Se
694	0.475	Silicon	Si
695	0.006	Silver	Ag
696	0.108	Sodium	Na
697	0.001	Strontium	Sr
699	0.808	Sulfate	SO4=
700	0.538	Sulfur	S
714	0.013	Tin	Sn
715	0.006	Titanium	Ti
767	0.002	Vanadium	V
778	0.265	Zinc	Zn
779	0.001	Zirconium	Zr
784	1.672	Ammonium	NH4+
795	0.080	Chlorine atom	Cl
797	19.004	Elemental Carbon	EC
810	0.006	Bromine Atom	Br
2669	13.731	Non-Carbon Organic Matter	PNCOM
2670	1.300	Metal-bound Oxygen	MOx
2671	6.146	Other Unspeciated $PM_{2.5}$	PMO

Table 5. CAMx CF GSPRO split factors generated by the Speciation Tool for profile 91122 $PM_{2.5}$. CF vs VBS.

CAMx CF				CAMx VBS SVOC		
ProfileID	Compound	Split Factor		ProfileID	Compound	Split Factor
91122	FPRM	0.0952		91122	FPRM	0.09520
91122	NA	1.08E-03		91122	NA	0.00108
91122	PCL	7.96E-04		91122	PCL	0.00080
91122	PEC	0.19		91122	PEC	0.19000
91122	PNH4	0.0167		91122	PNH4	0.01670
91122	PNO3	1.51E-03		91122	PNO3	0.00151
91122	POA	0.6866		~~91122~~	~~POA~~	~~0.68660~~
91122	POC	0.5493		91122	POC	0.54930
91122	PSO4	8.08E-03		91122	PSO4	0.00808
				91122	PAP0	0.18538
				91122	PAP1	0.10299
				91122	PAP2	0.17852
				91122	PAP3	0.10299
				91122	PAP4	0.11672

Table 6. CMAQ AE6 GSPRO split factors generated by the Speciation Tool for profile 91122 $PM_{2.5}$. AE6 vs VBS.

CMAQ AE6				CMAQ VBS SVOC		
ProfileID	Compound	Split Factor		ProfileID	Compound	Split Factor
91122	PAL	1.47E-03		91122	PAL	0.00147
91122	PCA	2.88E-03		91122	PCA	0.00288
91122	PCL	7.96E-04		91122	PCL	0.00080
91122	PEC	0.19		91122	PEC	0.19000
91122	PFE	4.04E-03		91122	PFE	0.00404
91122	PK	1.81E-04		91122	PK	0.00018
91122	PMG	5.29E-04		91122	PMG	0.00053
91122	PMN	4.03E-05		91122	PMN	0.00004
91122	PMOTHR	0.0813		91122	PMOTHR	0.08130
91122	PNA	1.08E-03		91122	PNA	0.00108
91122	PNCOM	0.1373		~~91122~~	~~PNCOM~~	~~0.13730~~
91122	PNH4	0.0167		91122	PNH4	0.01670
91122	PNO3	1.51E-03		91122	PNO3	0.00151
91122	POC	0.5493		~~91122~~	~~POC~~	~~0.54930~~
91122	PSI	4.75E-03		91122	PSI	0.00475
91122	PSO4	8.08E-03		91122	PSO4	0.00808
91122	PTI	5.54E-05		91122	PTI	0.00006
				91122	P_PVB0	0.18538
				91122	P_PVB1	0.10299
				91122	P_PVB2	0.17852
				91122	P_PVB3	0.10299
				91122	P_PVB4	0.11672

IVOC

The following is an example of modifying a VOC profile definition to include IVOC. This example represents speciation profile 8775, Diesel Exhaust Emissions from 2007 Model Year Heavy-Duty Diesel Engines with Controls. The NMOG fraction for diesel profiles is 0.2 (see Table 3).

Table 7. SPECIATE 4.4 profile definition for profile 8775, Diesel Exhaust Emissions from 2007 Model Year Heavy-Duty Diesel Engines with Controls with IVOC adjusted weight percents.

SPECIES_ID	WEIGHT_PER	SPECIES_PROPERTIES.NAME	SYMBOL	SPEC_MW	Adjusted WEIGHT_PER
		IVOD	IVOD	212.00	9.6726
3	0.2036	(2-methylpropyl)benzene; isobutylbenzene		134.22	0.1629
23	0.1562	1,2,3,5-tetramethylbenzene		134.22	0.1250
25	0.0579	1,2,3-trimethylbenzene	BZ123M	120.19	0.0463
28	0.0771	1,2,4,5-tetramethylbenzene		134.22	0.0617
30	0.7503	1,2,4-trimethylbenzene (1,3,4-trimethylbenzene)	BZ124M	120.19	0.6003
46	0.0439	1,3-butadiene	BUDI13	54.09	0.0351
48	0.0185	1,3-cyclopentadiene		66.10	0.0148
60	0.1219	1,4-dimethyl-2-ethylbenzene		134.22	0.0975
63	0.1275	1-(1,1-dimethylethyl)-3,5-dimethylbenzene (or ter		162.27	0.1020
64	0.0273	1-butene	LBUT1E	56.11	0.0218
65	0.2452	1-butyne		54.09	0.1961
78	0.0103	1-hexene		84.16	0.0082

SPECIES_ID	WEIGHT_PER	SPECIES_PROPERTIES.NAME	SYMBOL	SPEC_MW	Adjusted WEIGHT_PER
80	0.0543	1-Methyl-2-ethylbenzene	O_ETOL	120.19	0.0434
81	0.0648	1-Methyl-2-isopropylbenzene		134.22	0.0518
89	0.0782	1-Methyl-3-ethylbenzene (3-Ethyltoluene)	M_ETOL	120.19	0.0625
90	0.0500	1-Methyl-3-isopropylbenzene (1-Methyl-3-(1-me		134.22	0.0400
92	0.0151	1-Methyl-3-propylbenzene (3-n-propyltoluene)		134.22	0.0121
118	0.3739	2,2,4-trimethylpentane	PA224M	114.23	0.2992
121	0.0354	2,2,5-trimethylhexane		128.26	0.0283
124	0.6650	2,2-dimethylhexane		114.23	0.5320
125	0.0012	2,2-dimethyloctane		142.28	0.0009
126	0.0156	2,2-dimethylpentane		100.20	0.0125
127	0.6752	2,2-dimethylpropane		72.15	0.5402
128	0.5215	2,3,3-trimethylpentane		114.23	0.4172
130	0.5358	2,3,4-trimethylpentane	PA234M	114.23	0.4286
136	0.0877	2,3-dimethylbutane	BU23DM	86.18	0.0702
140	0.3511	2,3-dimethylpentane	PEN23M	100.20	0.2809
142	0.0429	2,4,4-trimethyl-2-pentene		112.21	0.0343
149	0.4194	2,4-dimethylhexane	HEX24M	114.23	0.3355
160	0.2037	2,6-dimethylheptane		128.26	0.1629
184	0.0103	2-methyl-1-pentene	P1E2ME	84.16	0.0082
187	0.0294	2-methyl-2-pentene	P2E2ME	84.16	0.0236
199	0.1349	2-methylpentane (isohexane)	PENA2M	86.18	0.1079
208	0.0047	3,3-dimethylpentane		100.20	0.0037
209	0.0663	3,4-dimethyl-1-pentene		98.19	0.0530
221	0.0099	3-ethyl-2-pentene		98.19	0.0079
226	0.0779	3-ethylhexane		114.23	0.0623
244	0.0703	3-methylheptane	HEP3ME	114.23	0.0562
245	0.1475	3-methylhexane	HEXA3M	100.20	0.1180
248	0.1373	3-methylpentane	PENA3M	86.18	0.1098
253	0.1601	4,4-dimethylheptane		128.26	0.1281
258	0.0555	4-methyl-1-pentene		84.16	0.0444
279	3.3576	Acetaldehyde	ACETAL	44.05	2.6861
281	0.7567	Acetone	ACETO	58.08	0.6053
282	0.5796	Acetylene	ACETYL	26.04	0.4637
283	0.5017	Acrolein (2-propenal)		56.06	0.4013
301	0.7877	Benzaldehyde	BENZAL	106.12	0.6301
302	0.6110	Benzene	BENZE	78.11	0.4888
313	0.1589	Butyraldehyde or butanal	BUAL	72.11	0.1271
391	0.0109	Cyclopentene		68.12	0.0088
438	1.3396	Ethane	ETHANE	30.07	1.0717
449	0.3147	Ethylbenzene	ETBZ	106.17	0.2518
452	3.0663	Ethylene	ETHENE	28.05	2.4531
465	10.0526	Formaldehyde	FORMAL	30.03	8.0421
491	0.4963	Isobutane	I_BUTA	58.12	0.3970
497	0.9742	Isobutylene (isobutene, 2-Methylpropene)	LIBUTE	56.11	0.7793
517	0.0817	Isovaleraldehyde		86.13	0.0654
522	1.0421	M & p-xylene	MP_X	106.17	0.8337
529	51.6372	Methane		16.04	51.6372
536	0.1589	Methyl ethyl ketone (2-butanone)	MEK	72.11	0.1271

SPECIES_ID	WEIGHT_PER	SPECIES_PROPERTIES.NAME	SYMBOL	SPEC_MW	Adjusted WEIGHT_PER
550	0.8940	Methylcyclohexane	MECYHX	98.19	0.7152
551	0.0153	Methylcyclopentane	MCYPNA	84.16	0.0122
592	1.1020	N-butane	N_BUTA	58.12	0.8816
598	0.3808	N-decane	N_DEC	142.28	0.3046
599	2.3395	N-dodecane	N_DODE	170.33	1.8716
600	0.2782	N-heptane	N_HEPT	100.20	0.2226
601	0.2368	N-hexane	N_HEX	86.18	0.1894
603	0.2796	N-nonane	N_NON	128.26	0.2236
604	0.2021	N-octane	N_OCT	114.23	0.1617
605	1.0143	N-pentane	N_PENT	72.15	0.8114
610	1.7458	N-undecane	N_UNDE	156.31	1.3966
611	0.0702	Naphthalene	NAPHTH	128.17	0.0561
620	0.6533	O-xylene	O_XYL	106.17	0.5226
671	0.5088	Propane	N_PROP	44.10	0.4071
673	0.1514	Propionaldehyde	PROAL	58.08	0.1211
678	0.9399	Propylene (1-Propene)	PROPE	42.08	0.7519
717	1.2404	Toluene	TOLUE	92.14	0.9923
840	0.1118	Hexaldehyde	HEXAL	100.16	0.0894
845	0.0451	Valeraldehyde	VALAL	86.13	0.0360
1655	0.0323	t-1-Butyl-2-Methylbenzene		148.24	0.0258
1711	0.4944	M- & p-tolualdehyde		120.15	0.3955
2297	4.3528	Unknown		137.19	3.4823
2568	0.0495	2-methyl-butyl-benzene	C11H16	148.25	0.0396

Chemical Mechanism Updates

We reviewed version 4.5 of the SPECIATE database, created CB05 and CB6 mechanism species mappings for newly added compounds. In addition, seven species mapping definitions were modified in existing CB6 and CB05 mechanism in order to promote consistency in methods used for some difficult-to-map compounds. The revised CB6 and CB05 chemical mechanisms were incorporated in the Speciation Tool version 4.0. With the release of Speciation Tool v4.0, there are no undefined species which are referenced in gas profiles.

Also provided in this release is a new mechanism option - SOA_CB6CAMX6P2. This would improve support for secondary organic aerosol (SOA) mechanism in CAMx 6.2. This mechanism generates BNZA, ISP, NONSOA, TOLA, TRP, and XYLA.

The latest chemical mechanism definitions are provided in "mechanism_forImport.26sep2016.csv".