Appendix A: Methodology to Revise VOC from Residential Wood Combustion

Purpose: Calculate corrected VOC emissions for EPA and State/local supplied sources with SCC=2104008001 which is Fireplaces (FP) and SCC=2104008000 (total RWC; i.e. it includes fireplaces AND woodstoves) because we have evidence that with the exception of Calif., an erroneously high emission factor (229 lb/ton) was used.

Note that the 229 lb/ton was the EF in AP-42, but numerous studies have shown it to be too high by approximately an order of magnitude. We chose to use the emission factor from the Mid-Atlantic Regional Air Management Association (MARAMA) study of 18.9 lbs VOC/ton.

The evidence for the State/local supplied data using the 229 lb/ton EF is the ratio of VOC to PM2.5 which is much greater than what is expected when computed at the state and/or county level. Using the the erroneous VOC emission factor of 229 lb/ton EPA factors, the VOC-to-PM2.5 ratio should be 9.7 (VOC = 229 lb/ton and PM25 = 23.6 lb/ton). But this ratio can vary if States use different PM2.5 ratios.

Because the RWC data is provided in different ways (one example is that states provide the data aggregated for fireplace and woodstove SCCs rather than use the separate SCCs) and we don't know what particular emission factors States used, we had to develop different adjustments for different cases. The caes are described below.

CASE 1: Adjustment of VOC from 2104008001 for **counties that have VOC emissions for BOTH fireplace SCCs (2104008001) and woodstove SCCs (any combination of 21040080XX, where XX not equal to 01 or 00)**

Except for California (which we don't change), recompute VOC from 2104008001 as follows:

VOCcorrected=VOCold*(EFcorrected/EFold)
Where EFcorrected=18.9 lbs VOC/tons of wood burned.
And EFold=229 lbs VOC/tons of wood burned.

Leave VOC from woodstove SCCs as is.

Apply FP VOC change to the following 35 States based on the value of their VOC to PM2.5 ratio for SCC=2104008001.

State	Comment regarding VOC to PM2.5 ratio
AZ CO DC FL GA IA KS KY LA MN MO MT NC ND NE NM NV OK OR(#1) PA RI SD TN WI(#2) WY	States appear to use the 229 EF (based on their VOC-to-PM2.5 ratio of 9.7). For these States, this correction is most accurate. Note that the top 2 VOC emitting states are in this list.
IL IN MI WV	have a VOC-to-PM2.5 ratio of 19.4, which may mean that they use a lower PM2.5 EF (11.8 lbs/ton?) or higher VOC EF (not likely). The calculation may be less accurate for these states, since we are unsure of the VOC EF that they used.
TX – EPA provided data	Ratio is 3.55. Wood stove EFs different (but not that far off) of EPA data for Colorado.
TX – State submitted data	Ratio is 10.73. Wood stove EFs different (but not that far off) of EPA data for Colorado.
VT	Ratio is 7.12. Other woodstove VOC to PM ratios are slightly higher than for the EPA data, but are not that far away.
NY	Ratio is 7.88. Same ratio for outdoor wood burning but woodstove ratio is on the order of the EPA
WA – local data only Counties 53-033, -035, -053, -061	ratio is 12.32. Wood stove ratios slightly higher than for the EPA data, but are not that far away.
MS	Ratio is 33.68. ratios for 2104008002, 2104008003, 2104008004 are also pretty different (higher) than EPA, but VOC emissions from these are not nearly as large as 21040080001.

CASE 2. Adjustment of VOC from 2104008000 from MARAMA states

State	Comment
CT DE MA MD ME NH	Ratio of VOC to PM2.5 is 4.7

They did not break out fireplace emissions from woodstove emissions. Need to know what EFs they used for fireplaces.

Madeleine contacted Marama on Friday June 27 (Julie R. McDill
Mid-Atlantic Regional Air Management Association
8900 LaSalle Road Suite 636
Baltimore, MD 21286
P. 443-901-1882
F. 443-901-1886
Email: jmcdill@marama.org
www.marama.org) to find out what they used so we know if/how to correct VOC.
She indicated that for the 2002v3 nonpoint, they had not used corrected VOC.

THUS USE CASE3 DIRECTIONS FOR CASE2

CASE 3. Adjustment of VOC from 2104008000 from non-MARAMA states and where 2104008000 is the only SCC used.

Approach: Divide out the VOC from the broad into fireplaces, uncontrolled woodstoves & controlled woodstoves using PM2.5 and then compute VOC from VOC/PM2.5 EFs, correcting the VOC EF for fireplaces.

Step 1. break out PM2.5 into fireplaces (FP), uncontrolled-woodstoves, controlled-woodstoves using the following factors: 0.194, 0.715, 0.091 (respectively)

Step 2. multiply **fireplaces** PM2.5 by (18.9/23.6) to get corrected FP VOC (numerator is corrected VOC EF for fireplaces, denominator is EF used for PM2.5 for fireplaces, NEI documentation, Table 4)
multiply **uncontrolled-woodstoves** PM2.5 by *(**53/30.6**) to get uncontrolled-woodstoves VOC (numerator is VOC EF for the uncontrolled-woodstove SCCs: 2104008002 and 2104008010. Denominator is PM2.5 EF for the uncontrolled woodstoves. These values are from the NEI documentation, table 5)
multiply **controlled-woodstoves** PM2.5 by *(12/19.6) to get controlled-woodstoves VOC (numerator/denominator are VOC&PM2.5 EFs for controlledwoodstove SCCs : 2104008003 and 8050 from NEI documentation, table 6 – assume most emissions are from 2104008003 and 8050 since other controlled-woodstoves SCC: 2104008004, has different ratios – (15/20.4))

Step 3. Sum up VOC and use that as the corrected VOC for 2108004000

Step 4. compute corrected ratio VOC to PM2.5 (NOTE THAT PM2.5 doesn't change from the original value) just to check. Should be about 1.45

Sample Calculation for AR is shown below.

Apply to:

State	Comment
AR	Ratio is 2.49. AR pm2.5 from broad SCC is 2485 tons. Example calc shows how to derive corrected VOC. Statewide VOC goes from 6177 tons to 3605 tons.
ID	PM2.5 has different data source code than VOC. PM2.5 total from ID is 2263 tons. Data source code for PM2.5 is S-02-X-PR. Shouldn't be a problem to do that calc. Statewide VOC goes from 15K to 3300.
AZ local data (Maricopa county only)	Pm2.5 is 409, VOC was 2912. corrected VOC is 593
NJ – EPA data ratio is 6.62 based on bad VOC and AP-42 PM2.5 for fireplaces	PM= 4419. VOC was 29K corrected VOC is 6405
NJ state data ratio is 1.73.	PM = 4392. VOC was 7607. corrected VOC is 6366.
Ohio VOC to PM2.5 ratio is 1.67	PM=8936. VOC was 14962 corrected VOC is 12952
TN local data VOC to PM2.5 ratio is 6.62	
UT state data. ratio is 3.05	
WA state data. Ratio is 3.9	

AR example calc: 2485 tons of PM2.5 and presumably bad VOC of 6177 tons
.194*2485=482 PM2.5 from FP
.715*2485=1779.6 from uncontrolled-woodstoves 2104008002, 2104008010, or 2104008051
.091*2485=223.69 from controlled-wood stoves. 2104008003, 2104008004, 2104008030, 2104008050, 2104008052 or 2104008053

Apply VOC to PM2.5 factor for FP: 482*(18.9/23.6)=386 tons VOC
Apply VOC to PM2.5 factor for uncontrolled-woodstoves (8002): 1779.6 *(**53/30.6**) = 3082 tons VOC
Apply VOC to PM2.5 factor for controlled-wood stoves (8003): 223.69*(12/19.6)=136.95 tons
Sum of VOC = 3605 tons ←-------this is the corrected VOC for 2104008000.

So corrected ratio is 3605/2485=1.45 looks good.

CASE 4. Virginia, which has no VOC for wood stoves, but there is PM. And has VOC (but no PM for broad SCC).

state_abbr	Scc	data_source	PM2_5	VOC
VA	2104008000	S-02-X		53825.14
VA	2104008001	E-01-G	831.2484	
VA	2104008002	E-01-G	3632.713	
VA	2104008003	E-01-G	144.1626	
VA	2104008004	E-01-G	60.54522	
VA	2104008010	E-01-G	4937.689	
VA	2104008030	E-01-G	82.29481	
VA	2104008050	E-01-G	195.95	

VA: remove all records with 2104008000 and compute VOC for all other SCCs using VOC to PM2.5 ratios.

For 2104008001 (fireplaces) use: (18.9/23.6)
For uncontrolled woodstoves: 2104008002, 2104008010, or 2104008051 use **(53/30.6)** because both 2104008002, 2104008010 use that and there are no factors for 2104008051
For controlled wood stoves use the following based on SCC:
2104008003 (12/19.6),
2104008004 (15/20.4 using Table 7),
2104008030 (15/20.4 using Table 7),
2104008050 (12/19.6),
2104008052: not there, so use same as 2104008050 (12/19.6),
Same for 2104008053

CASE 5: Alabama for which there is both broad and detailed woodstove SCCs

This case is unique because VOC is only in 2104008000 but PM2.5 (and HAPs) are in that SCC and numerous others

state_abbr	Scc	data_source	PM2_5	VOC
AL	2104008000	S-02-X	216.46	54987.12
AL	2104008002	S-02-X	1505.05	
AL	2104008003	S-02-X	59.76	
AL	2104008004	S-02-X	25.1	
AL	2104008010	S-02-X	2085.44	
AL	2104008030	S-02-X	34.67	
AL	2104008050	S-02-X	82.8	

I examined county-level inventory and it looks like the above is the pattern in very county.

Examples:

fips	Scc	poll	ann_emis	pm ratio
1001	2104008000	PM2_5	2.05	0.089716
1001	2104008002	PM2_5	10.55	0.461707
1001	2104008003	PM2_5	0.42	0.018381
1001	2104008004	PM2_5	0.18	0.007877
1001	2104008010	PM2_5	9.13	0.399562
1001	2104008030	PM2_5	0.15	0.006565
1001	2104008050	PM2_5	0.37	0.016193
fips	Scc	poll	ann_emis	PM ratio
1013	2104008000	PM2_5	0.77	0.028742
1013	2104008002	PM2_5	8.42	0.314296
1013	2104008003	PM2_5	0.33	0.012318
1013	2104008004	PM2_5	0.14	0.005226
1013	2104008010	PM2_5	16.22	0.60545
1013	2104008030	PM2_5	0.27	0.010078
1013	2104008050	PM2_5	0.64	0.02389
			26.79	

Approach is to remove current VOC from all counties and replace with VOC based on PM2.5 and the following PM2.5 to VOC ratios

The ratios to use: (by SCC) are in column 5

	scc	Ratio based on	PM2_5	factor num and denom	Factor	sum
AL	2104008000	FP: NEI documentation[2] Table 1 for PM2.5 and corrected VOC EF of 18.9 lb/ton	216.46	(18.9/23.6)	0.80084746	173.3514
AL	2104008002	NEI documentation Table 5	1505.05	**(53/30.6)**	1.73202614	2606.786
AL	2104008003	NEI documentation Table 6	59.76	(12/19.6)	0.6122449	36.58776
AL	2104008004	NEI documentation Table 7	25.1	15/20.4	0.73529412	18.45588
AL	2104008010	NEI documentation Table 5	2085.44	**(53/30.6)**	1.73202614	3612.037
AL	2104008030	NEI documentation Table 7	34.67	15/20.4	0.73529412	25.49265
AL	2104008050	NEI documentation Table 6	82.8	12/19.6	0.6122449	50.69388
					Grand total	**6523.404**

[2] ftp://ftp.epa.gov/EmisInventory/2002finalnei/documentation/nonpoint/2002nei_final_nonpoint_documentation0206version.pdf Appendix A. Residential Heating Using Wood

Case 6. SC, where VOC mass missing from some SCCs.

State	SCC	Data source code	PM2.5	VOC
SC	2104008001	S-02-X	157.93	43268.9
	2104008002	S-02-X	1667.88	
	2104008003	S-02-X	66.21	
	2104008004	S-02-X	27.79	
	2104008010	S-02-X	3163.31	5478.91
	2104008030	S-02-X	52.73	38.74
	2104008050	S-02-X	125.57	76.85

Compute VOC from 2104008002, 2104008003 & 2104008004
Using VOC to PM2.5 factors as follows:

For 2104008002, use **(53/30.6)**
For 2104008003 use (12/19.6),
For 2104008004 use (15/20.4)

Recompute VOC from 2104008001 as follows (case 1)
VOCcorrected=VOCold*(EFcorrected/EFold)
Where EFcorrected=18.9 lbs VOC/tons of wood burned.
And EFold=229 lbs VOC/tons of wood burned.

Case 7 -- SCC=2104008053 from Oregon and Washoe County (Nevada)
Multiply PM2.5 by (12/19.6)

Case 8 -- Selected New Jersey Counties
For counties of Bergen, Essex, Hudson, Middlesex and Union ,
VOC corrected = (18.9/229) * VOC old
ie, treat these as Case 1 counties.

Case 9 -- Selected Washington Counties
For counties of King (53-033), Kitsap(-035), Pierce (-053), and Snohomish (-061), calculate new VOC as in Case 3 .

Appendix B: Methodology to Speciate Partially-Speciated MOVES PM2.5 Emissions

Approach to adapt partially-speciated gasoline emissions from the draft MOVES model to air quality modeling species needed for CMAQ.

The MOVES output provided three components of PM2.5: two pre-speciated components of PM2.5 which are: 1) *PEC*, and 2) *PSO4*, and a a non-speciated component termed "*PM25OC*", which is defined as the difference between total $PM_{2.5}$ and PEC.

It is important to note that *PM25OC* is not organic carbon, but is defined as the following:

$$\text{MOVES total } PM_{2.5} = PEC + PM25OC \qquad (1)$$

The CMAQ PM2.5 species were computed from (1) the MOVES output pollutants: PEC, PSO4 and PM25OC, and (2) the speciation profile for total PM2.5 exhaust. The equations used are presented below. Since we had to adjust the PEC and POC emissions at 72 F to reflect the impact of colder actual temperatures prior to computing all of the species, the implementation of the equations does not follow the order presented. The order is described after the list of equations is presented.

MOVES total $PM_{2.5}$ is the sum of the two pre-speciated components of PM2.5 and a remainder term, *R*.

$$\text{MOVES total } PM_{2.5} = PEC + PSO4 + R \qquad (2)$$

The remainder term can be computed from the MOVES outputs of *PM25OC* and *PSO4* as

$$R = PM25OC - PSO4 \qquad (3)$$

The *R* term includes POM, which consists of POC and the hydrogen and oxygen atoms attached to the carbon as part of the organic matter, PNO3, soil oxides and metals (also known as "crustal" and called METAL here), ammonium, and water, and thus can be also written as:

$$R = POM + PNO3 + METAL + NH4 + H_20 \qquad (4)$$

To correctly calculate the five $PM_{2.5}$ species needed for CMAQ, we first needed to break out the POC, PNO3, and PMFINE from *R*. We used the proportional relationship of known species to unknown species from the speciation profile for exhaust PM2.5 for gasoline vehicles. All gasoline vehicles (e.g., Light Duty and Heavy Duty) use the same speciation profile for exhaust PM2.5, 92050: "Onroad Gasoline Exhaust – Simplified". This simplified profile is based on Composite profile 91022. Fractions of PNO3 and PEC can be obtained from either the detailed or composite profile (they are the same). The detailed composite profile is required in order to determine the METAL component in equation (4) since metal fractions are not included in the simplified profile. Profiles 92050 and 91022 are in version 4.0 of SPECIATE (Hsu et al., 2006), which can be downloaded at www.epa.gov/ttn/chief/software/speciate/

We computed the primary nitrate based on the ratio of nitrate to elemental carbon from speciation profile 91022 using equation (5) shown below.

$$\text{PNO3} = \text{PEC} \times F_{NO3} / F_{EC} \tag{5}$$

where,

F_{EC} = Fraction of elemental carbon in speciation profile 91022= **20.801136%**
F_{NO3} = Fraction of nitrate in speciation profile 91022 = **0.1015%**

Since CMAQ's PMFINE species is the sum of soil oxides, metals, ammonium, and water, we needed to calculate all of its components. First, the metals and ammonium are computed using equations (6) and (7). Equation (7) is based on stoichiometric calculations.

$$\text{METAL} = \text{PEC} \times F_{metal} / F_{EC} \tag{6}$$

$$\text{NH4} = (\text{PNO3}/MW_{NO3} + 2 \times \text{PSO4}/MW_{SO4}) \times MW_{NH4} \tag{7}$$

where,

F_{metal} = Fraction of metals in speciation profile 91022 = (**2.2256 %**[3])
F_{EC} = Fraction of elemental carbon in speciation profile 91022= **20.801136%**

MW_{SO4} = Molecular weight of sulfate (**96.0576**)
MW_{NO3} = Molecular weight of nitrate (**62.0049**)
MW_{NH4} = Molecular weight of ammonium (**18.0383**)

The final component of PMFINE is the non-carbon mass of organic carbon. To calculate the non-carbon mass, we first needed to compute organic carbon from the remainder term, *R*.

A key assumption is that POM is a factor of 1.2 greater than the mass of primary organic carbon, which is also used in the CMAQ postprocessing software at EPA.

$$\text{POM} = 1.2 \times \text{POC} \tag{8}$$

Using this assumption and assuming that the H_20 is negligible, the equation needed for the calculation of POC is shown in equation (9) below.

$$\text{POC} = 5/6 \times (R - \text{METAL} - \text{NH4} - \text{PNO3}) \tag{9}$$

From equation (8), the non-carbon portion of the organic carbon matter is 20%, of the POC. By definition, PMFINE is the sum of the non-carbon portion of the mass, METAL and NH4.

[3] To obtain this, all metals and other ions (e.g., Chlorine) with the exceptions of nitrate and ammonium were identified in the profile and the percentages were summed to give a total "METAL" percentage.

$$\text{PMFINE} = \text{METAL} + \text{NH4} + 0.2 \times \text{POC} \qquad (10)$$

For mobile sources, we assumed that PMC is 8.6% of the $PM_{2.5}$ mass.

$$\text{PMC} = 0.086 \times (\text{PMFINE} + \text{PEC} + \text{POC} + \text{PSO4} + \text{PNO3}) \qquad (11)$$

Order of Computations due to Temperature Adjustments

Due to the need to account for the impact of temperature on exhaust PEC and POC, some of the equations above were not implemented until after the temperature-adjusted PEC and POC were computed (after the spatial allocation and temporal allocation steps in SMOKE).

The input emissions to SMOKE and equations or MOVES outputs used to create them from the MOVES data are listed below. The pollutant name in SMOKE inventory file is italicized.

The following PM2.5 inventory “pollutants” were computed for input into SMOKE.

1. *PEC_72* (not computed, this is directly output from MOVES)
2. *PSO4* (not computed, this is directly output from MOVES)
3. *PNO3* (computed from Equation 5)
4. *POC_72* (computed from Equation 9)
5. *OTHER* = NH4 + METAL (computed from Equations 6 and 7)

Temperature adjustments were applied by hour and grid cell to the PEC_72 and POC_72 in the SMOKE intermediate files (prior to the final merge) using a Lookup Table (see Table A-1). Note that the same lookup table was used to adjust PEC_72 and POC_72.

The other CMAQ PM2.5 species at actual temperatures were created as follows:

PMFINE = *OTHER* + 0.2 × POC (computed from Equation 10)
PMC = 0.86 x (PMFINE + PEC + POC + PSO4 + PNO3) (computed from Equation 11)

A final merge of all sectors was then done.

Table A-1. Correction Factors to Adjust 72 F PM OC and EC Emissions for colder temperatures (supplied by Harvey Michaels, OTAQ, 9/5/2008)			
Year	Temperature (degrees F)	Correction Factor for Running Exhaust	Correction Factor for Start Exhaust
2005	-20	18.6454	70.7816
2005	-19	18.0618	67.5797
2005	-18	17.4965	64.5218
2005	-17	16.9488	61.6025
2005	-16	16.4183	58.8153
2005	-15	15.9045	56.1542
2005	-14	15.4067	53.6136
2005	-13	14.9244	51.1878
2005	-12	14.4573	48.8719
2005	-11	14.0048	46.6607
2005	-10	13.5665	44.5495
2005	-9	13.1418	42.5339
2005	-8	12.7305	40.6095
2005	-7	12.332	38.7722
2005	-6	11.9461	37.018
2005	-5	11.5721	35.3431
2005	-4	11.2099	33.744
2005	-3	10.8591	32.2173
2005	-2	10.5192	30.7596
2005	-1	10.1899	29.3679
2005	0	9.87099	28.0392
2005	1	9.56203	26.7706
2005	2	9.26275	25.5594
2005	3	8.97281	24.4029
2005	4	8.69197	23.2988
2005	5	8.41992	22.2447
2005	6	8.15638	21.2382
2005	7	7.90109	20.2773
2005	8	7.65378	19.3599
2005	9	7.41422	18.484
2005	10	7.18216	17.6477
2005	11	6.95736	16.8492
2005	12	6.73959	16.0868
2005	13	6.52865	15.359
2005	14	6.3243	14.6641
2005	15	6.12635	14.0006
2005	16	5.9346	13.3672
2005	17	5.74885	12.7624
2005	18	5.56891	12.1849
2005	19	5.39461	11.6337
2005	20	5.22576	11.1073
2005	21	5.06219	10.6048
2005	22	4.90375	10.125
2005	23	4.75026	9.66683
2005	24	4.60158	9.22946
2005	25	4.45755	8.81189
2005	26	4.31803	8.41321
2005	27	4.18288	8.03256
2005	28	4.05196	7.6691
2005	29	3.92513	7.32215
2005	30	3.80228	6.99088
2005	31	3.68327	6.67456

Table A-1. Correction Factors to Adjust 72 F PM OC and EC Emissions for colder temperatures (supplied by Harvey Michaels, OTAQ, 9/5/2008)

2005	32	3.56798	6.37257
2005	33	3.4563	6.08424
2005	34	3.34812	5.80897
2005	35	3.24333	5.54614
2005	36	3.14181	5.29521
2005	37	3.04347	5.05563
2005	38	2.94821	4.82689
2005	39	2.85593	4.6085
2005	40	2.76655	4.39999
2005	41	2.67995	4.20091
2005	42	2.59607	4.01085
2005	43	2.51481	3.82938
2005	44	2.4361	3.65612
2005	45	2.35985	3.4907
2005	46	2.28599	3.33277
2005	47	2.21444	3.18198
2005	48	2.14513	3.03801
2005	49	2.07799	2.90055
2005	50	2.01295	2.76932
2005	51	1.94994	2.64403
2005	52	1.88891	2.5244
2005	53	1.82979	2.41018
2005	54	1.77252	2.30114
2005	55	1.71704	2.19702
2005	56	1.66329	2.09762
2005	57	1.61123	2.00271
2005	58	1.5608	1.9121
2005	59	1.51195	1.82559
2005	60	1.46463	1.74299
2005	61	1.41878	1.66413
2005	62	1.37438	1.58883
2005	63	1.33136	1.51695
2005	64	1.28969	1.44832
2005	65	1.24932	1.38279
2005	66	1.21022	1.32022
2005	67	1.17234	1.26049
2005	68	1.13564	1.20346
2005	69	1.1001	1.14901
2005	70	1.06567	1.09703
2005	71	1.03231	1.04739
2005	72	1	1