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VOC Speciation Update for Texas Point Sources

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EXECUTIVE SUMMARY

Volatile Organic Compounds (VOC) are precursors to ozone and fine particulate matter which causes regional haze. Thousands of individual compounds make up the VOC emissions reported by regulated entities and tracked within the State of Texas Air Reporting System (STARS). When the Texas Commission on Environmental Quality (TCEQ) conducts photochemical modeling for the Texas State Implementation Plan (SIP), it is important to properly characterize the air quality impacts of VOC emissions which requires an accurate mapping of the VOC compounds present in the inventory to the model species used by air quality models.

This project improved how VOCs emitted by Texas point sources are represented in the TCEQ's SIP modeling by incorporating new information into TCEQ's emissions processing procedures. Ramboll updated two types of information needed to conduct VOC speciation: (1) speciation profiles that specify weight fraction of individual VOC emitted by a source (2) the compound database that contains the mapping of individual VOCs to model species of the CB6 chemical mechanism used by photochemical models (e.g. CAMx). Recently, we updated CB6 mappings for VOCs present in the EPA SPECIATE database to better represent oxygenates and low-volatility compounds. In this work, we reviewed and improved TCEQ's CB6 chemical mechanism mappings to be consistent with the most recent mechanism mapping guidelines. We also added many new speciation profiles from the latest version of the SPECIATE (v4.5) database to TCEQ's standard VOC speciation library.

1.0 INTRODUCTION

1.1 Background

Volatile Organic Compounds (VOC) are precursors to ozone and fine particulate matter which causes regional haze. Thousands of individual compounds make up the VOC emissions reported by regulated entities and tracked within the State of Texas Air Reporting System (STARS). When the Texas Commission on Environmental Quality (TCEQ) conducts photochemical modeling for the Texas State Implementation Plan (SIP), it is important to properly characterize the air quality impacts of VOC emissions which requires an accurate mapping of the VOC compounds present in the inventory to the model species used by air quality models. This step is part of the emissions processing where inventory pollutants are mapped to chemical mechanism model species in a step referred to as 'speciation'.

As new information becomes available for VOC speciation, the TCEQ's emissions processing procedures need to be updated. Two types of information are needed to conduct VOC speciation: (1) profiles that specify the weight fraction of individual VOCs emitted by each source type, and (2) the mechanism mapping that defines how individual VOCs are assigned to the model species of chemical mechanism (e.g. Carbon Bond version 6, CB6) of the photochemical model (e.g., the Comprehensive Air Quality Model with Extensions, CAMx).

1.2 Purpose and Objectives

The purpose of this work is to review and update the mechanism mapping used by the TCEQ to perform VOC speciation in SIP modeling.

2.0 DEVELOPMENT OF POINT-SPECIFIC SPECIATION PROFILES

The point source emissions data submitted to the TCEQ is stored in the STARS database. The major point sources are encouraged to report individual VOC species directly from each source in addition to the total VOC emissions. Each individual chemical species in the STARS is identified by a unique Contam code that is used by TCEQ for many internal analyses purposes. One use of speciated VOC emissions data is as input to regional scale photochemical models. The integration of individual VOC emissions improves speciation of VOC emissions in SIP modeling.

The STARS database contains speciated and unspeciated emissions data for VOC for each point source in Texas. The TCEQ has developed a unique processing methodology to retain all reported speciated data and characterize the remaining portion of unspeciated data according to default EPA speciation profiles (Cantu, 2003; PES, 2001). The processing approach is implemented in a SAS script to develop point-specific VOC speciation profiles. There are also QA/QC activities that are implemented in the SAS script such as removing non-VOC species from modeling inventory before processing and splitting generic chemical mixtures reported by industry (such as "crude oil" or "gasoline") into component hydrocarbons using existing chemical profiles.

The resulting point-specific VOC speciation profiles are used in EPS3 emissions processing. EPS3 maps point-specific speciated emissions information into model species of the photochemical reaction mechanism.

3.0 METHODOLOGY

The TCEQ provided all the existing information pertaining to creating point-specific VOC speciation profiles. This includes a current STARS VOC list with the VOC compounds identified by their Contam code and Chemical Abstracts Service (CAS) number, the existing Contam-SAROAD mapping file (contam_saroad_xref.map), the existing EPA VOC weight fraction profiles (emscvt.std_profiles.tog.Jul2002), and the existing mechanism mappings for the CB6 chemical mechanism (compound.database.cb6.05Aug2014). Each of these data inputs and updates are described in detail below.

3.1 SAROAD Assignment

In Emissions Preprocessor System (EPS3) individual VOCs are identified by a SAROAD code. Consequently, each Contam code in the STARS database must be cross-referenced to a SAROAD code so that EPS3 can process speciated point source emissions. This is accomplished by Contam-SAROAD cross-reference file (contam_saroad_xref.map). Ramboll updated this cross-reference file by adding new compounds found in the current STARS VOC list and assigning them to a SAROAD code. The cross-reference file contains all the Contam codes in the STARS database including generic raw material (like crude oil, gasoline etc) and individual compounds that are not VOC. As such, there are hundreds of VOC Contam code in the cross-reference file that do not have corresponding SAROAD code.

3.2 Refinement of Generic Chemical Mixtures

In the STARS database, generic chemical mixtures are sometimes reported by industry (such as "crude oil" or "gasoline") that need to be split into component hydrocarbons using chemical speciation profiles. In our review of the current STARS VOC list, we found one new Contam code "59100 - NATURAL GASOLINE" that should be speciated using "gasoline" profile.

3.3 Augmenting the Default Speciation Profiles

The unspeciated portion of the VOC inventory is speciated using chemical speciation profiles. For photochemical modeling, nationally recognized EPA speciation profiles are standard. Each emission point is assigned a default speciation profile based on its reported SCC according to an EPA SCC-Speciation Profile cross-reference.

EPA curates a comprehensive database of speciation profiles in the SPECIATE database which is updated frequently as new profiles become available from measurement studies. We identified 109 new profiles for point sources in the latest version of SPECIATE (v4.5) database that can be added based on EPA's 2011en platform[1] speciation cross reference file. Upon reviewing the VOC profile data from SPECIATE, we realized a couple of issues:

1. Not all species in SPECIATE have SAROAD code assigned which is a key for TCEQ's CB6 compound database.
2. There is no available standard procedure for assigning new SAROAD codes when needed.
3. Although SAROAD codes are present both in SPECIATE and TCEQ's CB6 compound database, there are many inconsistencies (i.e., the same code identifies different compounds in each database) which means that SAROAD code is unreliable for linking these two databases. In fact, SPECIATE does not rely upon SAROAD code but instead uniquely identifies compounds by their sequential number: "Species ID".

[1] https://www.epa.gov/air-emissions-modeling/2011-version-63-platform

To overcome the third issue, which could be a critical point of failure, we added all compounds from EPA's SPECIATE v4.5 database to TCEQ's CB6 compound database by assigning them a new SAROAD code that was previously unused within TCEQ's CB6 compound database. Simultaneously we imported the most recent CB6 mechanism mapping for these SPECIATE VOCs from the EPA Speciation Tool. The method for assigning unique SAROAD codes to all the species in SPECIATE is as follows. We padded each Species ID with leading 0s to make a 5 character long identifier that is consistent with the SAROAD system, e.g., Species ID 1234 becomes SAROAD code 01234. This approach has the advantages that: (1) we can use the mechanism mappings for SPECIATE Species ID available from the EPA Speciation Tool; (2) we can use profiles from SPECIATE. This approach will be easy to update in the future so that TCEQ can use new SPECIATE profiles as they become available.

We added 109 VOC speciation profiles from the SPECIATE v4.5 database to the existing file "emscvt.std_profiles.tog.Jul2002". We provided the updated file "emscvt.std_profiles.tog.24Apr2019" to the TCEQ in a format compatible with the SAS point source processing script.

3.4 Updating the CB6 Compound Database

The SAS script uses a compound database with mappings for the CB6 chemical mechanism. Ramboll recently updated CB6 mappings for VOCs present in SPECIATE to better represent oxygenates and low-volatility compounds (Ramboll, 2018). We reviewed and improved TCEQ's existing CB6 chemical mechanism mappings to be consistent with the most recent mechanism mapping guidelines (Ramboll, 2016, 2017 and 2018).

We updated mappings for 491 compounds and added 2,794 compounds from the latest version of SPECIATE database to the CB6 compound database. We provided the TCEQ with Excel workbook (TCEQ_CB6_Speciation_Update_noform_NASN_Apr18.xlsx) containing updated mappings and notes indicating which mappings were added, modified, or retained as is. We also provided the updated CB6 compound database file in a format compatible with the SAS script.

4.0 CONCLUSIONS AND RECOMMENDATIONS

This project improved how VOCs emitted by Texas point sources are represented in the TCEQ's SIP modeling by incorporating new information into TCEQ's emissions processing procedures. Ramboll updated two types of information needed to conduct VOC speciation: (1) speciation profiles that specify weight fraction of individual VOC emitted by a source (2) the compound database that contains the mapping of individual VOCs to model species of the CB6 chemical mechanism used by photochemical models (e.g. CAMx). Recently, we updated CB6 mappings for VOCs present in the EPA SPECIATE database to better represent oxygenates and low-volatility compounds. In this work, we reviewed and improved TCEQ's CB6 chemical mechanism mappings to be consistent with the most recent mechanism mapping guidelines. We also added many new speciation profiles from the latest version of the SPECIATE (v4.5) database to TCEQ's standard VOC speciation library. Testing the updated files for the Houston area (HGB) revealed small VOC differences. As such, this project succeeded in improving Texas point source VOC speciation used for SIP modeling.

5.0 REFERENCES

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