

Appendix B
Source Speciation Profile Development

**DEVELOPMENT OF SOURCE SPECIATION PROFILES
FROM THE TNRCC POINT SOURCE DATABASE**

Final Report

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Disclaimer

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INTRODUCTION

The Texas Natural Resource Conservation Commission (TNRCC) will be performing photochemical modeling of the Houston/Galveston area for ozone episodes that occurred during the 2000 Texas Air Quality Study (TexAQS). An accurate inventory of emissions of the primary ozone precursors NO_x , and VOC are essential to generate reliable model results. In the case of VOC, many different specific organic compounds that represent a range of reactivity in ozone formation mechanisms can be present in the emissions mix representing a complex industrial base such as that in the Houston/Galveston area. Reactivity in this application represents a measure of the contribution that each individual chemical has in the overall process that results in the formation and accumulation of ozone in urban systems.

An accurate representation of the individual chemical species that are emitted from each source is required to achieve meaningful results in this type of modeling exercise. To meet this need, VOC emissions are allocated to specific organic compounds by the application of a speciation profile. The speciation profile represents the weight percent of the specific organic compounds that are typically emitted from a particular process. Speciation profiles are typically used to characterize emissions at the source classification code (SCC) level. Much of the data used to develop these SCC-average profiles are based on national-level information. Major point sources of VOC emissions, such as, chemical, petrochemical and petroleum refining operations can vary and the use of an average SCC profile can rarely be expected to represent any individual facility exactly. Therefore, development of source-specific speciation profiles is one approach to improve the overall VOC speciation for urban and regional modeling applications. Alternatively, the use of SCC-specific profiles based on data collected for sources in a particular geographic region, will also result in improved speciation characteristics relative to the use of speciation profiles developed at the national-level.

In many areas of the United States where observed ozone concentrations exceed the National Ambient Air Quality Standard (NAAQS), the primary contribution of VOC is from mobile sources and dispersed stationary sources that are too small to track on an individual basis. Since point sources are not a major component of VOC in many areas, recent efforts at the national-level to develop more accurate VOC speciation profiles have focussed on area and mobile sources. In the Houston/Galveston area, however, significant point sources of VOC are present. The speciation profiles that are typically used for point sources in urban and regional modeling analyses are typically old and may be based on outdated measurement techniques. Add-on control devices and process changes have been implemented in many of the operations in the Houston/Galveston area that represent the largest point sources of VOC since the national default speciation profiles were developed. These activities have limited both the amount and reactivity of VOC emissions mix. For these reasons, many of the existing VOC speciation profiles that are routinely applied to point sources are not expected to accurately represent the VOC mix in the Houston/Galveston area, and therefore, may not accurately represent the reactivity of VOC in ozone formation processes.

Numerous studies using speciated ambient data available through the Photochemical Assessment Monitoring System (PAMS) network, along with assumed speciated emissions information have been completed in the past 5 to 10 years. In many of these studies, a

significant discrepancy has been observed between species that are represented in the inventory and the species that are actually observed in ambient air downwind of the sources. Since these types of discrepancies have been observed and reported for low reactivity species as well as high reactivity species, it is not simply a result of reactions that occur between the source and the monitoring location, but rather a real lack of accuracy in the application of many of the common speciation profiles.

TNRCC has recognized this weakness and the effects it can have on modeling analyses and has implemented a program to improve the situation. The major point sources in Texas are encouraged to report individual VOC species directly from each source in addition to the total VOC emission. These estimates of emissions of individual species can be easily aggregated to form speciation profiles for specific process-level point sources and for SCC-level processes representative of the conditions that exist in the Houston/Galveston area. These data have been compiled in the Point Source Data Base (PSDB).

OBJECTIVE

The objective of this project is to review the existing data from the 1999 TNRCC PSDB and develop source specific and SCC specific VOC speciation profiles that can be used to improve the point source speciation of VOC emissions for future modeling episodes. The focus of this effort is on point source information within the Houston/Galveston area, but data from outside this region were also used to develop source and SCC specific profiles.

SUMMARY

TNRCC provided data summaries from the 1999 PSDB for analyses in this study. The PSDB was divided into two separate files, one representing accounts within the Houston/Galveston area and the other representing accounts in the rest of the State, which is referred to as the outside Houston/Galveston database in the remainder of this report. The Houston/Galveston database included data for 12,536 individual points at 481 separate accounts, while the outside Houston/Galveston database included data for 19,677 points at 1,331 accounts.

Individual source-specific profiles and SCC-average profiles were constructed from data from those accounts that reported greater than 75% of the VOC emissions as species that can be identified as individual species. Source-specific profiles based on known VOC species that can be identified with a SAROAD/AIRS pollutant code were developed for 3,156 processes in the Houston/Galveston database. An additional 454 SCC-average profiles were developed from that database. The analysis of the outside Houston/Galveston database resulted in the development of 3,975 source-specific profiles and 637 SCC-average profiles. Application of the SCC-average profiles to the remaining points would result in speciation of 8,483 individual points, representing 73% of the VOC emissions in the Houston/Galveston database, and 12,666 individual points representing 64% of the VOC emissions in the outside Houston/Galveston database. The data have been compiled in a series of ACCESS® tables. The tables are included on a Compact Disk accompanying this report.

The methodology used to evaluate the original databases and develop the profiles is discussed. A more detailed presentation of the results is then provided, followed by a list of recommendations that could be implemented in the future to expand and improve the data available from the PSDB. Finally, a description of the ACCESS® table structures is presented as an attachment to the report.

METHODOLOGY

Data were received from the TNRCC from the 1999 Point Source Data Base (PSDB) in two EXCEL® files. One file contained data for sources from the Houston/Galveston area (speciated.emissions.HG.xls) and the second contained data for sources outside the Houston/Galveston area (speciated.emissions.xHG.xls). The information contained in these files is summarized in Table 1.

The data provided by TNRCC were reviewed and statistics on the content of these databases were prepared. A large fraction of the emissions in these databases are expressed as a general designation representing a collection of organic materials, as process raw materials, as industrial products, or as generic chemical classes. Examples of the general designations are non-methane VOC, and VOC gas mixture. Similarly examples of entries characterized as raw materials and products include crude oil and gasoline. Finally, examples of generic chemical classes represented in the database include alcohols undifferentiated, and aromatics undifferentiated. The databases also include entries for species that are not VOC (e.g., ethane, trichloroethane, acetone, hydrogen cyanide, etc.) For purposes of this analysis, only those species included in the general organic materials designation were considered unknown species. Table 2 is a summary of the content of the original database. A list of the species represented as unknown is presented in Table 3.

The quantity of emissions from each individual account number was totaled and the percent of emissions represented by unknown species (see Table 2) was calculated for each account number. The initial analyses were limited to those account numbers that have 75% or greater of the total VOC emissions represented by known species. The subsets of the two databases resulted in data for 99 account numbers from the Houston/Galveston database and for 246 accounts from the database representing sources outside of the Houston/Galveston area.

Separate profiles were created for each individual point and for the aggregate SCC level from the subsets of the two databases. The profiles that contained unknown species were normalized to develop a profile using the remaining known species. For example, if a profile contained 90% known species and 10% unknown species (e.g., non-methane VOC), the unknown specie would be removed from the profile, and each of the known species would be increased by 10%. In that way, 100% of the mass would be represented in the profile and all of the emissions could be associated with some particular chemical compound.

Each individual chemical specie in the PSDB is associated with a unique identification code referred to as the contam_code that is used by TNRCC for many internal analyses purposes. One of the uses of speciated VOC emissions data is as input to regional or urban scale

Table 1. Summary of PSDB Information

Parameter	Description	Notes
Pollutant	Reportable Criteria Pollutant	In this case, VOC
SIC	Standard Industrial Classification Code	Standard code to represent industry type, recently replaced by NAICS North American Industrial Classification System
SIC_cls	Industry Sector Identifier	Example: Organic Chemicals
Business	Subset of Industry	Example: Petrochemicals and Polymers
SCC	Source Classification Code	Code used to describe specific processes that result in air emissions
Fac_name	Process Description	Related to SCC
Account	Identifier code for a particular plant or industrial facility	Unique code used by TNRCC
Fac_id	Equivalent to an individual emission point	Identifier to represent different emission processes at an account
Point_id	Equivalent to an individual emission stack	Individual source resulting in emissions
Ozone Season	Emissions expressed in tons per day during the ozone season for specific contaminant	Emissions are specific for each process and contaminant
Contam code	Identifier used by TNRCC to represent individual chemical emissions species	Unique code used by TNRCC
CAS	Chemical Abstract Service Number	Nationally recognized pollutant code
Species	Preferred species name	Mnemonic identifier

Table 2. Overall Summary of the PSDB

	Houston/Galveston Database		Outside Houston/Galveston Database	
Unique species represented	467		449	
Total VOC emissions	177.41 (tpd)		395.41 (tpd)	
Unknown species	17		15	
Unknown species emissions	62.99 (tpd)	35.5%	224.16 (tpd)	56.7%
Known species	385		368	
Known species emissions	114.42 (tpd)	64.5%	171.24 (tpd)	43.3%
Generic species	65		66	
Generic species emissions	16.39 (tpd)	9.2%	26.92 (tpd)	6.8%

Note: Each generic specie is also identified as either a known or an unknown specie

Table 3. List of Chemicals Classified as Unknown

Chemical Name	Contam Code
non-methane VOC	50001
Organic acid	51100
Dibasic acids	51370
VOC with nitrogen	58200
VOC-oxygenated undifferentiated	58400
VOC gas mixture undifferentiated	59000
CCU feed	59050
Coker feed	59070
Condensate	59090
FCC feed	59175
Bunkers	59205
gas oil	59250
Platformate	59350
Raffinate	59400
Reformer feed	59410
Reduced crude	59425
Reformate	59450
Vacuum bottoms	59490

photochemical models. Emissions preprocessor programs combine source specific speciated emissions information into forms that can be used as input to representations of the photochemical reaction mechanism.

Currently, there are two primary formats that are used to represent VOC speciation in photochemical models. One is a lumped species type system in which many similar individual chemical species are summed into a single pseudo-specie with reaction characteristics that represent the average chemistry of the individual species. The other is the carbon bond type mechanism in which all individual species are treated as a combination of representative carbon bond types (e.g., single (alkane), double (alkene), or carbonyl carbon bonds.)

In both cases, the emissions preprocessor systems have to recognize the species represented in the profiles. These preprocessors use SAROAD or AIRS codes to identify chemicals, and will not recognize the TNRCC contam code system. Therefore, TNRCC provided a crosswalk lookup table that matched contam codes to SAROAD/AIRS species codes. The merger of files revealed that only 41% of the chemicals in the PSDB have a corresponding SAROAD/AIRS code. Those pollutants however, represent 94% of emissions in the Houston/Galveston database and 95% of the emissions in the outside Houston/Galveston database. Furthermore, the percentage of emissions represented by pollutants with SAROAD codes in the subsets representing 75% known species is 96% in the Houston/Galveston database and 93% in the outside Houston/Galveston database. Therefore, for this initial analysis the

profiles developed for the greater than 75% known species profiles were normalized to include only those species that are identified by an existing SAROAD/AIRS code.

RESULTS

General

The Houston/Galveston area database represents a total of 177.41 tons per day (tpd) of VOC emissions from 481 accounts or plants. Although the database is intended to represent speciated emissions, 60.84 tpd or 34% of the total emissions were reported simply as non-methane VOC undifferentiated. Data were reported entirely as non-methane VOC for 97 of the 481 accounts. The total non-methane VOC emissions represented at those 97 accounts, however, is only 4.97 tpd or 8% of the non-methane VOC in the database. Typically, those facilities reporting only non-methane VOC are small sources of less than 0.5 tpd total VOC emissions. Figure 1 is a map of the Houston/Galveston area showing the locations of the accounts that reported only non-methane VOC. Figure 1 includes data for 84 of the 97 accounts, since location data were not available for 13 of those accounts.

The outside Houston/Galveston database represents 395.41 tpd of VOC emissions from 1,331 accounts. The total emissions represented as non-methane VOC in that file is 212.12 tpd or 54% of the total emissions. Accounts that reported only non-methane VOC, number 400 and contribute 39.74 tpd or 19% of the total non-methane VOC in that database. The accounts for which all emissions are reported as non-methane VOC are small sources like those in Houston/Galveston database. Figure 2 shows the distribution of the 312 such facilities for which location data were available.

Source Specific and SCC Average Profiles

The subset of the Houston/Galveston database that represents accounts that had more than 75% of their emissions expressed as known VOC species includes data for 99 accounts. It was possible to develop 4,195 point specific profiles and 454 SCC average profiles using those data. Some of those profiles contain species that are either unknown or are species for which no SAROAD/AIRS pollutant code was available. Therefore, all profiles were normalized to represent only known species for which SAROAD identifiers were available. That step resulted in source specific profiles for 3,156 individual points. The total known emissions represented in the greater 75% known species database for the Houston/Galveston area are 61.21 tpd or 35% of the area wide total emissions. Figure 3 is a map showing the location of the accounts that were used to generate the subset database representing accounts that specified more than 75% of their emissions as specific known VOC species from the Houston/Galveston database. The data summarized in Figure 3 represent the location of 97 of the 99 accounts that have corresponding location data.

The analysis of the outside Houston/Galveston database resulted in a subset database of 246 accounts representing facilities that reported greater than 75% of their emissions as known species. That subset contributed 5,202 point specific profiles and 637 SCC average profiles. The further normalization to represent only profiles containing known species with SAROAD

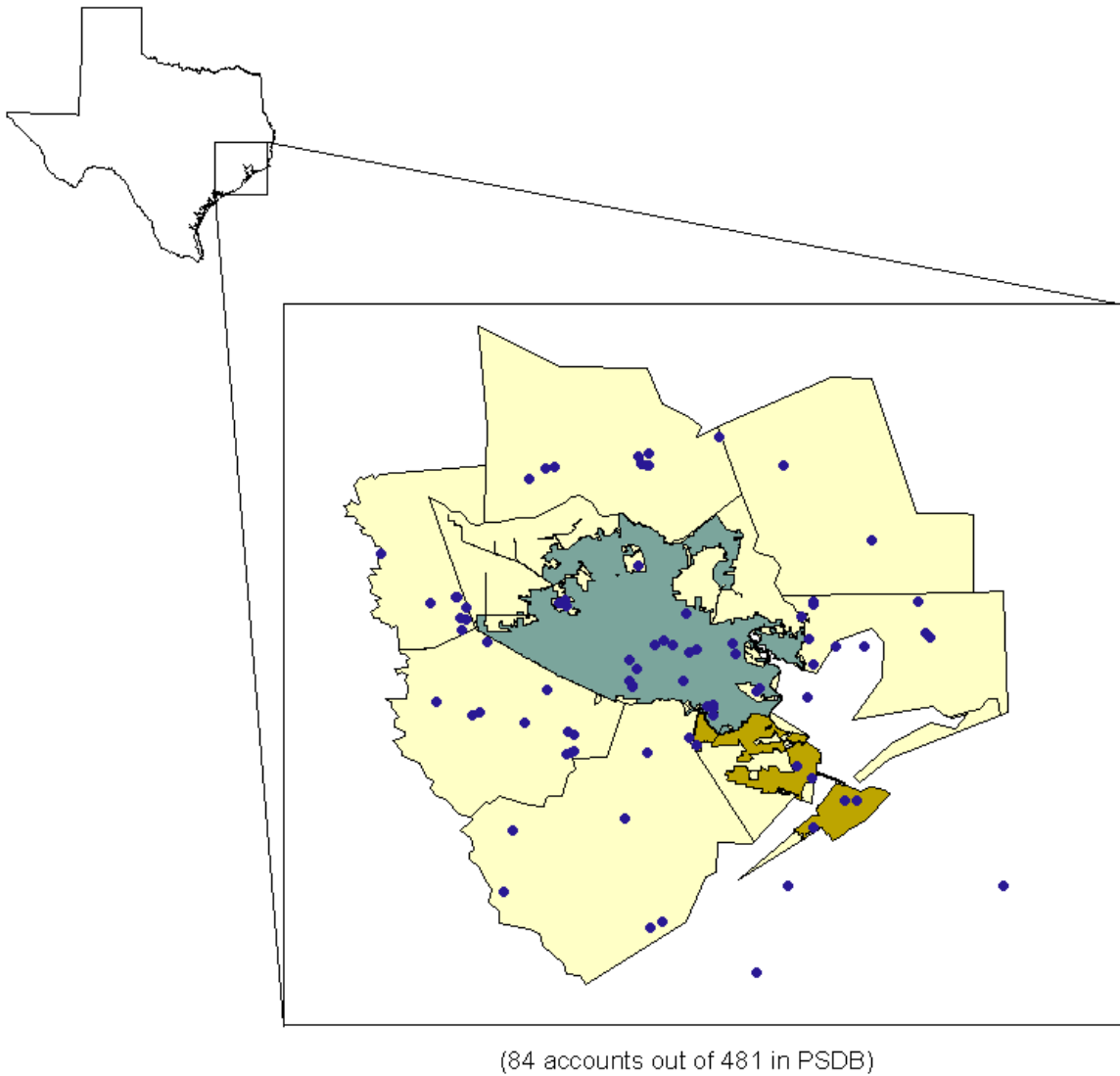


Figure 1. Location of Accounts Reporting All Emissions as "Non-Methane VOC-U" From the Houston/Galveston Database

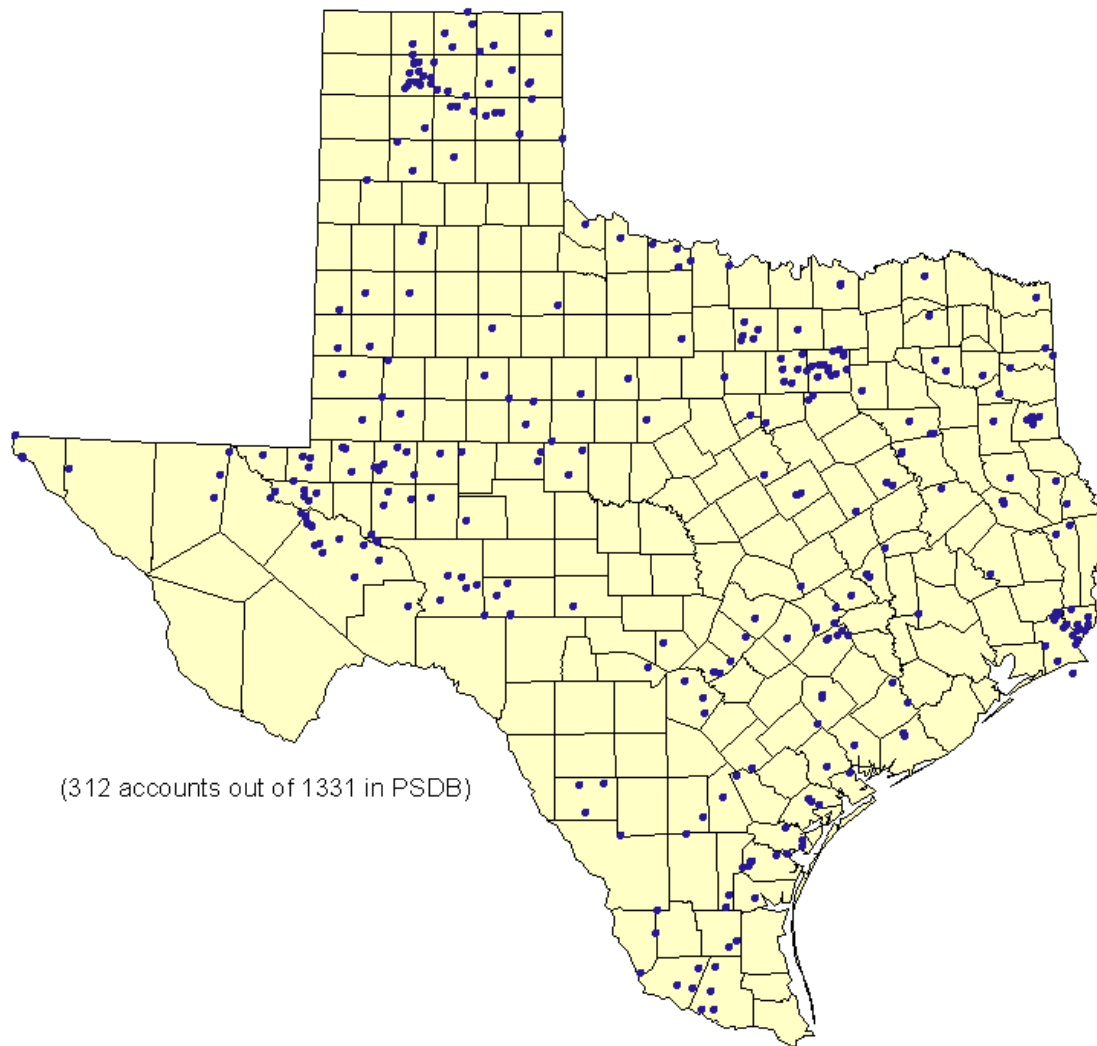


Figure 2. Location of Accounts Reporting All Emissions as
"Non-Methane VOC-U"
From the Outside Houston/Galveston Database

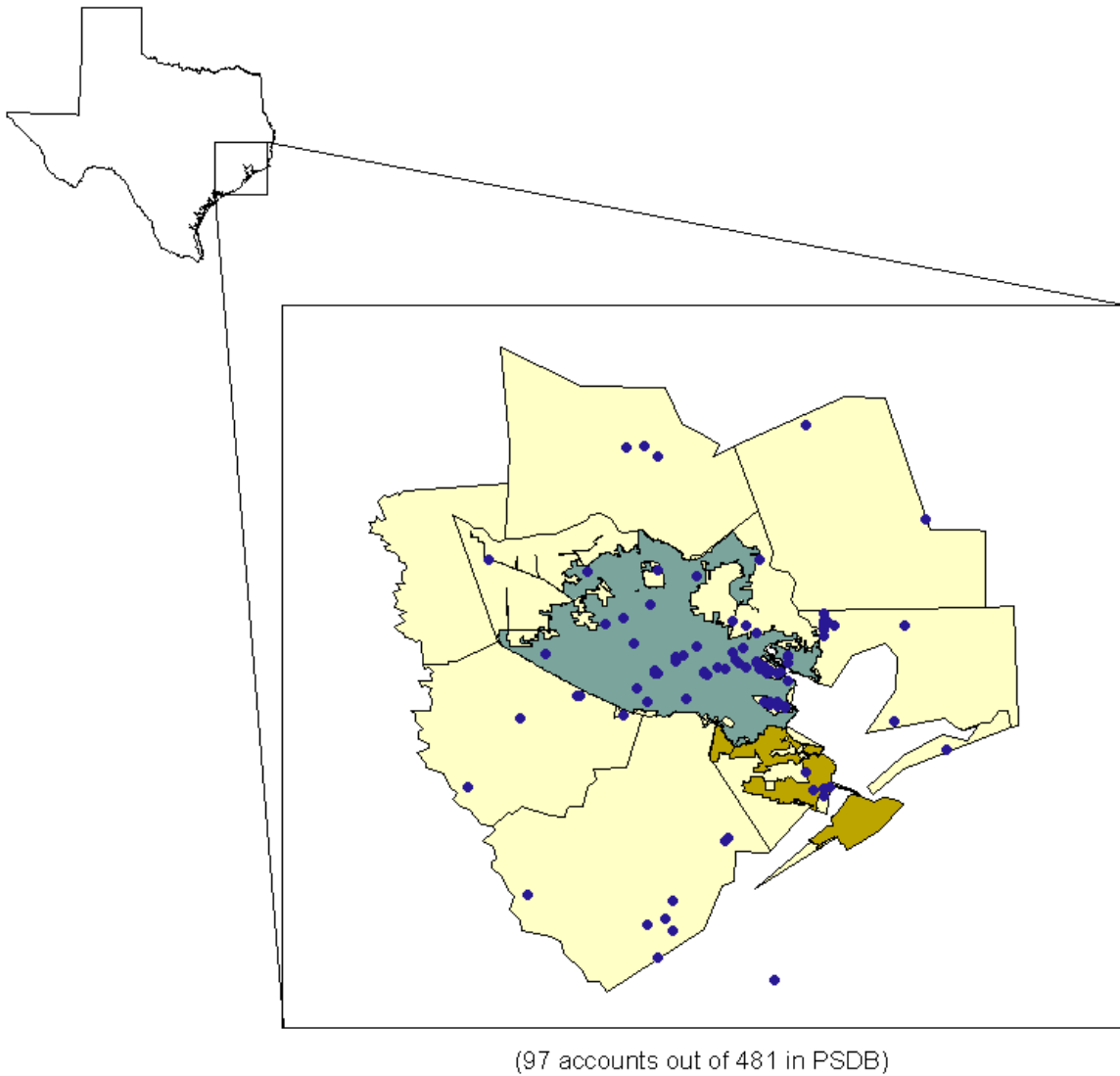


Figure 3. Location of Accounts with > 75% Known Emissions From the Houston/Galveston Database

codes resulted in profiles for 3,975 individual points. The total known emissions represented in the greater than 75% known species database for the outside Houston/Galveston area is 101.96 tpd or 26% of the total emissions. Figure 4 is a map showing the location of those accounts for the outside Houston Galveston database. The data in Figure 4 represent 240 of the 246 accounts for which location data are available.

Each of the SCC average profiles can be used to speciate any emissions source having an identical or similar SCC. This is the similar method used commonly to speciate emissions records using national-level speciation profiles. These profiles will improve the speciation of sources particularly when applied to the specific regions from which they are developed. The database was investigated to determine the effect of applying the regional SCC-average profiles to the data for accounts in the less than 75% known species categories. This process results in either point specific profiles or regionally representative SCC-average profiles for 8,483 individual points, and will speciate 73% of the Houston/Galveston database. The same process applied to the outside Houston/Galveston database accommodates 12,666 points and will speciate 64% of the total VOC emissions.

Sources of Ethylene and Propylene

Currently, sources of ethylene and propylene are of particular interest to TNRCC and are receiving attention in analyses of emissions information. Therefore, the data representing the largest contributions of ethylene and propylene were extracted and summarized. This exercise offers a good opportunity to use the data for an actual analysis of interest to demonstrate the utility of the PSDB.

Accounts were sorted to define the ranked list of contributors to the ethylene and propylene emissions sum. The top 25 accounts in each database were found to capture a significant amount of these emissions, and leave a manageable subset of data to review. In the Houston/Galveston database the total emissions of ethylene and propylene are 13.95 tpd or 8% of the total emissions. The top 25 accounts in terms of ethylene and propylene emissions contribute 12.19 tpd or 87% of the total ethylene and propylene emissions. Profiles based on the greater than 75% known species subset of the data, were developed for 15 of those top 25 sources. Figure 5 is a map showing the location of the top 25 accounts that emit the largest quantities of ethylene and propylene for the Houston/Galveston database. The 15 accounts for which point specific profiles were developed are represented by stars.

A similar analysis was completed for the outside Houston/Galveston database. The total ethylene and propylene emissions in that database are 17.05 tpd, which represents 4% of the total emissions. The top 25 accounts contribute 16.76 tpd or 98% of the total ethylene and propylene emissions from the outside Houston/Galveston database. Figure 6 is a map that shows the locations of the 25 accounts with the largest emissions of ethylene and propylene in the outside Houston/Galveston database.

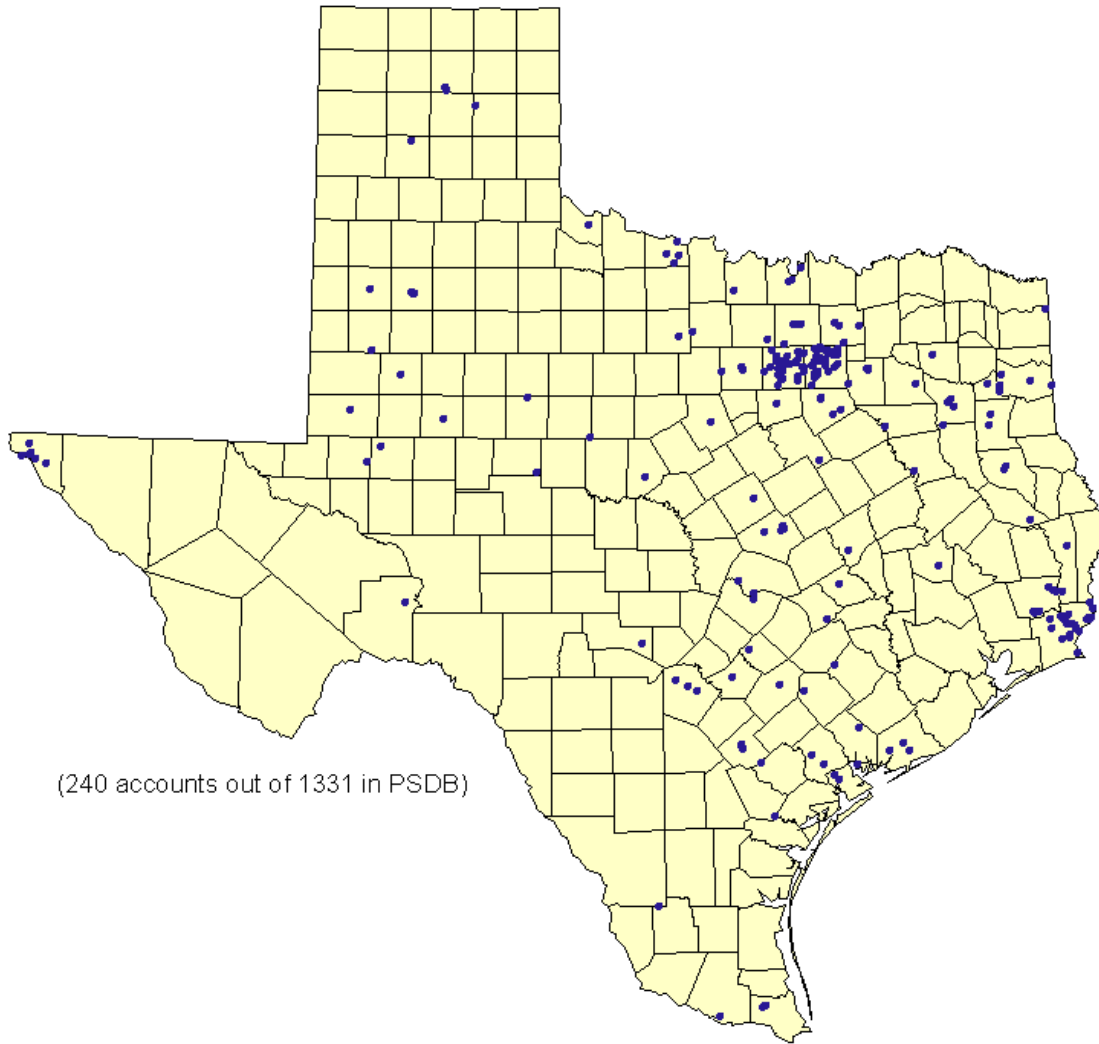
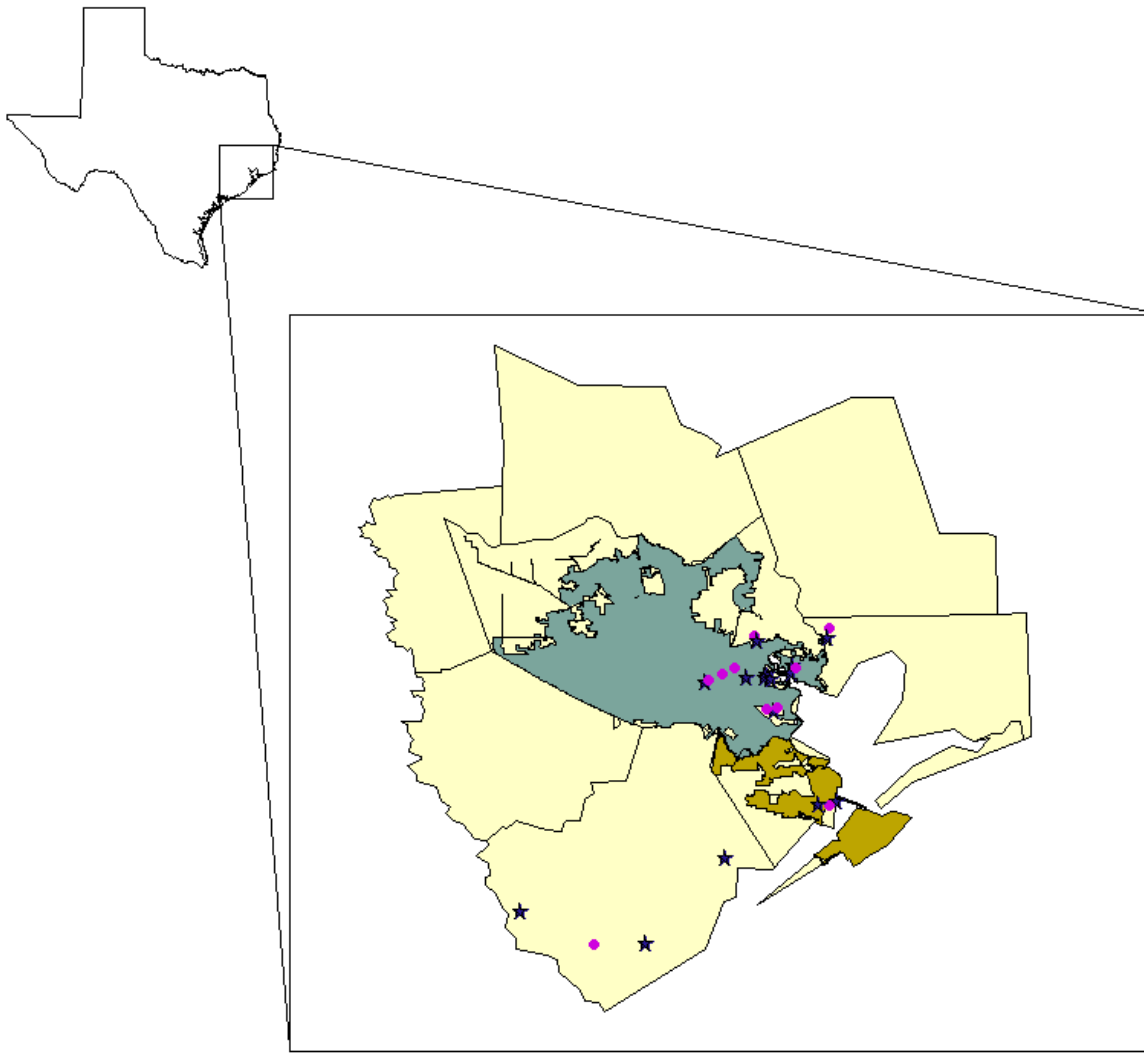


Figure 4. Location of Accounts with > 75% Known Emissions From the Outside Houston/Galveston Database



★ = account in the > 75% known emissions database

Figure 5. Location of the Top 25 Emitters of Ethylene and Propylene From the Houston/Galveston Database

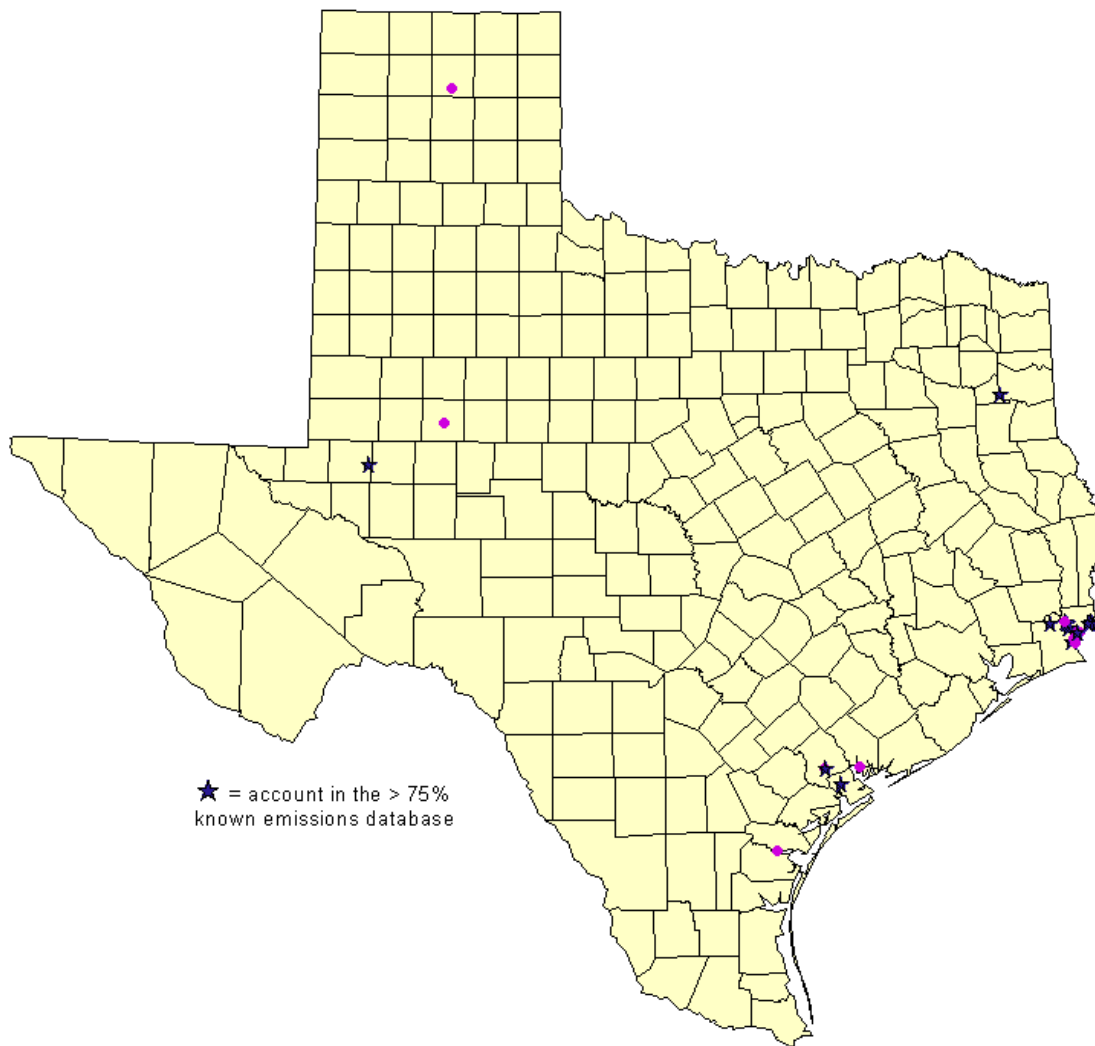


Figure 6. Location of the Top 25 Emitters of Ethylene and Propylene From the Outside Houston/Galveston Database

Recommendations

Time constraints limited the extent of analyses that could be conducted using the PSDB information provided by TNRCC. Additional activities can be completed to improve, and extend the usefulness of these data. The following list of recommendations provides a starting point for further study.

1. Review the list of known and suspected non-VOC compounds reported in the database and develop alternate approaches for removing all or part of them from the final profiles.
2. Similarly, establish rules for substituting some particular compound for cases where the generic compound class is reported.
3. A detailed review and summary of the extent of emissions reported as raw materials or products (e.g., gasoline, CCU feed, etc.) should be completed and an approach developed to represent specific VOC species for as much of that total as possible. NOTE: TNRCC has developed several profiles of gasoline composition that can be used for this purpose. These data were not available in time for use in this study.
4. A more detailed comparison of point specific and SCC-average profiles developed in the preliminary stage of this work can be completed in an attempt to find specific compounds to represent the unknown species in other similar sources. This type of analysis would allow the use of all of the specific species represented in the less than 75% known database instead of the use of a complete SCC-average profile.
5. Some of the compounds reported are included on lists of hazardous air pollutants (HAPs). The database could be reviewed to extract HAP species for use in improving the basis for an Air Toxics Emission Inventory.

ATTACHMENT 1

EMISSION PROFILE DESCRIPTIONS:

The structures of the MS ACCESS files are identical for the Houston-Galveston area profiles, and the profiles for outside the Houston-Galveston area. The “_all” files contain all the profiles we were able to generate from the >75% known subset; the “_air” profiles contain the profiles we created using only species we were able to match to AIRS/SAROAD codes from the >75% known subset; and the “_oth” profiles contain the sources that can be matched to the profiles in the “_air” database by SCC that were less than 75% known.

Point-Specific Speciation Profiles:

The data for the point-specific speciation profiles are contained in two tables. The table described as “Point Profile ID” contains one record for each profile. In this table, each profile is identified by a unique number assembled from a combination of the account id + fac id + point id. The “Point Profile ID” table also contains the name of the process, the total mass of compounds in tons per day emitted by the process, the mass of “known” compounds emitted by the process, the mass of AIRS/SAROAD species emitted by the process, and the number of species (known and unknown) included in the profile.

The table described as “Point Profile Data” contains one record for each chemical specie for each profile identified in “Point Profile ID”. As in “Point Profile ID”, the unique profile number is included in this table, and is the key connecting the two tables. The chemical specie is identified by a unique “contam_code” and CAS number, AIRS/SAROAD code where available, and of course the chemical name or class description. “Point Profile Data” also includes the account, SCC, fac_id, and point_id information. The amount of each chemical species emitted is described by the “Tonperday” field and the chemical species classification is identified by a logical field called “Know_unk”. A value of -1 identifies the species as known, and a value of 0 identifies the species as unknown. Due to the “unknown” chemical representation and lack of SAROAD/AIRS codes for all chemicals, in part or all of most of the profiles, each profile was calculated using three methods and the results of each calculation are included for every profile in the “_all” files. The first profile calculation was performed using all the chemical specie data; known and unknown. This profile calculation is expressed as a percentage value in the “Pro_total” field. If the “Pro_total” field is added for each chemical specie for a given profile, the total is 100% +/- 0.001%. A second profile calculation was performed including only the known chemical species for each profile. This profile calculation is expressed as a percentage value in the “Pro_known” field. If the “Pro_known” field is added for each chemical specie for a given profile, the total is 100% +/- 0.001%. If all species for a profile are known, the values of “Pro_total” and “Pro_known” for that profile are equal. If there are some unknown chemicals in a profile, the “Pro_known” values for that profile will differ from the “Pro_total” values. If all the chemicals for a given profile are unknown, no “Pro_known” values exist for that profile. A third profile calculation was performed including only the chemical species with AIRS/SAROAD codes for each profile. This profile calculation is expressed as a percentage value in the “Pro_airs” field. If the “Pro_airs” field is added for each chemical specie for a given profile, the total is 100% +/- 0.001%. If all species for a profile have AIRS/SAROAD codes, the

values of “Pro_total” and “Pro_airs” for that profile are equal. If there are some chemicals without AIRS/SAROAD codes in a profile, the “Pro_airs” values for that profile will differ from the “Pro_total” values. If none of the chemicals for a given profile have AIRS/SAROAD codes, no “Pro_airs” values exist for that profile. Since it is our understanding that only chemicals with matching AIRS/SAROAD codes will be used in modeling exercises, we created the “_air” files containing only AIRS/SAROAD profiles for convenience.

SCC-Specific Speciation Profiles:

The data for the SCC-specific speciation profiles are contained in two tables. The table described as “SCC Profile ID” contains one record for each profile. In this table, each profile is identified by SCC. The “SCC Profile ID” table also contains the total mass of compounds in tons per day emitted by the process, the mass of “known” compounds emitted by the process, the mass of AIRS/SAROAD species emitted by the process, and the number of species (known and unknown) included in the profile.

The table described as “SCC Profile Data” contains one record for each chemical specie for each profile identified in “SCC Profile ID”. As in “SCC Profile ID”, the unique profile number is included in this table, and is the key connecting the two tables. The chemical specie is identified by a unique “contam_code” and CAS number, AIRS/SAROAD code where available, CAS number, and of course the chemical name or class description. The amount of each chemical species emitted is described by the “Tonperday” field and the chemical species classification is identified by a logical field called “Know_unk”. A “Know_unk” value of -1 identifies the species as known, and a “Know_unk” value of 0 identifies the species as unknown. Due to the “unknown” chemical representation and lack of SAROAD/AIRS codes for all chemicals, in part or all of most of the profiles, each profile was calculated using three methods and the results of each calculation are included for every profile in the “_all” files. The first profile calculation was performed using all the chemical specie data; known and unknown. This profile calculation is expressed as a percentage value in the “Pro_total” field. If the “Pro_total” field is added for each chemical specie for a given profile, the total is 100% +/- 0.001%. A second profile calculation was performed including only the known chemical species for each profile. This profile calculation is expressed as a percentage value in the “Pro_known” field. If the “Pro_known” field is added for each chemical specie for a given profile, the total is 100% +/- 0.001%. If all species for a profile are known, the values of “Pro_total” and “Pro_known” for that profile are equal. If there are some unknown chemicals in a profile, the “Pro_known” values for that profile will differ from the “Pro_total” values. If all the chemicals for a given profile are unknown, no “Pro_known” values exist for that profile. A third profile calculation was performed including only the chemical species with AIRS/SAROAD codes for each profile. This profile calculation is expressed as a percentage value in the “Pro_airs” field. If the “Pro_airs” field is added for each chemical specie for a given profile, the total is 100% +/- 0.001%. If all species for a profile have AIRS/SAROAD codes, the values of “Pro_total” and “Pro_airs” for that profile are equal. If there are some chemicals without AIRS/SAROAD codes in a profile, the “Pro_airs” values for that profile will differ from the “Pro_total” values. If none of the chemicals for a given profile have AIRS/SAROAD codes, no “Pro_airs” values exist for that profile. Again, since it is our understanding that only chemicals with matching AIRS/SAROAD

codes will be used in modeling exercises, we created the “_air” files containing only AIRS/SAROAD profiles for convenience.

**Speciation of Texas Point Source VOC Emissions
for Ambient Air Quality Modeling**

**Gabriel Cantu
Texas Commission on Environmental Quality**

July 2003

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Introduction

Chemical speciation of point source emissions has always been an important issue in ambient air quality ozone modeling. With the recent adoption of species-specific highly reactive VOC (HRVOC) rules by the TCEQ it has become more important than ever to accurately represent each chemical species—by type and amount—emitted from each emission source. This report serves as a guide, as well as a case study, in a new method of speciation of Texas point source emissions for ozone modeling. The author of this paper assumes the reader is familiar with previous speciation methods used by TCEQ, most recently the method presented in, “Development of Source Speciation Profiles from the TNRCC 2000 Point Source Database”, PES August 2002

(ftp://ftp.tnrcc.state.tx.us/pub/OEPAA/TAD/Modeling/HGAQSE/Contract_Reports/EI/DevelopmentOfSourceSpeciationProfilesFrom2000PSDB.pdf), as well as the hierarchal profile application method presented in Attachment 3 to the Houston/Galveston/Brazoria Mid-Course Review Phase I Technical Support Document, “Emissions Inventory Development and Modeling for the August 25 - September 1, 2000 Episode”

(ftp://ftp.tnrcc.state.tx.us/pub/OEPAA/TAD/Modeling/HGAQSE/Modeling/Doc/TSD_PHASE1/attachment3-emissions_inventory.pdf).

Methodology

Limiting the Dataset

The first step in creating a fully speciated VOC modeling inventory is to perform some initial QA and general house-keeping on the modeling emissions extract. The current modeling inventory, hereafter referred to as PSDB2000v15a, contains emissions data for VOC (speciated and unspeciated), NO_x, CO, SO₂, etc..., for each point source emission point in Texas. Each emission point is uniquely identified by TCEQ and EPA identifiers. The first phase of QA includes, but is not limited to, removal of non-VOC species and limiting the number of points included in the dataset to those with species-specific emission rates greater than some predetermined limit.

Limiting the modeling extract to VOC results in data for 59,952 emission points. Imposing an emissions threshold of 0.0005 tons/day (1.0 lb/day) per VOC species per point reduces the dataset to 24,671 emission points.

Removal of Non-VOC Chemical Species

The second phase of QA/house-keeping begins with methodology adopted from PES 2002. All compounds labeled as VOC, as indicated by historical TCEQ contaminant codes, that do not meet the definition of VOC, according to TCEQ Chapter 101 General Air Quality Rules, (http://www.tnrc.state.tx.us/oprdrules/pdflib/101_ind.pdf), are removed from the data. A list of non-VOC compounds, developed by PES, is included in Table 1. Species such as Methane, Ethane, Acetone, and various Chlorofluorocarbons were removed from the dataset during the previously mentioned initial processing.

Table 1. Non-VOC Chemical Species Removed from Speciation Process

TCEQ CONTAM CODE	CAS	SPECIES
51051	19780111	DODECENYL SUCCINIC ANHYDRIDE
51890	9004700	CELLULOSE NITRATE
52261	8001205	MODIFIED VEGETABLE OILS
52785	9016006	LATEX
53209	7572294	DICHLOROACETYLENE
53320	75445	PHOSGENE
53390	79345	TETRACHLOROETHANE (1,1,2,2)
53391	630206	TETRACHLOROETHANE (1,1,1,2)
53524	76131	ETHANE (1,1,2-CL,1,2,2-FL)
54079	76164	HEXAFLUOROETHANE
54295	123319	HYDROQUINONE
55315	16219753	ETHYLIDENE NORBORNENE
55360	87683	HEXACHLOROBUTADIENE
56560	67721	HEXACHLOROETHANE
58240	74908	HYDROGEN CYANIDE GAS
58846	115866	TRIPHENYL PHOSPHATE
58921	62737	VAPONA
59869	9016459	NONYLPHENOXYPOLY(ETHYLENEOXY) ETHANOL
59872	99812	PARAMETHANE
50002		POLYCYCLIC ORGANICMATTER
51421		FATTY ALCOHOLS
51467		SULFOLANE
51475		GLYCERIN MIST
51492		POLYOL
51494		HYDROXYLAMINE
52471		ETHYL 3-ETHOXYPROPRION
52764		TRIMETHYL(2,2,4)PENTADIOL(1,1,3)
52912		EPOXY RESIN
53211		CARBON TETRAFLUORIDE
53340		TRICHLOROPROPANE
54021		HEXACHLOROACETONE
54025		ACETONE CYANOHYDRIN
58234		POLYAMIDES-U
58241		CYANIDE COMPOUNDS
58374		UREAA FORMALDEHYDE
58520		TRIOXANE
58625		DISULFIDES-U
58805		ETHYL SILICATE
58847		ORGANO PHOSPHATES
58850		ORGANIC SULFUR-OXIDES-U
59868		TERGITAL
59870		TERGITOL 15-5-3

Refinement of Generic Chemical Mixtures

After the non-VOC species were removed from the dataset, generic chemical mixtures reported by industry (such as “crude oil” or “gasoline”) were split into component hydrocarbons, using existing chemical profiles. When available, profiles from the TCEQ database were used; otherwise profiles from EPA’s SPECIATE database were applied. This process involves directly applying a profile to a generic chemical mixture and substituting the results in place of that mixture. A list of generic chemical mixtures, developed by PES, and their associated refinement profiles is included in Table 2.

Five profiles were used to resolve these generic mixtures. The methodology, developed by PES, for selecting them is as follows:

1. PES states that “an examination of the sources associated with the reported emissions of crude oil consisted mostly of large crude oil storage tanks and pipelines”. Therefore, SPECIATE profile 2487, “Composite of 7 Emission Profiles from Crude Oil Storage Tanks – 1993” was used as the “Crude Oil” refinement profile (Appendix A, Table A-1).
2. The “Gasoline” profile is derived from a gasoline vapor profile, for Houston Area gasoline from the summer of 2000, provided to PES by ENVIRON. This profile is included in Table A-2.
3. PES also states that “several generic species could be characterized as naphthas”, and therefore be resolved using a profile for naphthas from “Speciated VOC Emissions for the Dallas/Fort Worth Non-attainment Area”, ENVIRON October 1997. The “Naphthas” refinement profile is included in Table A-3.
4. Also, “several generic species could be characterized as stoddard solvents/mineral spirits”. Therefore, SPECIATE profile 1193, “Drycleaning” was used as the “Stoddard Solvent” profile (Table A-4). This profile is a composite of the headspace of five mineral spirit samples from two companies combined in equal amounts by volume.
5. The “Refinery” profile (Table A-5) is derived from SPECIATE profile 2457, “Composite of 10 Emission Profiles – Misc. Chemical and Refining Plants in Houston – 1993”. According to PES, “an evaluation of the remaining generic species in the PSDB showed that most could be described as refinery by-products, in-process refinery feedstocks, and general emissions from refinery processes or storage tanks. Generally, most of these generic chemicals are not defined well enough to speciate individually, but could be speciated effectively as a group – all associated as refinery emissions”.

Table 2. Generic Chemical Mixtures

PROFILE	SAROAD	TCEQ CONTAM CODE	CAS	SPECIES
CRUD		59001		CRUDE OIL
GASO		59003	8006619	GASOLINE
NAPH		59305		NAPHTHA, PETROLEUM, HYDRO TREAT
NAPH		51895	8032324	ALIPHATIC NAPHTHA
NAPH		59871	64742898	VM&P NAPHTHA
NAPH	45101	59300		NAPHTHA
NAPH		59330	8002742	PARAFIN WAX FUMES
NAPH	43118	59800		NAPHTHA, COAL-TAR
NAPH	81400	56500		PARRAFIN LINEAR-U
NAPH	81500	56001		PARRAFINS CYCLIC-U
NAPH	81400	56000		PARRAFINS-U
REFN		59002		DISTILLATE
REFN		59009		PETROLEUM DISTILLATE
REFN		52259		PETROLEUM DISTILLATES
REFN		59007		LUBRICATING OIL
REFN		59005	8008206	KEROSENE
REFN		58999		AROMATIC PETROLEUM DISTILLATE
REFN		52264		SWEETENED MIDDLE DISTILLATE
REFN		58997		PYROLYSIS GASOLINE
REFN		59050		CCU FEED
REFN		59200		FUEL OIL-U
REFN		58998		ALIPHATIC PETROLEUM DISTILLATE
REFN		59004		JET FUEL
REFN		59270		LIQUIFIED PETROLEUM GAS
REFN		59490		VACUUM BOTTOMS
REFN		59450		REFORMATE
REFN		59425		REDUCED CRUDE
REFN		59410		REFORMER FEED
REFN		59400		RAFFINATE
REFN		59150		DIESEL
REFN		59350		PLATFORMATE
REFN		59090		CONDENSATE
REFN		59250		GAS OIL
REFN		59225		NO 6 FUEL OIL
REFN		59220		NO 5 FUEL OIL
REFN		59215		NO 4 FUEL OIL
REFN		59210		NO 2 FUEL OIL
REFN		59175		FCC FEED
STOD		59360	8052413	STODDARD SOLVENT
STOD		59006		MINERAL OIL
STOD	43118	59275		MINERAL SPIRITS

SAROAD Assignment

After the "refinement" process, SAROAD codes were assigned to each TCEQ CONTAM Code/Species using the CONTAM-SAROAD mapping, developed by PES and ENVIRON, based on the existing EPS2x Compound Database. This cross-reference file is not included in this report but may be furnished upon request. The procedure for developing this map is as follows (from "Development of Source Speciation Profiles):

The master chemical table...was populated with SAROAD codes and CAS codes where those codes could be determined. PES contacted EPA personnel in an attempt to obtain a master list of SAROAD codes, but EPA is not maintaining such a list at this time. As there exists no recognized standard procedure for assignment of SAROADs, one had to be adopted to complete the SAROAD assignment exercise. The following hierarchical approach was obtained from ENVIRON and used to make the SAROAD assignments:

1. Find an exact match, e.g., toluene assigned to toluene.
2. Match to a general VOC category that includes the specific VOC isomer, e.g., 2,4,4-trimethyl-1-pentene assigned to "c7 olefins."
3. Match to a similar isomer, e.g., 2,2,4-trimethylhexane assigned to 2,2,5-trimethylhexane. Approach 2 is preferred to 3 because 2 shows more clearly that a reassignment has been performed. In this case, the assignment to a similar isomer is preferred over a general "c8 alkane" assignment because it permits the presence of a tertiary carbon to be identified, which impacts the resulting CB-IV split.
4. Match to the surrogate with the most similar properties, e.g., 2,4-dimethyl-1-pentene assigned to 3-ethyl-2-pentene. Here the surrogate is selected to show an alkene branched at the double bond.

Checking Extent of Speciation

At this point in the process we diverge from the methodology introduced in "Development of Source Speciation Profiles from the TNRCC 2000 Point Source Database", and continue with a process that will retain all speciated VOC data currently in the database and attempt to characterize the remaining portion of unspciated data according to augmented EPA speciation profiles.

An examination of the database after the "refinement" and SAROAD assignment processes reveals species with no SAROAD assignment as well as unspciated VOC mixtures for which no entry exists in the current modeling CB-IV Compound Database or for which a questionable entry exists. These species are presented in Table 3. Each of these compounds was replaced with SAROAD 43104, TCEQ CONTAM 50001, NONMETHANE VOC-U, and aggregated together for each emission point. There are many different reasons why these mixtures were reported in the first place, and they will not be discussed here as they are beyond the scope of this report. Theoretically, by aggregating them together and applying a detailed

profile, such as an EPA default specific to that point's process, results in a better approximation of the constituents of those mixtures than simply assigning them to some group of compounds or CB-IV species in arbitrary percentages.

Table 3. Unspecified VOC Mixtures

TCEQ CONTAM CODE	SAROAD	SPECIES
50001	43104	NONMETHANE VOC-U
59000	43104	VOC GAS MIXTURE-U
55320	43294	HEPTENES MIXED ISOMERS
52220	45701	ANILINE-U
51100	81000	ORGANIC ACID-U
51400	81100	ALCOHOLS-U
51600	81200	ALDEHYDES-U
55000	81300	OLEFINS-U
52200	81600	AMINES-U
51470	81700	GLYCOLS-U
51800	81800	ALKYNES-U
52400	81900	AROMATICS-U
52470	82100	POLYNUCLEAR AROMATICS
52600	82400	ESTERS-U
52800	82500	ETHERS-U
53200	82700	CHLORINATED HYDROCARBONS
54000	82800	KETONES-U
58400	83000	VOC - OXYGENATED-U
58700	83100	MERCAPTANS-U
58212	86031	PENTENE NITRILES-U
58216	86033	DINITRILES

A snapshot of the inventory at this point—post "refinement" (i.e. after resolution of generic species), SAROAD assignment, and replacement of unspecified mixtures—revealed that approximately 40% of the Texas inventory remained unspecified VOC (Table 4) and in the Eight County Houston-Galveston-Brazoria Nonattainment Area (HGB NAA) approximately 30% of the VOC remained unspecified (Table 5).

Table 4. Extent of Speciation, Post Refinement, for all of Texas

	TONS/DAY	PERCENT OF TOTAL
Total VOC	496.37	
Total Speciated VOC	296.59	59.75
Total Unspecified VOC	199.78	40.25

Table 5. Extent of Speciation, Post Refinement, for the HGB 8 County NAA

	TONS/DAY	PERCENT OF TOTAL
Total 8 County VOC	145.27	
Total 8 County Speciated VOC	101.62	69.95
Total 8 County Unspeciated VOC	43.65	30.05

Taking this analysis a step further and categorizing individual emission points based on their extent of speciation yields Tables 6 and 7, in which we associate extent of speciation with VOC tonnage and numbers of emission points. This data is also presented in a graphical format in Figures 1 and 2.

Table 6. Extent of Speciation, Post Refinement, for all of Texas

PERCENT SPECIATION	NUMBER OF POINTS	TONS/DAY	PERCENT OF TOTAL
90 - 100	7602	212.57	42.83
80 - 89.99	867	36.40	7.33
70 - 79.99	952	31.09	6.26
60 - 69.99	1017	17.76	3.58
50 - 59.99	269	9.69	1.95
40 - 49.99	410	15.57	3.14
30 - 39.99	319	5.48	1.10
20 - 29.99	305	7.57	1.53
10 - 19.99	402	13.34	2.69
0 - 9.99	12469	146.89	29.59

Table 7. Extent of Speciation, Post Refinement, for the HGB 8 County NAA

PERCENT SPECIATION	NUMBER OF POINTS	TONS/DAY	PERCENT OF TOTAL
90 - 100	3560	74.95	51.59
80 - 89.99	418	13.00	8.95
70 - 79.99	285	7.24	4.98
60 - 69.99	500	7.47	5.14
50 - 59.99	102	3.39	2.34
40 - 49.99	125	4.38	3.02
30 - 39.99	81	1.54	1.06
20 - 29.99	94	2.47	1.70
10 - 19.99	114	3.46	2.38
0 - 9.99	3751	27.37	18.84

Augmenting EPA Default Profiles

The next step in developing a fully speciated modeling inventory is to apply chemical speciation profiles to the unspiciated portion of the inventory. For photochemical modeling, nationally recognized EPA speciation profiles are standard. These profiles are based on national emissions data and may be used to represent emissions at the Source Classification Code (SCC) level. Each emission point is assigned a profile based on its reported SCC according to an EPA SCC-Speciation Profile cross-reference.

Since these profiles are based on national-level data they contain chemical species generally thought of as non-reactive for photochemical modeling or as not meeting the definition of a VOC. Therefore in order to accurately allocate the unspiciated portion of the modeling inventory according to these profiles, those species not included in the initial PSD2000v15a VOC inventory—because they are non-reactive or non-VOC—were removed and the profiles were re-normalized. A list of these species is included in Table 8. This list does not represent every species excluded from the VOC modeling inventory, rather, it only represents those found in the EPA speciation profiles.

Table 8. Species Removed from EPA Default Profiles

SAROAD	TCEQ CONTAM CODE	SPECIES
43201	60000	METHANE
43202	56550	ETHANE
43432	52760	METHYL ACETATE
43551	54020	ACETONE
43802	53230	DICHLOROETHANE, 1,1-
43811		TRICHLOROFLUOROMETHANE
43814		1,1,1-TRICHLOROETHANE
43817	55550	PERCHLOROETHYLENE
43821		TRICHLOROTRIFLUOROMETHANE
43823		DICHLORODIFLUOROMETHANE
43839		TETRAFLUOROMETHANE
43840		CHLORODIFLUOROMETHANE
43842		CHLOROPENTAFLUOROETHANE
43843		HEXAFLUOROETHANE
43845		CHLOROTRIFLUOROMETHANE
43950		OCTAMETHYLCYCLOTETRASILOXANE
46707		FLUORENE

An examination of all the resulting profiles and their associated unspiciated mass yields EPA profile 9012, "Petroleum Industry - Average", as the largest recipient of unspiciated VOC emissions with EPA profile 0007, "Natural Gas Turbine", as the next largest. Profile 0007 is also the largest profile by number of assigned points with 2,163 emission points across Texas, while

profile 9012 is ninth largest by assigned emission points. In all, 170 profiles were assigned to the 199.78 tons of unspciated VOC remaining in the modeling inventory. The top ten profiles by associated tonnage are presented in Table 9.

Table 9. Top Ten Profiles by VOC Tonnage

EPA PROFILE	NUMBER OF POINTS	TONS/DAY
9012	699	23.74
0007	2163	18.22
0003	1797	17.85
1012	913	14.38
9024	1571	10.03
1001	816	9.60
9004	1138	9.26
1014	1019	7.63
9001	266	7.58
0079	160	6.89

While it is true that some of the profiles originally existed as single compound profiles, more single species profiles are introduced after removal of non-reactive/non-VOC species. EPA profile 0007 is one such profile. It is transformed from 70% Methane, 30% Formaldehyde to 100% Formaldehyde. Table A-6 illustrates those SCCs assigned to EPA profile 0007. TCEQ Modeling staff believed this profile was inaccurate and inadequate and thus substituted California Air Resources Board (CARB) profile 0719, "Internal Combustion Engine - Reciprocating - Natural Gas", in its place and subjected it to the same non-reactive/non-VOC removal and normalization process as the EPA profiles, as well as a threshold of 0.01% per species in order to limit the profile to its major constituents and to avoid using a mixture of scientific and standard decimal notation in EPS2x inputs. The resulting augmented CARB profile 0719 is included in Table A-7.

Previous modeling inventory speciation analysis along with results from modeling staff ambient air reconciliation projects demonstrated the need for a replacement for EPA profile 1003, "Surface Coating Operations - Coating Application -Solvent-Base Paint". Therefore modeling staff replaced EPA profile 1003 with profile D404, "Coating profile, solvent based medium gloss/high gloss", from "Speciated VOC Emissions for the Dallas/Fort Worth Non-attainment Area", ENVIRON October 1997, and subjected it to the same non-reactive/non-VOC removal and normalization process as the EPA profiles, as well as a threshold of 0.01% per species in order to limit the profile to its major constituents and to avoid using a mixture of scientific and standard decimal notation in EPS2x inputs. The resulting profile is included in Table A-8.

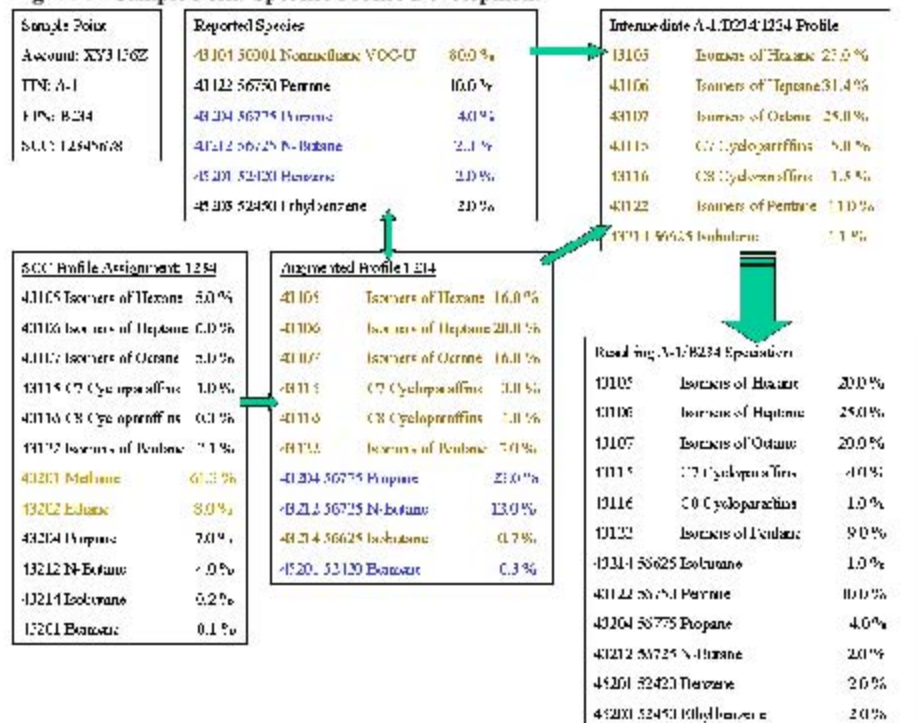
Summing the unspciated portion of the modeling inventory by assigned profile not only allows us to examine which profiles are most frequently used or which profiles have the potential to affect the most emissions, but it also identifies which points are not assigned a profile. This

occurs when an emission point's reported SCC does not match any of those included in EPA's official list of SCCs for one reason or another. Although, for this case study, only one point and 0.0010135 tons/day of unspciated VOC are not assigned a profile something must be done with those emissions. Modeling staff found a discrepancy between the SCC codes allowed into PSDB and those on EPA's official list, and determined that the rogue SCC was one such code allowed in PSDB and not on the EPA SCC list. As such, it was assigned EPA profile 0000, "Overall Average", which was consistent with profile assignments of those SCCs that most closely matched the unidentified code.

Applying Augmented Profiles to Unspciated VOC

The next step is to actually apply the augmented profiles assigned to each point to the unspciated VOC at that point. Recall, the goal of this entire speciation process is to retain all reported/refined speciated data and characterize the remaining portion of unspciated data according to augmented EPA speciation profiles. Therefore, we do not want to split the unspciated VOC into compounds already reported to PSDB or introduced during the refinement process. This introduces the need for a comparison—on a point-by-point basis—of reported compounds and potential, or profile, compounds regardless of amount or percentage. This process relies heavily on the two sources of compounds to agree on compound naming convention/spelling, since the SAROAD to CONTAM assignments are not necessarily unique. This work must be done prior to anything presented in this paper. Once completed we may continue with the speciation process. At this point we have two datasets, one with speciated VOC data and another with unspciated VOC and profile assignments. Any compound already contained in the speciated data for a given point is dropped from its assigned profile and the profile is normalized for that point. The resulting profile may then be applied to that point's unspciated VOC emissions. This is repeated for every point with unspciated data, essentially creating a unique point-specific unspciated VOC characterization profile for every point in the dataset as illustrated in the sample "Intermediate Profile" in Figure 3.

Figure 3. Sample Point-Specific Profile Development



One difficulty in applying this method is encountered when a point's reported VOC compounds (not including the unspciated portion) match those of the augmented profile assigned to at that point, resulting in no intermediate profile to apply to the unspciated VOC at that point. Modeling staff examined which profiles were associated with this phenomenon in order to determine if an alternate speciation profile was necessary. The analysis revealed a wide range of associated profiles, therefore staff assigned these unspciated emissions to EPA profile 0000, "Overall Average".

Creating Point-Specific Profiles for Ambient Air Quality Modeling

After a profile was applied to each point's unspciated VOC the resultant data was be merged with the spciated VOC data and a unique point-specific profile was created for each emission point, as shown in the sample "Resulting Speciation" in Figure 3. This step is simply a normalization of each point's emissions to obtain weight percentages per species per point. A unique profile "name" must also be created to correctly—and easily—identify each point-specific

profile. Modeling staff chose to identify each point-specific profile in the same manner as that presented in "Development of Source Speciation Profiles". Under this convention each profile "name" is a combination of TCEQ and EPA identifiers, namely TCEQ Air Account and EPA Facility and Point numbers. TCEQ's Air Account serves as a surrogate for EPA identifiers FIPS (County) and Plant number, while EPA Facility and Point numbers serve as a substitute for TCEQ FIN and EPN identifiers respectively. The result is a unique 14 character alpha-numeric identifier for each point-specific profile.

Applying Point-Specific Profiles

EPA requires that rule effectiveness (RE) be applied to VOC emission rates for ozone modeling. Reported emission rates assume maximum destruction efficiency for a given piece of control equipment 100% of operation time. Rule effectiveness attempts to account for the fact that controls/rules are not 100% effective due to noncompliance, malfunctions, maintenance, downtime, etc. Essentially, rule effectiveness is an estimate of actual in-use control efficiency over time.

EPA's policy on rule effectiveness can be found in the report "Guidelines for Estimating and Applying Rule Effectiveness for Ozone/CO State Implementation Plan Base Year Inventories" (http://www.epa.gov/ttn/chief/old/eidocs/454r92010_nov1992.pdf). The Emission Inventory Improvement Program Point Sources Committee has also developed a draft document, "Emission Inventories and the Proper Use of Rule Effectiveness" (http://www.epa.gov/ttn/chief/eiip/committee/point_sources/ruleef3.pdf). Further discussions on rule effectiveness can be found in the EPA report, "Rule Effectiveness Guidance: Integration of Inventory, Compliance, and Assessment Applications" (http://www.epa.gov/ttn/chief/old/eidocs/452494001_jan1994.pdf), and the Texas Air Control Board report, "Rule Effectiveness Development", TACB February 1993.

After creation of point-specific profiles, aggregation of emission rates by point, and application of rule effectiveness, each point-specific profile was applied to the resulting RE emission rates, thereby creating a fully speciated ozone modeling inventory. Those points with small emission rates, less than 1.0 lb/day, will have their emission rates aggregated by point and assigned an augmented EPA profile based on its SCC.

Results

Table A-9 presents an elementary analysis of species totals (post RE, post speciation allocation) compared to the results of the speciation methodology employed in the Dec. 2002 HGB SIP (the referenced 2002 report by PES). The species totals for the methodology presented in this report do not include those points with small emission rates, less than 1.0 lb/day, or the mass from those species presented in Table 1.

Overall, species totals are very similar for the eight county HGB NAA when comparing the speciation schemes presented in this report. The largest difference is seen in Isomers of

Pentane which increase almost 5.5 tons/day from the Dec. 2002 methodology. There is a significant decrease in Methane from 4.7 tons/day to 0.0 due to the exclusion of this species from the EPA default speciation profiles. Since the species totals are relatively unchanged, with the exception of a few noted compounds, the geographic distribution of selected species—Ethylene; Propylene; 1,3-Butadiene, and a grouping of Butenes—are compared to that of the previous speciation scheme for the HGB 8 County NAA in Appendix B. The maps show little or no change in the largest emitters of each species, indicating that those points were well speciated when reported to PSDB.

The speciation method presented in this report is currently planned as a sensitivity analysis in HGB Phase II Mid-Course Review modeling and is expected to replace the previous methodology.

Future Work

Obviously, chemical speciation is an important topic for ozone modeling and has received much attention as of late. The process presented in this report is by no means definitive and more work can be done to improve speciation of modeling inventories, most notably by obtaining better speciation information from industry, either voluntarily or in the form of a reporting rule. Also, since the augmented EPA profiles used in this speciation scheme are based on national level data, modeling staff may create profiles based on Texas inventory data similar to the Texas Average SCC profiles described in the PES 2002 report referenced in this document.

Appendix A

Table A-1. Crude Oil Profile

TCEQ CONTAM CODE	SPECIES	PERCENT
56725	N BUTANE	24.50
50001	NONMETHANE VOC-U	21.51
56775	PROPANE	16.90
56752	N-PENTANE	12.77
56575	HEPTANE	6.37
56730	N-HEXANE	6.30
56625	ISOBUTANE	4.42
56674	OCTANE	4.20
52420	BENZENE	1.04
52490	TOLUENE	0.79
56050	CYCLOHEXANE	0.66
55600	PROPYLENE	0.39
52450	ETHYL BENZENE	0.07
52440	CUMENE	0.04
52514	ORTHO-XYLENE	0.03
52416	TRIMETHYL BENZENE, 1,2,4-	0.01

Table A-2. Gasoline Profile

TCEQ CONTAM CODE	SPECIES	PERCENT
56527	NEOPENTANE	23.20
52878	METHYL TERT-BUTYL ETHER	16.21
50001	NONMETHANE VOC-U	10.88
56752	N-PENTANE	6.12
56528	ISOHEXANE	5.21
56725	N BUTANE	5.06
56601	METHYL PENTANE (3)	3.10
56751	PENTANE,224-TRIMETHYL	2.65
52490	TOLUENE	2.55
55475	BUTENE (2-METHYL-2)	2.52
56600	HEXANE	2.50
55526	PENTENE (2)	2.30
55476	BUTENE (2-METHYL-1)	1.50
56200	METHYL CYCLOPENTANE	1.43
56651	METHYLHEXANE, 3-	1.15
56650	ISOHEPTANE	1.15
55525	PENTENE (1)	1.08
51752	BUTENE (CIS-2-)	1.07
55179	TRANS-2-BUTENE	1.06
56625	ISOBUTANE	1.01
56605	TRIMETHYLPENTANE,2,3,4-	0.91
52420	BENZENE	0.71
56575	HEPTANE	0.70
56608	DIMETHYL PENTANE, 2,4-	0.62
56100	CYCLOPENTANE	0.61
56526	DIMETHYL BUTANE (2,2)	0.58
55477	BUTENE (3-METHYL-1)	0.50
56150	METHYL CYCLOHEXANE	0.45
56575	HEPTANE	0.34
56105	CYCLOPENTENE	0.32
55400	ISOBUTYLENE	0.29
52855	METHYLHEPTANE,3-	0.29
55176	BUTENE (1)	0.28
56050	CYCLOHEXANE	0.28
52514	ORTHO-XYLENE	0.25
52450	ETHYL BENZENE	0.23
56674	OCTANE	0.21
52416	TRIMETHYL BENZENE, 1,2,4-	0.15
56775	PROPANE	0.10
55450	ISOPRENE	0.07
52418	TRIMETHYL BENZENE, 1,3,5-	0.06
56615	DIISOBUTYLENE	0.06

56703	NONANE	0.06
55600	PROPYLENE	0.05
58711	ETHYL TOLUENE,0-	0.04
52428	TRIMETHYL BENZENE	0.03
52440	CUMENE	0.02
56681	DODECANE	0.01
52460	NAPHTHALENE	0.01
56683	UNDECANE	0.01
56680	DECANE	0.01

Table A-3. Naphthas Profile

TCEQ CONTAM CODE	SPECIES	PERCENT
56600	HEXANE	26
56750	PENTANE	25
56528	ISOHEXANE	25
56575	HEPTANE	22
56700	ISO PENTANE	2

Table A-4. Stoddard Solvents Profile

TCEQ CONTAM CODE	SPECIES	PERCENT
	ISOMERS OF DECANE	11.28
	ISOMERS OF UNDECANE	7.92
56703	NONANE	6.96
	DIMETHYLOCTANES	6.49
	METHYL PROPYLCYCLOHEXANE	5.99
	TRIMETHYLHEPTANES	5.89
	ETHYLMETHYLCYCLOHEXANE	4.27
	METHYLDECANES	4.19
	METHYLNONANE	4.17
	ISOMERS OF BUTYLBENZENE	3.74
	DIMETHYLNONANES	2.48
	M-XYLENE AND P-XYLENE	2.26
52428	TRIMETHYLBENZENE	2.23
	C10 OLEFINS	2.15
	PROPYLCYCLOHEXANE	2.11
	TRIMETHYLCYCLOHEXANOL	2.01
	BUTYLCYCLOHEXANE	1.68
52514	O-XYLENE	1.56
	METHYLOCTANES	1.49
	ISOMERS OF DODECANE	1.12
	C11 OLEFINS	0.98
	ISOMERS OF PROPYLBENZENE	0.98
	ETHYLDIMETHYLCYCLOHEXANE	0.95
	METHYLUNDECANE	0.91
	PROPENYLCYCLOHEXANE	0.77
	C10 PARAFFINS	0.70
	METHYLDECENE	0.67
	TETRAMETHYLPENTANONE	0.64
	DECALINS	0.60
	ETHYLCYCLOHEXANE	0.59
	DIETHYLMETHYLCYCLOHEXANE	0.55
	DIMETHYLHEPTANES	0.55
	METHYLDECALINS	0.55
	TETRAMETHYLCYCLOPENTANE	0.55
	PROPYLHEPTENES	0.55
52490	TOLUENE	0.50
	ETHYLPROPYLCYCLOHEXANE	0.50
	DIMETHYLCYCLOHEXANE	0.47
	DIETHYLCYCLOHEXANE	0.45
	ISOPROPYLMETHYLCYCLOHEXANE	0.43
	PENTYLCYCLOHEXANE	0.43
	C4 ALKYLPHENOLS	0.38

	ETHYLTOLUENE	0.38
	TRIMETHYLOCTANES	0.35
	TRIMETHYLHEXENE	0.35
52450	ETHYLBENZENE	0.35
52460	NAPHTHALENE	0.35
	ETHYLHEXANE	0.34
52440	CUMENE (ISOPROPYL BENZENE)	0.34
	ISOMERS OF C11H20	0.32
	T-BUTYLBENZENE	0.31
	DIMETHYLDECANE	0.29
52430	CHLOROBENZENE	0.26
	DIMETHYLUNDECANE	0.24
	ETHYLOCTANE	0.21
	NONADIENE	0.17
	C5 ALKYLPHENOLS	0.17
	PENTYLIDENECYCLOHEXANE	0.17
	OCTAHYDROINDENES	0.17
	TRIMETHYLCYCLOHEXANES	0.17
	DIMETHYLBENZYLALCOHOL	0.15
	TRIMETHYLCYCLOPENTANONE	0.15
	C12 OLEFINS	0.12
	DIMETHYLOCTYNE	0.10
	OCTANOL	0.10
	C10H16	0.10
	ETHYLMETHYLHEXANE	0.10
	OCTAHYDROPENTALENE	0.10
	C5 ALKYL BENZENES	0.10
	ISOMERS OF C10H18	0.07
	BENZOTHIAZOLE	0.05
	TETRAMETHYLTHIOUREA	0.05
	DIMETHYLBUTYLCYCLOHEXANE	0.05
	ISOMERS OF TRIDECANE	0.05
	METHYLHEPTANE	0.02
	TRIMETHYLDECANE	0.02
56150	METHYLCYCLOHEXANE	0.02
	C9 OLEFINS	0.02

Table A-5. Refinery Profile

TCEQ CONTAM CODE	SPECIES	PERCENT
50001	NONMETHANE VOC-U	32.27
56725	N BUTANE	24.61
56625	ISOBUTANE	10.31
56752	N-PENTANE	7.12
56775	PROPANE	3.98
56730	N-HEXANE	3.11
52490	TOLUENE	2.03
52420	BENZENE	1.72
56601	METHYL PENTANE (3)	1.71
55526	PENTENE (2)	1.45
56700	ISO PENTANE	1.44
56200	METHYL CYCLOPENTANE	1.44
55600	PROPYLENE	1.40
55179	TRANS-2-BUTENE	0.81
56575	HEPTANE	0.78
56526	DIMETHYL BUTANE (2,2)	0.75
56651	METHYLHEXANE, 3-	0.64
55177	CIS-2-BUTENE	0.63
55525	PENTENE (1)	0.61
56100	CYCLOPENTANE	0.48
56608	DIMETHYL PENTANE, 2,4-	0.40
52514	ORTHO-XYLENE	0.36
52416	TRIMETHYL BENZENE, 1,2,4-	0.31
56050	CYCLOHEXANE	0.29
56528	ISOHEXANE	0.25
52450	ETHYL BENZENE	0.23
56150	METHYL CYCLOHEXANE	0.20
56610	TRIMETHYL PENTANE, 2,2,4-	0.20
52440	CUMENE	0.16
52855	METHYLHEPTANE,3-	0.14
56674	OCTANE	0.07
56605	TRIMETHYL PENTANE,2,3,4-	0.07
52418	TRIMETHYL BENZENE, 1,3,5-	0.02
56703	NONANE	0.01

Table A-6. SCCs Associated with EPA Profile 0007.

SCC	MAJOR CATEGORY	MAJOR INDUSTRY	SPECIFIC INDUSTRY/EMISSION SOURCE CATEGORY/MAJOR PRODUCT, RAW MATERIAL, OR FUEL	PROCESS
20100201	Internal Combustion Engines	Electric Generation	Natural Gas	Turbine
20100205	Internal Combustion Engines	Electric Generation	Natural Gas	Reciprocating: Crankcase Blowby
20100206	Internal Combustion Engines	Electric Generation	Natural Gas	Reciprocating: Evaporative Losses (Fuel Delivery System)
20100207	Internal Combustion Engines	Electric Generation	Natural Gas	Reciprocating: Exhaust
20100208	Internal Combustion Engines	Electric Generation	Natural Gas	Turbine: Evaporative Losses (Fuel Delivery System)
20100209	Internal Combustion Engines	Electric Generation	Natural Gas	Turbine: Exhaust
20100801	Internal Combustion Engines	Electric Generation	Landfill Gas	Turbine
20100805	Internal Combustion Engines	Electric Generation	Landfill Gas	Reciprocating: Crankcase Blowby
20100806	Internal Combustion Engines	Electric Generation	Landfill Gas	Reciprocating: Evaporative Losses (Fuel Delivery System)
20100807	Internal Combustion Engines	Electric Generation	Landfill Gas	Reciprocating: Exhaust
20100808	Internal Combustion Engines	Electric Generation	Landfill Gas	Turbine: Evaporative Losses (Fuel Delivery System)
20100809	Internal Combustion Engines	Electric Generation	Landfill Gas	Turbine: Exhaust
20200201	Internal Combustion Engines	Industrial	Natural Gas	Turbine
20200203	Internal Combustion Engines	Industrial	Natural Gas	Turbine: Cogeneration
20200205	Internal Combustion Engines	Industrial	Natural Gas	Reciprocating: Crankcase Blowby
20200206	Internal Combustion Engines	Industrial	Natural Gas	Reciprocating: Evaporative Losses (Fuel Delivery System)
20200207	Internal Combustion Engines	Industrial	Natural Gas	Reciprocating: Exhaust
20200208	Internal Combustion Engines	Industrial	Natural Gas	Turbine: Evaporative Losses (Fuel Delivery System)
20200209	Internal Combustion Engines	Industrial	Natural Gas	Turbine: Exhaust
20200252	Internal Combustion Engines	Industrial	Natural Gas	2-cycle Lean Burn
20200253	Internal Combustion Engines	Industrial	Natural Gas	4-cycle Rich Burn

20200254	Internal Combustion Engines	Industrial	Natural Gas	4-cycle Lean Burn
20200255	Internal Combustion Engines	Industrial	Natural Gas	2-cycle Clean Burn
20200256	Internal Combustion Engines	Industrial	Natural Gas	4-cycle Clean Burn
20300203	Internal Combustion Engines	Commercial/Institutional	Natural Gas	Turbine: Cogeneration
20300204	Internal Combustion Engines	Commercial/Institutional	Natural Gas	Cogeneration
20300205	Internal Combustion Engines	Commercial/Institutional	Natural Gas	Reciprocating: Crankcase Blowby
20300206	Internal Combustion Engines	Commercial/Institutional	Natural Gas	Reciprocating: Evaporative Losses (Fuel Delivery System)
20300207	Internal Combustion Engines	Commercial/Institutional	Natural Gas	Reciprocating: Exhaust
20300208	Internal Combustion Engines	Commercial/Institutional	Natural Gas	Turbine: Evaporative Losses (Fuel Delivery System)
20300209	Internal Combustion Engines	Commercial/Institutional	Natural Gas	Turbine: Exhaust
20300701	Internal Combustion Engines	Commercial/Institutional	Digester Gas	Turbine
20300702	Internal Combustion Engines	Commercial/Institutional	Digester Gas	Reciprocating: POTW Digester Gas
20300705	Internal Combustion Engines	Commercial/Institutional	Digester Gas	Reciprocating: Crankcase Blowby
20300706	Internal Combustion Engines	Commercial/Institutional	Digester Gas	Reciprocating: Evaporative Losses (Fuel Storage and Delivery System)
20300707	Internal Combustion Engines	Commercial/Institutional	Digester Gas	Reciprocating: Exhaust
20300708	Internal Combustion Engines	Commercial/Institutional	Digester Gas	Turbine: Evaporative Losses (Fuel Storage and Delivery System)
20300709	Internal Combustion Engines	Commercial/Institutional	Digester Gas	Turbine: Exhaust
20300801	Internal Combustion Engines	Commercial/Institutional	Landfill Gas	Turbine
20300802	Internal Combustion Engines	Commercial/Institutional	Landfill Gas	Reciprocating
20300805	Internal Combustion Engines	Commercial/Institutional	Landfill Gas	Reciprocating: Crankcase Blowby
20300806	Internal Combustion Engines	Commercial/Institutional	Landfill Gas	Reciprocating: Evaporative Losses (Fuel Storage and Delivery System)
20300807	Internal Combustion Engines	Commercial/Institutional	Landfill Gas	Reciprocating: Exhaust
20300808	Internal Combustion Engines	Commercial/Institutional	Landfill Gas	Turbine: Evaporative Losses (Fuel Storage and Delivery System)
20300809	Internal Combustion Engines	Commercial/Institutional	Landfill Gas	Turbine: Exhaust
20300901	Internal Combustion Engines	Commercial/Institutional	Kerosene/Naphtha (Jet Fuel)	Turbine: JP-4

20300908	Internal Combustion Engines	Commercial/Institutional	Kerosene/Naphtha (Jet Fuel)	Turbine: Evaporative Losses (Fuel Storage and Delivery System)
20300909	Internal Combustion Engines	Commercial/Institutional	Kerosene/Naphtha (Jet Fuel)	Turbine: Exhaust
20400301	Internal Combustion Engines	Engine Testing	Turbine	Natural Gas
20400303	Internal Combustion Engines	Engine Testing	Turbine	Distillate Oil
20400304	Internal Combustion Engines	Engine Testing	Turbine	Landfill Gas
20400305	Internal Combustion Engines	Engine Testing	Turbine	Kerosene/Naphtha
20400399	Internal Combustion Engines	Engine Testing	Turbine	Other Not Classified

Table A-7. Augmented CARB Profile 0719 substituted for EPA profile 0007

SAROAD	TCEQ CONTAM CODE	SPECIES	PERCENT
43204	56775	PROPANE	32.26
43205	55600	PROPYLENE	18.74
43212	56725	N BUTANE	11.09
43502	51680	FORMALDEHYDE	8.98
43203	55300	ETHYLENE	6.98
43214	56625	ISOBUTANE	4.77
43206	51820	ACETYLENE	3.55
43120		ISOMERS OF BUTENE	2.88
43122		ISOMERS OF PENTANE	1.44
43216	55179	TRANS-2-BUTENE	1.44
43220	56752	N-PENTANE	1.44
45201	52420	BENZENE	1.22
43106		ISOMERS OF HEPTANE	0.44
43262	56200	METHYLCYCLOPENTANE	0.44
45202	52490	TOLUENE	0.44
43503	51620	ACETALDEHYDE	0.33
43105		ISOMERS OF HEXANE	0.22
43107		ISOMERS OF OCTANE	0.22
43109		ISOMERS OF DECANE	0.22
43215	55400	ISOBUTYLENE	0.22
43217	55177	CIS-2-BUTENE	0.22
43230	56601	METHYL PENTANE (3)	0.22
43231	56730	N-HEXANE	0.22
43232	56575	HEPTANE	0.22
43233	56674	OCTANE	0.22
43242	56100	CYCLOPENTANE	0.22
43261	56150	METHYLCYCLOHEXANE	0.22
43298	52855	METHYLHEPTANE,3-	0.22
43510	51660	BUTYRALDEHYDE	0.22
45102	52510	XYLENE-U	0.22
45207	52418	TRIMETHYL BENZENE, 1,3,5-	0.22
98040		2-METHYL-1-PENTENE	0.22

Table A-8 Augmented D40 profiles substituted to EP profile 003

SAROAD	TCEQ CONTAM CODE	SPECIES	PERCENT
43238	56680	DECANE	9.65
43241	56683	UNDECANE	7.99
90073		METHYLISOPROPYLCYCLOHEXANE	6.06
90076		DIMETHYLNONANES	5.10
90048		METHYLDECANES	4.87
45238		ETHYLTOLUENE	4.08
45208	52416	TRIMETHYLBENZENE, 1,2,4-	3.77
90047		METHYLNONANE	3.35
90049		METHYLUNDECANE	2.62
45243		ETHYLDIMETHYLBENZENE	2.60
43235	56703	NONANE	2.58
90055		PENTYLCYCLOHEXANE	2.45
90074		DIMETHYLDECANE	2.20
45205	52512	META-XYLENE	2.05
43255	56681	DODECANE	1.98
43109		ISOMERS OF DECANE	1.97
90120		PROPYLCYCLOHEXANE	1.94
99909		2,6-DIMETHYLOCTANE	1.92
90090		ETHYLPROPYLCYCLOHEXANE	1.89
98060		TRIMETHYLCYCLOHEXANES	1.81
90101		BUTYLCYCLOHEXANE	1.71
90083		ETHYLMETHYLCYCLOHEXANE	1.67
99918		2-METHYLDECANE	1.55
45225	52417	TRIMETHYLBENZENE, 1,2,3-	1.43
45207	52418	TRIMETHYLBENZENE, 1,3,5-	1.43
90089		ETHYLDIMETHYLCYCLOHEXANE	1.37
90070		DIMETHYLOCTANES	1.31
46753		DECALINS	1.31
45204	52514	ORTHO-XYLENE	1.29
46748		METHYLDECALINS	1.20
90128		ISOPROPYLCYCLOHEXANE	1.08
90077		ETHYLOCTANE	0.97
99908		2,3-DIMETHYLOCTANE	0.96
45203	52450	ETHYLBENZENE	0.81
45206	52516	PARA-XYLENE	0.76
45244		TETRAMETHYLBENZENE	0.75
99110		C10 COMPOUNDS (DIESEL EXHAUST)	0.74
99111		C11 COMPOUNDS (DIESEL EXHAUST)	0.73
46747		METHYLINDANS	0.65
99916		1-METHYL-3-N-PROPYLBENZE	0.61
90121		METHYLETHYLHEPTANE	0.61
99917		1-METHYL-3-ISOPROPYLBENZENE	0.58

99112		C12 COMPOUNDS (DIESEL EXHAUST)	0.52
99913		1-METHYL-2-ETHYLBENZENE	0.42
90015		3-METHYLOCTANE	0.37
90016		4-METHYLOCTANE	0.36
46701	52460	NAPHTHALENE	0.35
98149		2,4-DIMETHYLOCTANE	0.33
45106	52433	DIETHYL BENZENE	0.29
45209		N-PROPYLBENZENE	0.28
43233	56674	OCTANE	0.27
90071		DIMETHYLUNDECANE	0.25
98151		3,4-DIMETHYLOCTANE	0.25
98044		INDANE	0.21
90067		DIMETHYLHEXANES	0.21
45235		BUTYLBENZENE	0.18
99109		C9 COMPOUNDS (DIESEL EXHAUST)	0.17
90008		2-METHYLOCTANE	0.14
90085		ETHYLMETHYLOCTANE	0.14
98145		2,3-DIMETHYLHEPTANE	0.14
98061		ETHYLCYCLOHEXANE	0.14
98059		DIMETHYLCYCLOHEXANE	0.14
43296		2-METHYLHEPTANE	0.09
45202	52490	TOLUENE	0.07
43253		3-METHYLHEPTANE	0.06
43297		4-METHYLHEPTANE	0.04
43552	54065	METHYL ETHYL KETONE	0.03
43261	56150	METHYLCYCLOHEXANE	0.03
43258		N-TRIDECANE	0.02
43247	56608	DIMETHYL PENTANE, 2,4-	0.02
98139		2,3-DIMETHYLHEXANE	0.02
98143		2,5-DIMETHYLHEPTANE	0.02
99113		C13 COMPOUNDS (DIESEL EXHAUST)	0.02

Table-9. Comparison of Species Totals for Each Speciation Methodology

SPECIES	NEW SPECIATION METHODOLOGY TONS/DAY	DEC. 2002 METHODOLOGY TONS/DAY	ABSOLUTE DIFFERENCE
ISOMERS OF PENTANE	7.607127	2.168255	5.438872
METHANE	0.000000	4.700323	4.700323
METHANOL	8.406696	10.333420	1.926724
ISOMERS OF HEXANE	2.442412	0.700996	1.741416
FORMALDEHYDE	4.637015	3.025500	1.611515
N BUTANE	14.541068	13.254369	1.286698
PENTANE	5.821762	7.076858	1.255095
HEXANE	7.938597	8.923362	0.984765
ISOMERS OF HEPTANE	1.176564	0.225906	0.950658
NEOPENTANE	3.107383	4.045091	0.937708
PROPANE	14.432000	15.336817	0.904817
ETHANE	0.000000	0.892814	0.892814
CARBONYL SULFIDE	0.161269	1.051342	0.890073
TOLUENE	3.999675	4.878970	0.879296
BENZENE	6.284157	5.510771	0.773386
HEPTANE	3.513429	4.271227	0.757797
C7 CYCLOPARAFFINS	0.917611	0.175717	0.741894
METHYL TERT-BUTYL ETHER	5.007726	5.722530	0.714804
ISOHEXANE	3.289491	3.974688	0.685197
ISO PENTANE	2.508284	3.132707	0.624423
ISOMERS OF OCTANE	0.668304	0.070682	0.597622
ACETYLENE	1.325099	1.818465	0.493366
DECANE	0.951886	0.482210	0.469676
N-PENTANE	4.936645	4.506551	0.430094
N-TRIDECANE	0.703969	0.332853	0.371116
UNDECANE	0.765649	0.396954	0.368696
DIMETHYL ETHER	0.899935	0.554385	0.345550
ISOPROPANOL	1.305599	1.625473	0.319873
ISOBUTANE	8.584464	8.868379	0.283914
METHYL ETHYL KETONE	1.558531	1.823942	0.265410
GLYCOL ETHERS(CELLOSOL)	0.279910	0.023176	0.256734
ISOMERS OF BUTENE	0.423752	0.172661	0.251090
ETHANOL	1.425857	1.671940	0.246083
N-TETRADECANE	0.465486	0.219896	0.245590
DIMETHYL BUTANE (2,2)	0.517908	0.759140	0.241233
DIETHYL ETHER	1.059773	1.300621	0.240848
P-DICHLOROBENZENE	0.455822	0.219402	0.236419
MONOETHANOLAMINE	0.000000	0.234591	0.234591
N-HEXANE	1.109107	1.324498	0.215391
CYCLOHEXANE	1.192336	1.403082	0.210746

STYRENE	2.181965	1.976610	0.205355
BUTYL ACETATE	0.155260	0.338202	0.182942
BUTYRALDEHYDE	0.403601	0.586038	0.182437
ETHYLENE DICHLORIDE	0.528925	0.347545	0.181380
XYLENE-U	2.154636	2.335120	0.180484
ACROLEIN	0.238470	0.070415	0.168055
CHLORO BENZENE	0.949580	0.784291	0.165289
C8 CYCLOPARAFFINS	0.189995	0.027448	0.162547
TRIMETHYL BENZENE, 1,2,4-	0.283558	0.124872	0.158685
ACETONE	0.000000	0.155552	0.155552
N-PENTADECANE	0.289950	0.136690	0.153260
TRIMETHYL BENZENE	0.332222	0.178975	0.153247
BUTYL CELLOSOLVE	0.239675	0.390964	0.151290
DODECANE	0.822345	0.672730	0.149615
METHYL ACETYLENE	0.162944	0.016776	0.146168
ETHYL CHLORIDE	0.284451	0.147640	0.136812
BUTADIENE	1.942149	2.071629	0.129480
DIAMINO HEXANE (1,6)	0.165521	0.045339	0.120182
CHLOROPRENE	0.149900	0.030800	0.119100
BUTENE (1)	1.770920	1.652026	0.118894
2,4-DIMETHYLHEXANE	0.002276	0.119830	0.117553
SEC BUTYL ALCOHOL	0.175778	0.060591	0.115187
N-BUTYL ALCOHOL	1.430306	1.326046	0.104260
ACRYLONITRILE	0.620354	0.517579	0.102775
TRIFLUOROMETHANE	0.134009	0.036537	0.097472
ETHYLHEXALDEHYDE (DOT)	0.229612	0.324473	0.094860
VINYL CHLORIDE	0.456464	0.362256	0.094208
ISO-BUTENE	0.649815	0.742751	0.092937
METHYL BUTANAL, 2-	0.151727	0.242571	0.090844
UNIDENTIFIED	0.143876	0.053247	0.090629
PHTHALIC ANHYDRIDE	0.152733	0.065747	0.086986
VINYL ACETATE	1.625364	1.710919	0.085555
BUTENE (2-METHYL-2)	0.415689	0.496964	0.081274
METHYLISOPROPYLCYCLOHEXANE	0.080952	0.000000	0.080952
ORTHO-XYLENE	0.457818	0.538493	0.080675
METHYL PENTANE (3)	0.745802	0.825442	0.079640
ETHYL ACETATE	0.035072	0.113278	0.078206
TRANS-2-PENTENE	0.126027	0.047940	0.078087
HEXENE	0.684817	0.759160	0.074343
PERCHLOROETHYLENE	0.000000	0.073229	0.073229
METHYLCYCLOHEXANE	0.175226	0.248440	0.073214
ISOPHORONE	0.072338	0.000000	0.072338
METHYL FORMATE	0.213608	0.145256	0.068351
METHYLCYCLOPENTANE	0.532521	0.598688	0.066167
CUMENE	0.538693	0.604751	0.066058
ISO OCTANE	0.202973	0.137250	0.065723
DIMETHYLCYCLOHEXANE	0.011683	0.075658	0.063975

ISOHEPTANE	0.327652	0.391190	0.063538
PENTENE (1)	0.816376	0.754102	0.062274
ISOBUTANOL	0.339676	0.400653	0.060977
N-PROPANOL	0.211219	0.271692	0.060473
TRANS-2-BUTENE	0.539744	0.479300	0.060444
2-METHYL-3-HEXANONE	0.003176	0.063022	0.059846
PENTADIENE	0.322031	0.380988	0.058957
ETHYL ACRYLATE	0.128053	0.070338	0.057715
OCTANE	1.142294	1.198827	0.056532
MINERAL SPIRITS	0.081573	0.028023	0.053549
PROPIONALDEHYDE	0.180285	0.127272	0.053013
DIMETHYLNONANES	0.079114	0.026109	0.053005
METHYLHEXANE, 3-	0.237067	0.289396	0.052329
TRIMETHYLBENZENE	0.017634	0.069831	0.052196
ISOBUTYRALDEHYDE	0.071692	0.122554	0.050862
ETHYL TOLUENE	0.079882	0.029204	0.050678
ISOMERS OF DECANE	0.206572	0.156022	0.050551
ISOPRENE	0.475158	0.523985	0.048827
CIS-2-BUTENE	0.293685	0.245211	0.048475
ETHYL BENZENE	1.265158	1.313604	0.048447
METHYLDECANES	0.092638	0.045533	0.047104
META-XYLENE	0.585212	0.538247	0.046965
NAPHTHALENE	0.209052	0.163742	0.045310
PROPYLENE	11.858210	11.903516	0.045306
BUTENE (CIS-2-)	0.188253	0.232448	0.044195
ETHYLENE OXIDE	0.194782	0.150777	0.044006
1,1,1-TRICHLOROETHANE	0.000000	0.042368	0.042368
TETRAETHYLENE GLYCOL	0.006163	0.047628	0.041465
DIETHYL BENZENE	0.057482	0.016227	0.041255
CIS-2-PENTENE	0.062640	0.023240	0.039400
ISOBUTYLENE	0.812934	0.852277	0.039343
ETHYL HEXANOL (2)	0.141122	0.180310	0.039188
BUTENE	1.225642	1.264380	0.038738
BUTOXYETHANOL (2)	0.534450	0.496469	0.037980
ISOMERS OF PENTENE	0.044711	0.006798	0.037913
TRICHLOROFLUOROMETHANE	0.000000	0.037081	0.037081
HEXAFLUOROETHANE	0.000000	0.036586	0.036586
ETHYLDIMETHYLBENZENE	0.045018	0.008665	0.036353
METHYL ACETATE	0.000000	0.035776	0.035776
DICHLOROMETHANE	0.000000	0.035605	0.035605
TRIMETHYLBENZENE, 1,3,5-	0.088394	0.052876	0.035518
TRIMETHYLPENTANE, 2,3,4-	0.229862	0.263964	0.034102
TRIMETHYLBENZENE, 1,2,3-	0.035664	0.002582	0.033082
HEXANOL	0.138921	0.171273	0.032353
DICHLORODIFLUOROMETHANE	0.000000	0.032152	0.032152
CARBON TETRACHLORIDE	0.229529	0.197962	0.031567
ACETALDEHYDE	0.645383	0.614616	0.030767

PROPYLENE OXIDE	0.415769	0.446304	0.030535
ISOPROPYL ETHER	0.161893	0.192201	0.030307
OCTENE	0.046146	0.076419	0.030272
ACETIC ACID	0.782722	0.752660	0.030062
METHYLNONANE	0.076691	0.046634	0.030057
M-XYLENE AND P-XYLE	0.147127	0.117652	0.029475
PROPYL KETONE DI-N	0.044060	0.073308	0.029248
TRIMETHYL PENTANE, 2,2,4-	0.065082	0.036049	0.029033
ISOMERS OF ETHYL TOLUENE	0.032545	0.004014	0.028531
METHYLUNDECANE	0.037678	0.009388	0.028289
PARA-XYLENE	0.444895	0.472598	0.027703
PENTYLCYCLOHEXANE	0.031320	0.004168	0.027152
HEXAMETHYL DIAMINE	0.001011	0.026890	0.025879
ETHYLENE GLYCOL	0.233799	0.259503	0.025704
2,6-DIMETHYLOCTANE	0.025695	0.000000	0.025695
HEPTENE	0.078981	0.053477	0.025504
DIMETHYLDECANE	0.027885	0.003026	0.024859
DIETHYLENE GLYCOL	0.112100	0.087629	0.024471
METHYL CHLORIDE	0.166457	0.143218	0.023238
BUTENE (2-METHYL-1)	0.333827	0.356509	0.022682
BUTYL ACRYLATE	0.150741	0.128342	0.022399
FORMIC ACID	0.040956	0.018944	0.022013
ETHYLCYCLOHEXANE	0.009844	0.031833	0.021990
CREOSOL(ALL ISOMERS)	0.107098	0.128942	0.021844
ACETOPHENONE	0.053399	0.075163	0.021764
METHYL-2-PENTANOL,4-	0.072020	0.092857	0.020837
2-METHYLDECANE	0.020798	0.000091	0.020707
ETHYLPROPYLCYCLOHEXANE	0.025672	0.005057	0.020615
TOLUENE DIISOCYANATE-TD	0.035200	0.014753	0.020446
FURFURAL	0.095172	0.115386	0.020214
ANILINE-U	0.041949	0.021846	0.020104
C5 ESTER	0.000966	0.021056	0.020090
CIS-2-HEXENE	0.031143	0.011787	0.019357
TRICHLOROETHYLENE	0.040001	0.020936	0.019065
ISOPROPYL ACETATE	0.103930	0.122614	0.018684
ISOMERS OF NONANE	0.112997	0.094609	0.018388
DIMETHYL PENTANE, 2,4-	0.168553	0.186860	0.018307
HEPTANONE (2)	0.060450	0.042182	0.018268
CARBITOL CELLOSOLVE	0.027186	0.009023	0.018162
ISOBUTYL ACETATE	0.017881	0.035978	0.018097
TRICHLOROTRIFLUOROETHANE	0.000000	0.018043	0.018043
PROPYLCYCLOHEXANE	0.039869	0.022001	0.017868
ETHYLENE	12.406948	12.424674	0.017726
METHYL METHACRYLATE	0.269110	0.286731	0.017621
ISOBUTYRIC ACID	0.000000	0.017470	0.017470
ACETONITRILE	0.174038	0.191323	0.017285
C9 OLEFINS	0.019906	0.002796	0.017110

BUTYL CARBITOL	0.023753	0.006691	0.017061
ISOBUTYLISOBUTYRATE	0.022443	0.005609	0.016834
METHYL CARBITOL	0.022443	0.005670	0.016773
METHYL CELLOSOLVE	0.022443	0.005670	0.016773
ISOBUTYLACRYLATE	0.022148	0.005428	0.016720
DIPROPYLENE GLYCOL	0.031840	0.015219	0.016621
ISOMERS OF UNDECANE	0.071836	0.088369	0.016533
PINENE, ALPHA-	0.149917	0.166384	0.016467
BUTYLCYCLOHEXANE	0.034011	0.017731	0.016279
METHYL ISOBUTYL KETONE	0.515399	0.531587	0.016187
MALEIC ANHYDRIDE	0.055882	0.039728	0.016153
ETHYLENEAMINES	0.024726	0.008595	0.016131
ACETIC ANHYDRIDE	0.050157	0.034102	0.016055
BENZYLCHLORIDE	0.043152	0.027114	0.016038
METHYLALLEN	0.029567	0.013600	0.015967
PIPERYLENE	0.029567	0.013600	0.015967
SUBSTITUTED C9 ESTER (C12)	0.037031	0.052964	0.015933
ETHYLENE DIBROMIDE	0.049262	0.033428	0.015834
ETHANOLAMINE	0.046300	0.030710	0.015589
NITROBENZENE	0.022551	0.006978	0.015574
PROPYLENE GLYCOL	0.086608	0.102177	0.015569
ISOMERS OF PENTADECANE	0.024156	0.008661	0.015495
METHYLSTYRENE	0.024162	0.008849	0.015313
DIISOPROPYLBENZENE	0.022704	0.008028	0.014676
TRANS-2-HEXENE	0.024005	0.009341	0.014664
ISOPROPYLCYCLOHEXANE	0.014818	0.000291	0.014527
METHYLAL	0.073573	0.059112	0.014461
ISOMERS OF DODECANE	0.040608	0.026174	0.014434
CHLORODIFLUOROMETHANE	0.000000	0.014383	0.014383
C7-C16	0.039755	0.025510	0.014244
TOTAL C2-C5 ALDEHYDES	0.047312	0.033488	0.013823
DECALINS	0.019883	0.006129	0.013754
ETHYLDIMETHYLCYCLOHEXANE	0.023468	0.009718	0.013750
TRICHLOROETHANE (1,1,2)	0.048675	0.034999	0.013675
METHYL-2-PYRROLIDINE-P,N-	0.055591	0.042142	0.013448
METHYLPROPYLCYCLOHEXANE	0.049381	0.062816	0.013435
PENTANE,224-TRIMETHYL	0.480727	0.494126	0.013399
C9 CYCLOPARAFFINS	0.024512	0.011138	0.013374
NONANE	0.433712	0.420608	0.013104
2,3-DIMETHYLOCTANE	0.012870	0.000000	0.012870
METHYLDECALINS	0.018236	0.005493	0.012743
NONENE	0.041732	0.054140	0.012407
DIISOBUTYLENE	0.000000	0.012281	0.012281
CYCLODODECANE	0.000000	0.012175	0.012175
BENZOIC ACID	0.015021	0.002894	0.012128
AMYL ALCOHOL	0.056826	0.068880	0.012054
NAPHTHA	0.035351	0.047396	0.012045

BUTENE (3-METHYL-1)	0.097866	0.109894	0.012028
DIMETHYLAMINOETHANOL	0.083086	0.095014	0.011927
TRIMETHYLHEPTANES	0.051276	0.063199	0.011923
4-METHYL-TRANS-2-PENTENE	0.019202	0.007303	0.011899
POLYETHYLENE GLYCOL	0.011728	0.000000	0.011728
PENTENE (2)	0.440260	0.451907	0.011647
DI(2-ETHYLHEXYL) PHTHALATE (DE	0.011646	0.000000	0.011646
DIMETHYLHEPTANES	0.005979	0.017511	0.011532
2-METHYL-1-PENTENE	0.011619	0.000093	0.011526
CRESOL	0.024305	0.012945	0.011360
TETRAMETHYLBENZENE	0.018490	0.007184	0.011306
ETHYLOCTANE	0.012736	0.001765	0.010970
ETHYLTOLUENE,0-	0.022509	0.011756	0.010753
ETHYLMETHYLCYCLOHEXANE	0.057867	0.047161	0.010706
DIMETHYLDISULFIDE	0.019246	0.008649	0.010597
CYCLOPENTENE	0.208740	0.219297	0.010556
METHYLENE BROMIDE	0.018286	0.007849	0.010437
DIETHANOLAMINE	0.055484	0.065900	0.010416
METHYL PROPYL KETONE	0.002038	0.012153	0.010115
BUTYL ETHER-	0.006200	0.016308	0.010108
METHYL MERCAPTAN	0.067798	0.057837	0.009961
TETRAHYDROFURAN	0.072394	0.062434	0.009960
C10 COMPOUNDS (DIESEL EXHAUST)	0.009879	0.000000	0.009879
CYCLOPENTADIENE	0.105494	0.115332	0.009838
C11 COMPOUNDS (DIESEL EXHAUST)	0.009713	0.000000	0.009713
DIETHYLAMINOETHANOL	0.009000	0.018704	0.009704
METHYL ACRYLATE	0.055427	0.045834	0.009593
METHYLINDANS	0.013030	0.003580	0.009449
PROPYL ACETATE	0.049924	0.040899	0.009025
CYCLOHEXANONE	0.097217	0.088259	0.008958
DECYL ALCOHOL	0.037000	0.045884	0.008884
DIMETHOXYMETHANE	0.000000	0.008682	0.008682
TRIMETHYLFLUOROSILANE	0.031219	0.022647	0.008572
METHYLHEPTANE,3-	0.070165	0.061681	0.008484
1-METHYL-3-N-PROPYLBENZE	0.008187	0.000000	0.008187
METHYLETHYLHEPTANE	0.008157	0.000000	0.008157
MALEIC ACID	0.049654	0.057737	0.008083
1-METHYL-3-ISOPROPYLBENZ	0.007749	0.000000	0.007749
ACRYLIC ACID	0.153138	0.145402	0.007735
PROPYL PROPIONATE	0.013124	0.020753	0.007629
PROPASOL	0.077135	0.084572	0.007437
DICHLOROBENZENES	0.008872	0.001521	0.007351
PYRIDINE	0.035517	0.028277	0.007240
DIMETHYLPHTHALATE	0.008283	0.001064	0.007219
BISPHENOL-A	0.096766	0.103965	0.007199
DIMETHYL SULFIDE	0.021258	0.014131	0.007126
C12 COMPOUNDS (DIESEL EXHAUST)	0.006994	0.000000	0.006994

PENTADIENE (E-1,3)	0.062528	0.069389	0.006862
METHYL ISOAMYL KETONE	0.055464	0.062017	0.006554
METHYLBUTANOL,2-	0.026197	0.032742	0.006545
2-METHYLPROPANE	0.007348	0.001116	0.006233
TERPENE	0.652060	0.658291	0.006231
ISOMERS OF PROPYLBENZENE	0.026383	0.020166	0.006217
VINYL CYCLOHEXENE	0.017968	0.024168	0.006200
PROPYLENE DICHLORIDE	0.033322	0.027123	0.006199
PHENOL	0.631199	0.625030	0.006169
PINENE, BETA-	0.085275	0.079137	0.006138
LACTOL SPIRITS	0.012415	0.006312	0.006103
CRESOL, P	0.006075	0.000000	0.006075
2,5-DIMETHYLHEXANE	0.009913	0.003901	0.006012
N-PROPYLBENZENE	0.012483	0.006543	0.005940
3,5,5-TRIMETHYLHEXANE	0.009740	0.003914	0.005826
METHOXY-2-ACETOXYPROPANE, 1-	0.037743	0.043450	0.005707
TRIMETHYLCYCLOHEXANES	0.024709	0.030382	0.005673
1-METHYL-2-ETHYLBENZENE	0.005609	0.000018	0.005591
DODECENE	0.086566	0.080981	0.005584
EPICHLOROHYDRIN	0.166230	0.160715	0.005515
DIMETHYLAMINE	0.025489	0.019983	0.005507
TERT BUTYL ALCOHOL	0.233528	0.238993	0.005465
DIMETHYL FORMAMIDE	0.115076	0.120539	0.005463
CELLOSOLVE ACETATE	0.016631	0.011368	0.005264
M-XYLENE AND P-XYLENE	0.017872	0.023104	0.005233
C8 PARAFFIN	0.032509	0.027298	0.005211
CELLOSOLVE SOLVENT	0.012415	0.007291	0.005124
TERTIARY BUTYL AMINE	0.030414	0.035529	0.005115
GLYCOLONITRILE	0.063312	0.068343	0.005031
CARBON DISULFIDE	0.089785	0.084791	0.004994
3-METHYLOCTANE	0.004970	0.000000	0.004970
CYCLOHEXANOL	0.056141	0.051215	0.004925
DIISOBUTYL KETONE	0.013076	0.008170	0.004906
4-METHYLOCTANE	0.004773	0.000000	0.004773
ETHYLENE GLYCOL M-ETHYL	0.000000	0.004736	0.004736
TRIETHYLENE GLYCOL	0.007593	0.002926	0.004667
ISOMERS OF DIETHYLB	0.005726	0.001111	0.004615
TRIMETHYLCYCLOHEXANOL	0.015965	0.020561	0.004596
CHLOROTRIFLUOROMETHANE	0.000000	0.004506	0.004506
ETHYL-3-PROPYL ACRYLEIN, 2-	0.007823	0.012327	0.004504
M-ETHYLTOLUENE	0.004962	0.000461	0.004501
C10 AROMATIC	0.004744	0.000259	0.004485
2,4-DIMETHYLOCTANE	0.004478	0.000000	0.004478
C6 OLEFINS	0.007910	0.003471	0.004439
C3/C4/C5 ALKYL BENZENES	0.004741	0.000370	0.004372
3-METHYL-TRANS-2-PENTENE	0.006466	0.002137	0.004329
DIMETHYLHEXANES	0.009785	0.005580	0.004205

O-DICHLOROBENZENE	0.108442	0.112485	0.004043
BENZOYL CHLORIDE	0.004012	0.000000	0.004012
BUTYNEDIOL 1,4	0.033680	0.037668	0.003988
DIOXANE (1,4)	0.004934	0.000951	0.003983
CYCLOPENTANE	0.278745	0.274766	0.003980
METHYL(3)PYRROLIDONE(2)	0.020184	0.024034	0.003850
DIOCTYLPHTHALATE, N-	0.007267	0.003446	0.003821
C10 OLEFINS	0.027317	0.023579	0.003738
METHYL SILOXANE	0.003704	0.000000	0.003704
PROPIONIC ACID	0.120333	0.116648	0.003685
1-UNDECENE	0.003617	0.000024	0.003592
BUTYLBENZOATE	0.006988	0.003436	0.003552
INDANE	0.006561	0.003063	0.003497
METHYLHEXANE	0.019519	0.016030	0.003489
CYCLODODECATRIENE	0.000000	0.003449	0.003449
PALMITIC ACID	0.006638	0.003254	0.003383
ALPHA METHYL STYRENE	0.027152	0.023781	0.003371
3,4-DIMETHYLOCTANE	0.003394	0.000062	0.003332
ETHYLCYCLOPENTANE	0.000752	0.004059	0.003307
HEXAMETHYLENEIMINE	0.003337	0.006595	0.003258
C7 OLEFINS	0.004854	0.001635	0.003219
DIMETHYLBUTANE	0.019271	0.016110	0.003161
ETHYLBENZENE	0.005352	0.002342	0.003010
1-METHYLCYCLOHEXENE	0.004624	0.001712	0.002912
C5 PARAFFIN	0.017612	0.014706	0.002905
ETHANETHIOL	0.055073	0.057976	0.002902
HEXAMETHYLENE DIISOCYANATE	0.014761	0.017661	0.002900
VALERIC ACID	0.005136	0.008021	0.002885
DICYCLOPENTADIENE	0.162543	0.159679	0.002864
CHLOROETHANE	0.002822	0.000000	0.002822
N BUTYL CHLORIDE	0.008124	0.005330	0.002794
DIMETHYLUDECANE	0.004829	0.002039	0.002791
ETHYLISOPROPYL ETHER	0.006843	0.009608	0.002765
MESITYL OXIDE	0.009398	0.012137	0.002738
TETRAFLUOROMETHANE	0.000000	0.002711	0.002711
CHLOROFORM	0.168524	0.165841	0.002683
C5 OLEFIN	0.016118	0.013443	0.002675
DIHYDROXYBENZENE (1,4)	0.002671	0.000000	0.002671
CYCLOOCTADIENE	0.000688	0.003309	0.002621
METHYL-2,4-PENTANEDIOL (2-)	0.099866	0.102434	0.002568
METHYLPENTANE	0.014900	0.012384	0.002516
DIKETENE	0.030361	0.032866	0.002506
PROPROXYETHANOL (2)	0.006663	0.004182	0.002481
C5 ALKYL BENZENES	0.014204	0.011745	0.002459
BUTYLBENZENE	0.002462	0.000024	0.002437
METHYLHEPTENE	0.000022	0.002438	0.002416
ACRYLONITRILE MONOMER	0.004107	0.006453	0.002346

PROPYLENE GLYCOL MONOMETHYL	0.014532	0.016793	0.002261
ISOMERS OF BUTYLBENZENE	0.069399	0.071638	0.002238
C9 COMPOUNDS (DIESEL EXHAUST)	0.002236	0.000000	0.002236
CAPROLACTAM	0.108388	0.110497	0.002109
ETHYLMETHYLOCTANE	0.002184	0.000105	0.002079
CYMENE, P-	0.006311	0.004266	0.002045
METHYLNAPHTHALENES	0.012282	0.010251	0.002031
TRIMETHYLCYCLOPENTANE	0.002946	0.004938	0.001992
BIPHENYL	0.009241	0.007277	0.001964
PROPROXYPROPANOL	0.019483	0.021429	0.001946
METHYLSTEARATE	0.003651	0.001713	0.001938
SUBSTITUTED STYRENES	0.001923	0.000000	0.001923
BUTYL CELLOSOLVE ACETATE	0.025709	0.027630	0.001922
ETHYLENE DIAMINE	0.019818	0.021738	0.001920
2-METHYLOCTANE	0.001904	0.000000	0.001904
2,3-DIMETHYLHEPTANE	0.001888	0.000000	0.001888
DICHLOROPROPANE (1,2)	0.000704	0.002530	0.001826
B-METHYL STYRENE	0.001805	0.000000	0.001805
ALIPHATICS (PER CARBON)	0.003319	0.001548	0.001771
2,2,5-TRIMETHYLHEXANE	0.002509	0.000801	0.001708
DIPHENYL ETHER	0.009113	0.010816	0.001703
DIMETHYLOCTANES	0.071002	0.069310	0.001692
DI-(2-ETHYLHEXYL)PHTHALATE (DE	0.000000	0.001665	0.001665
NHEXYL CELLOSOLVE	0.039195	0.040840	0.001645
2,4,4-TRIMETHYL-1-PENTENE	0.001955	0.000312	0.001643
C6H18O3SI3	0.003780	0.002156	0.001625
TEREPHTHALIC ACID	0.001834	0.000212	0.001623
PHENYLISOCYANATE	0.005554	0.003942	0.001613
C11 OLEFINS	0.008744	0.010344	0.001600
O-XYLENE	0.012463	0.010918	0.001546
METHYLOCTANES	0.019828	0.021369	0.001541
ETHYL HEXANOIC ACID,2-	0.002857	0.004344	0.001487
METHOXYETHANOL, 2-	0.000000	0.001467	0.001467
BUTANEDIOL (1,3)	0.009828	0.011290	0.001462
C5 PARAFFIN/OLEFIN	0.008962	0.007537	0.001425
METHYL ISOPROPYL KETONE	0.000000	0.001397	0.001397
DECYCLENE	0.021965	0.023352	0.001386
TRIETHANOLAMINE	0.012327	0.010982	0.001346
PROPENYLCYCLOHEXANE	0.006642	0.007967	0.001325
NITROETHANE	0.000000	0.001298	0.001298
NAPHTHALENE	0.003628	0.002342	0.001286
METHYLPALMITATE	0.003106	0.001824	0.001282
C10 PARAFFINS	0.005861	0.007141	0.001280
NONMETHANE VOC-U	0.000000	0.001269	0.001269
METHYLPENTENES	0.007359	0.006104	0.001255
ISOBUTYRONITRILE	0.000000	0.001253	0.001253
TRIETHYLAMINE	0.004933	0.003693	0.001241

2-METHYLHEPTANE	0.001242	0.000016	0.001226
METHYLHEXANAL	0.007635	0.006420	0.001214
CHLOROPENTAFLUOROETHANE	0.000000	0.001196	0.001196
D-LIMONENE	0.005874	0.004688	0.001186
C8 OLEFINS	0.003446	0.002277	0.001169
METHYLDECENE	0.005729	0.006838	0.001109
PHENANTHRENE	0.001768	0.000663	0.001105
TETRAMETHYLPENTANONE	0.006630	0.007735	0.001105
1-CHLOROBUTANE	0.002951	0.004012	0.001061
C2 ALKYLINDAN	0.007144	0.006083	0.001061
PYRROLIDONE,2-	0.007379	0.008435	0.001056
DIMETHYLHEPTANE	0.006018	0.007058	0.001039
INDENE	0.007134	0.006123	0.001011
DIMETHYLCYCLOPENTANE	0.003726	0.002751	0.000975
TRIMETHYLPENTANE	0.005643	0.004691	0.000952
BUTYLISOPROPYLPHthalate	0.001856	0.000908	0.000948
METHYLAMYLALCOHOL	0.000000	0.000942	0.000942
ISOPROPYL FORMATE	0.000000	0.000940	0.000940
DICHLOROPROPYLENE, 1,3-	0.006735	0.007673	0.000938
M-DICHLOROBENZENE	0.005149	0.004218	0.000931
AMYL ACETATE	0.001693	0.002606	0.000913
DIETHYLMETHYLCYCLOHEXANE	0.004589	0.005480	0.000891
PROPYLHEPTENES	0.004589	0.005480	0.000891
1-ETHOXY-2-PROPANOL	0.001757	0.002626	0.000869
3-METHYLHEPTANE	0.000861	0.000000	0.000861
TETRAMETHYLCYCLOPENTANE	0.004715	0.005547	0.000833
PROPADIENE	0.002635	0.003446	0.000810
DIBUTYLPHthalate	0.001507	0.000704	0.000803
NONENONE	0.007597	0.006802	0.000795
A-CHLOROTOLUENE	0.000779	0.000000	0.000779
1,4-BUTANEDIOL	0.001379	0.000600	0.000779
OXOHEXYL ACETATE	0.002466	0.003203	0.000737
TRICHLOROBENZENE, 1,2,4-	0.000000	0.000731	0.000731
METHYL IODIDE	0.007826	0.008554	0.000728
PIVALIC ACID	0.000721	0.000000	0.000721
CUMENE HYDROPEROXIDE	0.006119	0.006830	0.000710
CHLOROETHANOL (2)	0.000703	0.000000	0.000703
BENZALDEHYDE	0.019264	0.019955	0.000691
C9 PARAFFIN	0.003983	0.003294	0.000689
DIETHYLENE TRIAMINE	0.005436	0.006125	0.000688
SEC-BUTYL CHLORIDE	0.001815	0.002480	0.000665
DIMETHYLINDANS	0.003537	0.002882	0.000655
ETHYLSTYRENE	0.000996	0.000349	0.000647
METHYLMYRISTATE	0.000996	0.000349	0.000647
BENZYLALCOHOL	0.006140	0.006769	0.000629
BUTYL METHACRYLATE	0.006220	0.006848	0.000628
2-METHYL-2-PENTENE	0.000987	0.000361	0.000627

METHYLCYCLOPENTENE	0.003710	0.003084	0.000625
TRIMETHYLDECENE	0.003588	0.002970	0.000618
C8H24O4SI4	0.001246	0.000639	0.000607
BUTYL ETHYL ETHER, TERT-	0.000000	0.000604	0.000604
ACETYLACETONE	0.000000	0.000603	0.000603
ETHYLHEXANE	0.010800	0.010203	0.000597
METHYLHEPTANE	0.003036	0.002440	0.000596
DIMETHYLCYCLOPENTENES	0.002546	0.001959	0.000587
NITROPROPANE (1)	0.001392	0.001962	0.000570
4-METHYLANILINE	0.001362	0.000795	0.000567
ISOMERS OF TETRADECANE	0.002202	0.001636	0.000567
ISOPROPYLMETHYLCYCLOHEXANE	0.003602	0.004168	0.000566
VINYLDENE CHLORIDE	0.008589	0.009149	0.000560
MORPHOLINE	0.000558	0.000000	0.000558
CUMENE (ISOPROPYL BENZENE)	0.002800	0.002252	0.000549
DIACETONE ALCOHOL	0.002168	0.002708	0.000540
CYCLOBUTANE	0.003298	0.003826	0.000528
DIMETHYLPENTANE	0.002987	0.002462	0.000526
HEXADIENE	0.004989	0.005503	0.000514
4-METHYLHEPTANE	0.000542	0.000038	0.000504
BUTADIENE, 1,2-	0.003929	0.004418	0.000488
BUTYLENE OXIDE, 1,2-	0.007402	0.007880	0.000478
ADIPIC ACID	1.211939	1.212413	0.000474
HEPTANOL (3-1)	0.001160	0.001631	0.000471
DIMETHYLBUTENE	0.002490	0.002023	0.000467
BUTOXYETHOXYETHANOL	0.004228	0.003762	0.000466
PARAFFINS (C16-C34)	0.000664	0.000200	0.000464
METHYLGLYOXAL	0.000833	0.000379	0.000455
TRIETHYLENETETRAMINE	0.001471	0.001912	0.000441
ETHYLMETHYLHEXANE	0.002545	0.002107	0.000438
2-(2-BUTOXYETHOXY)ETHANOL	0.000940	0.001377	0.000436
CYCLOHEXENE	0.000969	0.000535	0.000434
O-CHLOROTOLUENE	0.000000	0.000434	0.000434
GLYOXAL	0.000904	0.000472	0.000432
N-PENTYLCYCLOHEXANE	0.001465	0.001041	0.000423
METHYLGLUTARONITRILE	0.000000	0.000423	0.000423
XYLENOL 3,4-	0.000000	0.000423	0.000423
ACENAPHTHYLENE	0.000589	0.000166	0.000423
METHYLHEXADIENE	0.002048	0.001628	0.000420
ISOMERS OF C10H18	0.000966	0.000548	0.000418
VINYL-2-PYRROLIDONE,N-	0.003338	0.003748	0.000409
C6 SUBSTITUTED CYCLOHEXANE	0.001953	0.001544	0.000409
C5 SUBSTITUTED CYCLOHEXANE	0.002506	0.002101	0.000405
2,2-DICHLORONITROANILINE	0.002394	0.001994	0.000400
ISOMERS OF C11H20	0.002639	0.003039	0.000400
C4 SUBSTITUTED CYCLOHEXANONE	0.001556	0.001162	0.000394
C4 ALKYLPHENOLS	0.003235	0.003618	0.000383

ETHYL-B-ETHOXYPROPIONATE	0.001255	0.001630	0.000375
C6 ALKYL BENZENE	0.000907	0.000534	0.000373
MYRCENE	0.001327	0.000962	0.000365
B-PHELLANDRENE	0.001231	0.000873	0.000358
BUTOXYBUTENE	0.002106	0.001753	0.000353
3-(CHLOROMETHYL)-HEPTANE	0.000745	0.001094	0.000349
T-BUTYLBENZENE	0.002604	0.002952	0.000349
AMYL METHYL ETHER, TERT-	0.000000	0.000336	0.000336
2-METHYLPROPENE	0.000374	0.000039	0.000336
AMINOETHYLPIPERAZINE, (N-)	0.001158	0.001493	0.000335
CAMPHENE	0.000989	0.000665	0.000324
ETHYLHEXYL ACRYLATE (2)	0.002144	0.002468	0.000324
TERPENES	0.000329	0.000013	0.000316
ETHYLHEPTENE	0.000398	0.000084	0.000314
ANTHRAQUINONE	0.000350	0.000038	0.000313
TRICHLOROBENZENES(ALL)	0.000350	0.000038	0.000313
2,3-DIMETHYLHEXANE	0.000302	0.000000	0.000302
C3 ALKYL CYCLOHEXANE	0.000333	0.000038	0.000295
BROMODINITROBENZENE	0.000332	0.000038	0.000294
ETHYLPHENYLPHENYLETHANE	0.000332	0.000038	0.000294
ETHYLMETHYLCYCLOPENTANE	0.001139	0.000848	0.000291
MONONONYLPHENOL	0.007441	0.007730	0.000289
TRIMETHYLHEXENE	0.003247	0.003533	0.000286
METHYLCYCLOHEXENE	0.001162	0.000880	0.000281
CHLOROPROPENE (3)	0.014039	0.014320	0.000281
C4 ALKYLSTYRENES	0.000554	0.000274	0.000280
C2 ALKYL CYCLOHEXANE	0.000349	0.000076	0.000273
C4 SUBSTITUTED CYCLOHEXANE	0.000349	0.000076	0.000273
HEXADECANE	0.000409	0.000144	0.000264
ISOMERS OF HEPTADECANE	0.000405	0.000143	0.000262
2-HEXENE	0.000311	0.000051	0.000260
ISOMERS OF OCTADECANE	0.000345	0.000086	0.000259
2-BUTYNE	0.000295	0.000038	0.000257
CHRYSENE	0.000295	0.000038	0.000257
CIS-3-HEXENE	0.000295	0.000038	0.000257
FLUORANTHENE	0.000295	0.000038	0.000257
PYRENE	0.000295	0.000038	0.000257
METHACRYLIC ACID	0.001203	0.001455	0.000253
ISOMERS OF C9H16	0.000425	0.000182	0.000243
ISOPROPYLAMINE	0.004064	0.004305	0.000241
TRIMETHYLOCTANES	0.003571	0.003810	0.000238
ETHYLDIMETHYLPENTANE	0.001052	0.000815	0.000237
METHYLDIETHANOLAMINE	0.007247	0.007014	0.000233
ISOAMYL ALCOHOL	0.000279	0.000047	0.000232
TETRAETHYLENEPENTAMINE	0.000850	0.001077	0.000226
2,5-DIMETHYLHEPTANE	0.000281	0.000061	0.000219
C13 COMPOUNDS (DIESEL EXHAUST)	0.000211	0.000000	0.000211

C2 ALKYL NAPHTHALENE	0.000830	0.000620	0.000210
DIMETHYLHEXADIENE	0.000830	0.000620	0.000210
TRIMETHYLDECANE	0.000390	0.000188	0.000201
DIMETHYLETHYLCYCLOHEXANE	0.000720	0.000527	0.000193
DIMETHYLCYCLOBUTANONE	0.000506	0.000313	0.000193
METHYLHEXENES	0.000463	0.000275	0.000189
ETHER, TERT-BUTYL-METHYL	0.000000	0.000182	0.000182
BUTYL CARBITOL ACETATE	0.000000	0.000177	0.000177
DIHYDRO NAPHTHALENE	0.000498	0.000334	0.000164
ETHYLCYCLOPENTENE	0.000498	0.000334	0.000164
METHYLBUTENE	0.000498	0.000334	0.000164
TRIMETHYLINDAN	0.000498	0.000334	0.000164
BUTYRIC ACID	0.000000	0.000159	0.000159
ISOBUTYL ISOBUTYRATE	0.000000	0.000156	0.000156
BUTYROLACTONE (4)	0.006418	0.006567	0.000150
HYDROXYPROPYL ACRYLATE	0.001302	0.001448	0.000147
DINITROTOLUENE (ALL ISOMERS)	0.001996	0.002140	0.000144
3-HEPTENE	0.000164	0.000021	0.000143
CIS-2-OCTENE	0.000164	0.000021	0.000143
VALERALDEHYDE	0.046982	0.047124	0.000142
ISOMERS OF TRIDECANE	0.000445	0.000314	0.000131
DIBUTYL ETHER	0.000290	0.000419	0.000130
TETRAMETHYLCYCLOBUTENE	0.000335	0.000206	0.000128
ISOVALERIC ACID	0.000819	0.000947	0.000128
C10H12	0.000332	0.000206	0.000126
C7 PARAFFINS	0.000332	0.000206	0.000126
C7H12O	0.000332	0.000206	0.000126
ETHYLINDAN	0.000332	0.000206	0.000126
METHYLCYCLOPENTADIENE	0.000332	0.000206	0.000126
PROPARGYL ALCOHOL	0.003513	0.003636	0.000123
C5 ALKYL BENZENES (U)	0.000388	0.000266	0.000122
TRIMETHYLPENTADIENE	0.000388	0.000266	0.000122
DIMETHYLPENTENE	0.000166	0.000051	0.000115
ETHYLHEPTANE	0.000166	0.000051	0.000115
HEPTADIENAL	0.000166	0.000051	0.000115
METHYLCYCLOHEXADIENE	0.000166	0.000051	0.000115
METHYLHEPTYNE	0.000166	0.000051	0.000115
METHYLAMINE	0.044461	0.044571	0.000110
CHLOROPROPANE (2)	0.001250	0.001359	0.000109
N-PROPYL CHLORIDE	0.001250	0.001359	0.000109
BENZOTHIAZOLE	0.000411	0.000314	0.000097
DIMETHYLBUTYLCYCLOHEXANE	0.000411	0.000314	0.000097
ALLYL ALCOHOL	0.014614	0.014526	0.000088
ETHYLPENTENE	0.000222	0.000138	0.000084
HEXADIENAL	0.000222	0.000138	0.000084
PENTENYNE	0.000222	0.000138	0.000084
TETRAMETHYLTHIOUREA	0.000395	0.000314	0.000081

MEK PEROXIDE	0.000000	0.000081	0.000081
TOLUIDINE, O-	0.000976	0.001058	0.000081
C10H16	0.000829	0.000749	0.000080
DIMETHYLOCTYNE	0.000829	0.000749	0.000080
OCTAHYDRO PENT ALENE	0.000829	0.000749	0.000080
OCTANOL	0.000829	0.000749	0.000080
ETHYL-1,3-HEXANEDIOL,2-	0.000000	0.000079	0.000079
TRIMETHYLHEXANES	0.000776	0.000704	0.000072
2-BUTYLTE TRAHY DROFURAN	0.000183	0.000255	0.000072
METHYLISOPROPYLCYCLOHEXANE	0.000115	0.000045	0.000071
ETHYLHEXANOATE	0.000114	0.000043	0.000070
LIMONENE	0.000114	0.000043	0.000070
DIPROPYLENE GLYCOL METHYL	0.000000	0.000067	0.000067
BUTYL BENZYL PHTHALATE (BBP)	0.001211	0.001147	0.000064
OCTAHYDROINDENES	0.001478	0.001415	0.000064
BUTYNE	0.002897	0.002839	0.000058
HEXAMETHYLENE-1, 6-	0.000000	0.000058	0.000058
C5 ALKYLPHENOLS	0.001464	0.001410	0.000055
PROPYLENE GLYCOL T-BUTYL	0.000728	0.000783	0.000054
DIHYDROXYNAPHTHALENE DIONE	0.000052	0.000000	0.000052
DIMETHYLHEXANEDIOATE	0.000083	0.000032	0.000051
TETRAMETHYLHEXANE	0.000083	0.000032	0.000051
ETHYL-3-ETHOXYPROPIONATE	0.000000	0.000051	0.000051
PENTYLIDENE CYCLOHEXANE	0.001344	0.001395	0.000050
NONADIENE	0.001462	0.001412	0.000050
EPOXY (1,2) PROPANOL (3)	0.006987	0.006939	0.000048
FURFURYL ALCOHOL	0.000125	0.000077	0.000048
DIAMINO CYCLOHEXANE (1,3)	0.000000	0.000047	0.000047
DIMETHYLINDENE	0.000056	0.000012	0.000044
ETHYLBICYCLOHEPTANE	0.000056	0.000012	0.000044
METHYLBUTADIENE	0.000056	0.000012	0.000044
METHYLDIHYDRONAPHTHALENE	0.000056	0.000012	0.000044
OCTATRIENE	0.000056	0.000012	0.000044
DIMETHYLPENTANEDIOATE	0.000838	0.000794	0.000044
DICHLORO (1,3) PROPANOL (3)	0.004113	0.004157	0.000044
DIETHYLCYCLOHEXANE	0.004921	0.004879	0.000042
C12 OLEFINS	0.001035	0.000994	0.000041
ETHYLOCTENE	0.000075	0.000035	0.000040
DIMETHYLPENTANOL	0.000424	0.000385	0.000039
FLUORENE	0.000000	0.000038	0.000038
OCTAMETHYLCYCLOTETRA SILOXA	0.000000	0.000038	0.000038
DIBUTYLAMINOETHANOL (2-N)	0.003290	0.003326	0.000037
CARENE,3-	0.002154	0.002118	0.000037
METHYLPROPYLNONANE	0.000063	0.000027	0.000036
METHYLNONENE	0.000058	0.000022	0.000035
ACETYLENE DICHLORIDE	0.004344	0.004377	0.000034
METHYLDODECANE	0.000046	0.000015	0.000031

THIOPHENE	0.001642	0.001672	0.000030
DECENE,1-	0.008907	0.008876	0.000030
DIPHENYLMETHANE DIISOCYANATE	0.001158	0.001186	0.000029
BUTYRONITRILE	0.000000	0.000027	0.000027
DIMETHYLBENZYLALCOHOL	0.001283	0.001256	0.000027
DI-N-BUTYL PHTHALATE	0.000000	0.000025	0.000025
P-TOLUALDEHYDE	0.000022	0.000000	0.000022
DIMETHYLNAPHTHALENE	0.000019	0.000000	0.000019
DIPHENYLETHANE	0.000019	0.000000	0.000019
DIVINYLBENZENE	0.000019	0.000000	0.000019
SILOXANE	0.000019	0.000000	0.000019
METHYL BROMIDE	0.003244	0.003262	0.000018
C5 ALKYL CYCLOHEXANE	0.000016	0.000000	0.000016
CHLOROHYDRIN	0.000614	0.000598	0.000016
2,3-DIMETHYLPENTANE	0.000133	0.000118	0.000015
EICOSANE	0.000014	0.000000	0.000014
NONADECANE	0.000027	0.000012	0.000014
2,3,3-TRIMETHYLPENTANE	0.000104	0.000092	0.000013
1-METHYL-3-ETHYLBENZENE	0.000102	0.000089	0.000012
2,3-DIMETHYLBUTANE	0.000071	0.000058	0.000012
METHYL-3-PENTANOL (2-)	0.000521	0.000510	0.000011
2,4-DIMETHYLHEPTANE	0.000010	0.000000	0.000010
SEC-BUTYLBENZENE	0.000010	0.000000	0.000010
DIMETHYLETHYLBENZOIC ACID	0.000010	0.000000	0.000010
HEXADECANOIC ACID	0.000010	0.000000	0.000010
HENEICOSANE	0.000009	0.000000	0.000009
2,3,5-TRIMETHYLHEXANE	0.000009	0.000000	0.000009
1,2-DIETHYLBENZENE	0.000056	0.000050	0.000007
M-DIETHYLBENZENE	0.000056	0.000050	0.000006
ISOBUTYLBENZENE	0.000052	0.000046	0.000006
NEOHEXENE	0.001539	0.001533	0.000006
ISOVALERALDEHYDE	0.000005	0.000000	0.000005
1-METHYL-3-ISOPROPYLBENZENE	0.000037	0.000032	0.000005
2,2-DIMETHYLHEXANE	0.000005	0.000000	0.000005
HEXANAL	0.000026	0.000021	0.000005
PENTYLBENZENE	0.000024	0.000019	0.000004
N,N-DIMETHYLACETOACETAMIDE	0.000802	0.000799	0.000003
TRANS-3-HEXENE	0.000028	0.000024	0.000003
C16 BRANCHED ALKANE	0.000017	0.000014	0.000003
TRIMETHYLCYCLOPENTANONE	0.001241	0.001244	0.000003
CARYOPHYLLENE	0.000003	0.000000	0.000003
2,4,5-TRIMETHYLHEPTANE	0.000025	0.000022	0.000003
METHYLHEPTANOL	0.000002	0.000000	0.000002
1-METHYL-3-N-PROPYLBENZENE	0.000016	0.000014	0.000002
DIMETHYLOCTANOL	0.000002	0.000000	0.000002
CROTONALDEHYDE	0.000002	0.000000	0.000002
METHYLENE(b)4-	0.000002	0.000000	0.000002

DIMETHYLHEPTANOL	0.000002	0.000000	0.000002
METHOXYETHOXYETHANOL	0.000002	0.000000	0.000002
DIMETHYLHEXENE	0.000012	0.000010	0.000001
N-HEPTADECANE	0.000001	0.000000	0.000001
METHYLETHYLPENTANOATE	0.000001	0.000000	0.000001
4,4-METHYLENE DIANILINE	0.000001	0.000000	0.000001
3,5-DIMETHYLHEPTANE	0.000000	0.000000	0.000000
VINYLTOLUENE	0.002152	0.002152	0.000000
GLYOXYLIC ACID	0.001900	0.001900	0.000000
METHYLPYRIDINE (3)	0.000930	0.000930	0.000000
DICHLOROMONOFLUOROMETHANE	0.000735	0.000735	0.000000
2,2-DIMETHYLPROPANE	0.000000	0.000000	0.000000
2,3-DIMETHYL-1-BUTENE	0.000000	0.000000	0.000000
2-ETHYL-1-BUTENE	0.000000	0.000000	0.000000
3-METHYL-1-PENTENE	0.000000	0.000000	0.000000

Appendix B

Figure B-1. HGB 8 County NAA Ethylene Emissions (Tons/Day), New Speciation Methodology

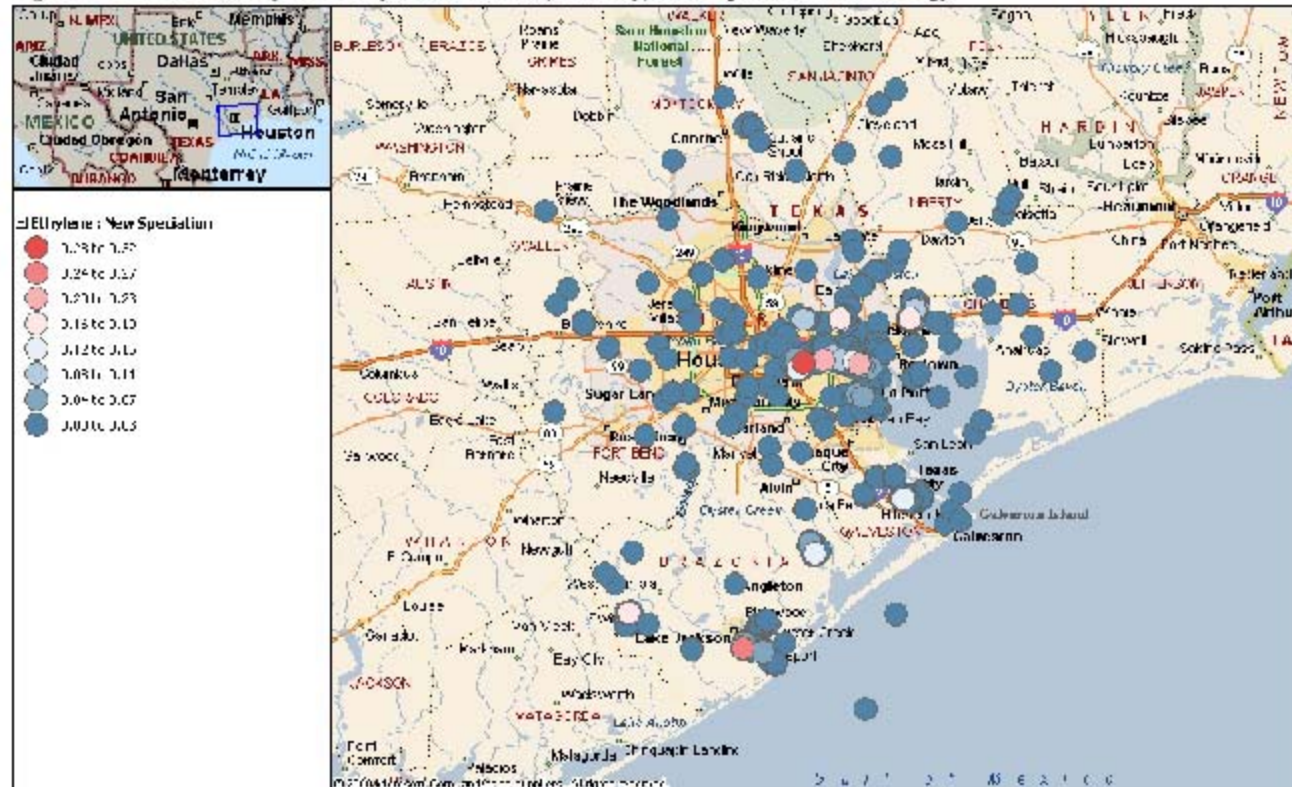


Figure B-2. HGB 8 County NAA Ethylene Emissions (Tons/Day), Dec. 2002 Speciation Methodology

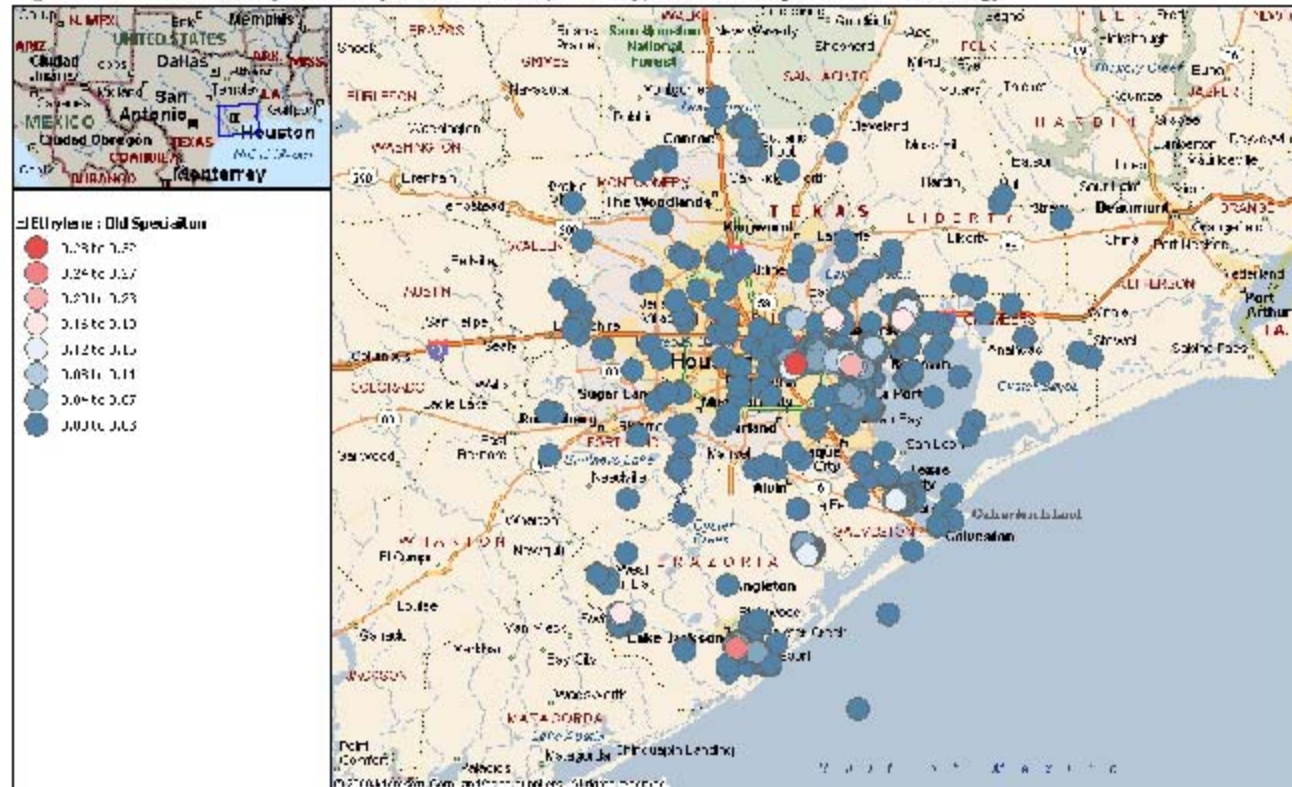


Figure B-3. HGB 8 County NAA Propylene Emissions (Tons/Day), New Speciation Methodology

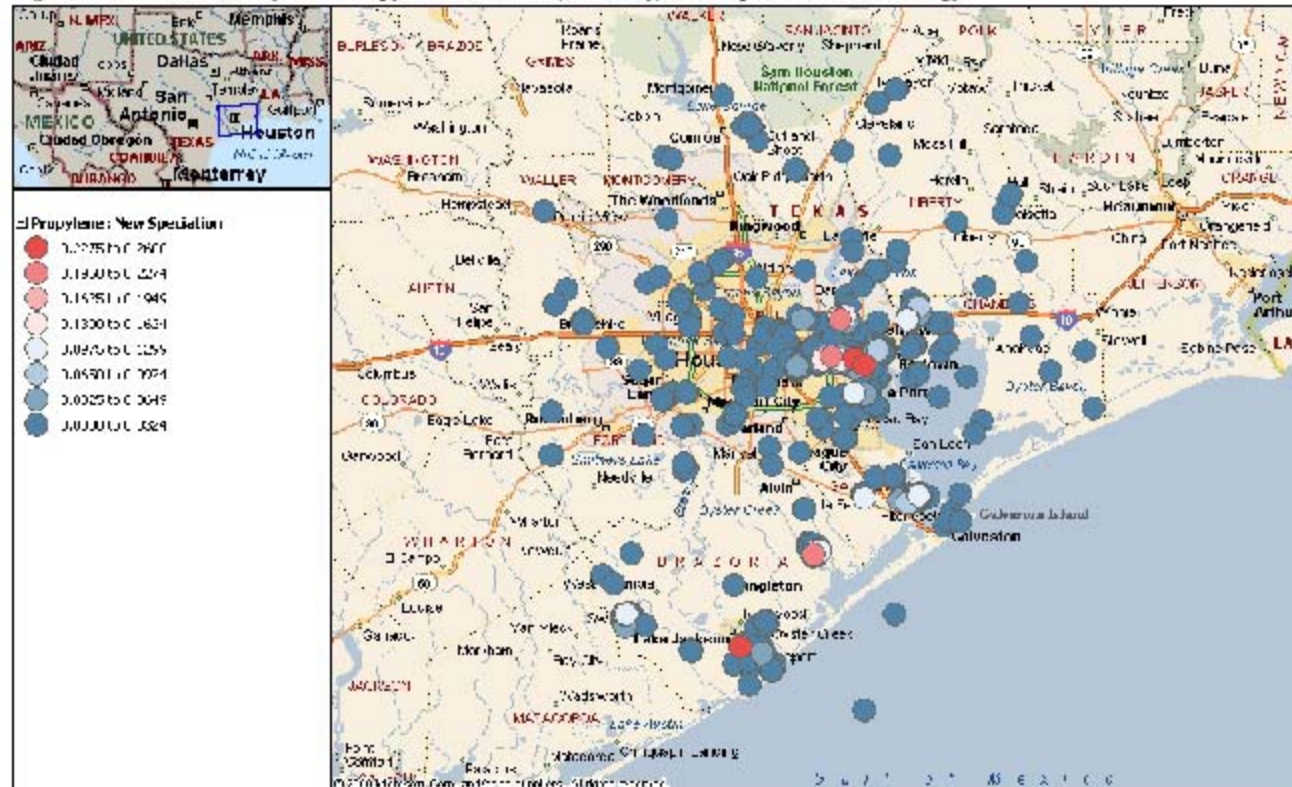


Figure B-4. HGB 8 County NAA Propylene Emissions (Tons/Day), Dec. 2002 Speciation Methodology

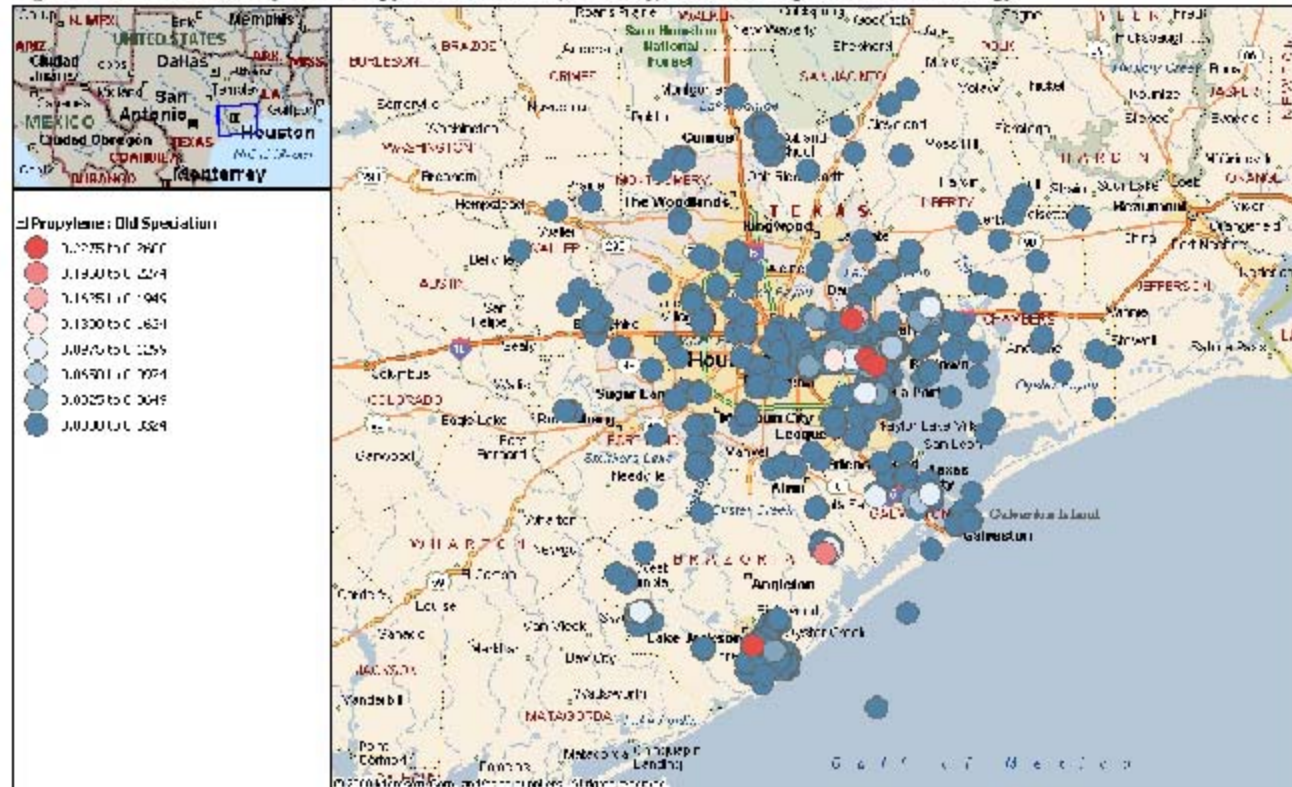


Figure B-5. HGB 8 County NAA 1,3-Butadiene Emissions (Tons/Day), New Speciation Methodology

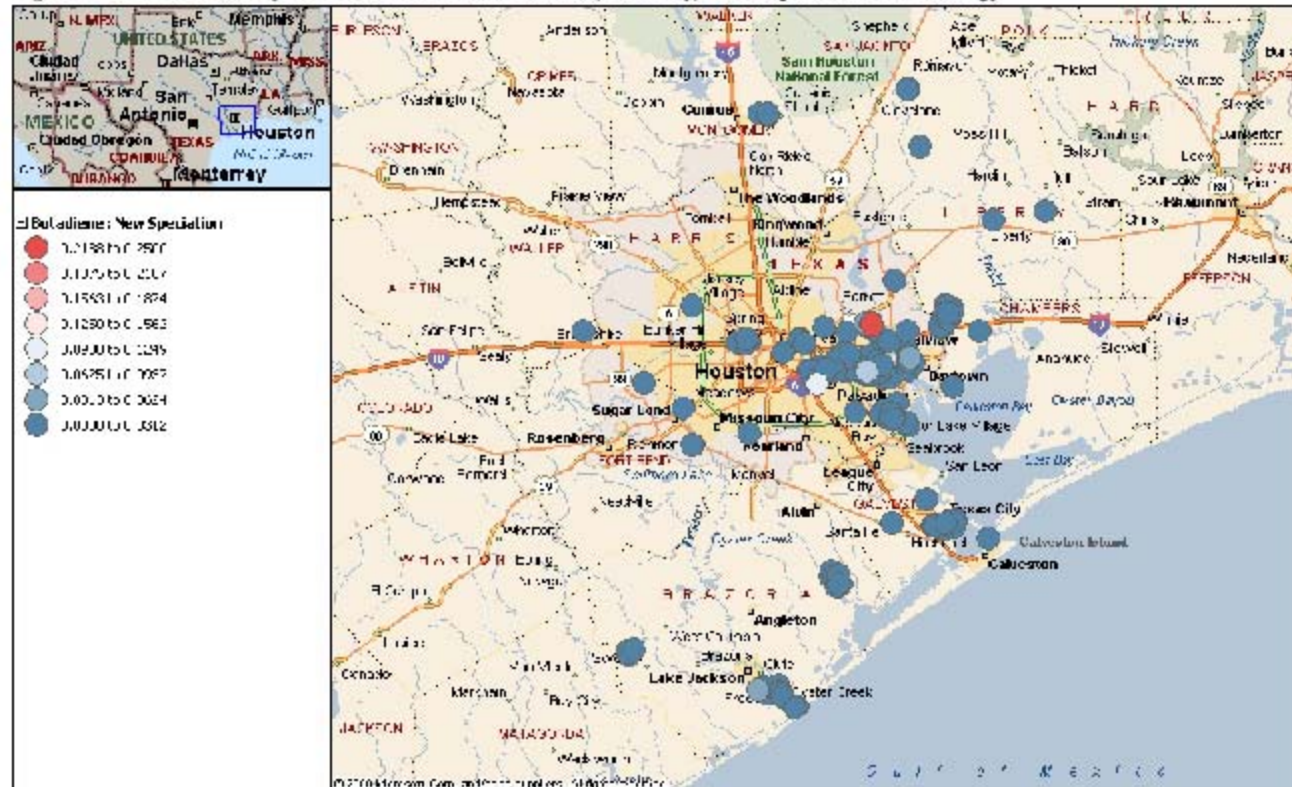


Figure B-6. HGB 8 County NAA 1,3-Butadiene Emissions (Tons/Day), Dec. 2002 Speciation Methodology

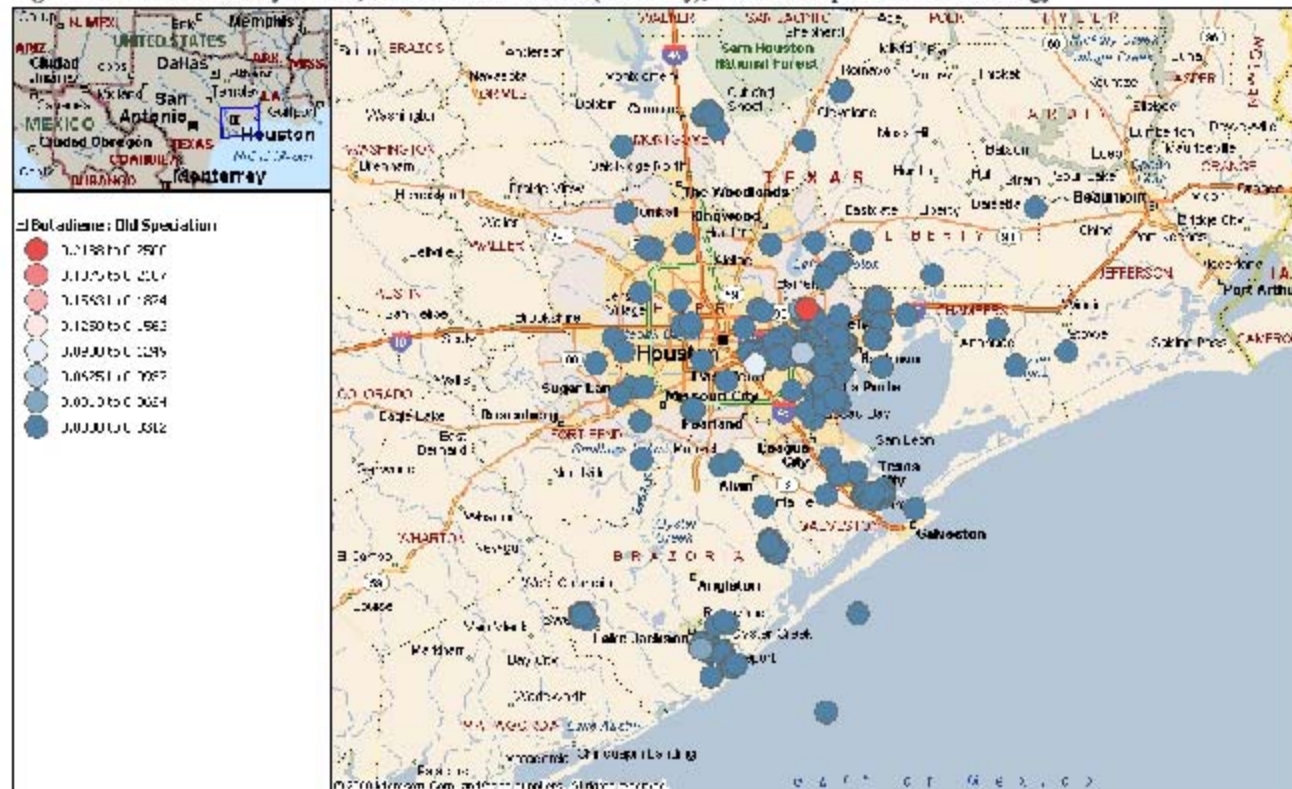


Figure B-7. HGB 8 County NAA Butenes (Tons/Day), New Speciation Methodology

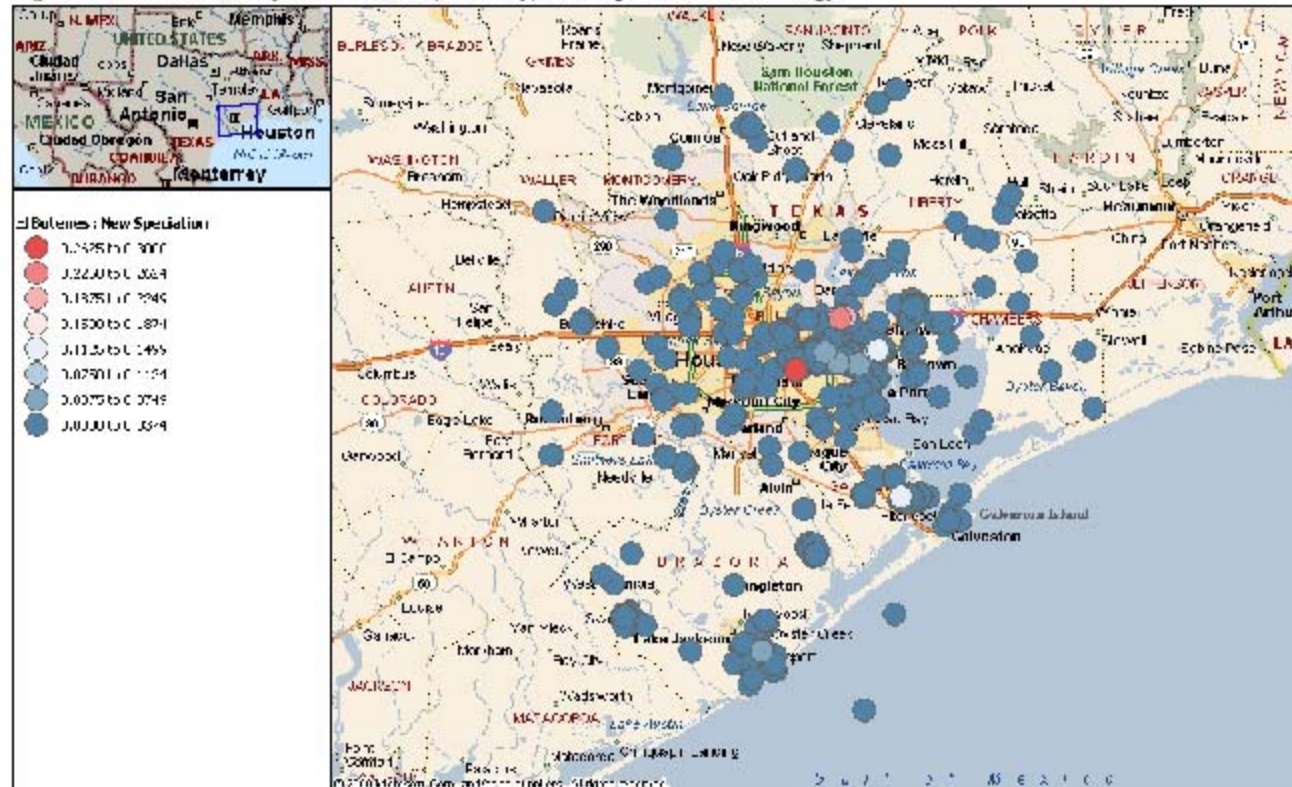
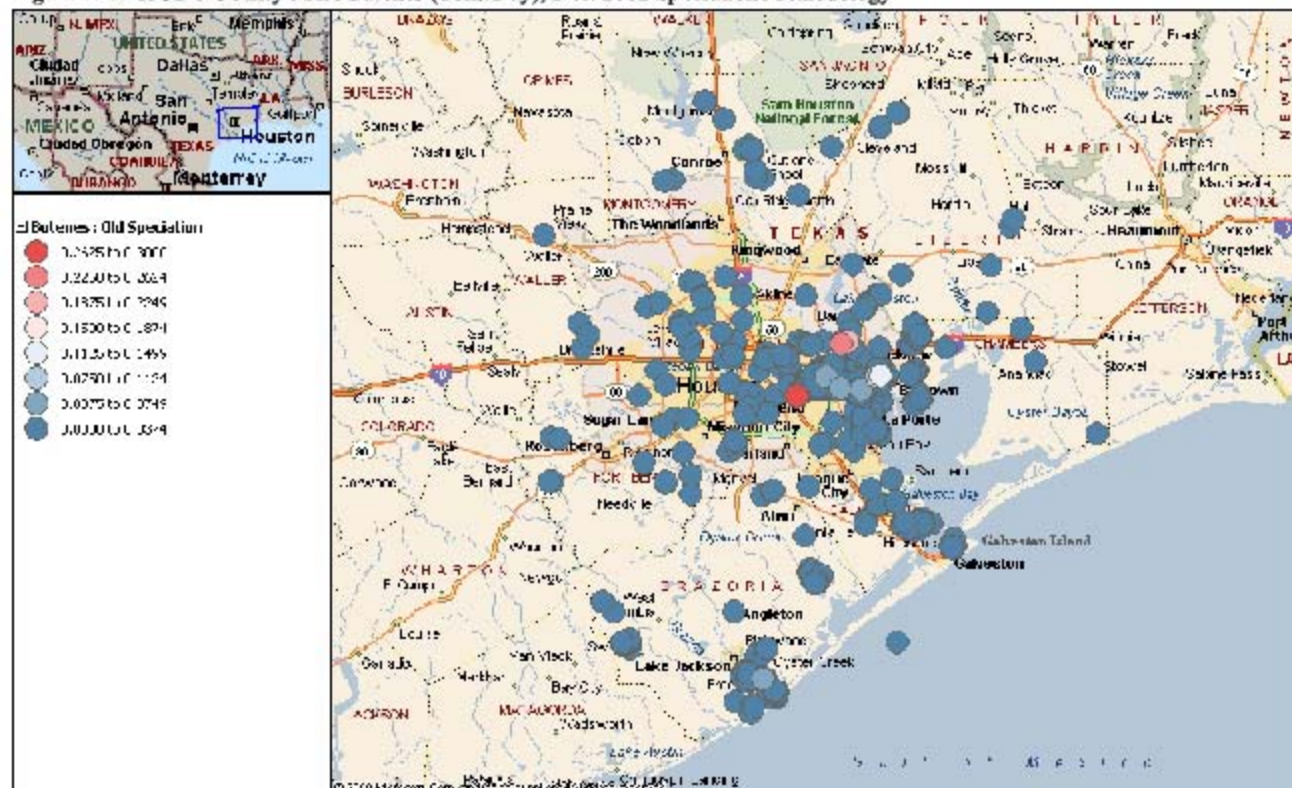


Figure B-8. HGB 8 County NAA Butenes (Tons/Day), Dec. 2002 Speciation Methodology



Emissions Modeling of Specific Highly Reactive Volatile Organic Compounds (HRVOC) in the Houston-Galveston-Brazoria Ozone Nonattainment Area

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ABSTRACT

The 2006 Texas Air Quality Study (TexAQS II) confirmed many of the results from the 2000 Texas Air Quality Study (TexAQS 2000). Both of these studies rank among the most extensive and comprehensive studies of their kind undertaken to date. Chief among many important findings was the discovery of the role played by certain light olefins in the rapid, intense formation of ozone in the Houston-Galveston-Brazoria (HGB) ozone nonattainment area. Atmospheric concentrations of species such as ethylene and propylene were often found to be many times larger than could be explained by reported emissions inventories. Successfully modeling pollutant concentrations observed during the study necessitated adjustments to these reported emissions. As a consequence of these findings, in 2001, the Texas Natural Resource Conservation Commission (now Texas Commission on Environmental Quality) began developing regulations targeting specific highly-reactive VOCs (HRVOC). Adjusting the modeling inventories to account for unreported HRVOC emissions and later test-driving controls on emissions of these specific compounds presented a set of unique challenges to emissions modelers, since emission processing software typically is not designed to apply adjustments or controls to individual VOC species. This paper describes a set of procedures developed by TCEQ which allowed us to successfully adjust and control (in processing for the photochemical model) emissions of individual hydrocarbon species in the TexAQS 2000 modeling episode. This paper also provides an introduction to ongoing efforts to reconcile more recent inventories with ambient measurements made at twelve automatic gas chromatographs (auto-GCs) currently operating continuously in the HGB nonattainment area.

INTRODUCTION

Background and Motivation

The development of a strategy for reducing ozone in HGB is complicated by the many factors contributing to ozone formation in this area. A hot, sunny climate, a large urban population, a massive refining/petrochemical industry, and complex coastal meteorology all work together to make the area one of the worst in the nation for ground-level ozone, and at the same time one of the most challenging areas to model.

In December 2000, TCEQ adopted an HGB Attainment Demonstration Ozone SIP that included rules requiring a 90 percent nitrogen oxides (NO_x) reduction from industrial sources within the HGB area. Shortly after the SIP revision was adopted, a group of Houston-area industrial companies challenged the December 2000 HGB SIP and some of the associated rules. Among other things, the group contended that the last 10 percent of the NO_x reductions (i.e. requiring a 90% reduction instead of 80%) was not cost effective and that the ozone plan would fail because TCEQ did not account for volatile organic compound emissions associated with upset conditions. As part of a settlement agreement reached in June, 2001 TCEQ committed to investigate whether attainment could still be reached under alternatives to the 90 percent industrial NO_x reduction strategy, specifically whether reductions to emissions of Highly-Reactive VOCs (HRVOCs) could be substituted for the last 10% of NO_x reductions.

reconciliation of more recent modeling inventories with HRVOC and other VOC measured at several auto-GCs in HGB.

This paper will cover the following topics in individual sections of the body of the text:

- Reactivity
- Speciation
- Developing and Defining HRVOC Adjustment
- Modeling the Adjustment
- HRVOC Controls
- HRVOC Rules
- Recent Developments in Emissions Reconciliation

Highlights of Results

Relying on results of the TexAQS 2000 field campaign, TCEQ was able to improve the performance of the photochemical model in HGB by adjusting the amount of modeled HRVOC emissions available for rapid ozone formation in 2000. A key component of this process involved developing a process to fully speciate the reported emissions of industrial sources. Using the adjusted inventory, TCEQ was able to demonstrate that 80 percent NO_x reduction combined with overall 36 percent HRVOC reductions is equivalent to the 90 percent industrial NO_x reduction. To achieve the necessary HRVOC reductions, TCEQ developed a dual approach: (1) address variable short-term emissions through a 1200 lb/hour, not-to-exceed, emission limit, and (2) address steady-state and routine emissions through an annual cap. The paper concludes with a preview of current work TCEQ is undertaking to reconcile monitored ambient emissions with the reported inventory.

DISCUSSION

Reactivity

As modelers and atmospheric scientists, we ask the question, "What drives local ozone production?" One answer is reactivity, or reaction rates among the contaminants in the ozone soup. Looking at the VOC part of the equation, not all VOCs are created equal – some VOCs make ozone much more effectively than others. We can define reactivity as the potential of a given compound to make ozone.

One result of TexAQS 2000 was a list of twelve reactive compounds groups developed by TCEQ with the assistance of Brookhaven National Laboratory (BNL) during the field study¹. This list of compounds is referred to as the original "Big 12". Table 1 lists the original "Big 12" HRVOC species as modeled for the December 2002 SIP revision.

Table 1. Original "Big 12" HRVOC.

Propylene
Ethylene
Formaldehyde
Acetaldehyde
Isoprene
Butenes
1,3-butadiene
Toluene
Pentenes
Trimethylbenzenes

Xylenes
Ethyltoluenes

Subsequent analyses were performed¹ in order to refine the list by using data collected over a longer time period (1996-2001) to assess which compounds contributed most to ozone reactivity. Automated gas chromatograph (auto-GC) data were available for seven different sites in Houston and vicinity during this time period. The analysis concluded that, while some compounds (e.g., alkanes) occasionally caused high reactivity, those *frequently* responsible for high reactivity days were propylene, ethylene, butenes (1-butene, cis-2-butene, trans-2-butene), and 1,3-butadiene.

Reactivity Scales

There are several reactivity scales in use today. The two most popular are the OH and the MIR. MIR (maximum incremental reactivity) is a measure of the maximum amount of ozone that can be formed by adding an incremental amount of a particular VOC to a mixture of NO_x-rich air. Units are grams of ozone produced per gram of VOC injected into the system. In the urban core and the Ship Channel, MIR is a suitable metric to use, given the large amount of NO_x in those areas.

MIR is calculated from smog chamber experiments and photochemical modeling. William Carter of the University of California at Riverside is the pioneer and leading expert in this field³. TCEQ downloaded (2002) Carter's MIR reactivity scales⁴ -- an excerpt of the MIR table that TCEQ used (2002) is provided as Table 3.

Table 2. MIR table excerpt.

Compound	MIR
2-Methyl-2-Butene	14.45
trans-2-Butene	13.91
1,3-Butadiene	13.58
cis-2-Butene	13.23
Propene	11.58
1,2,3-Trimethyl Benzene	11.26
1,3,5-Trimethyl Benzene	11.22
Isoprene	10.69
m-Xylene	10.61
1-Butene	10.29
cis-2-Pentene	10.24
trans-2-Pentene	10.23
Ethene	9.08
1-Pentene	7.79
o-Xylene	7.49
. . .	
Acetylene	1.25
2,3,4-Trimethyl Pentane	1.23
2-Methyl Heptane	1.20
2,3-Dimethyl Butane	1.14
n-Octane	1.11
n-Nonane	0.96
n-Decane	0.83
Benzene	0.82

Propane	0.56
Methane	0.0139

A map of the TCEQ analysis¹ area of the auto-GC data represented in Table 2 is provided as Figure 1.

Figure 1. HGB auto-GC locations.

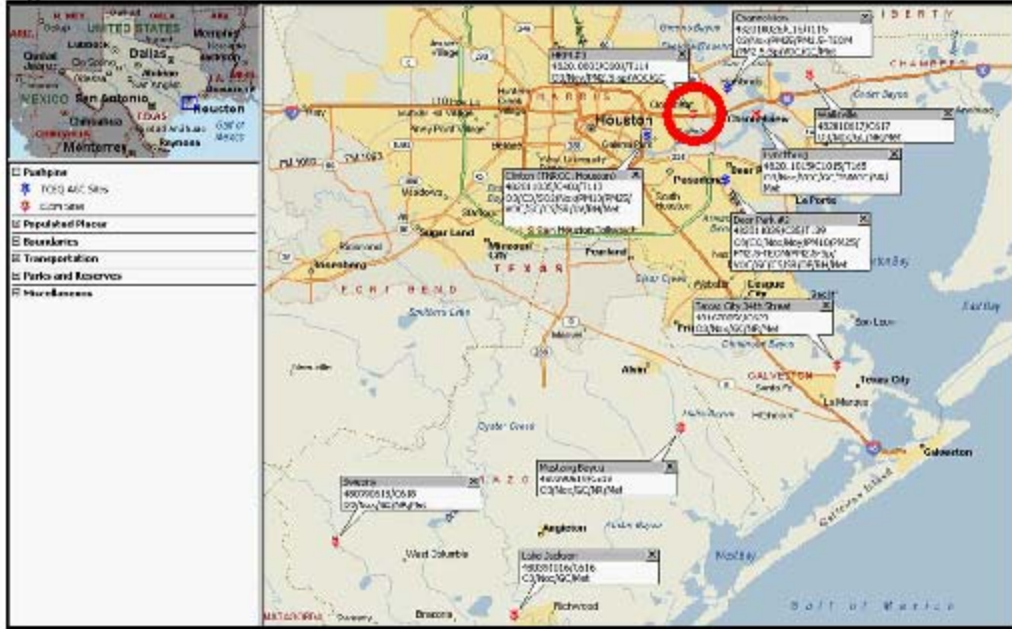
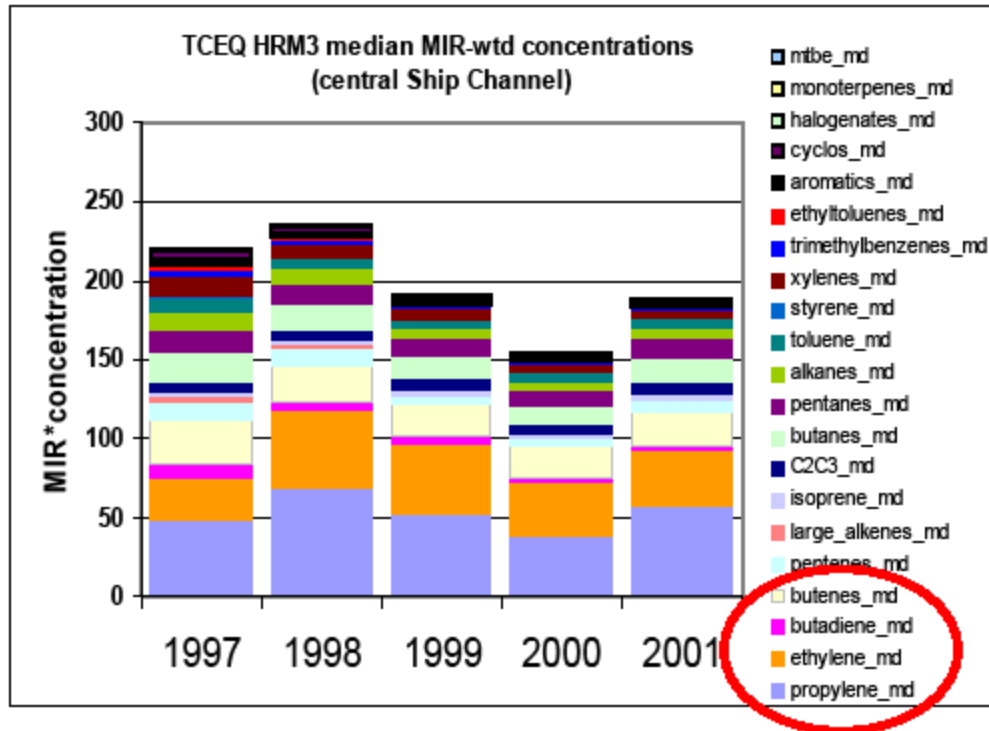


Figure 2 shows mean concentrations by year of canister samples taken at site HRM3 (circled in red in Figure 1). When the compounds are weighted by MIR (Figure 3) the true importance of highly-reactive compounds to ozone production becomes evident.

Figure 3. MIR-weighted concentrations of canister compounds from Figure 2.



Speciation

Photochemical modelers would prefer to have an EI of individual chemical species to place into their models. Unfortunately, the EI is generally not available in that level of detail, because continuous emissions monitors (CEMs) and automated gas chromatographs (auto-GCs) are expensive, and the vast majority of process units are not required to monitor in that level of detail, if they are required to monitor at all.

Speciation is the top-down process of breaking a prepared EI of criteria pollutants into its constituents, preferably compound-specific. For the purpose of this paper, we will limit discussion to volatile organic compounds (VOCs). Historically, professionals involved in speciation (EI preparers, modelers, scientists) have relied on national databases such as SPECIATE or AP-42/FIRE. It has become fairly commonplace for modelers to share and compare speciation profiles and cross-references among themselves. A speciation profile for an emission-generating process is a list of constituent compounds and the mass fraction of each. Since many speciation profiles may exist for one type of process (one SCC), depending on area of the country and the specifics of the process, it is necessary to tie a specific profile to a specific process, via cross-reference. It is possible for several units/processes to use the same speciation profile, so many units/processes can point to one speciation profile. For example, take gasoline: a novice in this business might believe that gasoline is gasoline, but experienced professionals know that what's being emitted as gasoline vapor (volatilization) in a storage tank is very different from gasoline being burned (combusted) in a commuter vehicle engine. Additionally, summer gasoline differs from winter gasoline in composition, and gasoline in certain nonattainment areas may have a special formulation designed to reduce emissions of NO_x .

In recent years, TCEQ has aggressively solicited speciation information directly from major sources in the state, and as a result the VOC inventory in the HGB area is now approximately 85 percent speciated. However, some sources still report sizable quantities of mixtures or unspciated VOCs, and so it is necessary to speciate these fractions in the best way we can, for two reasons: (1) ozone production is very sensitive to the amount of HRVOC being emitted, and the model needs good speciation in order to make valid predictions, and (2) Texas has an HRVOC banking and trading system, which requires complete and accurate (as much as possible) speciation. In addition to speciation routinely collected as part of the EI process, TCEQ requested a Special Inventory (SI) from targeted regulated entities in southeast Texas during each of the past three major field studies. Even if the annual inventory for a source is completely speciated, the speciation can vary from hour to hour within the year (for example, refineries produce different blends of gasoline for different seasons, docks may vary the product loaded from one ship to the next, and the same tank may hold several different products within a given year).

TCEQ Speciation procedure

TCEQ has employed a number of approaches to speciation over the years. For the December 2004 SIP revision modeling analysis, a new process was developed which retains virtually all speciated hydrocarbon data reported to the PSDB/STARS and the SI, regardless of the completeness of the speciation of each point's emissions. Also new for the December 2004 SIP is the exclusion of non-VOC species, as defined by EPA, from all point-source speciation profiles. These procedures are described in "Speciation of Texas Point Source VOC Emissions for Ambient Air Quality Modeling"². This TCEQ report is now referenced in EPA's SPECIATE 4 QAPP document, September 2006. It is also referenced in William Carter's "ei13 paper" (13th International EI Conference), "Development of a Chemical Speciation Database...", 2004.

Companies (regulated entities) supplied chemical speciation profiles for their hourly emissions as part of the 2000 SI (used in the 2004 SIP revision). When available, these data were used to develop speciation profiles used in the emissions preprocessor (EPS3) to CAMx. In cases where 2000 SI speciation data were incomplete or not available, the procedure described in the speciation report² above was used. The same was performed for the unspciated portion of the ozone season daily (OSD) EI, which was used for point sources that were not required to submit hourly 2000 SI data. An outline of these procedures follows:

1. Extract STARS (State of Texas Air Reporting System) Report.
2. Remove non-VOC compounds.
3. Replace mixtures (crude oil, gasoline, naphtha, Stoddard solvent, and "refinery") with refined profiles.
4. Import EPA Default SCC Profiles.
 - After Deletion of non-VOC/non-reactives.
 - And re-normalization of this dataset.
 - Check for profiles composed of only one compound after removal of non-VOC/non-reactives.
 - Replace such profile with a more appropriate profile (SPECIATE, CARB, TCEQ); e.g., EPA 0007 is replaced with CARB 0719
5. Assign profile to each point that had unspciated VOC.
6. Compare reported speciated emissions with profile assigned to each point.
 - Retain reported speciated emissions and remove common species from assigned profile for each emission point.
 - Normalize resulting profile for each point, thereby creating a unique speciation profile (for each point) to be assigned to each emission point's unspciated VOC.
 - Apply to unspciated VOC on a point-by-point basis.

7. Substitute resulting speciation in place of unspciated VOC in reported emissions.
8. Create a point-specific profile for each path in STARS, where a path is a process-unit and emission point combination.

For hourly SI sources, a company may report a different composition for each hour for a given path. For example, a flare may report eight VOC compounds for 10 hours of the day, then a new feed stream may be added that adds six more compounds to that flare for the next 7 hours. For the 2000 SI, when this occurred, an average composition profile was created for that path, and this was the procedure through the December 2004 SIP revision. Figure 4 shows the results of the fully-speciated 2000 point source EI, and Figure 5 shows the same for Harris County only.

Figure 4. HGB 8-county VOC speciation for year 2000.

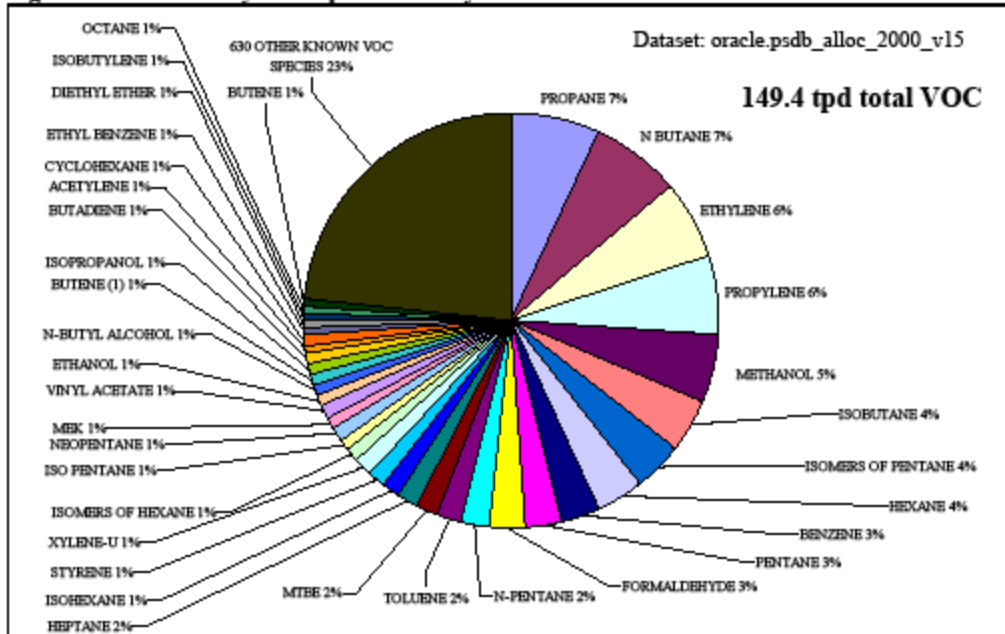
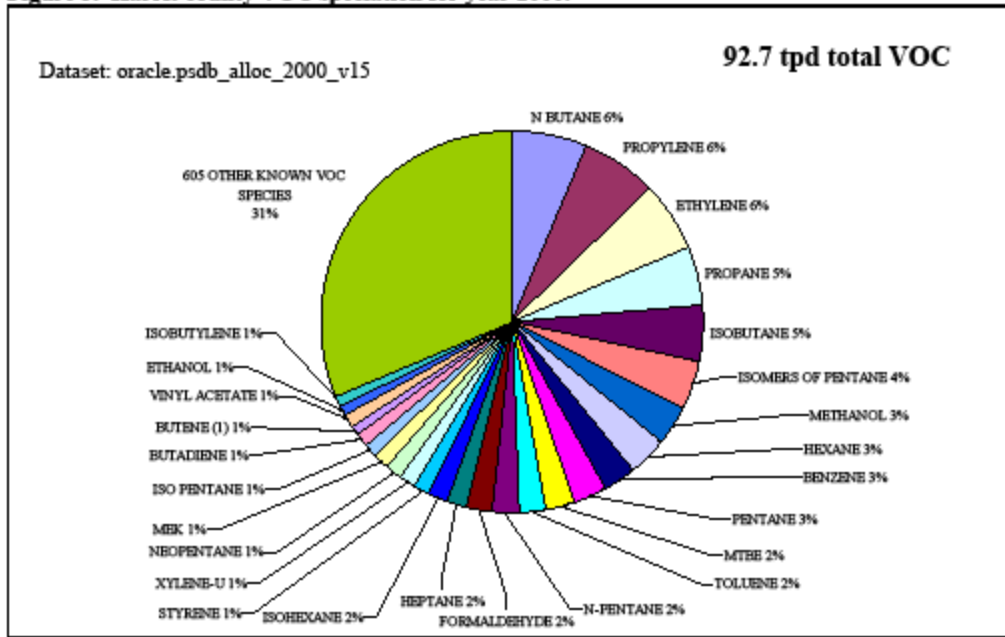


Figure 5. Harris county VOC speciation for year 2000.



Current Speciation Work

For the current SIP modeling project work, TCEQ modelers have created a speciation profile for every hour for every path in a SI dataset, rather than an average profile for each path for entire episode. This greatly increases the number of speciation profiles and cross-references for processing with EPS3, but this procedure only occurs once, and we want to take advantage of every bit of information that a regulated entity provides, especially for a Special Inventory request. This also caused TCEQ modelers to develop a new scheme for profile code names, adding a bit of complexity to the profile/cross-reference system. This improved process for handling the TexAQs II Special Inventory of 2005-06 was facilitated by the organization of the hourly data as it was collected by the Hourly Emissions Inventory Reporting System (HEIRS)⁵ and uploaded into STARS.

Speciation as Modeled

Photochemical models, such as CAMx, use simplified chemical mechanisms by computational necessity. Today, there are more than 100 chemical reactions that are computed inside the photochemical model for each time step for each 3-D face of each grid cell in the modeling domain. Imagine the computing time that would be required for one day of a modeling episode if we modeled every single possible species and its interaction with all of the other species it would encounter in each grid cell. Ozone modelers typically use about 15 of those species as model input emissions. If we modeled each species, instead of lumping them, as all photochemical models do, we would be modeling approximately 300 individual hydrocarbon species (and that's if all the insignificant species were dropped). Hence, to obtain photochemical modeling results in a human timeframe, like species are lumped into categories, or more accurately, like parts of molecules are lumped with like parts of other molecules.

Most of the chemical mechanisms are based on a molecular structure approach. The Carbon Bond IV (CB-IV) chemical mechanism uses the carbon bond as its criteria. CB-IV has been a standard for most of the nation for more than 20 years. CB05 is an upgrade to CB-IV. EPA incorporated CB05 into the CMAQ model in 2006. Environ incorporated CB05 into CAMx in 2006-07, and TCEQ is currently using it in all of its photochemical modeling studies. Table 4 is an excerpt of the speciation conversion of some of the most reactive species into modeled CB-IV lumped categories. The table for CB05 would look similar. To read the table, for example, half of the reported propylene mass is modeled as PAR (parafins) and half as OLE (olefins). Table 5 shows the overall MIR for each CB-IV category. Hence, it is still important to know how much of each individual species is present, so that the allocation to CB-IV/CB05 is performed as accurately as possible.

Table 3. HRVOC reported species mapping to CB-IV modeled categories.

SPECIES	PAR	OLE	TOL	XYL	FORM	ALD2	ETH	ISOP	MEOH	ETOH
ETHYLENE	0.00	0.00	0.00	0.00	0.00	0.00	1.00	0.00	0.00	0.00
PROPENE	1.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1-BUTENE	2.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1,3-BUTADIENE	0.00	2.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PENTENE	3.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
HEXENE	3.00	0.33	0.00	0.00	0.00	1.17	0.00	0.00	0.00	0.00
ISOPRENE	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00	0.00	0.00

Table 4. MIR for the CB-IV modeled categories.

CB-IV SPECIES	CB-IV MIR (g O3 / g CB-IV ROG)
FORM	17.313
OLE	14.493
ISOP	13.125
ALD2	9.021
XYL	7.149
ETH	7.146
ETOH	1.995
TOL	1.5417
MEOH	1.2303
PAR	1.0374

Comparing Reported Emissions with Ambient Measurements

Beginning with the 2002 SIP revision, TCEQ has made adjustments to emissions of HRVOCs in the HGB eight-county ozone nonattainment area. These adjustments are justified by a strong scientific consensus that the reported emissions of certain light olefins are not sufficient to explain concentrations observed in the many aircraft flights downwind from industrial sources. As stated above, data collected and analyzed from the TexAQS field studies provided valuable insight regarding the ambient concentrations of ozone precursors in the HGB area. Again, one conclusion of TexAQS (and reaffirmed by TexAQS II) was that ambient concentrations of certain VOCs, in particular terminal olefins, were not consistent with the reported industrial emissions. Specifically, the ratio of terminal olefins to NO_x measured by aircraft-borne monitors was generally much higher than would be expected from the reported emissions of VOCs and NO_x.

Because of the greater certainty associated with the NO_x emissions estimates, TCEQ concluded that industrial emissions of terminal olefins were likely understated in earlier emissions inventories. This conclusion has been reviewed and documented in numerous scientific journals^{6,7}. The question of whether emissions estimates of other VOCs should be adjusted has arisen. Adjustments to the emission inventory are only warranted when strong evidence and substantial analysis and review indicates that an adjustment would be necessary. Because most of the research has been directed at emissions of highly-reactive compounds, there is only tenuous support available to warrant an inventory adjustment beyond the terminal olefin adjustment. "Other" VOCs (those not described as "highly reactive") have not been adjusted for TCEQ SIP modeling to date. TCEQ continues to investigate whether other VOCs should be adjusted.

Ambient monitoring shows that other less-reactive VOCs can sometimes contribute an equivalent amount of reactivity to the airshed as HRVOC. However, the reactivity measure does not indicate the speed at which a VOC component helps create ozone. Recall that reactivity is typically grams of ozone generated per gram of VOC injected into the system. HRVOC react quickly to form ozone, thus making them the most important VOCs with regard to the 1-hour ozone standard. The scientific evidence and photochemical modeling shows that additional reductions in other less-reactive VOCs are not necessary in order to attain the 1-hour ozone standard. However, TCEQ intends to continue to research the role of other VOCs in ozone formation with respect to the 8-hour ozone standard and will address emissions of those compounds if additional VOC controls are necessary to achieve the 8-hour ozone standard.

Defining HRVOC

The term HRVOC generically applies to any VOC with the potential to efficiently and rapidly form ozone in an urban environment. For TCEQ regulatory purposes, HRVOC applies specifically to the four olefin compounds listed in Table 6. For modeling purposes, HRVOC is operationally defined in terms of which VOCs are adjusted in the modeling. As of December 2002, the list of highly-reactive VOCs was that given in Table 1 (the "Big 12"). For the December 2004 SIP, that list was refined to the terminal olefins, as given in Table 7. The reason for the change is that one of the key instruments used in TexAQS 2000 (and upon whose measurements the original inventory adjustment was based) actually measures total *terminal* olefins, which is somewhat different from the "Big 12". Current work on reconciling the 2005 and 2006 inventories with ambient measurements is focused on the four compounds in Table 6, but may be expanded to consider additional compounds.

For control strategy modeling in the December 2004 SIP, TCEQ demonstrated that the four highly-reactive VOCs: ethylene, propylene, 1,3-butadiene, and butenes (all isomers) make the biggest difference of the HRVOCs. These four compounds are common in all the lists, except for *trans-2* and *cis-2* butene, which are *internal* olefins, not terminal olefins, and have been found to frequently cause high total reactivity conditions, and often dominate the total reactivity. Substantial emission reductions of these compounds were hypothesized to make a large impact on high ozone, rapid ozone formation, and transient high ozone observed in the Houston area. This hypothesis is the result of analyzing 57,307 hours of TCEQ routine VOC monitoring data collected between 1996-2001, and 666 airborne VOC samples collected by TexAQS 2000 scientists¹, as summarized in Table 2 and Figures 2 and 3, above. Modeling analysis indicates that emission reductions in these four compounds alone can compensate for the change of industrial NO_x controls to 80% reductions, as agreed upon in the lawsuit settlement, but additional controls on many VOC sources will be necessary to actually reach attainment of the new 8-hour ozone standard. TCEQ will continue to study VOC data available now and in upcoming years to determine whether additional compounds should be added. For now, the list of HRVOC regulated in Texas is given in Table 6.

Table 6. HRVOC species chosen for control/regulation.

Ethylene (ethene)
Propylene (propene)
1,3-Butadiene
Butenes (all isomers)

Table 7. Terminal olefins selected for 2004 "HRVOC" adjustment.

Ethylene
Propylene
1-Butene
1,3-Butadiene
1,2-Butadiene
Pentene
2-Methyl-1-Butene
3-Methyl-1-Butene
Hexene
Isoprene
1-Decene
Propadiene
1,3-Pentadiene

Modeling the HRVOC adjustment

The adjustment used in modeling for the 2002 SIP revision consisted of creating a second point source emissions file containing all emission points for the largest reactive VOC-emitting accounts in the 8-county nonattainment area. This file was used to provide the extra emissions of "Big 12" VOCs necessary to make the selected facilities' emissions of these specific VOCs equal their individual NO_x emissions. This specific VOC-to-NO_x adjustment was first proposed by Greg Yarwood of Environ, based on data collected by an instrumented aircraft operated by Baylor University. On October 19, 2001 the aircraft monitored a number of industrial plumes where high concentrations of terminal olefins coincided with high NO_y concentrations (NO_y consists of NO_x plus other nitrogen compounds which are typically products of photochemical reactions such as nitric acid). In four of these plumes, the concentration ratio of light olefin to NO_y was observed to be between 0.8 and 1, consistent with the assumption of roughly equal emissions of light olefins and NO_x from the plume sources.

For the 2004 SIP revision modeling analysis, the adjustment to terminal olefins was made. The extra terminal olefin emissions were explicitly speciated as individual compounds in this phase of modeling, based on the speciation profiles of individual accounts, whereas in previous modeling, 12 selected VOCs were increased for all accounts using a generic olefin mixture. The specific compounds selected for adjustment were the "terminal olefins," which have a specific chemical structure that is easily detectable by an instrument carried aboard the Baylor research aircraft.

Two types of adjustments were developed using this method, a non-varying adjustment similar to that used in previous modeling and an adjustment that incorporates Special Inventory daily and hourly emission fluctuations. Overall, these enhancements changed the modeled reactivity only slightly from

previous modeling, but provided for much more flexibility in control strategy modeling. The improved non-varying HRVOC adjustment added 155 tons/day of VOC to the HGB 8-county area. The time-varying adjustment fluctuated from 163 to 203 tons/day, depending on the day analyzed.

HRVOC Controls

The modeling indicated that a reduction of approximately 36% of industrial HRVOC emissions, combined with overall point source NO_x reductions of approximately 80%, achieved air quality benefits commensurate with those achieved by the 90% NO_x reductions case in the attainment year. This is critical, not only because TCEQ demonstrated that it did not have to rely solely on a NO_x reduction strategy for attainment demonstration, but that it satisfied the settlement agreement with the industry group.

In the 2004 SIP Revision, the question to TCEQ was, “Can we obtain the equivalent of the last 10% reduction in industrial NO_x with VOC (HRVOC) controls?” The answer was yes. TCEQ calculated the reactivity that the 10% represents, decided on the species to control, and devised a control strategy. A solution was a 36% overall reduction in the four HRVOC in HGB, which amounted to approximately 50% reduction in the four HRVOC species in Harris County and less reduction required for the “big two” (ethylene and propylene) species in the seven adjacent counties. All of the reductions were modeled as controls to the “EXOLE” (extra olefins) file – the same file that represented the HRVOC adjustment. This was possible because the controlled future-case emissions of HRVOCs were actually slightly higher than the originally reported 2000 emissions of these compounds.

Figures 6, 7 and 8 are emissions tileplots that TCEQ modelers use as a quality assurance tool. Figure 6 shows the HGB area VOC base case (unadjusted) for one of the days of the modeled episode (August 30, 2000). Figure 7 shows the same after we applied the HRVOC adjustment. Figure 8 shows the HGB VOC total after we applied the overall 36% HRVOC controls. Each grid cell is 2km by 2km. The total emissions for the HGB eight counties are tabulated. Note that Harris County and Brazoria County received the largest HRVOC reductions. Keep in mind that the tileplots actually show the CB-IV hydrocarbon mass modeled, not VOC or HRVOC, so totals may not exactly match the tons/day of input emissions. Also note that “reported” in the tileplots is actually “reported plus rule effectiveness”.

Figure 6. Unadjusted (reported) total modeled VOC in HGB

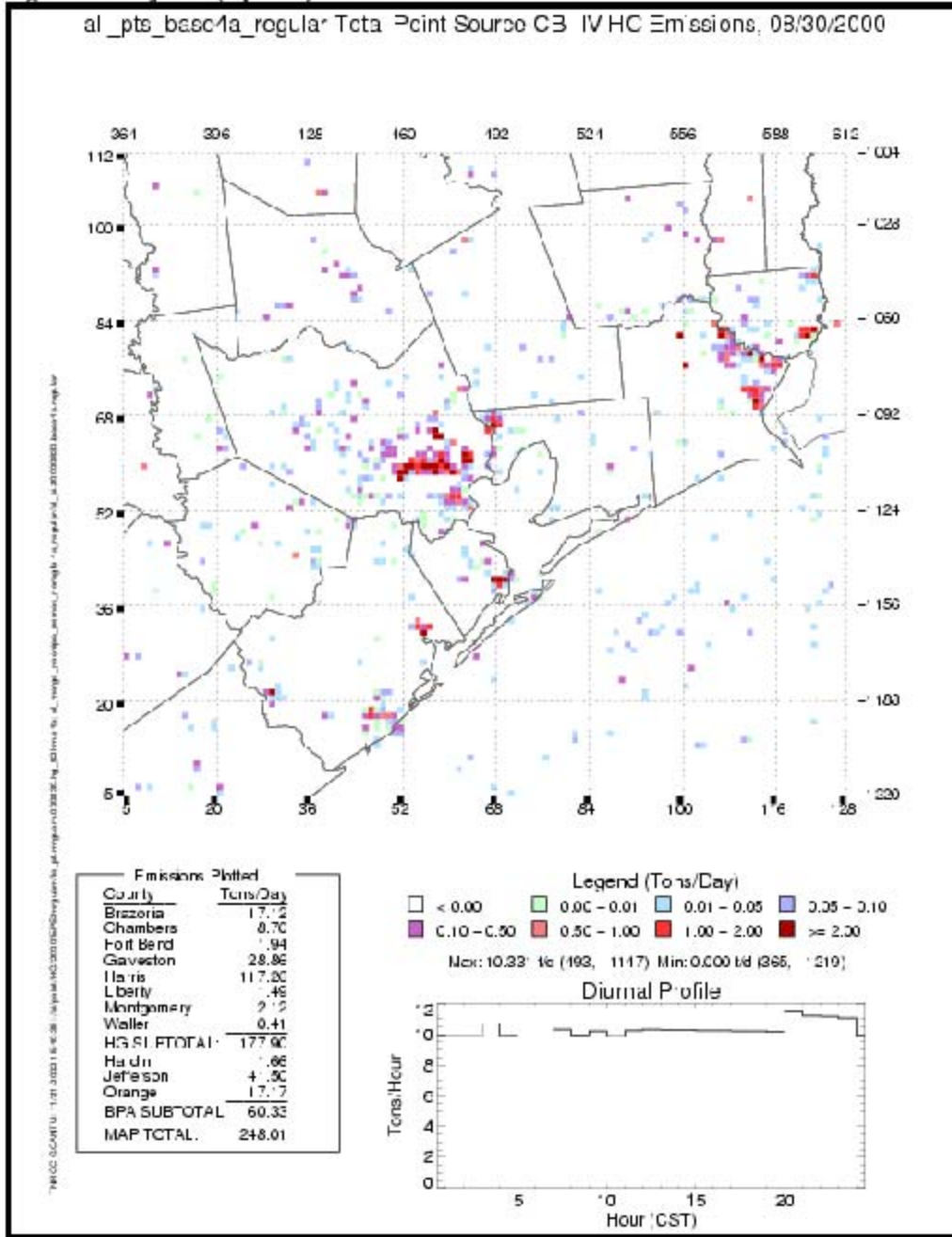


Figure 7. Total (reported+adjusted) modeled VOC in HGB.

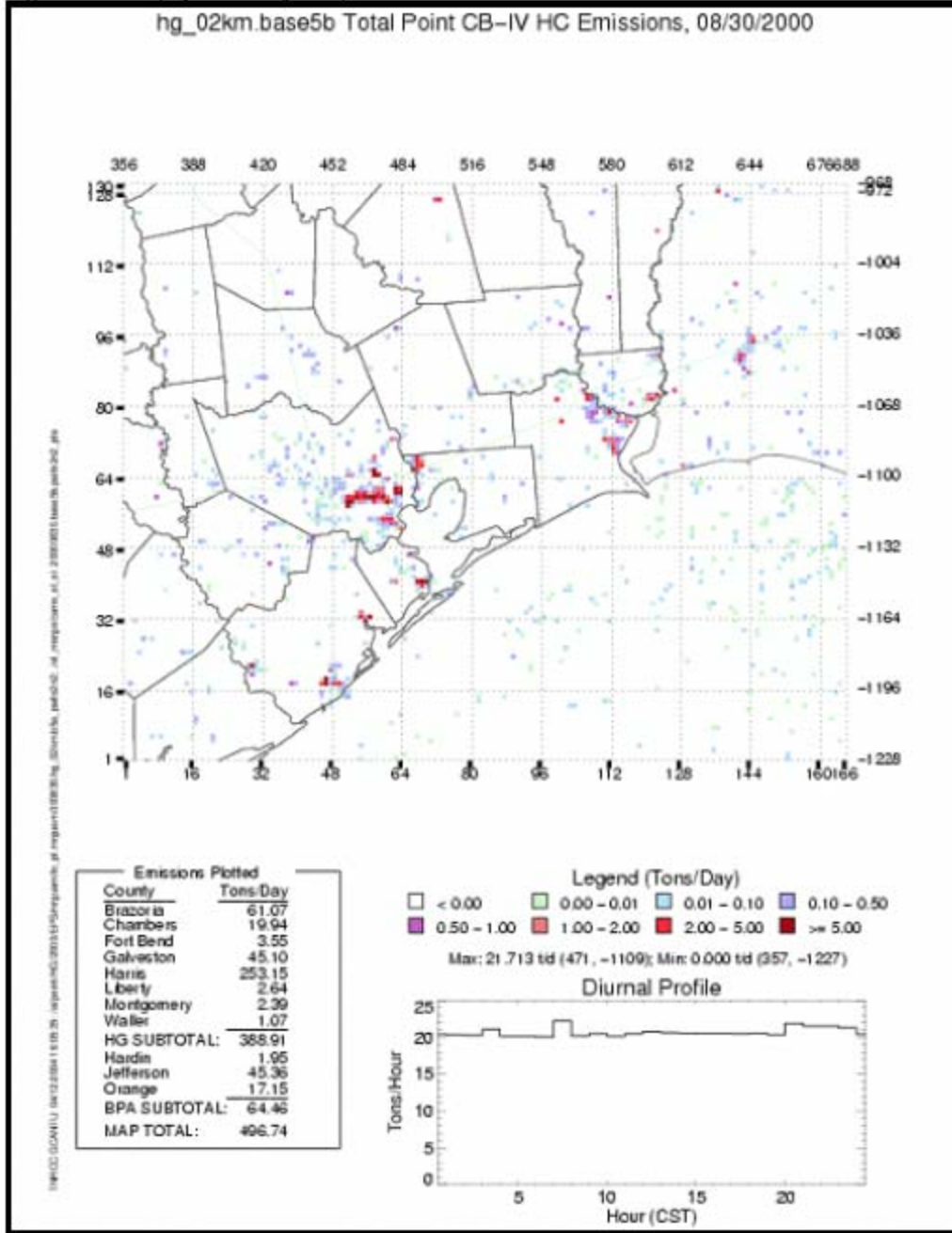
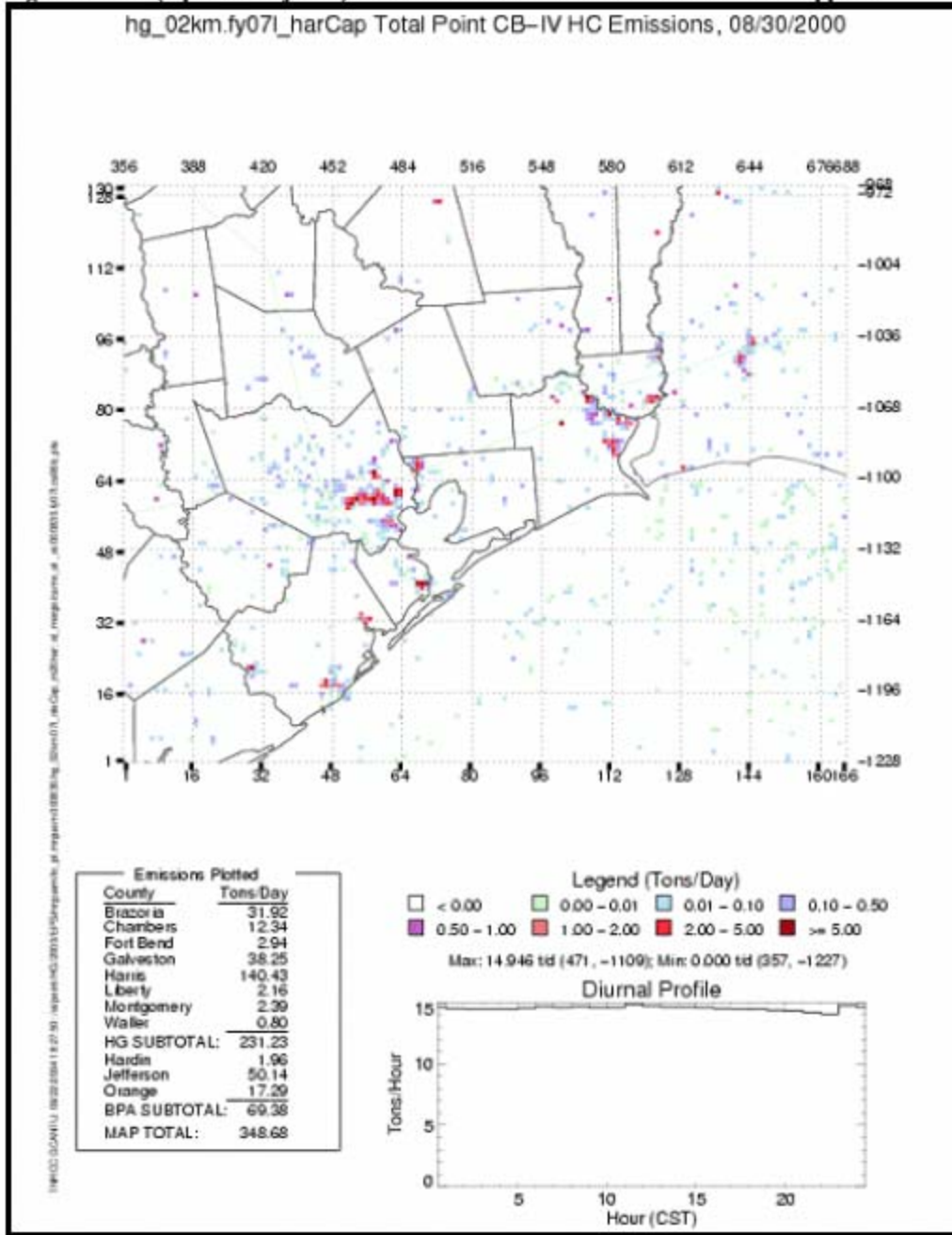


Figure 8. Total (reported+adjusted) modeled VOC in HGB after HRVOC controls applied.



HRVOC Rules

TCEQ adopted HRVOC rules in the December 2002 SIP and revised them in the December 2004 SIP revision. The rules addressed the two concerns that TCEQ agreed to address as part of the Consent Order: (1) Rapid formation of ozone and short-term variability, and (2) Steady-state and routine emissions. To address (1), the HRVOC rules call for a short-term cap of 1200 lb/hr sitewide limit on total HRVOC for all sites in HGB subject to the HRVOC rules of TCEQ Chapter 115. HRVOC is defined in the seven adjacent counties as ethene and propene. Sites in the seven adjacent counties agreed to an enforceable limit based on permit representations. To address (2), the HRVOC rules call for a long-term cap, an annual sitewide cap on total HRVOC for all sites in Harris County subject to the HRVOC rules of TCEQ Chapter 115. Trading is allowed under TCEQ Chapter 101 HECT (HRVOC Emissions Cap and Trade) program.

In general, fugitives are not subject to the HRVOC caps since they are not easily monitored at the levels that would be required to be effective. Everything else is essentially subject to the rule and some sort of monitoring, including the following units in HRVOC service: flares, cooling tower heat exchangers, and vent gas streams. The HRVOC process flow monitoring program was implemented in 2005.

The rules, as adopted through the December 2002 SIP revisions can be found at <http://www.tceq.state.tx.us/implementation/air/sip/dec2002hgb.html>

The rules, as adopted through the December 2004 SIP revisions, including HECT (HRVOC Emissions Cap and Trade) can be found at http://www.tceq.state.tx.us/implementation/air/sip/dec2004hgb_mcr.html

The enhanced HRVOC monitoring requirements of Chapter 115 (TCEQ's VOC rules) will provide TCEQ additional information regarding the emissions of less-reactive VOCs in two different ways. First, the point source HRVOC monitors will collect information on other VOCs as well. TCEQ is evaluating changes to the emission inventory data collection process to ensure that companies include this information with their emissions inventory. Second, the HRVOC monitoring will provide information on which types of sources (i.e., flares, cooling towers, vents) are contributing most to the emission under-estimation problem. This information will be used to focus any subsequent efforts on the sources that will provide the biggest air quality benefit.

Collateral VOC Reductions

Additional and less predictable emission reductions are also expected to occur as industries improve their monitoring capabilities and become more knowledgeable about their own HRVOC emissions. Collateral reductions of other VOCs that are present in HRVOC streams will also occur when the HRVOC streams are controlled. For example, a cooling tower that handles an HRVOC stream that has other VOC present will have extensive monitoring of the water to determine when a leak is present. When leaks are fixed, not only are HRVOC emissions controlled, but VOC emissions as well.

TCEQ rules require owner/operators of flares in HRVOC service to install flow meters and comply with maximum tip velocity and minimum heat content requirements to ensure proper combustion by the flare. The tip velocity and heat content requirements apply at all times, not only when the flare is combusting HRVOC streams. Because many of these flares are also used for non-HRVOC streams, the regulations will result in better combustion of other VOC streams as well. This improved combustion will reduce emissions of less-reactive VOCs.

Potential Reductions Resulting From Enhanced Monitoring and EMRS

Since 2003 TCEQ and the HRVOC regulated community have significantly expanded the real-time ambient monitoring network of specific VOCs. Evaluation of data collected since the installation of these monitors in the summer of 2003 has increased the confidence in the direction of this SIP strategy. Likewise, there is an indication that HRVOC concentrations are trending downward in advance of the HRVOC rule requirements. This downward trend is expected since, as with the experience of the Toxic Release Inventory, the awareness by industry of ambient concentrations often results in reductions of emissions well in excess of any mandatory regulatory program.

To increase the potential for success of this SIP strategy, a program to help industry respond rapidly to increases in ambient HRVOC concentrations detected by these monitors is under development. The Environmental Monitoring Response System (EMRS) is a cooperative monitoring venture between Houston Regional Monitoring Network, HGB area Industry and TCEQ which is designed to measure Photochemical Assessment Monitoring Sites (PAMS) VOC species close to point source clusters.

A primary goal of EMRS is to prevent HRVOC emissions from creating situations that may lead to high levels of ozone. This goal will be accomplished by the near real time monitoring and rapid response built into the program.

Other goals of EMRS include the ability to measure the effectiveness of HRVOC rules, to correlate HRVOC levels with ozone, to determine which other VOCs should also be considered HRVOC, to provide high resolution data that will allow Emissions Inventory improvements, and to provide a reasonable alternative to costly fence line monitoring.

Recent developments in emissions reconciliation

The HGB area has an extensive network of automatic gas chromatographs (auto-GCs), which measure ambient concentrations of many hydrocarbon species. During TexAQ5 II, in 2005 and 2006, twelve sites operated in Harris (8), Galveston (1), and Brazoria (3) counties. TCEQ is just one of many groups analyzing those data. This uniquely extensive and intensive sampling of hydrocarbons provides a rare opportunity to examine the reported hydrocarbon inventory and determine how well it correlates with ambient measurements. TCEQ is taking advantage of this opportunity by investigating improved methods to compare inventories with ambient measurements in a data-rich environment. One new technique being worked on now at TCEQ involves the use of the ISC (Industrial Source Complex) model, coupled with a technique known as Potential Source Contribution Function (PSCF)⁵.

The main difficulty in using ambient measurements to validate emissions inventories is the fundamental difference between the two kinds of data. Ambient monitors measure mixing ratios, which in this case are represented in "parts per billion carbon", while emission inventories are reported as mass emissions per unit time, usually "tons per day", making it impossible to compare the two directly. To make such a comparison, a good approach is to use an atmospheric dispersion model to estimate mixing ratios at monitor locations, based on reported emissions. TCEQ is using the ISC model to estimate what concentrations would be expected at the monitor locations, assuming the reported inventory is accurate.

The PSCF technique is commonly used to identify likely locations of emission sources based on ambient measurements at monitoring locations. It associates back trajectories ending at the site with measured mixing ratios observed at the ending time of the trajectory, then composites a large number of trajectories to see which areas were most often associated with high pollutant concentrations. Simply put, if trajectories passing through a given location were frequently associated with unusually high

concentrations at the monitor where the trajectory ends, there is a good chance there is an emission source at or near that location.

The technique being developed by TCEQ applies the PSCF to ambient measurements at the 12 auto-GCs, then repeats the process using the concentrations predicted with the ISC model at the same locations. The differences between the two resulting PSCF maps serve to estimate both the magnitude and locations of discrepancies between reported emissions and actual emissions. Figure 9 shows an original PSCF plot using observed mixing ratios of propylene (propene). Figure 10 shows the same plot using the ISC-modeled concentrations at these locations. Note that the darker areas indicate areas where emission sources likely reside. These areas largely coincide with the locations where point source emissions of propylene were reported in 2005. Differences in shading between the two plots indicate possible discrepancies between reported and actual emissions.

Figure 9. Original PSCF plot for propene.

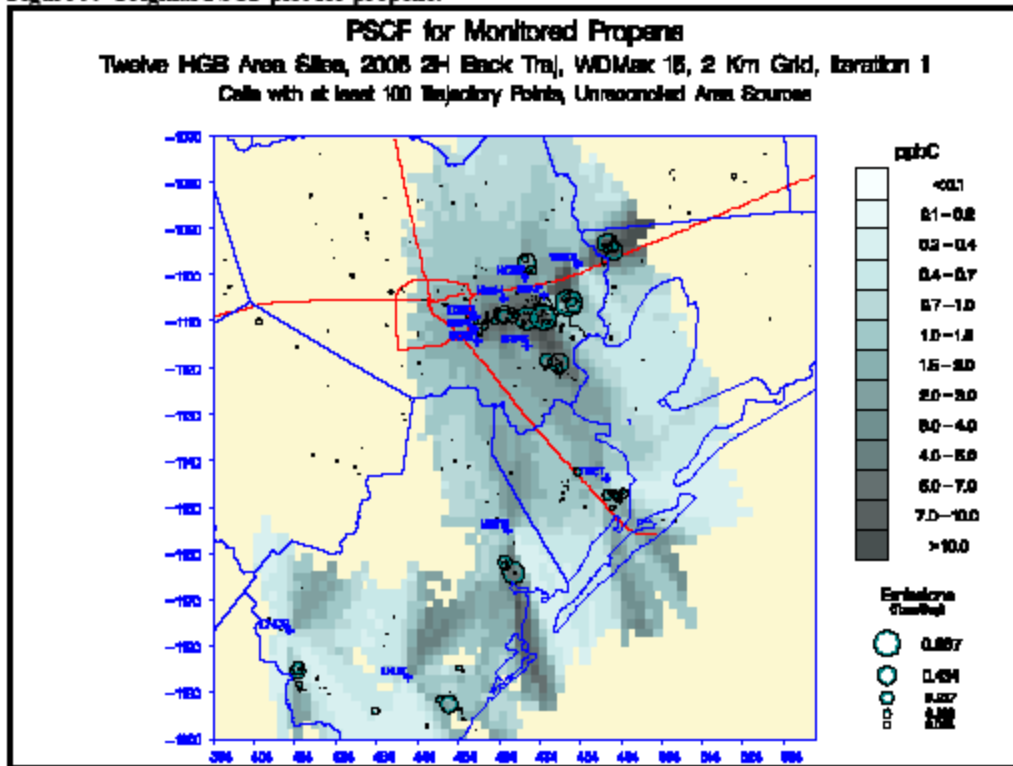
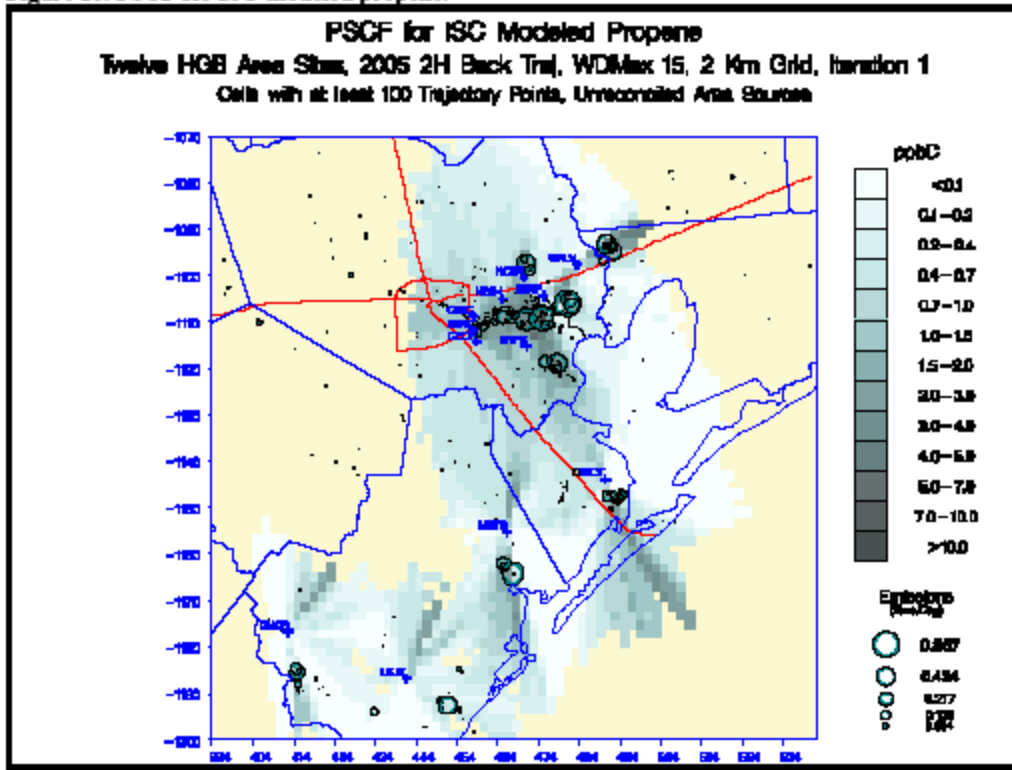
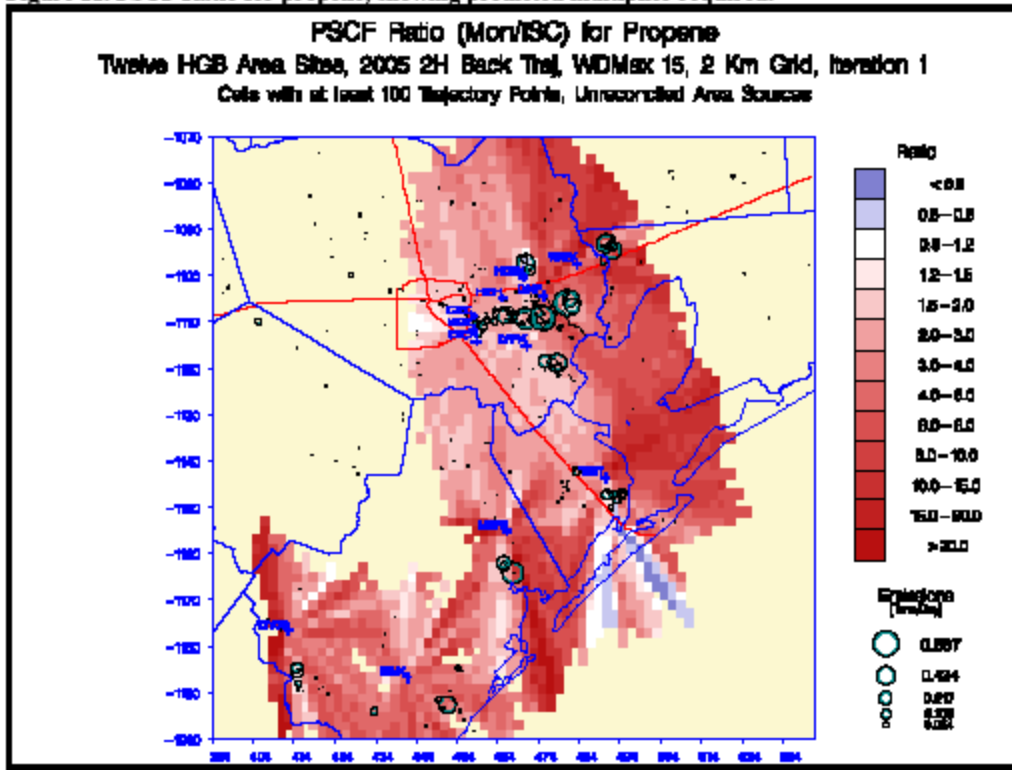


Figure 10. PSCF for ISC-modeled propene.



Generally, potential source areas are lighter than in the plot using measured concentrations, indicating that reported emissions do not fully explain measured concentrations. Taking the ratio of Figures 9 and 10 provides an estimate of how much additional emissions are needed and where, in order to reconcile the reported emissions with ambient concentrations. Figure 11 shows the ratio (monitored/ISC) for propene, in which the deeper the color, the higher the predicted multiplier needed for that grid cell. Note that the plot shows large areas of dark red which do not correspond to any point sources. The underlying discrepancies might be associated with area and/or mobile sources in these locations, or may simply be a result of proximity to large sources. In any case these areas have relatively low emissions compared with the larger point sources, so even a large ratio amounts to a fairly small discrepancy in total tons.

Figure 11. PSCF Ratio for propene, showing predicted multiplier required.



TCEQ has conducted some preliminary photochemical modeling using HRVOC emissions adjusted using the ISC/PSCF analysis and the results look promising. We are currently working on resolving the point sources from other emission sources in the analysis and expect to improve significantly on the results presented in this paper shortly.

EI Improvement Projects

The Emissions Assessment Section of TCEQ has also attacked the under-reporting issue head-on from several angles. First is the ever-improving EI Guidance Document that instructs EI preparers on the main issues that QA staff will be looking for in reported annual EIs. Topics of recent special interest have been flares, equipment leak fugitives, and cooling towers. Additional guidance is provided not only in the EI Guidance Document, but at semi-annual workshops.

Flares are of major concern. There is much uncertainty, and TCEQ has discovered many examples of flares that are labeled "emergency flares" that are operated more like routine thermal oxidizers. Topics for flares include flare minimization (i.e., what else can an operator do besides sending a stream to the flare) and DRE (destruction removal efficiency). Besides modifying our standard guidance on use of "default DRE", TCEQ funds many studies, such as flare speciation modeling using current CFD (computational fluid dynamics) software and projects with manufacturers and industry to study design parameters and alternatives to flaring.

TCEQ is a leader in the use of remote sensing of emissions. We now have hands-on experience with Differential Absorption LIDAR (DIAL), HAWK infrared video camera flyovers, and GasFindIR cameras onsite. The GasFindIR camera has been such a hit with industry safety managers, that several have been purchased to not only find potential safety hazards (leaking flammable or toxic VOCs), but to identify more routine leaks.

TCEQ has found several previously unreported sources of enormous amounts of VOC. One of these is Tank Landing Losses, originally found using a remote sensing technique. TCEQ discovered that many of the large tank farm operators (usually bulk tank-for-hire) allowed their floating roofs to land on the legs, allowing the volatile heel (leftovers in the bottom) to fill the head space and escape out the normal pathway of tank VOC loss. This amounted to more than 7000 tpy VOC increase in HGB alone. While these are rarely in HRVOC service, the total amount of VOC is significant. The retroactive emissions fees associated with these now-captured losses was significant. Similarly flash emissions from upstream oil and gas storage tanks amount to an estimate 80,000 tpy VOC increase in HGB and more than 750,000 tpy increase in statewide area source VOC emissions increase. Again, these were previously unreported, but the quantity of small oil and gas patches across Texas are enormous. Leaking barges in the intercoastal waterways or ship channels are another purported source of unreported or under-reported VOCs (again, not likely HRVOC, but may be in large quantity). The Coast Guard has agreed to maintain records of barge activity.

CONCLUSIONS

TCEQ has adopted new rules into its SIPs that will better quantify and reduce HRVOC emissions from four key industrial sources: fugitives, flares, process vents, and cooling towers. The adopted rules target HRVOC emissions. Analysis showed that limiting emissions of ethylene, propylene, 1,3-butadiene, and butenes in conjunction with an 80 percent reduction in NO_x is equivalent or better in terms of air quality benefit to that resulting from a 90 percent point source NO_x reduction requirement alone.

Ethylene, propylene, 1,3-butadiene, and butenes have been found to frequently cause high total reactivity conditions, and often dominate the total reactivity. Substantial emission reductions of these compounds are likely to make a large impact on high ozone, rapid ozone formation, and transient high ozone observed in the Houston area. Yet additional controls on many VOC sources will be necessary to reach attainment. TCEQ will continue to study VOC data available now and in upcoming years to determine whether additional compounds should be added.

Through the research conducted as a part of TexAQS and TexAQS II, HRVOC emissions have been acknowledged as a priority area needing both improved emission controls and better emission quantification. The enhanced monitoring requirements that have been established as part of the HRVOC rules will improve emission quantification. The HRVOC emissions in future models will be based on measured HRVOC emissions rather than on estimated emissions based on ambient ratios.

“What drives local ozone production?” This may be a changing answer that is already being addressed, as we transition away from the 1-hour ozone standard to the new 8-hour ozone standard for HGB. This is partially being addressed with the new ISC/PSCF emissions reconciliation technique in that the auto-GC data represent 8-hour averaging times.

EI reconciliation is being addressed feverishly from an EI Improvement perspective, with many ongoing and proposed projects and contracts. The bottom line for modelers is that we can always use higher resolution data – better spatial precision, better temporal precision, and better chemical (speciation) precision.

REFERENCES

1. Estes, Wharton, Boyer, Fang, et al, TCEQ report, "Analysis of Automated Gas Chromatograph Data from 1996-2001 to Determine VOCs with Largest Ozone Formation Potential", Nov 2002
http://www.tceq.state.tx.us/assets/public/implementation/air/am/docs/hgb/tsd1/attachment6-agc_voc.pdf
2. Cantu, G; TCEQ Report, "Speciation of Texas Point Source VOC Emissions for Ambient Air Quality Modeling"; July 2003
ftp://ftp.tceq.state.tx.us/pub/OEPAA/TAD/Modeling/HGAQSE/Modeling/EI/PointEI_VOC_Speciation_Report-GabrielCantu.pdf
3. Carter, William, University of California at Riverside, latest database work,
<http://pah.cert.ucr.edu/~carter/emitdb/>
4. Carter, William, University of California at Riverside, MIR reactivity scales, 2002
<ftp://ftp.cert.ucr.edu/pub/carter/SAPRC99/r02tab.xls>
5. Thomas, Ron, presentation, HEIRS referenced in
http://www.tceq.state.tx.us/assets/public/implementation/air/am/committees/pmt_set/20070227/07.02.27-rthomas-ei_update.pdf
6. TexasAQS findings, Bibliography of Technical Support Information Reviewed and Considered for Dec 2002 SIP
<http://www.tceq.state.tx.us/assets/public/implementation/air/am/docs/hgb/tsd1/AppendixD-bibliography.pdf>
7. TexAQS II findings, Bibliography on TCEQ webpage:
<http://www.tceq.state.tx.us/nav/eq/texaqsII.html>
8. Smith, Jim and Jarvie, John, TCEQ, personal correspondence, 2008

KEY WORDS

TCEQ
Texas Commission on Environmental Quality
Highly Reactive VOC
HRVOC
TexAQS 2000
TexAQS II
Houston-Galveston-Brazoria nonattainment area
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Photochemical modeling
TCEQ SIP
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