

MEMORANDUM

Date: June 27, 2006

To: Lee Beck, U.S. Environmental Protection Agency, Office of Research and Development

From: Y. Hsu and R. Strait, E.H. Pechan & Associates, Inc.

Subject: Develop an SCC-Profile Cross Reference Table for SPECIATE4.0
EPA Contract No. 68-D-02-063, WA No. 4-04¹

Introduction

Air quality modelers and emission inventory preparers rely on the SCC-Speciation Profile Cross Reference Table (Cross Reference Table) to identify appropriate speciation profiles to use for calculating species needed for air quality models from VOC and PM_{2.5}. Applications of the Cross Reference Table are wide and essential, from photochemical modeling inputs to characterizing speciated emissions (e.g., toxics) and global warming pollutants (methane and elemental carbon), etc. In order to take advantages of the new speciation profiles, the Cross Reference Table has been updated to include the latest speciation profiles available in the new SPECIATE4.0 database.

Updates

Pechan started this task by acquiring the latest Cross Reference Table (gsref) used in SMOKE from EPA (Houyoux, 2005). Pechan reviewed the assigned speciation profiles covering the SCCs that account for 80% of the VOC emissions in the draft 2002 National Emission Inventory (NEI). A total of 146 SCCs for nonpoint and mobile sources accounted for 80% of total VOC emissions. After evaluating the assigned speciation profiles in SMOKE and the new profiles available in the SPECIATE4.0 database, Pechan assigned new speciation profiles for 135 SCCs which account for 72.4% of the draft 2002 NEI VOC emissions. New profiles were not available for improving on existing profile assignments for the remaining 11 SCCs included in the top 80% of VOC emissions; therefore, the existing profile assignments were retained in the Cross Reference Table.

PM_{2.5} speciation profiles for all SCCs were reviewed and updated by the EPA Workgroup, which provided 106 simplified profiles – some new, some revised, and some based on data in SPECIATE3.2. No profiles were identical to any old EPA profiles because the new profiles do not use a 1.2 multiplier to increase the organic aerosol (POA) fraction and decrease the PM Other fraction. Note that POA was calculated as 1.2 times of organic carbon (OC) to account for molecules associated with carbon atoms. Recent finding has shown that the 1.2 multiplier is not representative for all emission sectors. Therefore, the EPA Workgroup has decided not to adjust OC to account for molecules associated with it and to let air quality modelers decide on the appropriate correction factors. Most of these profiles were assigned to

¹ This memorandum was initially delivered to EPA on June 20, 2005, under EPA Contract No. 68-D-00-265, WA No. 4-49. It was undated to reflect revisions to and the addition of new profiles in SPECIATE4.0.

SCCs with PM_{2.5} emissions in the 1999 and 2001 NEI. Work is ongoing at EPA to update the Cross Reference Table for all SCCs with PM_{2.5} emissions in the 2002 NEI.

Some profiles were created but not assigned because they were not appropriate for a default SCC-only assignment. The profiles that have not been used could be assigned by SPECIATE4.0 users by adding to the cross-reference location-specific profile assignments to certain counties or facilities, to support the particular needs of users. For example, the profile “Residential Wood Combustion: Eucalyptus” is not used in any default profile assignments, but could be applied in counties where Eucalyptus is a primary source of emissions from residential wood combustion sources.

Through this process, EPA made the following major improvements to the available PM_{2.5} profiles and assignments:

- New and separate profiles for subbituminous coal combustion and controlled lignite coal combustion are being used for appropriate processes.
- Different natural gas profiles for residential use, natural gas as used by industry, and process gas.
- A revised profile for wildfires is being used.
- Prescribed burning is now using a new profile that is specific to prescribed burning and not the profile for wildfires.
- Household waste combustion is now using the agricultural burning profile instead of an incineration profile, to reflect the lower combustion temperature and “smokier” profile that household waste combustion would be expected have.
- Meat frying is now using a profile that is specific to meat frying and not the profile for charbroiling.
- The default profile assignment for residential wood combustion is a composite profile based on hardwood and softwood profiles. However, more detailed simplified profiles are also available in SPECIATE4.0 that are not being used because they are not appropriate for a national default.
- A new steel desulfurization profile is being used for steel desulfurization processes, instead of sintering furnace and open-hearth furnace profiles used previously.
- A tire burning profile is being used for tire burning instead of a solid waste combustion profile.
- A dairy soil profile is being used for dairy soil dust instead of a generic soil dust profile.

The new Cross Reference Table better characterizes source chemical compositions which should result in improvements in inventories and air quality modeling. The recommended profile, comments, and rationale by SCC are provided for the VOC portion of work conducted by Pechan.

Discussion

The following provides general rationale for updates to profile assignments that are recommended by Pechan.

1. Representativeness – composite profiles are generally based on several new, individual profiles whereas the previous composite profiles used in SMOKE were developed from one or a few legacy profiles.
2. Profile quality – many profiles adopted in SMOKE do not appropriately characterize emission sources. For example, for fireplace and wood smoke (the top VOC emissions sector), the VOC profile (# 1167) contains 44% of naphthalene and over 90% of polycyclic aromatic hydrocarbons (PAHs) which over estimates toxic emissions. Pechan recommends the use of profile # 4642 based on Schauer et al. (1998) which includes 22% methane and many other total organic gases (TOG) species. The recommended profile significantly reduces toxic estimates and changes photochemical reactivity for this sector. Similar situations exist for forest fires (SCC 2810001000) and prescribed burning (SCC 2801500170, 2810015000). These SCCs are now assigned to a new composite profile by EPA Hays et al. (2002).

Another example is the diesel exhaust VOC profile # 1201 which identifies compounds as C2 compounds, C3 compounds, etc. Individual species of these compounds are not provided in this diesel exhaust profile. Pechan recommends a detailed speciation profile by Schauer et al. (1998) to replace the dated profile.

3. Appropriateness – multiple VOC profiles assigned to motor vehicles and petroleum marketing emissions were based on dated non-oxygenated gasoline (leaded and non-reformulated gasoline [RFG]). Due to regulation and technology changes, profiles for motor vehicles exhaust and evaporative emissions and petroleum marketing emissions are recommended to be based on RFG, methyl tertiary butyl ether (MTBE), and ethanol blended gasoline. These updates will significantly change toxic emissions and photochemical reactivity.

Also, the legacy profile (# 1190) assigned for gasoline marketing does not contain oxygenates like MTBE and ethanol, indicating that this profile does not properly characterize the source compositions. Based on recent EPA gasoline speciation data (Lewis, 2004), this sector is dominated by pentanes, MTBE, butanes, and other highly-volatile species as shown in the recent profiles in the new SPECIATE4.0 database. The previous legacy VOC profile (# 1190) contains xylenes (the largest constituent) at 22% by weight, compared to more recent data showing xylenes at less than 2%.

Note that profiles for petroleum marketing are available for many regions. Pechan recommends applying appropriate profiles to reflect regional specific compositions. For example, Milwaukee, WI and California adopted ethanol blended gasoline in these regions. Composite ethanol blended gasoline and headspace profiles are recommended in these regions. For areas (e.g., Houston, TX) use MTBE blended gasoline, speciation profiles collected from this region should apply. For areas (e.g., Research Triangle Park, NC) that do not require oxygenated fuels, there are profiles developed from these areas in the SPECIATE

database. Note that the profiles from Research Triangle Park,, NC area could slightly (mainly less than 3%) contain ethanol, MTBE, and/or t-amylmethyl ether (TAME) due to mixed batches of gasolines supplied from refineries.

The other example is the legacy profile (# 289) assigned to SCC: 2460100000 “Solvent Utilization: Miscellaneous Non-industrial: Consumer and Commercial: All Personal Care Products”. This profile is based on a surface coating solvent and not appropriate for personal care consumer product. This profile has only one species – n-butyl alcohol. Pechan recommends the use of a California Air Resources Board (CARB) composite consumer products profile (# 3147) to characterize personal care products emissions. This new profile (# 3147), which contains 46 species, is based on a composite of all personal care products for this sector that CARB developed from information it collected through a 1997 consumer products survey.

Future Work

The following provides recommendations by the EPA Workgroup and Pechan for future work in developing new profiles for SPECIATE:

1. The EPA Workgroup has identified the need for developing profiles for the following categories:

- Coal combustion for eastern bituminous coal and subbituminous coal from both controlled and uncontrolled sources. It should be combined with efforts to also improve PM_{2.5} emission factors and establish differences in emissions factors between filterable and condensable PM_{2.5} for different coal and control technologies;
- Nonroad diesel engines (e.g., construction equipment);
- Gasoline-powered boats;
- On-road gasoline exhaust under different conditions (e.g., temperatures/seasons);
- Updated process refinery gas outside of California, which would be more representative of other sources; and
- Measurements of new woodstoves.

2. Adopt new speciation profiles not yet available in the new SPECIATE4.0 database – as listed in the memorandum, “Candidate Profiles for Integration into SPECIATE” (Pechan, 2005), which Pechan has recommended many important speciation datasets. These speciation data are essential for multiple top emission SCCs. For example, the 7th and 8th ranked VOC emissions categories in the draft 2002 NEI are associated with “Industrial Processes: Oil and Gas Production”. The legacy profile (# 9015) assigned to these categories in SMOKE is in the simplified model species format showing 63% of TOG as nonreactive and 37% of TOG as paraffin.

For the oil and gas production sector, Pechan recommends a CARB study that collected 38 samples from many oil production facilities for speciation (Censullo, 1999). The speciation data are not available in the CARB speciation database and, therefore, not incorporated into the new SPECIATE4.0 database. Preliminary review of the cited CARB study shows that the photochemical reactivities of the new speciated data are significantly higher than the

legacy profile (# 1010) assigned for point source oil production (i.e., SCC 31000101) and the legacy profile (# 9015) assigned for area sources (i.e., SCCs 2310001000 and 2310002000).

The CARB-sponsored Censullo study speciated many olefins and aromatics, whereas older profiles contain only a few paraffins (paraffins have lower reactivity). Note that olefins and aromatics have much high ozone formation potentials than paraffins. For example, in the Censullo study, trimethyl benzene was about 4% by mass, however, the photochemical reactivity is about 800 times higher than methane (or 10 times higher than butanes). Applying these new speciation data can significantly change photochemical modeling results. Since these raw speciated data have not yet been incorporated into the new SPECIATE4.0 database, the Censullo study is added to the high priority list. This is a highly recommended work due to the large emissions and the needs for air quality modeling and speciated emissions inventory.

3. Currently, the Cross Reference Table in SMOKE is not in the format to provide speciation profiles with temporal (summer and winter) and spatial (e.g., MTBE, ethanol, and non-oxygenated fuels) resolutions. For the gasoline marketing and evaporative emission sectors, profiles are available to differentiate MTBE, ethanol, and non-oxygenated fuels in the database. Pechan is working with the Workgroup (Houyoux and Strum, 2005) to continuously enhance the Cross Reference Table with this capability.

Reference

Censullo, 1999. A.C. Censullo, California Polytechnic State University, Development of Species Profiles – Oil Field Fugitive Emissions prepared for California Air Resources Board.

Houyoux, 2005. Marc Houyoux of EPA personal communication with Ying Hsu of Pechan, June 2005.

Houyoux and Strum, 2005. Marc Houyoux and Madeleine of EPA personal communication with Ying Hsu of Pechan, June 2005.

Pechan, 2005. Memorandum from Pechan to EPA SPECIATE Workgroup titled “Candidate Profiles for Integration into SPECIATE”, May 17.

Hays et al., 2002. Hays, M.D.; Geron, C.D.; Linna, K.J.; Smith, N.D.; Schauer, J.J., 2002, “Speciation of Gas-Phase and Fine Particle Emissions from Burning of Foliar Fuels” *Environmental Science & Technology*, vol. 36, no. 11, pp. 2281-2295.

Lewis, 2004. Lewis, C., EPA, personal communication (EPA internal data collection effort) with Ying Hsu, E.H. Pechan & Associates, Inc., June 29, 2004.

Schauer et al., 1998. *Characterization and Control of Organic Compounds Emitted from Air Pollution Sources*, prepared by Schauer, J.J., Kleeman, M.J.; Cass, G.R.; Simoneit, B.R.T., prepared for the California Air Resources Board, contract number 93-329, April 1998.