Fuel-Cycle Emissions for Conventional and Alternative Fuel Vehicles: An Assessment of Air Toxics

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Fuel-Cycle Emissions for Conventional and Alternative Fuel Vehicles: An Assessment of Air Toxics

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Notation

Acronyms and Abbreviations

3WPFI	three-way catalytic converter with fuel injection
AAQIRP	Auto/Oil Air Quality Improvement Research Program
AC	acetaldehyde
AFV	alternative fuel vehicle
ANL	Argonne National Laboratory
AP42	EPA Compilation of Air Pollutant Emission Factors
Bi-CNGV	Bi-fuel Compressed Natural Gas Vehicle
BU	1,3-butadiene
BZ	benzene
C_2H_5OH	ethanol
C_3H_8	propane
C_4H_6	1,3-butadiene
C_6H_6	benzene
CAAA	Clean Air Act Amendments
CARB	California Air Resources Board
CARFG3	California Phase 3 reformulated gasoline
CATEF	California Air Toxic Emission Factor database
CD	conventional diesel
CG	conventional gasoline
CH_3CHO	acetaldehyde
CH_4	methane
CI	compression ignition
CIDI	compression ignition, direct injection
CNG	compressed natural gas
CNGV	compressed natural gas vehicle
CO	carbon monoxide
CO_2	carbon dioxide
CR	catalytic reduction
CURE	Cancer Unit Risk Estimate
CV	conventional vehicle
DFA	direct-flame afterburner
DOE	U.S. Department of Energy
E200	percent volume of the distillation fraction at 200 ºF
E300	percent volume of the distillation fraction at 300 ºF
E50	mixture of 50% ethanol and 50% gasoline (by volume)
E85	mixture of 85% ethanol and 15% gasoline (by volume)
EF	emission factor
EIA	Energy Information Administration

EPA	U.S. Environmental Protection Agency
ETBE	ethyl tertiary butyl ether
EtOH	ethanol
EV	electric vehicle
FBC	fluidized bed combustion
FCC	fluid catalytic cracking
FFV	flexible fuel vehicle
FGR	flue gas recirculation
FIRE	EPA Factor Information Retrieval database
FRFG2	federal Phase 2 reformulated gasoline
GHG	greenhouse gas
GREET	Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation
GRI	Gas Research Institute
GV	gasoline vehicle
HAP	hazardous air pollutant
HC	hydrocarbon
HCHO	formaldehyde
HDE	heavy-duty engine
HEV	hybrid electric vehicle
HEV1	grid-connected hybrid electric vehicle operating on CARFG3
HEV2	grid-independent hybrid electric vehicle operating on FRFG2
HEV3	grid-independent hybrid electric vehicle operating on CD
IGCC	integrated gasification with combined cycle
IRIS	Integrated Risk Information System
L&E	EPA Locating and Estimating emissions documents
LDGT1	light-duty truck with a gross vehicle weight of less than 6,000 pounds
LDGT2	light-duty truck with a gross vehicle weight of 6,001–8,500 pounds
LDGV	light-duty gasoline vehicle
LDV	light-duty vehicle
LNB	low-NO_x burner
LNG	liquefied natural gas
LPG	liquefied petroleum gas
LPGV	liquefied petroleum gas vehicle
M50	mixture of 50% methanol and 50% gasoline (by volume)
M85	mixture of 85% methanol and 15% gasoline (by volume)
MeOH	methanol
MPV	maximum possible value
MTBE	methyl tertiary butyl ether
MY	model year
N_2O	nitrous oxide
NAFDC	National Alternative Fuels Data Center
NG	natural gas
NMHC	nonmethane hydrocarbon
NMOG	nonmethane organic gas
NMTOC	nonmethane total organic compound
NO	nitrogen oxide

NO_x	nitrogen oxides
NREL	National Renewable Energy Laboratory
O_2	oxygen
OEM	original equipment manufacturer
$OH^\bullet$	hydroxyl radical
PAH	polynuclear aromatic hydrocarbon
PAN	peroxyacetyl nitrate
PFB/CC	pressurized fluidized-bed combustion with combined cycle
PM	particulate matter
PM_{10}	particulate matter with aerodynamic diameter of less than 10 microns
POM	polycyclic organic matter
RFG	reformulated gasoline
RVP	Reid vapor pressure
SCR w/NH_3	selective catalytic reduction with ammonia injection
SI	spark ignition
SI/SCR	steam injection/selective catalytic reduction
SI-AFV	spark-ignition alternative fuel vehicle
SO_x	sulfur oxides
T&S	transportation and storage
T&S&D	transportation, storage, and distribution
T/TOG	toxic/total organic gas fraction
T/VOC	toxic/volatile organic compound fraction
TCC	thermal catalytic cracking
TECA	total energy-cycle analysis
THC	total hydrocarbon
TOC	total organic compound
TOG	total organic gas
VMT	vehicle mile traveled
VOC	volatile organic compound

Units of Measure

°C	degree Celsius
°F	degree Fahrenheit
μg	microgram
atm	atmosphere
bbl	barrel
Btu	British thermal unit
g	gram
gal	gallon
h	hour
J	Joule
L	liter
lb	pound
m^3	cubic meter

mi	mile
mL	milliliter
ng	nanogram
ppb	part per billion
ppm	part per million
psi	pound per square inch

Acknowledgments

Abstract

This report provides information on recent efforts to use the Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation (GREET) fuel-cycle model to estimate air toxics emissions. GREET, developed at Argonne National Laboratory, currently addresses greenhouse gas emissions and such regulated emissions as volatile organic compounds, nitrogen oxides, and carbon monoxide. Because mobile sources are major contributors to air toxic inventories, GREET is being modified to account for the following important toxic pollutants: *acetaldehyde, benzene, 1,3-butadiene,* and *formaldehyde*. This study is significant because it is the first to consider fuel-cycle emissions of these pollutants for alternative transportation fuels and advanced vehicle technologies.

For this study, we evaluated air toxics emissions of the following fuels and vehicle technologies: conventional gasoline, conventional diesel, federal reformulated gasoline, California reformulated gasoline, compressed natural gas, liquefied natural gas, methanol, ethanol, battery-powered electric vehicles, and hybrid electric vehicles. Fuel-cycle analysis results show that all of these fuels and vehicle technologies help reduce benzene emissions. Almost all of them help reduce 1,3-butadiene emissions. Use of ethanol in E85 or reformulated gasoline, however, leads to increased acetaldehyde emissions, and use of methanol, ethanol, and compressed natural gas may result in increased formaldehyde emissions. When the modeling results for the four air toxics are considered together with their cancer risk factors, all the fuels and vehicle technologies demonstrate air toxics emission reduction benefits.

Section 1
Introduction

Recent data indicate that, in many parts of the country, mobile sources are responsible for the largest portion of emissions of certain air toxic pollutants. These airborne pollutants are either carcinogenic or pose some other significant human health threat. Mobile source toxic emissions are attributed to vehicles powered by petroleum-based fuels that release a variety of complex chemicals when the fuels are burned or evaporated. The use of alternative fuel vehicles (AFVs) that operate on nonpetroleum-based fuels is being promoted in many parts of the country. Although the transition to AFVs will likely lead to lower toxic emissions, the extent of these emissions reductions is not clear.

The purpose of this project is to extend our understanding of toxic emissions from conventional vehicles (CVs) and AFVs by considering the total fuel cycle for selected transportation technologies. The Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation (GREET) model, developed at Argonne National Laboratory (ANL), provides a mechanism to analyze fuel-cycle emissions; however, GREET does not currently include toxic components.[1] On the basis of the results of this project, GREET will eventually be modified to include the following four air toxics: *acetaldehyde, benzene, 1,3-butadiene*,[2] and *formaldehyde*.

The project consists of two phases. The first focused on data collection and an "off-line" calculation of toxic fuel-cycle emissions for near-term CVs and AFVs.[3] The second phase will focus on the reprogramming of GREET and the refinement of data, especially for upstream and long-term technologies. This report presents the background and results for the first phase of the project.

During phase 1, we addressed toxic emissions from near-term light-duty vehicles (LDVs) operating on the following fuels: conventional gasoline (CG), reformulated gasoline (RFG) (Federal Phase 2 [FRFG2] and California Phase 3 [CARFG3]), M85 (a mixture of 85% methanol and 15% gasoline by volume), E85 (a mixture of 85% ethanol and 15% gasoline by volume), compressed natural gas (CNG) (for both dedicated and bi-fuel vehicles), and liquefied petroleum gas (LPG) (for dedicated vehicles). We also evaluated fuel-cycle emissions from electric vehicles (EVs) and hybrid electric vehicles (HEVs).

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[1] For a detailed description of GREET, including its analytical methodology and descriptions of each of the technologies considered, see Wang 1999a,b.

[2] We use "1,3-butadiene" and "butadiene" interchangeably throughout this report.

[3] We considered an "off-line" calculation because GREET has not been completely recoded to conduct this analysis transparently.

Data for the downstream (i.e., vehicle operation) components of the fuel cycle are more readily available than upstream data, although there are some gaps and uncertainties associated with the data for vehicles operating on RFG and alternative fuels. Because data for upstream processes are somewhat limited at this time, we analyzed only certain processes in our study. However, researchers generally believe that the processes chosen are the greatest contributors of toxic emissions along the upstream pathway. This report accounts for toxic emissions from the following components of the upstream process: fuel combustion that occurs throughout the upstream process; fuel production processes (e.g., venting during petroleum refining); and transportation, storage, and distribution (T&S&D) of fuels.

The report is divided into seven sections. Section 2 provides background information on each of the four air toxic pollutants considered, including chemical properties and toxic characteristics. Section 3 presents data for the upstream fuel cycle for the fuels and upstream components listed above. Data for the downstream component of the fuel cycle are provided in Section 4. Section 5 presents our estimated toxic emissions results based on calculations using the GREET model. Sections 6 and 7 present a summary and references.

2.1 Air Toxics and Mobile Sources

Section 112 of the Clean Air Act Amendments (CAAA) of 1990 tasked the U.S. Environmental Protection Agency (EPA) with regulating 188 hazardous air pollutants (HAPS) that present a "significant risk" to human health.[4] EPA was further assigned to identify those toxic pollutants that "posed the greatest potential threat to public health in the largest number of urban areas" (EPA 1998a). In its *Draft Integrated Urban Air Toxics Strategy*, EPA listed 33 of the most threatening air toxics for urban areas (EPA 1998a); these are provided in Table 2.1.

Of all air toxics emitted in 1993, EPA estimated that about 24% (by mass) were from major stationary sources, 34% were from area sources, and 42% were from mobile sources. The four air toxics highlighted in Table 2.1 and evaluated in our study — *acetaldehyde, benzene, 1,3-butadiene,* and *formaldehyde* — are generated primarily by mobile sources.[5] EPA estimates that 60% of total benzene emissions, 56% of 1,3-butadiene emissions, 39% of acetaldehyde emissions, and 33% of formaldehyde emissions are from mobile sources[6] (EPA 1993; 1999d).

Table 2.1 Air Toxics Identified by EPA[a]

Acetaldehyde	Coke oven emissions	Mercury compounds
Acrolein	1,4-dichlorobenzene	Methyl chloride
Acrylonitrile	1,3-dichloropropene	Methylene diphenyl disocynate
Arsenic compounds	2,3,7,8-tetrachlorodibeno-p-dioxin	Methylene chloride
Benzene	Ethylene dibromide	Nickel compounds
Bis(2-ethylhexyl)phthalate	Ethylene dichloride	Polycyclic organic matter
1,3-Butadiene	Ethylene oxide	Propylene dichloride
Cadmium compounds	***Formaldehyde***	Quinoline
Carbon tetrachloride	Hydrazine	Tetrachloroethylene
Chloroform	Lead compounds	Trichloroethylene
Chromium compounds	Manganese compounds	Vinyl chloride

[a] From EPA 1998a (Table 1).

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[4] Section 112(b) of the CAAA of 1990 actually lists 189 air toxics, but one, *caprolactam*, was later de-listed.

[5] In tables and equations in this report, we commonly refer to acetaldehyde as "AC," benzene as "BZ," butadiene as "BU," and formaldehyde as "HCHO."

[6] The four toxic pollutants studied in this report are not the *only* toxics generated by mobile sources. For example, polycyclic organic matter (POM) is an important class of toxics representing organic compounds made up of multiple, fused benzene rings. POM can be released as a gas (at weights less than 230 grams per mole [g/mole]) but is more frequently adsorbed on the surface of particulate matter (PM). Mobile sources are estimated to contribute 63% of POM inventories in urban areas (Rosenbaum et al. 1999). However, sufficient data are unavailable for POM and other compounds to justify a fuel-cycle analysis at this time. As more data surface, our study may be expanded to include additional toxics.

Similar estimates were made by Rosenbaum et al. (1999), who report that 46% of acetaldehyde, 63% of benzene, 59% of 1,3-butadiene, and 45% of formaldehyde concentrations found in the ambient environment are contributed by mobile sources.

These mobile source pollutants are either presumed or known human carcinogens. The expected numbers of additional annual cancer deaths caused by these pollutants are listed in Table 2.2; EPA calculated these values in a study conducted in 1993 (EPA 1993). Table 2.2 also lists each pollutant's Cancer Unit Risk Estimate (CURE) — the increased lifetime cancer risk caused by a continuous lifetime (i.e., 70-year) exposure to a 1.0 microgram per cubic meter ($\mu g/m^3$) increase in a given pollutant's concentrations. For example, the CURE for acetaldehyde implies an increased risk of cancer of 2.2×10^{-6} for every 1.0 $\mu g/m^3$ increase in lifetime exposure.[7]

The CURE values are taken from EPA's most recent published estimates (EPA 2000). EPA is required to consider regulating these mobile source emissions under Section 202(l) of the Clean Air Act. According to the EPA values, the order of toxicity (from highest to lowest) for the four toxics considered in our study is 1,3-butadiene, formaldehyde, benzene, and acetaldehyde. Although they have been the focus of EPA investigations primarily because of their carcinogenic potential, these air toxics pose other, non-carcinogenic health concerns. Some of these additional problems are discussed in the following sections.

Besides the four pollutants examined in our study, Table 2.2 also includes diesel PM, because PM may be a major cause of cancer in urban areas. Earlier versions of GREET include PM fuel-cycle emissions estimates. We chose to include PM in Table 2.2 to allow readers to compare the relative toxicity of PM to that of the other four pollutants. As the table shows, if the PM CURE value adopted by EPA in 1993 is used, the number of PM-caused cancer deaths is smaller than the number caused by 1,3-butadiene. However, the California Air Resources Board (CARB) recently concluded that the PM CURE is much higher than previously estimated (CARB 1998). If the CARB-adopted CURE value for PM is used, the number of cancer deaths caused by PM would be much higher than the number caused by the four air toxics combined. Woodruff et al. (2000) recently published a study on the cancer risk from inhaled HAPs based on 1990 exposure estimates. Woodruff and his colleagues concluded that POM (the major carcinogenic constituent in diesel PM) was responsible for 40% of the total estimated lifetime HAP cancer cases. Butadiene, formaldehyde, and benzene were responsible for 17%, 8%, and 7% of these cancer cases, respectively. These differences are attributable to a combination of the pollutants' different CURE values and the higher exposure levels associated with PM. Nevertheless, this finding implies that PM can be potentially more dangerous that the four air toxics together. Obviously, there is a large uncertainty in the PM CURE value. Evaluation of PM emissions is beyond the scope of this study.

The purpose of the following section is to present background information on each of the four air toxics considered in this report, including chemical properties, toxic effects, and major

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[7] For more information on lifetime cancer risks and interpretation of CUREs, see EPA 1999. Calabrese and Kenyon (1991) and Gratt (1996) also provide an overview of air toxics and risk assessment.

Table 2.2 Cancer Unit Risk Estimates and Annual Expected Cancer Deaths Caused by Exposure to Mobile Source Air Toxics[a]

Pollutant	CURE[b] $(\mu g/m^3)^{-1}$	Annual Expected Cancer Deaths			
		1990	1995	2000	2010
Acetaldehyde	2.2×10^{-6}	5.3	3.6	2.8	3.0
Benzene[c]	8.3×10^{-6}	70	43	35	35
1,3-Butadiene[d]	2.8×10^{-4}	304	209	176	204
Formaldehyde	1.3×10^{-5}	44	28	21	22
Totals		**423**	**283**	**235**	**264**
Diesel PM[e]	1.7×10^{-5}	109	66	39	27
Diesel PM[f]	3.0×10^{-4}	19,235	1,165	688	476

[a] From EPA 1993 (using base-case analysis results) and EPA 2000.

[b] CURE is the "Cancer Unit Risk Estimate," which is the increased lifetime cancer risk caused by continuous lifetime exposure to a 1.0 $\mu g/m^3$ increase in the concentration of a given pollutant. These CURE values are taken from EPA 2000 unless otherwise noted. The annual expected cancer deaths are based on emissions and exposure modeling from 1993, which may no longer be current. In addition, the CURE values identified in EPA 1993 vary somewhat from CURE values used by other regulatory agencies. For example, CARB (1997a) has identified the following CURE values for the pollutants under study:

- Acetaldehyde 2.7×10^{-6} $(\mu g/m^3)^{-1}$
- Benzene 2.9×10^{-5} $(\mu g/m^3)^{-1}$
- 1,3-Butadiene 1.7×10^{-4} $(\mu g/m^3)^{-1}$
- Formaldehyde 6.0×10^{-6} $(\mu g/m^3)^{-1}$

[c] The benzene CURE value is from EPA 1993. Newly released data by EPA (2000) indicate benzene inhalation CURE values between 2.2×10^{-6} and 7.8×10^{-6}. These values are not significantly different than the 1993 values. Because EPA calculated expected cancer deaths by using the 1993 values, we use that value in the table.

[d] Note that the 1,3-butadiene CURE information is largely based on data from mice. EPA has concluded that the metabolism of this compound in mice is not applicable to humans, and a revised risk assessment is now under way (Cook 1999). We retain the "official" CURE value reported in the Integrated Risk Information System (IRIS) database (EPA 2000) because the final revised value has not yet been released.

[e] This diesel PM CURE is from EPA 1993. New health assessments to revise this CURE value are under way.

[f] This diesel PM CURE is from CARB 1998. Expected cancer deaths were calculated by multiplying the EPA expected deaths by the ratio of the CARB CURE to the EPA CURE.

sources. Emission factors for each of the upstream and downstream sources of each pollutant are considered in later sections.

2.2 Properties and Inventory of Toxic Emissions Sources

2.2.1 Acetaldehyde

2.2.1.1 Chemical and Physical Properties

Acetaldehyde (CH_3CHO) is a saturated *aldehyde* with a "pungent and suffocating odor" at high concentrations, but a "fruity and pleasant" odor at diluted concentrations (EPA 1993). Acetaldehyde is colorless, volatile, and flammable at room temperature. Its chemical structure is shown in Figure 2.1. EPA classifies acetaldehyde as a *B2 Probable Human Carcinogen*, a classification for chemicals with inadequate human data but sufficient animal study evidence to suggest carcinogenicity (EPA 2000).

Important chemical and physical properties of acetaldehyde are listed in Table 2.3. Acetaldehyde is lighter than water, but its vapor is heavier than air. It is soluble in water, alcohol, ether, acetone, and benzene. Acetaldehyde is very reactive in the atmosphere, and is a major component of photochemical smog.
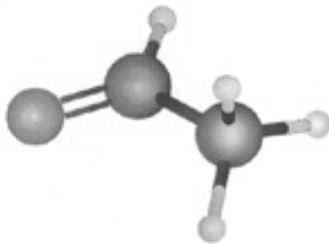
Figure 2.1 Structure of Acetaldehyde

2.2.1.2 Toxic Effects

The destruction and formation of acetaldehyde in the atmosphere is similar to the same processes for formaldehyde, discussed in Section 2.2.4. Acetaldehyde is frequently formed through the oxidation of *olefins* and *paraffins* such as propane (C_3H_8) and ethanol (C_2H_5OH) (EPA 1993; NRC 1981). Acetaldehyde is destroyed in the atmosphere through reactions with the hydroxyl radical ($OH^\bullet$) and other chemical species to ultimately form formaldehyde or peroxyacetyl nitrate (PAN), a major constituent of photochemical smog. Acetaldehyde can also undergo photolysis, in which the products that are formed can react with nitrogen oxide (NO) to form formaldehyde. The residence time of acetaldehyde in the atmosphere is on the order of a few hours during clear summer days and more than 60 hours on clear winter days (EPA 1993, Table 8-5).

Table 2.3 Chemical and Physical Properties of Acetaldehyde[a]

Property	Value
Molecular weight	44.06 g/mole
Melting point	-123.5°C
Boiling point	20.16°C
Density at 20°C	0.783 g/mL
Vapor pressure at 25°C	0.97 atm
Flash point (closed cup)	-38.0°C
Solubility in water at 25°C	Infinite

[a] From EPA 1993 (Table 8-1).

Acetaldehyde concentrations in ambient air have been measured for a number of urban and rural areas. Concentrations are typically less than 3 $\mu g/m^3$; mobile source contributions represent about one-third of that value (EPA 1993, Tables 8-6, 8-7, and 8-8). These estimates include both primary and secondary acetaldehyde formation. More recently, EPA has estimated that exposure

to acetaldehyde caused by mobile sources ranged from 0.2 µg/m^3 to 0.4 µg/m^3 in 1996, depending on vehicle populations and the predominant fuel used (EPA 1999a, Table 7-6).[8]

Inadequate human data (based on only one occupational exposure study) but sufficient animal data are available to suggest that acetaldehyde is a probable human carcinogen. In animal studies, rats and hamsters exposed to acetaldehyde through inhalation had an increased incidence of nasal and laryngeal tumors. Thus, EPA has identified acetaldehyde as a *B2 Probable Human Carcinogen* (EPA 2000).

Recent assessments have estimated acetaldehyde's CURE at 2.2×10^{-6} (µg/m^3)$^{-1}$. This value means that, for every increase in lifetime exposure of 1.0 µg/m^3, an individual's lifetime cancer risk increases by 2.2×10^{-6}.

2.2.1.3 Major Sources

Acetaldehyde is formed during the incomplete combustion of hydrocarbon-based fuels. It is present as a primary pollutant in tailpipe emissions from both gasoline- and diesel-fueled vehicles. Catalytic converters have been shown to reduce acetaldehyde in approximate proportion to reductions in total hydrocarbons (EPA 1993). Acetaldehyde can be formed as a secondary pollutant in the atmosphere. Under the right conditions, volatile organic compound (VOC) precursors react to form acetaldehyde. Much ongoing debate and research have been focused on the secondary formation of acetaldehyde. For this report, we consider only primary acetaldehyde emissions, although secondary acetaldehyde formation might surpass primary emissions under some atmospheric conditions (CARB 1999).

Major sources of acetaldehyde, annual tons emitted for 1990 (the most recent year in which data are available), and percent of total acetaldehyde emissions are listed in Table 2.4. Note that on-road vehicles represent the second-largest source of acetaldehyde emissions in the nation.

2.2.2 Benzene

2.2.2.1 Chemical and Physical Properties

Benzene (C_6H_6) is a clear, colorless, aromatic hydrocarbon that has a "sickly, sweet odor." Its structure, a hexagonal ring of carbon atoms with bonded hydrogen atoms, is a common building block for many other chemical species (those in the family of *aromatics*). Figure 2.2 depicts benzene's chemical structure. The chemical and physical properties of benzene are listed in Table 2.5.

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[8] This exposure estimate is not corrected for atmospheric transformation, such as the formation of secondary acetaldehyde from other emissions components or the decay of acetaldehyde caused by atmospheric processes.

Table 2.4 1990 National Acetaldehyde Emission Estimates by Source Category for Sources with 2% or Greater Contribution[a]

	Annual Emissions	
Source Category	**Ton/yr**	**Percent[b]**
Mobile		
Nonroad vehicles and equipment	35,300	25.7
On-road vehicles	28,200	20.5
Stationary		
Forest and wildfires	27,600	20.0
Prescribed burnings	21,800	15.9
Pulp and paper (noncombustion)	8,950	6.5
Pulp and paper (combustion)	3,860	2.8
Other	11,850	8.6
Totals	137,560	100

[a] From EPA 1999b (adapted from Table 6-7).

[b] Numbers may not add up to 100% because they have been rounded.

2.2.2.2 Toxic Effects

Figure 2.2 Structure of Benzene

Table 2.5 Chemical and Physical Properties of Benzene[a]

Property	Value
Molecular weight	78.11 g/mole
Melting point	5.5°C
Boiling point	80.1°C
Density at 20°C	0.879 g/mL
Vapor pressure at 25°C	0.13 atm
Flash point (closed cup)	-11.1°C
Solubility in water at 25°C	1.8 g/L

[a] From EPA 1993 (Table 5-1).

Benzene has low solubility and is relatively stable in the atmosphere, with residence times of 2 to 6 days under summer conditions (EPA 1988; Ligocki et al. 1991; CARB 1984; Nielsen et al. 1983). Exposure to benzene from motor vehicle emissions makes up about 25% of the total population exposure (tobacco smoke accounts for roughly 50%) (Wallace 1989).

Benzene concentrations in ambient air have been measured for a number of urban and rural areas. Concentrations vary from less than 1 $\mu g/m^3$ to upwards of 7 $\mu g/m^3$, but usually range from around 2 to 3 $\mu g/m^3$ in urban areas, with motor vehicles contributing about 60% of that total (EPA 1993, Table 5-6). In some microenvironments (e.g., gasoline service stations), benzene concentrations of over 250 $\mu g/m^3$ have been measured, although these are short-term, acute exposures for the majority of the population (Wilson 1991). More recent estimates by EPA indicate that on-road vehicles may increase exposure by 0.5 to 1.5 $\mu g/m^3$ in the urban environment, depending on vehicle populations and predominant fuel formulations (EPA 1999a, Table 7-5).

Benzene has been found to cause cancers and leukemia in laboratory animals and human populations subjected to long-term exposure (EPA 2000). EPA has classified benzene as a *Group A Known Human Carcinogen* on the basis of various human epidemiological studies that focused on occupational inhalation exposure (Rinsky et al. 1981; Wong et al. 1983; Ott et al. 1987). This classification is reserved for pollutants for which there is sufficient evidence from

epidemiological studies to develop a causal relationship between the substance and the incidence of cancer.

Recent assessments have estimated benzene's CURE to be between 2.2×10^{-6} and 7.8×10^{-6} (recently adjusted from 8.3×10^{-6}) (EPA 2000). This value implies that, for every increase in lifetime exposure of 1.0 μg/m^3, an individual's lifetime cancer risk increases by 2.2 to 7.8×10^{-6}.

2.2.2.3 Major Sources

The major source of benzene, on-road vehicles, represents almost 50% of the total benzene emissions inventory. Benzene is a volatile component of gasoline and other fuels and is emitted from vehicles as both an exhaust gas and in evaporative emissions. Depending on control technology and fuel type, benzene makes up about 3–5% of the total organic gas (TOG) exhaust emissions and about 1% of the evaporative emissions for conventional gasoline vehicles. Exhaust benzene is from either unburned benzene or benzene formed during the combustion of other aromatic and non-aromatic compounds found in gasoline (EPA 1988). Data have shown that benzene emissions from motor vehicles are predominantly from gasoline vehicles; diesel vehicles contribute only about 3% of the total mobile source benzene emissions (Carey 1987). In addition, evaporative emissions of benzene are relatively small compared to exhaust emissions (EPA 1993).

Other sources of benzene include biomass combustion, oil and gas production, petroleum refining, and gasoline distribution, discussed at greater length in Section 3. These sources and their annual emissions are listed in Table 2.6.

2.2.3 1,3-Butadiene

2.2.3.1 Chemical and Physical Properties

Butadiene (C_4H_6) is a colorless, flammable, aromatic hydrocarbon that has a pungent odor (EPA 1993). Its structure is shown in Figure 2.3. Butadiene is structurally related to known carcinogens and, like acetaldehyde, has been classified as a *B2 Probable Human Carcinogen* by EPA (2000).

The chemical and physical properties of 1,3-butadiene are listed in Table 2.7. Butadiene is relatively insoluble in water and slightly soluble in methanol and ethanol. Butadiene has a very high rate of reactivity in the atmosphere, and thus a short atmospheric lifetime.

2.2.3.2 Toxic Effects

Butadiene is a straight-chain molecule, as shown in Figure 2.3. The double bonds that make 1,3-butadiene an *alkene* also create opportunities for quick reaction with OH$^\bullet$. Thus, 1,3-butadiene has a very short residence time in the atmosphere: less than an hour during summer days (EPA 1993). Oxidation of 1,3-butadiene can form formaldehyde and acrolein, two toxic substances in their own right (Ligocki et al. 1991). Although the secondary production of

Table 2.6 1990 National Benzene Emission Estimates by Source Category for Sources with 2% or Greater Contribution[a]

Source Category	Annual Emissions	
	Ton/yr	Percent[b]
Mobile		
On-road vehicles	209,000	53.4
Nonroad vehicles and equipment	71,400	18.3
Stationary		
Forest and wildfires	29,900	7.6
Prescribed burning	25,700	6.6
Oil and gas production	18,200	4.7
Gasoline distribution stages I and II	10,800	2.8
Petroleum refining	7,830	2.0
Other	18,600	7.4
Totals	391,400	100

[a] From EPA 1999b (adapted from Table 6-12).

[b] Numbers may not add up to 100% because they have been rounded.

Figure 2.3 Structure of Butadiene

Table 2.7 Chemical and Physical Properties of 1,3-Butadiene[a]

Property	Value
Molecular weight	54.09 g/mole
Melting point	-108.91°C
Boiling point	-4.41°C
Density at 20°C	0.6211 g/mL
Vapor pressure at 25°C	1.2 atm
Flash point (closed cup)	-105.0°C
Solubility in water at 25°C	0.735 g/L

[a] From EPA 1993 (Table 7-1).

formaldehyde from 1,3-butadiene oxidation is not expected to be a significant portion of total formaldehyde content in the atmosphere, this is not the case for acrolein, for which 1,3-butadiene is the major precursor species. Note that acrolein is included with 1,3-butadiene on the EPA's list of the 33 most threatening air toxics (Table 2.1).

Exposure to 1,3-butadiene is primarily caused by vehicle emissions in urban areas. Butadiene concentrations in ambient air have been measured for a number of urban and rural areas. Concentrations typically are less than 1 $\mu g/m^3$, with on-road vehicles responsible for about 50% of that concentration (EPA 1993, Table 7-7). More recent analysis suggests that, in some areas of the country, mobile sources may increase exposure by 0.06 to 0.13 $\mu g/m^3$, depending on vehicle populations and the predominant fuel blend in use (EPA 1999a, Table 7-8).

There are inadequate human data (based on only a few occupational exposure studies) but sufficient animal data to suggest that 1,3-butadiene is a human carcinogen. In animal studies, rats exposed to airborne concentrations of 1,3-butadiene developed multiple tumor types. In addition, chemical compounds related in structure to 1,3-butadiene are known carcinogens. Thus, like acetaldehyde, 1,3-butadiene is classified by EPA as a *B2 Probable Human Carcinogen* (EPA 2000).

Recent assessments have estimated 1,3-butadiene's carcinogenicity, as measured by its CURE, at 2.8×10^{-4} $(\mu g/m^3)^{-1}$. This value means that for every increase in exposure of

1.0 $\mu g/m^3$, an individual's lifetime cancer risk increases by 2.8×10^{-4}. On the basis of its CURE, 1,3-butadiene is the most toxic of the four pollutants considered in this study.

2.2.3.3 Major Sources

The major source of 1,3-butadiene is incomplete combustion of fuel in motor vehicles. Butadiene is primarily emitted from vehicle tailpipes. Because of low concentrations of butadiene in conventional fuels, the evaporative emissions of 1,3-butadiene from motor vehicles are assumed to be negligible (EPA 1993).

Other major sources, annual tons emitted, and percent of total emissions of 1,3-butadiene are listed in Table 2.8.

2.2.4 Formaldehyde

2.2.4.1 Chemical and Physical Properties

Formaldehyde (HCHO), the simplest aldehyde, is a colorless gas with a "pungent, irritating odor" (EPA 1993). Formaldehyde is soluble in polar solutions. Its structure is shown in Figure 2.4. The chemical and physical properties of formaldehyde are listed in Table 2.9. Formaldehyde has been classified as a *B1 Probable Human Carcinogen* (EPA 2000). This classification is reserved for chemicals for which there is *limited information*, based on epidemiological studies, of a causal relationship between the substance and the incidence of cancer. *Limited information* implies that the evidence is based on studies that focus on a single species or that the experimental design was potentially flawed by inadequate doses, exposures, or other complicating factors (Calabrese and Kenyon 1991).

2.2.4.2 Toxic Effects

Formaldehyde is the simplest of the organic compounds known as aldehydes. Because formaldehyde is both a primary and secondary pollutant, it is ubiquitous in the atmosphere, with background concentrations of approximately 0.6 parts per billion (ppb) during daylight hours (EPA 1993; NRC 1981). Formaldehyde is also a major precursor to photochemical smog, reacting with other chemical species to ultimately form ozone. Because of its reactivity and ability to undergo photolysis, the residence time of formaldehyde ranges from a few hours on clear summer days to 10–20 hours during clear winter days (EPA 1993).

In urban areas, exposure to formaldehyde comes from vehicle emissions and from photo-oxidation of organic compounds. Formaldehyde concentrations in ambient air have been measured for a number of urban and rural areas. Concentrations typically are less than 4.0 $\mu g/m^3$ in urban areas (EPA 1993, Table 6-7). Motor vehicles are estimated to contribute approximately 28% of the primary formaldehyde emissions and 35% of the secondary formaldehyde emissions

Table 2.8 1990 National Emission Estimates of 1,3-Butadiene by Source Category for Sources with 2% or Greater Contribution[a]

Source Category	Annual Emissions	
	Ton/yr	Percent[b]
Mobile		
On-road vehicles	36,900	51.4
Nonroad vehicles and equipment	10,100	14.0
Stationary		
Forest and wildfires	10,700	14.9
Prescribed burning	9,200	12.8
Other	2,800	4.4
Totals	77,500	100

[a] From EPA 1999b (adapted from Table 6-4).

[b] Numbers may not add up to 100% because they have been rounded.

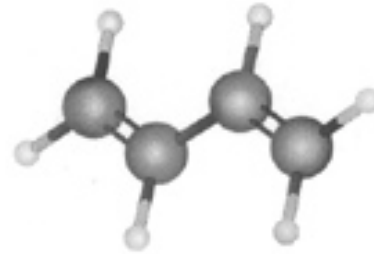
Figure 2.4 Structure of Formaldehyde

Table 2.9 Chemical and Physical Properties of Formaldehyde[a]

Property	Value
Molecular weight	30.03 g/mole
Melting point	-92.0°C
Boiling point	-19.5°C
Density at -20°C	0.8153 g/mL
Vapor pressure at -19.5°C	1 atm
Flash point (closed cup)	-60°C at a 40% solution
Solubility in water at 25°C	Very soluble (up to 55%)

[a] From EPA 1993 (Table 6-1).

(caused by photo-oxidation of hydrocarbons emitted from vehicles) (Carey 1987).[9] Recent studies suggest that in 1996, mobile sources may have increased formaldehyde exposure by 0.3 to 0.7 μg/m^3, depending upon vehicle populations and fuel type used (EPA 1999a). [10]

EPA has classified formaldehyde as a *B1 Probable Human Carcinogen* (EPA 2000). This classification is based on a limited number of studies that show some relationship between formaldehyde exposure and lung cancer in humans, and on more definitive studies with rats, mice, and monkeys that show an increase in cancer caused by long-term inhalation exposure. In

[9] This study focuses on direct (primary) formaldehyde emissions. EPA (1993) estimates that about 30% of formaldehyde concentrations in the atmosphere are from primary emissions, and the other 70% are from secondary emissions. Of the primary formaldehyde emissions, EPA estimates that about 28% are from mobile sources; of the secondary formaldehyde emissions, EPA estimates that about 35% are from mobile sources. In recent exposure assessment work, EPA has only considered primary formaldehyde emissions, under the assumption that primary formaldehyde destruction in the atmosphere is offset by secondary formaldehyde formation (Cook 1999). Thus, data on secondary formaldehyde formation from mobile sources are uncertain. As better data become available, we will attempt to include secondary formaldehyde formation in our fuel-cycle analysis.

[10] This exposure estimate is not corrected for atmospheric transformation, such as the formation of secondary formaldehyde from other emissions components or the decay of formaldehyde caused by atmospheric processes.

addition, formaldehyde has a structure similar to that of other carcinogenic aldehydes, such as acetaldehyde.

EPA estimates formaldehyde carcinogenicity, as measured by its CURE, at 1.3×10^{-5} $(\mu g/m^3)^{-1}$. This value implies that for every increase in exposure of 1.0 $\mu g/m^3$, an individual's lifetime cancer risk increases by 1.3×10^{-5} (EPA 2000).

2.2.4.3 Major Sources

Formaldehyde comes from a variety of sources; the most prevalent is the incomplete combustion of fuel in motor vehicles. Formaldehyde is both a primary and a secondary pollutant because it is also formed through the oxidation of many organic compounds. Formaldehyde can be controlled using a catalytic converter at efficiencies similar to those for total hydrocarbons (Carey 1987). Major sources of formaldehyde are listed in Table 2.10. This table identifies sources of formaldehyde for 1990, tons emitted, and percent of total formaldehyde emissions.

Formaldehyde is also emitted directly during petroleum refining processes, although total emissions from refineries represent only about 0.2% of the total formaldehyde inventory (EPA 1999b). Emissions are generated mainly from catalytic cracking, coking operations, and fuel combustion. These processes are discussed in Section 3.

Table 2.10 1990 National Emission Estimates of Formaldehyde by Source Category for Sources with 2% or Greater Contribution[a]

Source Category	Annual Emissions	
	Ton/yr	Percent[b]
Mobile		
On-road vehicles	97,500	27.8
Nonroad vehicles and equipment	72,900	20.8
Stationary		
Forest and wildfires	68,200	19.5
Prescribed burnings	58,600	16.7
Stationary internal combustion engines	28,300	8.1
Other	25,200	7.1
Totals	350,700	100

[a] From EPA 1999b (adapted from Table 6-25).

[b] Numbers may not add up to 100% because they have been rounded.

Section 3
Upstream Air Toxics Emissions

3.1 Background and Methodology

3.1.1 Overview

Fuel-cycle emissions are usually separated into two groups: upstream and downstream. Upstream emissions include emissions from all activities associated with recovering and transporting fuel feedstock, as well as refining, storing, and delivering fuel to refueling stations. Downstream emissions include those from vehicle refueling and operation.[11] Downstream activities are also referred to as *vehicle operation stages* in this report. The components of each of the three stages are shown in Figure 3.1.

Feedstock-Related Stages:	*Fuel-Related Stages:*	*Vehicle Operation:*
Feedstock recovery, transportation, storage, and distribution	Fuel processing, transportation, storage, and distribution	Refueling and operation
Upstream		*Downstream*
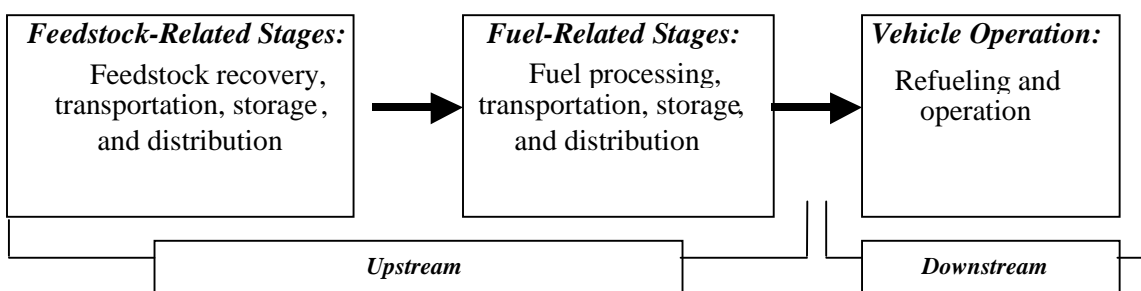
Figure 3.1 Components of a Total Fuel Cycle

Each stage in the total fuel cycle shown in Figure 3.1 includes activities that involve HAP emissions. These emissions are caused by either fuel combustion during a particular stage or non-combustion sources such as evaporation during refueling or fugitive emissions at a refinery. The goal of a total fuel-cycle analysis is to account for each of the emissions events along the entire fuel-cycle chain. In this way, we hope to determine the total emissions (upstream and downstream) associated with the consumption of a given amount of fuel in the vehicle.

This section of the report estimates upstream air toxic emission factors and toxic/VOC (T/VOC) fractions for each of the four air toxics included in this study. T/VOC fractions represent the toxic component of a particular VOC emission stream. These fractions are specific to each toxic pollutant and emissions event.[12] In the GREET model, the fractions are fixed

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[11] We also separate upstream activities into two groups: feedstock-related stages and fuel-related stages. Downstream activities are also referred to as "vehicle operation" in later sections of this report.

[12] An "emissions event" is any point along the upstream pathway at which VOC emissions occur. The size of the emissions event is a function of fuel type, process technology, and control equipment.

parameters that are multiplied by VOC emission levels to calculate toxic emissions. This approach is used for the following reasons:

1. Under the reasonable assumption that T/VOC fractions remain relatively constant as VOC emissions change for a given event, using T/VOC fractions allows us to calculate toxic emissions without having to input new toxic emission factors each time that VOC emission factors are modified. That is, with fixed T/VOC fractions, we need only modify VOC emission levels, and our toxic emissions will be adjusted accordingly. This approach provides a much more efficient method for conducting sensitivity analysis and other types of analyses within the GREET model.

2. Because of data collection constraints, using T/VOC fractions is often the only way to estimate toxics for different emissions events. Toxic emissions data are not always available for each individual stationary and mobile source event. However, if T/VOC *fractions* can be estimated, we can use the fractions and the relatively more abundant VOC emissions data to determine total toxic emissions. EPA uses this approach for many of its analyses for precisely this reason (EPA 1999a).

3. Using T/VOC fractions allows us to structure the GREET model so that the calculation of toxic emissions is relatively transparent to the user. This benefit will be realized mostly during the second phase of the project (i.e., when GREET is revised to integrate air toxics).

Upstream activities include energy feedstock production, feedstock transportation and storage, fuel production, and fuel T&S&D. Not all of these components are involved for every fuel, and not all of the components lead to increased toxic emissions. Wang (1999a) includes a well-defined list of upstream and downstream processes for each of the fuels listed in Table 3.1. For Phase I of this project, we limited our analysis to the fuels and upstream processes listed in Table 3.1.

3.1.2 General Approach for Estimating Emissions from Upstream Processes

We employed the GREET model to calculate toxic emissions from upstream processes. GREET's approach to fuel-cycle analysis is described in detail in Wang 1999a; the information provided there will help the reader to better understand the calculations that follow.

In order to better understand the GREET approach, the reader must recognize that process fuel consumed in each upstream stage (for example during the energy-intensive petroleum refining process) also has its own fuel-cycle chain that must be considered. We call these activities up-upstream processes. Likewise, the fuel used to produce the process fuel has an upstream chain associated with it (i.e., up-up-upstream processes). Because these upstream chains go on *ad infinitum*, we call them the up^n-stream process. Because the amount of fuel used in each chain of the up^n-stream process grows smaller with each incremental increase in *n*, the emissions values ultimately converge mathematically in a value that captures all the up^n-stream processes.

Table 3.1 Fuels and Processes Analyzed

Fuel/Vehicle Technology	Process Analyzed
Conventional gasoline (CG)	*Upstream*
Federal RFG Phase 2 (FRFG2)	Process fuel combustion[a]
California RFG Phase 3 (CARFG3)	Fuel production (non-combustion)
Conventional diesel (CD)	Fuel transportation, storage & distribution
Bi-fuel compressed natural gas (bi-CNG)	*Downstream*
Dedicated compressed natural gas (CNG)	Vehicle refueling
85% methanol blend FFV (M85)[b,c]	Vehicular fuel combustion
85% ethanol blend FFV (E85)[d]	Vehicular fuel evaporation
Dedicated liquefied petroleum gas (LPG)[e]	Brake and tire wearing
Battery-powered electric vehicle (EV)[f]	
Grid-connected hybrid electric vehicle (HEV1)[g]	
Grid-independent HEV (HEV2/HEV3)	

[a] Process fuel combustion refers to the burning of any fuel during the upstream recovery, production, and T&S&D processes. T/VOC fractions for fuel combustion depend on the type of fuel burned, the type of technology used (e.g., steam boiler or gas turbine), and the emissions control equipment used for the combustion process.

[b] FFV = flexible-fuel vehicle.

[c] The analysis is conducted for M85 assuming natural gas (NG) as the feedstock for methanol.

[d] The analysis is conducted for E85 assuming corn as the feedstock for ethanol.

[e] The analysis is conducted for LPG assuming both NG and crude oil as the feedstocks. Currently, 60% of the LPG consumed in the United States originates from NG and 40% originates from crude oil.

[f] The analysis is conducted for EV and HEV1 assuming an average U.S. electric generation mix. See Wang (1999a,b) for detailed information regarding the mix.

[g] HEV1 = HEVs fueled by CARFG3. HEV2 = HEVs fueled by FRFG2. HEV3 = HEVs fueled by CD.

The GREET model was designed in Microsoft Excel®, which allows so-called circular calculations to take into account the up^n-stream processes. We incorporated circular calculations in GREET. Figure 3.2 illustrates the circular calculations for three simplified upstream chains for which we considered only fuel use in the fuel production process.

GREET calculates energy use (in Btu per mile [Btu/mi]) and emissions (in grams per mile [g/mi]) by taking into account energy use and emissions of combustion and non-combustion events during the upstream and downstream stages of the total fuel cycle. The model calculates total energy use (all energy sources), fossil energy use (petroleum, natural gas, and coal), and petroleum use and emissions of three major greenhouse gases (carbon dioxide [CO_2], methane [CH_4], and nitrous oxide [N_2O]) and five criteria pollutants (VOCs, carbon monoxide [CO], nitrogen oxides [NO_x], particulate matter with aerodynamic diameters of 10 microns or less [PM_{10}], and sulfur oxides [SO_x]).
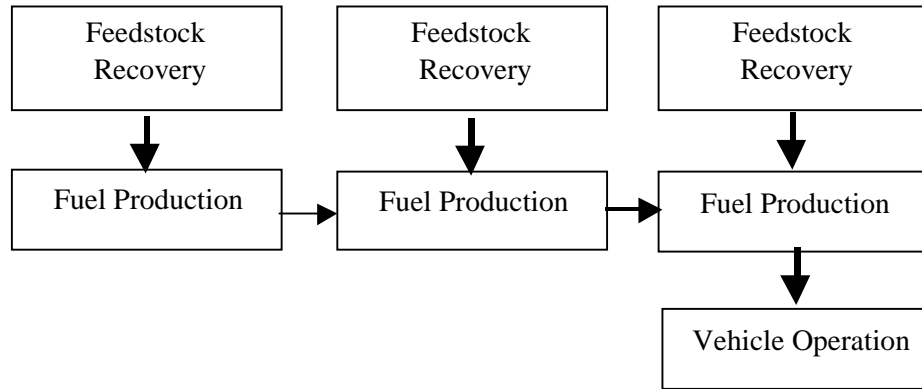
Figure 3.2 The Up^n-Stream Process for N=3

Upstream emissions of these pollutants were first calculated in grams per million Btu (g/10^6 Btu) of fuel throughput from each upstream stage. Emissions occurring during a stage include those resulting from the combustion of process fuels and from non-combustion processes such as chemical reactions, fuel leakage, and evaporation.

Emissions from the combustion of process fuels for a particular stage were calculated by using the following formula:

$$EM_{cm,i} = (\sum_j \sum_k EF_{i,j,k} \times EC_{j,k}) \div 1{,}000{,}000 \qquad [1]$$

where:

$EM_{cm,i}$ = Combustion emissions of pollutant i in g/10^6 Btu of fuel throughput,

$EF_{i,j,k}$ = Emission factor of pollutant i for process fuel j with combustion technology k (g/10^6 Btu of fuel burned), and

$EC_{j,k}$ = Consumption of process fuel j with combustion technology k (Btu/10^6 Btu of fuel throughput).

$EC_{j,k}$ for a given stage was, in turn, calculated by using the following formula:

$$EC_{j,k} = EC \times Share_{fuelj} \times Share_{techk,j} \qquad [2]$$

where:

$EC_{j,k}$ = Total energy consumption for the given stage (in Btu/10^6 Btu of fuel throughput);

$Share_{fuelj}$ = Share of process fuel j out of all process fuels consumed during the stage ($\sum_j$fuel$_j$ = 1); and

Share$_{techk,j}$ = Share of combustion technology k out of all combustion technologies for fuel j ($\sum_k$tech$_{k,j}$ = 1).

Combustion technology shares (Share$_{techk,j}$) for a given process fuel are influenced by technology performance, technology costs, and emissions regulations for stationary sources. For this study, we assumed combustion technologies and emissions control systems consistent with current conditions.

Once VOC emissions were determined for upstream combustion processes, we applied T/VOC fractions to calculate total toxic emissions from these processes. This important task involved the acquisition and manipulation of various data to determine T/VOC fractions (discussed in more detail in Section 3.2). We used the following three primary data sources for both VOC emission factors and toxic emissions:

- Factor Information Retrieval (FIRE) Database (EPA 1998b),

- Compilation of Air Pollutant Emission Factors (commonly called AP42) (EPA 1995a), and

- Locating and Estimating Emissions Documents (L&E) (EPA 1988, 1991, 1996, and 1998c).

Besides the upstream toxic air emissions generated during process fuel combustion, VOCs and air toxics are emitted during fuel production and fuel T&S&D (i.e., the process-related, or non-combustion, emissions that occur during chemical processes, fuel evaporation, fuel leakage, and venting). To calculate these non-combustion process emissions, we used the databases listed above to calculate toxic emission factors. The units for these emission factors were ultimately converted into g/10^6 Btu or mg/10^6 Btu of fuel product throughput. By multiplying these emission factors by GREET's estimates of product throughput, we were able to calculate total toxic emissions directly. These noncombustion, process-related emissions are discussed in more detail in Sections 3.3 and 3.4.

3.2 Air Toxics Emissions from Upstream Process Fuel Combustion

Emission factors for VOCs and air toxics for upstream fuel combustion processes were obtained from the three emission factor databases listed above. Several hydrocarbon categories are used in the three databases: VOCs, total organic compounds (TOCs), nonmethane total organic compounds (NMTOCs), total hydrocarbons (THCs), and nonmethane hydrocarbons (NMHCs). To calculate T/VOC fractions, we converted all emissions into VOCs using the conversion factors listed in Table 3.2.

We assumed that the upstream combustion technologies we examined are current technologies equipped with emissions control systems in accordance with current regulations. The upstream combustion fuels and technologies we considered in this study are listed in Table 3.3. For each combustion technology identified in this section, we obtained data on VOC

Table 3.2 Hydrocarbon Emission Categories and Conversion Factors

Hydrocarbon Categories	Differences in Hydrocarbon Categorization	Conversion Factors[a]	
		Mobile Sources[b]	Stationary Sources[c]
VOC	= TOC – methane – ethane	1	1
TOC	= All organic compounds	0.808	Varies[d]
NMTOC	= TOC – methane	NA[e]	1
THC	= TOC – aldehydes	NA	Varies
NMHC	= THC – methane	0.944	1

[a] Conversion factors are the multiplication factors for converting the given category to VOCs.

[b] Mobile source conversion factors are adapted from EPA (1999a).

[c] Stationary source conversion factors are estimated according to the FIRE database, Version 6.1, August 1998.

[d] The conversion factor varies depending upon the combustion technology employed.

[e] NA = not applicable.

and air toxic emissions as a function of the combustion process (usually in $g/10^6$ Btu for VOC and $mg/10^6$ Btu for toxic pollutants). Using these data, we calculated T/VOC fractions for each combustion technology. These fractions were applied to final VOC estimates generated from the GREET model to calculate total toxic emissions from fuel combustion processes. Air toxic emission factors are not available from the three databases listed above for some combustion technologies. In those cases, assumptions were made on the basis of characteristics of similar combustion technologies and emission controls.

3.2.1 Coal Combustion

Coal combustion can occur in utility boilers, industrial boilers, and other advanced technologies. Table 3.4 lists VOC and toxic emission factors for a variety of coal combustion technologies. Blank spaces indicate that no data are available for that technology.

For the most part, the emission factors listed in AP42, L&E, and the FIRE database are consistent. However, benzene emission factors in the L&E are one magnitude lower than those reported in AP42 and the FIRE database.

3.2.1.1 Utility and Industrial Boilers

More than 80% of the coal consumed in the United States is used for electricity generation. Most of this coal is burned in pulverized-coal-fired boilers (U.S. Department of Energy [DOE] 1995). The most commonly used pulverized-coal boilers are "dry-bottom" boilers in which coal ash does not reach the fusion temperature. A small amount of coal in electric power plants is burned in stoker furnaces, in which crushed coal is supplied on a moving grate, and in cyclone furnaces, in which crushed coal is carried in a whirling stream of air. Some advanced power plants use fluidized-bed combustion, in which crushed coal in a bed behaves like a boiling fluid

Table 3.3 Combustion Fuels and Technologies Included in this Analysis

Fuel	Technology
Coal	Utility boilers
	Industrial boilers
Residual and fuel oil	Utility boilers
	Industrial boilers
	Commercial boilers
	Barges
Distillate and diesel fuel	Utility boilers
	Utility turbines
	Industrial boilers
	Commercial boilers
	Stationary reciprocating engines and turbines
	Locomotives
	Heavy-duty trucks
	Farm tractors
NG, LPG, and liquefied natural gas (LNG)	Utility boilers
	Utility turbines
	Industrial boilers
	Industrial turbines
	Commercial boilers
	Commercial turbines
	Stationary reciprocating engines and turbines
	Flaring in oil fields
Gasoline	Reciprocating engines
	Heavy-duty trucks
	Farm tractors
Wood	Fluidized bed combustion
	Stoke boilers

with high-velocity airflow (DOE 1995). Bituminous and sub-bituminous coal is primarily used in electric power plants (DOE 1995).

Because of the dominant use of dry-bottom boilers for coal combustion, we used the emission factors for these boilers to calculate T/VOC fractions. Available data from EPA's FIRE database (see Table 3.3) indicate that emission factors for utility boilers are similar to those for industrial boilers. Therefore, we assumed identical T/VOC fractions for both utility and industrial boilers. These fractions are listed in Table 3.5.[13]

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[13] Note that in this case and others, data are not always available for all air toxics (particularly for butadiene). Although these cases are indicated by an "NA" in the tables that follow, we treat them as generating zero emissions in our analysis. Although we believe that the emissions in such cases are negligible, the reader should be aware that our analysis may underestimate these emissions because we used this approach.

Table 3.4 Emission Factors for Coal Combustion Technologies[a]

Combustion Technology	Coal Type	Combustion Configuration	Emission Factor (per 10⁶ Btu)				
			VOC (g)	HCHO (mg)	AC (mg)	BU (mg)	BZ (mg)
Utility/ industrial boiler	Anthracite[b]	Pulverized	1.72				
		Traveling grate	1.72				
		Hand fired	24.55				
	Bituminous and subbituminous	Pulverized, wet bottom	0.98				
		Pulverized, dry bottom	1.47	5.89	14.0		31.9
		Cyclone furnace	2.70	5.89	14.0		31.9
		Spreader	1.23	0.22			
		Traveling grate (overfeed)	1.23	0.14			
		Underfeed	31.91				
		Cogeneration	1.72				
		Fluidized bed combustion	1.23	5.89	14.0		31.9
	Lignite	Dry bottom	5.43	18.6	44.2		101
		Dry tangential	5.43	18.6	44.2		101
		Cyclone furnace	5.43	18.6	44.2		101
		Traveling grate	5.43	18.6	44.2		101
		Spreader	5.43	18.6	44.2		101
Gasification turbine							

[a] From FIRE Database (EPA 1998b).

[b] Only small amounts of anthracite coal are now used.

3.2.1.2 Integrated Gasification Combined-Cycle Turbines

No air toxic data are currently available for integrated gasification combined-cycle (IGCC) turbines.

3.2.2 Residual and Fuel Oil Combustion

The available emission factors for boilers and barges are listed in Table 3.6.

Table 3.5 T/VOC Fractions for Coal-Fired Utility and Industrial Boilers

Air Toxic	T/VOC Fraction (%)
Formaldehyde	0.4
Acetaldehyde	0.9
1,3-Butadiene	NA[a]
Benzene	2.1

[a] Data for 1,3-butadiene are not available.

The L&E data are different from the AP42 data in several ways. First, the L&E lists an emission factor for formaldehyde of 0.069 nanograms per Joule (ng/J) (0.0224 pounds per 10,000 gallons [lb/10³ gal]) for industrial usage, which is slightly lower than the value listed in AP42. The L&E also lists an emission factor for benzene of 9.38×10^{-5} lb/10⁶ Btu (0.0131 lb/10³ gal) for industrial usage, which is greater than the value listed in AP42. The FIRE data are identical to those listed in AP42.

Table 3.6 Emission Factors for Residual and Fuel Oil Combustion Technologies[a]

Technologies	Oil Grade	Combustion Configuration	Emission Factor (per 10^6 Btu) VOC (g)	HCHO (mg)	AC (mg)	BU (mg)	BZ (mg)
Utility boiler	6	Normal firing	2.465	78–197 (72.6)[b]	10.7[c]	36.9[c]	25.0[c]
		Tangential fire	2.465	107			1.0
	5	Normal firing	2.465	213			
		Normal firing with FGR[d]		156			
	6/5	Tangential fire	2.465				
Industrial boiler	6	Large boiler[e]	0.908	78–197			4.0
		Medium boiler[f]	0.908				
		Small boiler[g]	0.908				
	5		0.908				
	6/5	Cogeneration	0.908				
Commercial boiler	6	Large boiler	3.664	78–197			
		Medium boiler	3.664				
		Small boiler	3.664				
	5		3.664				
Barge			2.21	109	16		1.0

[a] From EPA (1998b).

[b] From EPA's L&E database (EPA 1991).

[c] From CARB's California Air Toxic Emission Factor (CATEF) database (1996).

[d] FGR = flue gas recirculation.

[e] Size is greater than 10^8 Btu/h.

[f] Size is greater than 10^7 Btu/h and less than 10^8 Btu/h.

[g] Size is less than 10^7 Btu/h.

3.2.2.1 Utility, Industrial, and Commercial Boilers

Using the emission factors listed in Table 3.6, we calculated the T/VOC fractions provided in Table 3.7.

3.2.2.2 Barges

The air toxic emission factors for barge operations listed in Table 3.6 were obtained from EPA (1999c) (on the basis of factors for residual oil-fueled commercial marine vessels). The VOC emission factor was obtained from AP42. From these values, T/VOC fractions were calculated as shown in Table 3.8.

Table 3.7 T/VOC Fractions for Residual Oil-Fired Boilers

Air Toxic	T/VOC Fraction (%)[a]		
	Utility	Industrial	Commercial
Formaldehyde	8.03	8.6	8.03
Acetaldehyde	0.44	0.44	0.44
1,3-Butadiene	1.50	1.50	1.50
Benzene	1.01	1.01	1.01

[a] Acetaldehyde-, 1,3-butadiene-, and benzene-to-VOC fractions for industrial and commercial boilers were assumed to be the same as those for utility boilers. Although benzene emissions are available for industrial boilers, the data are not consistent with benzene emissions from utility boilers. We adopted the utility boiler data for industrial and commercial boilers because these data are more reliable.

Table 3.8 T/VOC Fractions for Barges

Air Toxic	T/VOC Fraction (%)
Formaldehyde	4.93
Acetaldehyde	0.7
1,3-Butadiene	NA[a]
Benzene	0.05

[a] Data for 1,3-butadiene are not available.

3.2.3 Distillate and Diesel Fuel Combustion

Distillate and diesel fuel are burned in utility boilers, industrial boilers, commercial boilers, locomotives, trucks, and farming tractors. Estimates of VOC and air toxic emission factors for these combustion categories are listed in Table 3.9.

3.2.3.1 Utility, Industrial, and Commercial Boilers

T/VOC fractions were calculated by dividing air toxic emission factors by the VOC emission factors listed in Table 3.9 for utility, industrial, and commercial diesel-fired boilers. These fractions are shown in Table 3.10. To calculate the T/VOC fraction for formaldehyde, the lowest value within the range of formaldehyde emission factors was adopted. Note that no data for butadiene are available at this time.

3.2.3.2 Locomotives

T/VOC fractions for locomotives were determined on the basis of the freight locomotive emission rates for line haul locomotives that are listed in Table 3.9. By using these emissions factors, we estimated the T/VOC fractions for locomotives that are shown in Table 3.11.

3.2.3.3 Stationary Reciprocating Engines and Turbines

On the basis of the emission rates listed in Table 3.9, we estimated the T/VOC fractions for stationary reciprocating engines and turbines that are shown in Table 3.12.

Table 3.9 Air Toxic Emission Factors for Distillate and Diesel Fuel Combustion Technologies[a]

Category	Fuel Grade	Combustion Configuration	Emission Factor (per 10^6 Btu)				
			VOC (g)	HCHO (mg)	AC (mg)	BU (mg)	BZ (mg)
Utility	1/2	Boilers	0.707	124–216			
		Turbine[b]	1.802	113	15	29	27
		Turbine plus DFA[c]		4.0			41
		Reciprocating		234			456
	4	Normal firing	2.685				
		Tangential fire	2.367				
Industrial	1/2	Large boilers	0.707	124–216			10
		Middle boilers	0.707				
		Small boilers	0.707				
		Reciprocating			348		3.0
		Reciprocating/ cogeneration			486		2.0
		Cogeneration	0.707				
	4		0.707				
Commercial	1/2	Large boilers	1.201	124–216			10
		Middle boilers	1.201				
		Small boilers	1.201				
		Reciprocating	37.183	536	348	18	424
Locomotive[d]	Diesel	Line haul	0.022[e]	3.3		0.33[f]	0.22[f]
		Yard	0.046[e]			0.8[f]	0.54[f]
HDE truck[g,h]	Diesel			88		50[f]	35[f]
Farming tractor[d]	Diesel		0.0607[i]	7.26[i,j]		1.3[f]	80.7[f,k]

[a] From EPA's FIRE database (EPA 1998b).

[b] Data from EPA (1998h).

[c] DFA = direct-flame afterburner.

[d] Emissions are in lb/gal for VOC and lb/10^3 gal for toxics.

[e] From EPA (1997).

[f] From EPA (1996; 1998c).

[g] Emissions are in g/mi.

[h] HDE = heavy-duty engine.

[i] From EPA (1995a).

[j] Emissions were calculated using aldehyde emissions data and assuming aldehyde emissions are 60% formaldehyde.

[k] The benzene emission factor for farming tractors is from EPA's L&E database; the VOC emission factor for farming tractors is from AP42. Benzene emissions here exceed VOC emissions for farming tractors. We have no way to reconcile the data from the two EPA sources. In our analysis, we did not use the benzene emission factors listed in this table to generate our benzene/VOC fraction for farming tractors. Table 3.13 provides our assumptions regarding the final approach.

Table 3.10 T/VOC Fractions for Diesel-Fired Boilers

	T/VOC Fraction (%)	
Air Toxic	Industrial Boiler	Commercial Boiler
Formaldehyde	17.5	10.3
Acetaldehyde	4.78[a]	2.81[a]
1,3-Butadiene	NA[b]	NA
Benzene	1.4	1.4[c]

[a] Acetaldehyde emissions were calculated on the basis of the ratio of AC/HCHO (0.273 for oil-fired boilers according to EPA 1998d).

[b] Data for butadiene are not available.

[c] The benzene emission factor for commercial boilers was not available; the T/VOC fraction for industrial boilers (1.4%) was adopted.

3.2.3.4 Heavy-Duty Trucks and Farming Tractors

The estimated T/VOC fractions for heavy-duty trucks and farming tractors are based on data listed in Table 3.9, as well as information from EPA (1999a). The calculated T/VOC fractions generated from these data are listed in Table 3.13.

3.2.4 Natural Gas, Liquefied Petroleum Gas, and Liquefied Natural Gas Combustion

NG combustion technologies include utility and industrial boilers, gas turbines, and reciprocating engines. Available toxic emissions factors for these technologies are listed in Table 3.14.

No air toxics emission factors are available for LPG or LNG. The T/VOC fractions for LPG and LNG combustion sources are assumed to be the same as those for NG sources.

Air toxic data among the three EPA databases are similar, with the exception of formaldehyde emissions from reciprocating engines and turbines (the L&E data are much higher than those found in other databases).

3.2.4.1 Utility, Industrial, and Commercial Boilers

On the basis of the emissions factors listed in Table 3.14, we estimated the T/VOC fractions for NG-fueled boilers that are shown in Table 3.15.

Table 3.11 T/VOC Fractions for Diesel Locomotives

Air Toxic	T/VOC Fraction (%)
Formaldehyde	15.00
Acetaldehyde	0.94[a]
1,3-Butadiene	1.50
Benzene	1.00

[a] Value for acetaldehyde is based on data from stationary diesel reciprocating engines.

Table 3.12 T/VOC Fractions for Stationary Reciprocating Engines and Turbines

	T/VOC Fraction (%)	
Air Toxic	Reciprocating Engines	Turbines
Formaldehyde	1.44	6.27
Acetaldehyde	0.94	0.84
1,3-Butadiene	0.05	1.61
Benzene	1.14	1.49

3.2.4.2 Stationary Reciprocating Engines and Turbines

In our study, we considered four upstream, stationary internal combustion technologies that burn NG: NG turbine, combined-cycle gas turbine, pipeline turbine, and reciprocating engine. Emissions factors were estimated assuming a combination of several emission control technologies. Estimated T/VOC fractions for NG-fueled stationary reciprocating engines and turbines are listed in Table 3.16.

3.2.4.3 Natural Gas Flaring in Oil Fields

No data are available in the three primary databases listed in Section 3.1.2 for toxic emissions from NG flaring in oil fields. However, the EPA Industrial Combustion Coordinator Rulemaking database (incinerators/flares) (EPA 1998f) lists air toxic emission factors for some specific NG flare facilities. These data were analyzed, and the T/VOC fractions were calculated as shown in Table 3.17.

3.2.5 Gasoline Combustion

Three gasoline combustion technologies used for upstream processes were considered in this study: stationary reciprocating engines, heavy-duty trucks, and farming tractors. Emissions data for each of these processes are listed in Table 3.18.

3.2.5.1 Reciprocating Engines

No air toxics data are available in the three primary databases listed in Section 3.1.2 for gasoline-fueled reciprocating engines. However, EPA's Industrial Combustion Coordinator Rulemaking database (turbines) (EPA 1998g) lists air toxic emissions factors for some specific gasoline reciprocating engines. These emissions factors, listed in Table 3.18, were used to calculate the T/VOC fractions listed in Table 3.19.

3.2.5.2 Heavy-Duty Trucks and Farming Tractors

VOC emissions factors, as presented in Wang (1999a), were used to calculate T/VOC fractions for gasoline-fueled heavy-duty trucks and farming tractors. The calculated fractions are presented in Table 3.20.

3.2.6 Wood Combustion

The only wood combustion technology considered in this study was fluidized bed combustion (FBC). VOC and air toxic emissions data are not available for FBC. However, data

Table 3.13 T/VOC Fractions for Diesel Trucks and Farming Tractors

Air Toxic	T/VOC Fraction (%)	
	Heavy-Duty Truck[a]	Farming Tractors
Formaldehyde	9.68	11.96
Acetaldehyde	3.56	3.56[b]
1,3-Butadiene	0.75	2.15
Benzene	1.29	1.29[c]

[a] From EPA (1999a, Appendix C). Values were modified to T/VOC using a 0.808 VOC conversion factor. The value assumes no evaporative emissions from diesel fuel.

[b] Data for acetaldehyde emissions from farming tractors were not available, so we employed the T/VOC fraction for heavy-duty trucks.

[c] This value was assumed to be the same as the value for heavy-duty trucks (EPA 1999b).

Table 3.14 Emission Factors for Natural Gas Combustion Technologies[a]

Category	Fuel	Combustion Configuration	VOC (g)	HCHO (mg)	AC (mg)	BU (mg)	BZ (mg)
Utility	NG	Large boilers	2.691	37			1.0
		Large boilers plus FGR		18			
		Small boilers	2.691	37			1.0
		Small boilers plus FGR	0.000	89			
		Tangential	2.691	37			1.0
		Turbine	0.489				
		Turbine plus SI/SCR[b]	1.644	1226			
		Turbine plus afterburn	0.000	156			
		Reciprocating[c]	230.4	2,151	242	0.46	65
		Reciprocating cogeneration		627			
	Process gas	Large boilers	2.691				
		Small boilers	2.935				
Industrial and commercial boilers	NG	Large boilers	2.691	37			1.0
		Medium boilers	2.691	37			1.0
		Small boilers	2.691	37			1.0
		Cogeneration	0.685				
		Reciprocating	56.750				
		Turbine[c]	1.37	54	39	0.2	7
		Turbine plus afterburn			10		
		Turbine plus SCR with NH$_3$[d]			2.0		
		Turbine plus CR[e]		73			
	Process gas	Boilers	1.468	65			2.0
		Boilers plus LNB[f] plus FGR			3.0		
		Boilers plus LNB	2.740		1.0		
Flaring			2.74	196	39	0	64

[a] From EPA's FIRE database (EPA 1998b).

[b] SI/SCR = steam injection/selective catalytic reduction.

[c] Values are from CARB's CATEF database (CARB 1998).

[d] SCR with NH$_3$ = selective catalytic reduction with NH$_3$ (ammonia) injection.

[e] CR = catalytic reduction.

[f] LNB = low NO$_x$ burners.

Table 3.15 T/VOC Fractions for Natural Gas-Fueled Boilers

Air Toxic	T/VOC Fraction (%)
Formaldehyde	1.36
Acetaldehyde	0.00[a]
1,3 butadiene	NA[b]
Benzene	0.04

[a] Aldehyde emissions from NG combustion have been estimated to be 100% (by weight) formaldehyde (EPA 1991).

[b] Data for butadiene are not available.

Table 3.16 T/VOC Fractions for Natural Gas-Fueled Stationary Reciprocating Engines and Turbines

Air Toxic	T/VOC Fraction (%)		
	Large Gas Turbine	Pipeline Turbine	Reciprocating Engine
Formaldehyde	3.93	3.93	9.33
Acetaldehyde	2.86	2.86	1.05
1,3-Butadiene	0.02	0.02	0.02
Benzene	0.50	0.50	0.28

Table 3.17 T/VOC Fractions for Natural Gas Flaring

Air Toxic	T/VOC Fraction (%)
Formaldehyde	7.14
Acetaldehyde	1.43
1,3-Butadiene	0.00
Benzene	2.32

Table 3.18 Air Toxics Emission Factors for Gasoline Combustion[a]

Combustion Technology	Emission Factor				
	VOC (g)	HCHO (mg)	AC (mg)	BU (mg)	BZ (mg)
Reciprocating engine (per 106 Btu)	1,089.3	19,500	9,800	980	57,600
Heavy-duty truck (per mi)		640		60	425
Farming tractor (per hp-h)	6.59	180		131	10,500

[a] From EPA (1998c; 1991; 1996; 1998g).

Table 3.19 T/VOC Fractions for Gasoline Reciprocating Engines

Air Toxic	T/VOC Fraction (%)
Formaldehyde	1.79
Acetaldehyde	0.90
1,3-Butadiene	0.09
Benzene	5.29

for stoke boilers are available and reveal the following emission factors: 0.22 lb/ton for TOC, 0.1 lb/ton for CH_4, 0.00995 lb/ton for benzene, 0.0082 lb/ton for formaldehyde, and 0.00192 lb/ton for acetaldehyde (EPA 1998e). Here, we assumed that the T/VOC fractions for FBC are the same as those for stoke boilers. The estimated T/VOC fractions for wood FBC are listed in Table 3.21.

3.3 Air Toxics Emissions from Fuel Production Processes

Air toxics emissions occur not only during process fuel combustion, but also during the non-combustion stages of fuel production (i.e., petroleum refining). These emissions, which result from such events as chemical reactions, fuel leakage, and fuel evaporation, are both fuel- and stage-specific.

This section, unlike Section 3.2, addresses each of the four air toxics individually. Because these emissions are not associated with combustion, emission factors are often described in terms of emissions per 1,000 barrels (bbl) crude product output or per 1,000 bbl of crude input (fresh feed). For use in the GREET model, we converted these emission factors into units of $g/10^6$ Btu or $mg/10^6$ Btu of fuel throughput. We then used GREET to apply these factors to total fuel throughput for each stage to calculate total air toxics emissions.

Figure 3.3 depicts several stages of the petroleum refining process in which non-combustion VOC and air toxics emissions may be released. The figure represents material flow in terms of the percentage of crude feedstock input. Some VOC and air toxics data are available for the three highlighted processes in this figure (*vacuum distillation*, *catalytic cracking*, and *coking*). The availability of VOC and air toxics data is discussed in each of the following sections.

3.3.1 Acetaldehyde Emissions

Potential sources of acetaldehyde emissions from petroleum refineries include asphalt blowing and incineration. Because these emissions are small and can be controlled to negligible levels, they were not included in this study.

Table 3.20 T/VOC Fractions for Gasoline-Fueled Heavy-Duty Trucks and Farming Tractors

Air Toxic	T/VOC Fraction (%)	
	Heavy-Duty Trucks[a]	Farming Tractors
Formaldehyde	4.29	2.73
Acetaldehyde	0.83	0.83
1,3-Butadiene	0.92	1.99
Benzene	3.62	3.62[b]

[a] From EPA (1999b, Appendix C). Values were modified to T/VOC using a 0.808 VOC conversion factor. Acetaldehyde values for farming tractors are assumed to be the same as the values for heavy-duty trucks.

[b] Because data from AP42 and L&E are not consistent for benzene (benzene emissions are higher than total VOC emissions), the T/VOC fraction for benzene was assumed to be the same as that for heavy-duty trucks .

Table 3.21 T/VOC Fractions for Wood Fluidized Bed Combustion

Air Toxic	T/VOC Fraction (%)
Formaldehyde	6.83
Acetaldehyde	1.60
1,3-Butadiene	Na[a]
Benzene	8.29

[a] Data for butadiene emissions are not available.
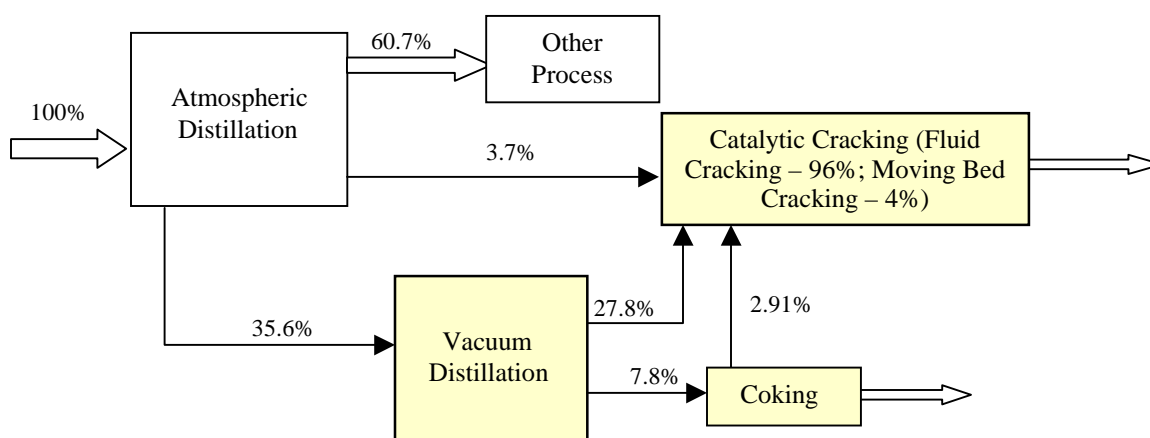
Figure 3.3 Material Flows in Air-Toxic-Related Processes for a Typical Petroleum Refinery

(Note: Percentages represent the fractions of total crude oil feedstock; they were calculated on the basis of data from Gaines and Wolsky (1981) and DOE (1998). The percentages in the catalytic cracking box represent the technology shares for the two cracking methods used in the United States (fluid catalytic cracking [FCC] and moving bed cracking). These values were obtained from the L&E document and EPA (1995b).)

3.3.2 Benzene Emissions

Benzene emissions occur in two areas in petroleum refineries: process venting and fugitive emissions. In both cases, benzene emissions are generated from evaporation of unburned fuel. Thus, the level of benzene emissions is directly related to benzene concentrations within the refined fuel. The methods used to calculate benzene emission factors are described for each of these sources below.

3.3.2.1 Process Venting

Process venting, or the direct release of emissions during refining, occurs during the distillation and cracking processes. During these processes, release of high-pressure gas into the atmosphere is required for safety. Table 3.22 lists VOC emission factors for venting from three refining processes and the average benzene concentrations for this emissions stream.

To calculate benzene emission factors from process venting, we first multiplied the VOC emission factors by the benzene concentrations. We then calculated an average benzene emission factor for catalytic cracking by applying the material flow percentages and the technology shares for the two technologies (FCC and TCC) discussed above and shown in Figure 3.3. Finally, we added this average cracking emission factor to the vacuum distillation factor, which we also

Table 3.22 VOC Emission Factors and Benzene Concentrations in Refining Process Stream

Process	VOC Emission Factor (lb/1,000 bbl)[a]	Benzene Concentration (%)[b]
Vacuum distillation	50	0.72
FCC	220	0.39
Moving bed cracking: TCC	87	0.24

[a] From EPA (1995a); VOC emission factors were assumed to be identical to emission factors for TOC, because methane and ethane levels for these processes are negligible (less than 1%) (EPA 1995a).

[b] From L&E document (EPA 1998c).

adjusted on the basis of its material flow percentage (provided in Figure 3.3). This calculation is shown in the following equation:

$$
\begin{aligned}
\text{Emission factor} \quad = \quad & 220 \times 0.39\% \times 34.4\% \times 96.1\% + \\
& 87 \times 0.24\% \times 34.4\% \times 3.9\% + \\
& 50 \times 0.72\% \times 35.6\% \\
\\
= \quad & 0.488 \text{ lb benzene/1,000 bbl crude input}
\end{aligned}
\qquad [3]
$$

3.3.2.2 Fugitive Emissions

Fugitive emissions occur from process equipment components such as valves, pump seals, compressor seals, pressure relief valves, connectors, open-ended lines, and sampling connections. VOC emissions were calculated using emissions factors (in lb/h for each source) estimated by EPA (1995b). Benzene emissions from equipment leaks can be estimated by multiplying equipment counts (obtained from the L&E document), equipment leak factors, and benzene concentrations of the leaked stream. We assumed that the weight composition of a stream inside a process line is the same as the weight composition of the leaked stream. On the basis of this assumption, we estimated an overall average T/VOC fraction for benzene from leaking emissions of 0.83%. Total VOC emissions caused by fugitive emissions from a typical petroleum refinery are 136.3 lb/1,000 bbl crude input (EPA 1995a). Therefore, benzene emissions were estimated as 1.13 lb/1,000 bbl crude input.

Given this fugitive emission factor and the process venting factor (as calculated in Section 3.3.2.1), we estimated that the *total* benzene emission factor for noncombustion petroleum refining processes is 158 mg/10^6 Btu petroleum output (assuming an 85% efficiency factor).

3.3.3 1,3-Butadiene Emissions

Butadiene emissions from refinery processes are primarily from blow-down vents, catalyst regeneration process vents, and miscellaneous vents at vacuum distillation, alkylation, and

thermal cracking units. No emission factors are available for butadiene from refining processes. However, total butadiene emissions from petroleum refining in 1990 were 159.1 metric tons; the total crude oil input to refineries from that year was 13.5×10^6 bbl/day (Beck 1997). From these estimates, we calculated the butadiene emission factor from the refineries: 6.9 mg/10^6 Btu of crude product output (assuming an 85% efficiency factor).

3.3.4 Formaldehyde Emissions

Various stages of the petroleum refining process emit formaldehyde. The stages for which data are available include catalytic cracking (fluid and moving bed) and coking. These stages and their formaldehyde emission factors are listed in Table 3.23.

Total formaldehyde emissions from petroleum refineries in 1990 were 696.4 metric tons; the total crude oil input to refineries from that year was 13.5×10^6 bbl/day (Beck 1997). From these estimates, we calculated the formaldehyde emission factor from refineries: 30.4 mg/10^6 Btu of crude product output (assuming an 85% efficiency factor).

3.4 Air Toxics Emissions from Fuel Transportation, Storage, and Distribution

The T&S&D of fuels represents another avenue for air toxic emissions. Fuel combustion-related emissions from T&S&D activities (e.g., tailpipe emissions from fuel delivery tanker trucks) were calculated by using the methodology described in Section 3.2. That is, total fuel use for combustion-related processes of the T&S&D process was determined, and appropriate T/VOC fractions were applied.

Evaporative benzene emissions also occur during refueling and fuel transfer processes. In most cases, we assumed that the concentration of benzene in evaporative VOC emissions is the same as the concentration in the fuel itself. This is not entirely true, because benzene's chemical makeup does not allow it to evaporate as readily as many other VOCs. So we would expect to see

Table 3.23 Formaldehyde Emission Factors for Petroleum Refining Processes[a]

Process	Emission Factor (lb/1,000 bbl fresh feed)
FCC regenerator	4.86
Moving bed regenerator: TCC[b]	2.20
Fluid coker burner	1.19

[a] From L&E document (EPA 1991).

[b] TCC = thermal catalytic cracking.

slightly lower concentrations of benzene in evaporative VOC emissions than in the fuel. However, except for CG and RFG, we did not have data on the T/VOC fractions for evaporative benzene emissions. Thus, except for gasoline blends, we used the benzene concentration of the fuel as the concentration in the evaporative emissions, understanding that the values may be *slightly* overestimated. The resulting T/VOC values are listed in Table 3.24.

Table 3.24 Evaporative T/VOC Fractions for Benzene[a]

Fuels	T/VOC Fraction (%)[b]
Aviation gasoline	0.51
Crude oil	0.45
Diesel/distillate	0.008
Conventional gasoline	1.1
FRFG 2	0.61
CARFG2	0.71
Heavy gas oil	0.0002
Jet fuel	1.05
Jet kerosene	0.004
Naphtha	1.24
Residual fuel oil	0.001

[a] From EPA's L&E document (EPA 1998c).

[b] Values for gasoline blends are determined using EPA's *Unconsolidated Complex Model for RFG* (see Section 4). Values for other fuels are based on the weight percentage of benzene in the fuel.

Section 4
Downstream Air Toxics Emissions

4.1 Background and Methodology

4.1.1 Overview

Downstream emissions are those generated by vehicle operation. Sources for downstream emissions include vehicle refueling, vehicle tailpipe exhaust emissions, and evaporative emissions from vehicle operation. This section provides our estimated T/VOC fractions for each of the air toxics and fuels identified in this report.

As in our treatment of upstream emissions, we employed T/VOC fractions to calculate downstream air toxics emissions (Section 3.1 provides a discussion of the rationale behind the T/VOC fraction approach). Using this approach, we determined air toxics emissions by multiplying a vehicle's estimated downstream VOC emissions by a particular pollutant's T/VOC fraction for that vehicle technology. This approach, generally accepted and used by EPA (EPA 1993; 1999a), demands that we identify T/VOC fractions for acetaldehyde, benzene, butadiene, and formaldehyde for vehicles operating on the conventional and alternative fuels listed in Table 4.1. We considered these fuels as operating in vehicle technologies currently available or expected to be available within the next several years. We will analyze long-term technologies (i.e., those that will be available in the next 5–10 years) during the second phase of this project.

One issue that arose in researching T/VOC fractions for LDVs was the distinction between the following classes of LDVs: light-duty gasoline vehicle (LDGV) (passenger cars), light-duty trucks with a gross vehicle weight of less than 6,000 lb (LDGT1), and light-duty trucks with a gross vehicle weight of 6,001 to 8,500 lb (LDGT2). EPA (1999a) has shown that the differences in T/VOC fractions among these vehicle types are negligible with respect to RFG.[14] Therefore, in this phase of the project, we chose to conduct the analysis on the basis of assumptions for LDGVs.[15]

T/VOC data for AFVs are less certain. There have been no studies that attempt to distinguish T/VOC fractions among LDV classes (i.e., cars, LDGT1, and LDGT2). As discussed in the following sections, there are very few studies that estimate air toxics emissions from AFVs. Because of this lack of data, we cannot say whether T/VOC fractions from different classes of AFVs would vary significantly. Therefore, as we did for conventional vehicles, we assumed that calculations of T/VOC fractions for AFVs can be applied equally to the three vehicle classes.

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[14] Of course, mass emissions of air toxics from different classes of LDVs will be different because of the differences in VOC emissions from these vehicles.

[15] For a more complete discussion of the LDGV assumptions, see Wang 1999a,b.

4.1.2 General Methodology for Conventional Fuels

T/VOC fractions for conventional fuels (i.e., gasoline and diesel) were determined on the basis of existing literature and original analysis using EPA's *Unconsolidated Complex Model for Reformulated Gasoline*.[16] The most useful published report was one recently released in draft form by EPA entitled *Estimation of Motor Vehicle Toxic Emissions and Exposure in Selected Urban Areas* (EPA 1999a). This report was a followup to a 1993 EPA report entitled *Motor Vehicle Related Air Toxics Study* (EPA 1993). The 1999 report was prepared partly in response to Section 202(l) of the CAAA of 1990, which require EPA to promulgate regulations that control toxic air pollutants from mobile sources. The study also supports EPA's regulatory impact analysis for proposed Tier 2 tailpipe standards.

Table 4.1 Vehicle Technologies Included in the Downstream Analysis

Fuel/Vehicle Technologies
CG
FRFG2[a]
CARFG3[a]
CD
Bi-CNG
CNG
M85
E85
Dedicated LPG
Battery-powered EV
Grid-connected HEV operating on CARFG3 (HEV1)
Grid-independent HEV operating on FRFG2 (HEV2)
Grid-independent HEV operating on CD (HEV3)

[a] For our analysis, we include several formulations of FRFG2 and CARFG3. We define these fuel blends in later sections.

In the new EPA work (EPA 1999a), toxic/total organic gas (T/TOG) fractions are estimated using EPA's *Unconsolidated Complex Model for Reformulated Gasoline* (Cook 1999). The T/TOG fractions reported by EPA (1999a) are for various conventional fuel blends that are currently in use or may be used in nine urban areas over the next decade. For this study, we also used the *Unconsolidated Complex Model* to establish T/VOC fractions for conventional and reformulated fuels. The model can be used to explore the impacts of an infinite number of fuel blends. However, for this phase of the project, we defined the following fuel blends for each of our conventional fuels:

- CG: an average blend of conventional gasoline sold in non-RFG areas of the country;

- FRFG2a: FRFG2 containing 2.1% oxygen by weight and using methyl tertiary butyl ether (MTBE) as an oxygenate;

- FRFG2b: FRFG2 containing 3.5% oxygen by weight and using ethanol as an oxygenate;

- CARFG3a: CARFG3 with no oxygenate added; and

- CARFG3b: CARFG3 containing 2.0% oxygen by weight and using ethanol as an oxygenate.

---

[16] The "unconsolidated" model separates emissions by control technology type, so that the user can identify T/VOC fractions for different control technologies. We obtained the model from Cook 1999.

Each of these fuels is discussed in more detail below. Using these pre-defined fuel blends, we ran the *Complex Model* for each conventional fuel type. For each fuel, we determined T/VOC fractions on the basis of the assumption that a three-way catalytic converter with fuel injection (3WPFI) would be used.[17] All T/VOC estimates are for tailpipe exhaust emissions, except for benzene, for which we determined both exhaust and evaporative fractions. Evaporative fractions for benzene are totals that include hot soak, diurnal, running loss, and refueling emissions. These T/VOC fractions were applied to VOC emissions (in g/mi) within the GREET model to determine emission factors for our toxic pollutants (see Section 5).

4.1.3 General Methodology for Alternative Fuels

The method for determining T/VOC emissions fractions for alternative fuels was based largely on analyzing existing empirical data from published studies or publicly available databases.[18] No standard method was applied because the data were in disparate forms and required various kinds of manipulation and analysis. In the appropriate sections, we note the studies that we used and the analytical methods that we employed. Once these T/VOC estimates were obtained, we applied them to VOC emissions estimates (in g/mi) in the GREET model to calculate air toxic emissions factors.

T/VOC fractions for CVs and AFVs are listed in Table 4.2. The data sources and methodology for generating the values listed are discussed in Section 4.2.

4.2 Detailed T/VOC Fraction Estimates

4.2.1 Conventional Gasoline Vehicles

To estimate T/VOC fractions for CG, we first defined our CG fuel blend. We used an average CG blend similar to the one studied in Wang (1999a). The Reid vapor pressure (RVP) for this summer blend is kept under 8.7 pounds per square inch [psi]). The specific parameters that were used in the *Complex Model* are listed in Table 4.3. These values were taken from 1998 survey data contained in the *Report of the Blue Ribbon Panel on Oxygenates in Gasoline* (BRP 1999).

From these fuel parameters, we ran the EPA *Complex Model* and determined the T/VOC fractions listed in Table 4.4.

4.2.2 Federal Phase 2 Reformulated Gasoline (FRFG2a and FRFG2b) Vehicles

To estimate T/VOC fractions for FRFG2, we first defined our two FRFG2 blends (described in Table 4.5). FRFG2 is a summer blend with an RVP averaged over northern and southern

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[17] EPA expects 100% of LDVs and over 90% of LDGTs sold in 2001 to be equipped with this type of catalytic converter (EPA 1999a).

[18] Most notably, the National Alternative Fuel Data Center (NAFDC) collects emissions data on hundreds of AFVs operating in the federal government fleet. These data are available for download from NAFDC's web site (www.afdc.doe.gov).

Table 4.2 T/VOC Fractions for Downstream Emissions

	T/VOC Fractions (%)				
Fuel	Benzene	Acetaldehyde	Formaldehyde	Butadiene	Benzene (Evaporative)
CG	5.64	0.48	1.25	0.62	1.13
FRFG2a	4.35	0.51	1.73	0.67	0.56
FRFG2b	4.37	1.25	1.58	0.67	0.61
CARFG3a	3.85	0.53	1.68	0.56	0.49
CARFG3b	3.88	0.89	1.69	0.57	0.49
CD	5.09	0.53	1.29	0.67	0.00
Bi-CNG	0.20	0.46	6.21	0.03	0.00
CNG	0.20	0.46	6.21	0.03	0.00
M85	1.00	0.20	9.00	0.10	0.08
E85	1.00	12.70	5.20	0.15	0.08
LPG	0.41	0.36	1.17	0.08	0.00

Table 4.3 Fuel Parameters for Conventional Gasoline

Parameter	Value
Oxygenate (O_2 % wt)[a]	0.4
Sulfur (ppm)	339
RVP (psi)	8.25
E200 (%)	41
E300 (%)	83
Aromatics (%)	32
Olefins (%)	13
Benzene (%)	1.5

[a] Oxygenate in this case is MTBE.

Table 4.5 Fuel Parameters for FRFG2a and FRFG2b

Parameter	FRFG2a	FRFG2b
Oxygenate (O_2 % wt)	2.1[a]	3.5[b]
Sulfur (ppm)	150	150
RVP (psi)	6.7	6.7
E200 (%)	49	49
E300 (%)	87	87
Aromatics (%)	25	25
Olefins (%)	11	11
Benzene (%)	0.68	0.68

[a] Oxygenate in this case is MTBE.

[b] Oxygenate in this case is ethanol.

Table 4.4 T/VOC Fractions for Conventional Gasoline

Air Toxic	T/VOC Fraction (%)
Benzene	5.64
Acetaldehyde	0.48
Formaldehyde	1.25
1,3-Butadiene	0.62
Benzene (evaporation)	1.13

markets (BRP 1999). The BRP report also presents a national average in which the oxygenate percentage is 2.26%; however, this average includes both MTBE and ethanol oxygenates. Ethanol oxygenates, most commonly added to RFG sold in Chicago and Milwaukee, tend to have higher oxygenate percentages (3.5%) that increased the average oxygenate percentage to above 2.1% (the percent that would be expected with MTBE as the sole oxygenate). So we established two fuels. The first (FRFG2a) uses the expected 2.1% (by weight) MTBE oxygenate percentage. The second (FRFG2b) uses the 3.5% (by weight) ethanol oxygenate percentage. We also used a value of 0.68% benzene (although the FRFG2 requirements

indicate a 0.95% average) because BRP (1999) states that this lower percentage was used throughout the FRFG1 program. We expect these lower values to continue with FRFG2.

The T/VOC fractions resulting from our *Complex Model* run are listed in Table 4.6. These results are consistent with those of other studies that indicate lower benzene emissions and higher formaldehyde emissions from MTBE blended fuels (Kirchstetter et al. 1996).

4.2.3 California Phase 3 Reformulated Gasoline (CARFG3a and CARFG3b) Vehicles

Recently, CARB defined a CARFG3 fuel formulation (CARB 1999, Table 3.1) that was approved on December 19, 1999, and will go into effect in 2002. This fuel will eliminate the use of MTBE and will likely contain ethanol as an oxygenate. There is another possibility — that CARFG3 will not contain any oxygenate — if EPA grants a waiver from the oxygenate rule, which California has requested.

For this study, we used two CARFG3 blends, both of which assume the formulation presented in CARB (1999) and BRP (1999). In the first blend (CARFG3a), we assumed no oxygenate; in the second (CARFG3b), we assumed 2.0% oxygen (by weight) using ethanol as an oxygenate. This second case represents an average of the ethanol "flat limit" under the CARFG3 rule. Our CARFG3 fuel blends are described in Table 4.7.

On the basis of these fuel parameters, we used the *Complex Model* to calculate the T/VOC fractions listed in Table 4.8.

Table 4.6 T/VOC Fractions for FRFG2

	T/VOC Fraction (%)	
Air Toxic	FRFG2a	FRFG2b
Benzene	4.35	4.37
Acetaldehyde	0.51	1.25
Formaldehyde	1.73	1.58
1,3-Butadiene	0.67	0.67
Benzene (evaporation)	0.56	0.61

Table 4.7 Fuel Parameters for CARFG3

Parameter	CARFG3a	CARFG3b
Oxygenate (O_2 % wt)[a]	0.0	2.0
Sulfur (ppm)	15.0	15.0
RVP (psi)	6.8	6.8
E200 (%)	51.0	51.0
E300 (%)	89.0	89.0
Aromatics (%)	22.0	22.0
Olefins (%)	4.0	4.0
Benzene (%)	0.55	0.55

[a] The oxygenate in this case is ethanol.

Table 4.8 T/VOC Fractions for CARFG3

	T/VOC Fraction (%)	
Air Toxic	CARFG3a	CARFG3b
Benzene	3.85	3.88
Acetaldehyde	0.53	0.89
Formaldehyde	1.68	1.69
1,3-Butadiene	0.56	0.57
Benzene (evaporation)	0.49	0.49

4.2.4 Conventional Diesel Vehicles

EPA (1999a) estimates of T/VOC fractions for diesel-fueled passenger cars are listed in Table 4.9. These values are based on several previous studies of available speciation data (Springer 1977, 1979; Bass and Newkirk 1995; Norbeck et al. 1998; CARB 1991).[19]

4.2.5 Bi-Fuel and Dedicated Compressed Natural Gas Vehicles

Bi-fuel and dedicated CNG vehicles offer an opportunity to dramatically reduce toxic emissions from vehicle tailpipes. The most recent published analyses of speciated emissions data from light-duty CNG vehicles is in Winebrake and Deaton (1999a) and Kelly et al. (1999). In those studies, the researchers analyze data collected at NAFDC on CNG vehicles operating in the federal government fleet. On the basis of that analysis (of dedicated CNG Dodge Ram vans operating on NG), we determined the T/VOC fractions listed in Table 4.10.

The values in Table 4.10 represent T/VOC fractions from studies of dedicated CNG vehicles. For this study, we assumed that these fractions remain the same for bi-fuel CNG vehicles when those vehicles operate on CNG. When those vehicles operate on gasoline, we assumed the gasoline T/VOC fractions.

Table 4.9 T/VOC Fractions for Conventional Diesel Fuel[a]

Air Toxic	T/VOC Fraction (%)
Benzene	5.09
Acetaldehyde	0.53
Formaldehyde	1.29
1,3-Butadiene	0.67
Benzene (evaporation)	0.00

[a] From EPA (1999a, Appendix C). Values were modified to T/VOC using VOC conversion factors. No evaporative emissions occur with diesel fuel.

Table 4.10 T/VOC Fractions for Dedicated Compressed Natural Gas Vehicles and Bi-Fuel Vehicles Fueled by Compressed Natural Gas

Air Toxic	T/VOC Fraction (%)[a]
Benzene	0.20
Acetaldehyde	0.46
Formaldehyde	6.21
1,3-Butadiene	0.03
Benzene (evaporation)	0.00

[a] Values based on Winebrake and Deaton (1999a) and Kelly et al. (1999) using average T/NMHC estimates for CNG vehicles, modified to T/VOC using 1.169 TOG/NMHC (from EPA 1999a) and 0.808 VOC/TOG conversion factors.

These values are not entirely consistent with those obtained in other studies. For example, Black, et al. (1998) tested one model year (MY) 1994 CNG Dodge Caravan and obtained much higher T/non-methane organic compound (NMOG) values (1.67% for benzene and 11.67% for formaldehyde). Winebrake and Deaton (1999a) analyzed 145 CNG vehicle tests for formaldehyde and acetaldehyde, but only five vehicle tests for butadiene and benzene. We chose to use the Winebrake and Deaton (1999a) estimates, with a slight modification to 1,3-butadiene on the basis of Kelly et al. (1999).

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[19] These studies and others often rely on emissions tests from only a handful of vehicles. We also suspect that most, if not all, diesel vehicles tested were indirect-injection diesel engines. In our analysis of near-term technologies, we include direct-injection diesel engines. Fractions could be different between the two engine types.

Other earlier studies suggest that, compared to gasoline, CNG vehicles will offer similar formaldehyde and acetaldehyde emissions, virtually eliminate benzene emissions, and significantly reduce 1,3-butadiene emissions (EPA 1990; CARB 1989; CARB 1991).

4.2.6 Liquefied Petroleum Gas Vehicles

Little speciation analysis has been conducted for LPG vehicles. LPG vehicles were not included in the published Winebrake and Deaton (1999a) study because of the limited sample sizes (three bi-fueled vehicles, tested on both LPG and CARFG2). However, the data for these three vehicles (MY96 Ford pickup trucks) were made available for this report. After conducting an analysis similar to that described in Winebrake and Deaton (1999a), we determined the T/VOC estimates listed in Table 4.11.

The values listed in Table 4.11 are based on emissions tests of bi-fuel vehicles operating on LPG. We understand that these values may not be identical to fractions for dedicated LPG vehicles. Earlier studies indicate that, compared to gasoline, LPG vehicles will have increased acetaldehyde emissions, lower benzene emissions, and significantly reduced 1,3-butadiene emissions (EPA 1989; CARB 1989).

4.2.7 Methanol Flexible-Fuel Vehicles

Relatively more speciation data are available for methanol FFVs than for the gaseous fuels. The Winebrake and Deaton (1999a) study and the Kelly et al. (1999) report contain T/NMHC analyses of Dodge Intrepids, Dodge Spirits, and Econoline vans operating on methanol fuel blends. The fractions are affected by the amount of methanol in these blends. Table 4.12 presents T/VOC fraction results for M85.

The values in the middle column of Table 4.12 are somewhat higher than values in Kelly et al. (1996a), who tested six MY93 M85 Dodge Spirits and obtained values of 1.23% benzene, 0.22% acetaldehyde, 10.86% formaldehyde, and 0.09% butadiene. They are also higher than values from Black et al. (1998), who presented data from a single MY93 Ford Taurus (0.59% benzene, 0.07% acetaldehyde, and 4.90% formaldehyde). Finally, the results are higher than those obtained by Durbin et al. (1999), who tested 20 M85 vehicles and obtained the following average values: 0.71% benzene, 0.03% butadiene, 6.14% formaldehyde, and 0.45% acetaldehyde. The recommended T/VOC fractions in Table 4.12 have been adjusted on the basis of these lower values.

The final recommended results are consistent with earlier studies. For example, according to EPA (1989), the Auto/Oil Air Quality Improvement Research Program (AAQIRP) (1992), and

Table 4.11 T/VOC Fractions for Dedicated Liquefied Petroleum Gas Vehicles

Air Toxic	T/VOC Fraction (%)[a]
Benzene	0.41
Acetaldehyde	0.36
Formaldehyde	1.17
1,3-Butadiene	0.08
Benzene (evaporation)	0.00

[a] Values are based on data from Winebrake and Deaton (1999b) and average T/NMHC estimates for LPG vehicles, modified to T/VOC using 1.169 TOG/NMHC and 0.808 VOC/TOG conversion factors.

Table 4.12 T/VOC Fractions for Methanol-Fueled Flexible Fuel Vehicles

Air Toxic	T/VOC Fraction (%)[a]	Recommended T/VOC (%)[b]
Benzene	2.25	1.00
Acetaldehyde	0.48	0.20
Formaldehyde	24.13	9.00
1,3-Butadiene	0.61	0.10
Benzene (evaporative)[c]	NA[d]	0.08

[a] Values are based on data from Winebrake and Deaton (1999a) and average T/NMHC estimates for M85 vehicles, modified to T/VOC using 1.169 TOG/NMHC and 0.808 VOC/TOG conversion factors.

[b] Values are modifications of the T/VOC data based on Kelly at al. (1999) and other studies described below.

[c] Evaporative benzene emissions are estimated to depend entirely on the percent of gasoline found in the methanol blends. Thus, for M85, we calculate a benzene evaporative fraction that is 15% of the fraction for CG.

[d] Not available. Evaporative benzene emissions were not calculated by Winebrake and Deaton (1999a).

Kirwan (1993), primary formaldehyde emissions from M85 vehicles are expected to be 4–6 times higher than those from gasoline vehicles. However, because M85 vehicles are also expected to have lower THC emissions than gasoline vehicles, secondary formaldehyde emissions are expected to be approximately 40% lower (EPA 1989). Gabele (1990) has also pointed out that most of the primary formaldehyde emissions occur during the cold-start portion of emissions tests. Modifications in the catalytic converters installed on these vehicles may significantly reduce formaldehyde emissions (CARB 1997b).

Earlier studies also suggest that M85 vehicles will have 90% lower butadiene emissions, significantly lower benzene emissions, and lower acetaldehyde emissions (EPA 1989; AAQIRP 1992).

4.2.8 Ethanol Flexible-Fuel Vehicles

Like methanol-fueled vehicles, a number of studies have been conducted for ethanol-fueled FFVs. Winebrake and Deaton (1999a) included MY92 and MY93 Chevrolet Lumina and MY95 Ford Taurus models in their data analysis (96 vehicle tests for formaldehyde and acetaldehyde and nine vehicle tests for benzene and butadiene). Kelly et al. (1996b, 1999) analyzed Chevrolet Luminas and obtained similar results. From those studies, we recommended the T/VOC estimates listed in Table 4.13.[20]

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[20] Like M85, E85 is a common ethanol fuel blend found at ethanol fueling facilities. Most vehicles operating on E85 are "flexible-fuel" vehicles. These vehicles can operate on fuel blends ranging from pure gasoline (E0) to 85% ethanol (E85). Flexible-fuel vehicles that are powered by E85 *and* gasoline will operate on blends containing ethanol at concentrations below 85%.

Table 4.13 T/VOC Fractions for Ethanol-Fueled Flexible Fuel Vehicles

Air Toxic	T/VOC Fraction (%)[a]	Recommended T/VOC (%)[b]
Benzene	1.30	1.00
Acetaldehyde	12.66	12.70
Formaldehyde	5.22	5.20
1,3-Butadiene	0.20	0.15
Benzene (evaporative)[c]	NA[d]	0.08

[a] Values are based on data from Winebrake and Deaton (1999a) and average T/NMHC estimates for E85 vehicles, modified to T/VOC using 1.169 TOG/NMHC and 0.808 VOC/TOG conversion factors.

[b] Values are modifications of the T/VOC data based on Kelly at al. (1999) and other studies described below.

[c] Evaporative benzene emissions are estimated to depend entirely on the percent of gasoline found in the ethanol blends. Thus, for E85, we calculate a benzene evaporative fraction that is 15% of the fraction for CG.

[d] Not available. Evaporative benzene emissions were not calculated by Winebrake and Deaton (1999a).

Our estimates are supported by earlier studies that suggest that, when compared to gasoline, ethanol vehicles have excessive acetaldehyde emissions, lower benzene emissions, lower butadiene emissions, and similar formaldehyde emissions (EPA 1989, 1990; AAQIRP 1992). Even vehicles operating on E10 fuel have showed significantly higher acetaldehyde emissions compared to gasoline (Black et al. 1998).

4.2.9 Electric Vehicles

Electric vehicles have no toxic tailpipe emissions. Toxic emissions for electric vehicles occur only during upstream processes (mainly electricity generation). For this analysis, we assumed that EVs are charged using an average U.S. generation mix: natural gas (15%), coal (54%), nuclear power (18%), residual oil (1%), and other (12%).

4.2.10 Grid-Connected Hybrid Electric Vehicles Fueled by CARFG3b (HEV1)

HEVs operating on grid power will have no toxic tailpipe emissions. Grid-connected HEVs operating on electricity and an internal combustion engine fueled by RFG will have T/VOC fractions identical those of the RFG blends discussed earlier. For this analysis, we assumed that 30% of the vehicle miles traveled (VMT) for the HEV1 will be powered by grid electricity and 70% will be powered by the internal combustion engine.

4.2.11 Grid-Independent Hybrid Electric Vehicles Fueled by FRFG2a (HEV2)

We assumed that grid-independent HEVs operating on electricity and an internal combustion engine fueled by RFG will have T/VOC fractions identical to those of the gasoline blends discussed earlier.

4.2.12 Grid-Independent Hybrid Electric Vehicles Fueled by Conventional Diesel Fuel (HEV3)

We assumed that grid-independent HEVs operating on electricity and an internal combustion engine fueled by CD will have T/VOC fractions identical to those for CD.

This section of the report presents air toxic emissions results for each of the fuels discussed in this study. To generate these results, we used default assumptions in the GREET model for near-term fuels and vehicle technologies, as discussed in Wang (1999a). From these assumptions, we generated VOC emissions for each stage of the total fuel cycle. We multiplied these VOC estimates by the T/VOC fractions discussed in Sections 3 and 4 of this report (see Section 3.1 for the rationale in using this approach). This method allowed us to calculate toxic emissions for each stage of the total fuel cycle and for each type of fuel/vehicle technology. A summary table of our results is included as Table 5.1. The data in Table 5.1 form the basis of the graphs that follow.

Table 5.1 lists emissions from passenger cars in mg/mi for each of the three fuel-cycle stages analyzed in this study. Emissions values are for both urban and non-urban areas.[21] Because light-duty trucks have higher VOC emissions in the downstream stages of the fuel cycle, we would expect slightly higher per-mile emissions estimates for those types of vehicles. However, we reserve that analysis for future work.

In Table 5.1, we also include a "combined air toxics emissions" metric, calculated by multiplying each toxic emissions value by its CURE and then dividing the result by the benzene CURE value.[22] We applied the following formula to our results:

$$X_{CURE} = X_i \frac{CURE_i}{CURE_{benzene}}$$ [4]

where:

X_i = the emissions value for the pollutant,

$CURE_i$ = the CURE value for the pollutant,

$CURE_{benzene}$ = the CURE value for benzene, and

X_{CURE} = the benzene-weighted result.

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[21] The urban versus non-urban emissions apportionment discussed in Section 5.2 was determined on the basis of estimates of the geographic locations of emissions points throughout the fuel cycle. See Wang (1999a) for a detailed discussion of issues surrounding urban versus rural emissions apportionment.

[22] We could have chosen to use the CURE for another toxic pollutant (instead of benzene) as the normalizing parameter. We chose benzene because of its familiarity and the fact that its CURE was neither the highest nor the lowest available CURE.

Table 5.1 Estimated Per-Mile Air Toxics Emissions for Selected Fuels (g/mi for VOC and mg/mi for air toxics)[a]

Vehicle	Stage	VOC	Formaldehyde	Acetaldehyde	Butadiene	Benzene	Four Air Toxics Combined (mg/mi) EPA CUREs	CARB CUREs
CG	Feedstock	17.11	0.244	0.050	0.004	0.212	0.750	0.292
	Fuel	71.64	0.753	0.177	0.073	1.515	5.198	2.114
	Vehicle	207.00	1.000	0.384	0.496	5.947	24.348	9.097
	Total	295.76	1.996	0.611	0.573	7.674	30.296	11.503
FRFG2a	Feedstock	17.11	0.244	0.050	0.004	0.212	0.750	0.292
	Fuel	71.48	0.818	0.187	0.072	1.112	4.861	1.719
	Vehicle	160.90	1.246	0.367	0.482	3.630	21.952	6.750
	Total	249.49	2.308	0.603	0.558	4.954	27.563	8.760
FRFG2b	Feedstock	17.11	0.244	0.050	0.004	0.212	0.750	0.292
	Fuel	90.99	0.668	0.211	0.094	1.146	5.414	1.854
	Vehicle	160.90	1.138	0.900	0.482	3.689	21.983	6.836
	Total	269.00	2.050	1.160	0.580	5.046	28.147	8.981
CARFG3a	Feedstock	17.11	0.244	0.050	0.004	0.212	0.750	0.292
	Fuel	71.68	0.818	0.187	0.072	1.112	4.861	1.719
	Vehicle	160.90	1.210	0.382	0.403	3.208	18.805	5.857
	Total	249.69	2.272	0.618	0.479	4.532	24.416	7.868
CARFG3b	Feedstock	17.11	0.244	0.050	0.004	0.212	0.750	0.292
	Fuel	82.89	0.668	0.211	0.094	1.146	5.414	1.854
	Vehicle	160.90	1.217	0.641	0.410	3.229	19.150	5.946
	Total	260.90	2.129	0.901	0.508	4.587	25.314	8.092
CD	Feedstock	12.67	0.180	0.037	0.003	0.157	0.555	0.216
	Fuel	21.22	0.440	0.103	0.043	0.489	2.651	0.841
	Vehicle	80.00	1.032	0.424	0.536	4.072	23.883	7.467
	Total	113.89	1.653	0.564	0.582	4.718	27.089	8.524
Bi-CNG	Feedstock	17.70	1.387	0.178	0.005	0.153	2.554	0.488
	Fuel	12.60	0.912	0.111	0.007	0.051	1.741	0.291
	Vehicle	111.50	2.981	0.221	0.014	0.096	5.309	0.818
	Total	141.80	5.279	0.510	0.027	0.300	9.603	1.596
CNG	Feedstock	17.13	1.342	0.172	0.005	0.148	2.471	0.472
	Fuel	12.19	0.882	0.108	0.007	0.050	1.685	0.281
	Vehicle	44.70	1.987	0.147	0.010	0.064	3.539	0.545
	Total	74.02	4.211	0.427	0.021	0.262	7.695	1.298
LPG	Feedstock	10.34	0.301	0.054	0.003	0.150	0.751	0.238
	Fuel	24.80	0.632	0.147	0.051	0.217	2.980	0.663
	Vehicle	76.70	0.749	0.230	0.051	0.262	3.224	0.739
	Total	111.84	1.682	0.431	0.106	0.630	6.954	1.639
M85	Feedstock	8.38	0.299	0.052	0.003	0.130	0.716	0.215
	Fuel	54.31	0.525	0.098	0.042	0.432	2.706	0.798
	Vehicle	175.95	6.120	0.136	0.068	0.766	12.682	2.444
	Total	238.64	6.943	0.286	0.113	1.328	16.104	3.456
E85	Feedstock	-89.45	1.581	0.488	0.284	0.439	12.622	2.476
	Fuel	394.14	1.579	0.219	0.113	0.477	6.830	1.488
	Vehicle	175.95	3.536	8.636	0.102	0.766	12.035	2.900
	Total	480.65	6.695	9.343	0.499	1.682	31.487	6.864

Continued

Table 5.1 Estimated Per-Mile Air Toxic Emissions for Selected Fuels
(g/mi for VOC and mg/mi for air toxics)[a] (Cont.)

Vehicle	Stage	VOC	Formaldehyde	Acetaldehyde	Butadiene	Benzene	EPA CUREs	CARB CUREs
				Pollutant (mg/mi)			**Four Air Toxics Combined (mg/mi)**	
EV	Feedstock	27.61	0.653	0.072	0.046	0.124	2.720	0.536
	Fuel	5.79	0.061	0.056	0.002	0.092	0.275	0.123
	Vehicle	0.00	0.000	0.000	0.000	0.000	0.000	0.000
	Total	33.40	0.713	0.128	0.048	0.217	2.995	0.659
HEV1	Feedstock	9.00	0.224	0.036	0.004	0.101	0.605	0.176
	Fuel	33.02	0.280	0.093	0.036	0.449	2.138	0.729
	Vehicle	103.74	0.852	0.449	0.287	2.217	13.361	4.119
	Total	145.76	1.356	0.578	0.328	2.768	16.104	5.024
HEV2	Feedstock	9.01	0.128	0.026	0.002	0.111	0.395	0.154
	Fuel	37.62	0.431	0.098	0.038	0.585	2.559	0.905
	Vehicle	148.20	1.246	0.367	0.482	3.559	21.881	6.678
	Total	194.82	1.805	0.491	0.522	4.256	24.834	7.737
HEV3	Feedstock	8.55	0.122	0.025	0.002	0.106	0.375	0.146
	Fuel	14.32	0.297	0.070	0.029	0.330	1.789	0.568
	Vehicle	80.00	1.032	0.424	0.536	4.072	23.883	7.467
	Total	102.87	1.451	0.518	0.567	4.508	26.047	8.181

[a] Upstream stages include a host of activities, each contributing to the per-mile values listed. This fact alleviates some apparent contradictions in the table. For example, because ethanol plants produce animal feeds together with ethanol, emission "credits" from produced animal feeds are calculated by using the so-called "displacement method" (Wang et al. 1999). So E85 gains a "VOC credit," represented by a negative VOC value in the table; however, the T/VOC fractions for these credit-generating activities are quite small, while the fractions are large for other upstream activities. Thus, the feedstock stage for E85 vehicles shows an overall VOC credit, while still demonstrating positive toxic emissions.

As shown in Table 5.1, we applied this metric using both EPA and CARB CURE values.

Our results are discussed in three major sections. The first section (5.1) discusses toxic emissions as a function of fuel-cycle stages. From those results we can determine where in the total fuel cycle most toxic emissions arise for each fuel. The second section (5.2) presents per-mile emissions results in a fuel-by-fuel comparison for each of the toxic pollutants. Section 5.2 also partitions the data into urban versus non-urban emissions so that the relative impacts of each fuel can be studied as they relate to potential exposure sites. Finally, Section 5.3 provides the results of our sensitivity analysis of the uncertainty associated with our upstream butadiene data.

5.1 Toxic Emissions for Each Stage of the Fuel Cycle for Conventional and Alternative Fuels

This section presents results of the apportionment of per-mile fuel-cycle emissions for three primary stages of the total fuel cycle: feedstock stage, fuel production and distribution stage, and vehicle operation stage. In the graphs that follow, these stages are noted as "feedstock," "fuel," and "vehicle," respectively. Note that the feedstock stage and the fuel production and distribution

stage account for all *upstream* fuel-cycle emissions; the vehicle operation stage accounts for *downstream* fuel-cycle emissions. Each of these stages includes a number of processes discussed in Sections 3.2 through 3.4.

Figures 5.1 through 5.5 show emissions apportionment for each of the pollutants studied. VOCs, acetaldehyde, total benzene, butadiene, and formaldehyde values are shown (in mg/mi) in each figure.
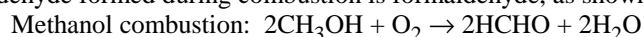
Figure 5.1 shows the contributions of various fuel-cycle stages to total VOC emissions for each of the fuels studied. Downstream emissions tend to dominate the totals, especially for the alternative fuels, but conventional fuel production adds a significant amount of VOCs. Several alternative fuels (CNG, LPG, and M85) demonstrate large reductions in VOC emissions during the fuel production and vehicle operation stages. Vehicles fueled by E85 have much higher fuel production emissions, primarily because of the distillation process, in which a large amount of energy is consumed. However, E85 vehicles also have a negative VOC contribution (i.e., a "VOC credit") in the feedstock phase of the fuel cycle because of VOC emission credits from co-products of ethanol in ethanol plants (see footnote to Table 5.1 for more information regarding VOC credits).

Figure 5.2 shows that acetaldehyde emissions are released primarily during vehicle operation. The scale for this graph is set at a maximum 1.50 mg/mi; acetaldehyde emissions from E85 vehicles far exceed this value (the actual value is noted next to the E85 bar). It is well known that combustion of ethanol generates a large amount of acetaldehyde emissions.[23] Acetaldehyde emission standards (like those for formaldehyde) may be needed to limit acetaldehyde emissions from ethanol-fueled vehicles.
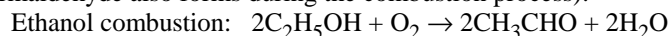
Figure 5.3 shows total benzene emissions (evaporative and combustion) throughout the fuel cycle for our studied fuels. Benzene emissions occur primarily during the vehicle operation stage of the fuel cycle, with the exception of some emissions that occur during the refining of conventional fuels.

Figure 5.4 provides butadiene emissions for each stage of the fuel cycle for each of the fuels studied. As the figure shows, most emissions occur in the downstream (vehicle operation) stage of the fuel cycle. Only E85 results in emissions during upstream stages (in particular, feedstock production) that are significant relative to total emissions.
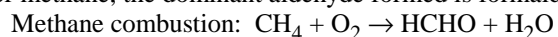
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[23] The combustion of alcohol and NG fuels proceeds in several stages. For methanol, the dominant aldehyde formed during combustion is formaldehyde, as shown in the following reaction:
   Methanol combustion: $2CH_3OH + O_2 \rightarrow 2HCHO + 2H_2O$
For ethanol, the dominant aldehyde formed is acetaldehyde, as shown in the following reaction (although formaldehyde also forms during the combustion process):
   Ethanol combustion: $2C_2H_5OH + O_2 \rightarrow 2CH_3CHO + 2H_2O$
For methane, the dominant aldehyde formed is formaldehyde, as shown in the following reaction:
   Methane combustion: $CH_4 + O_2 \rightarrow HCHO + H_2O$
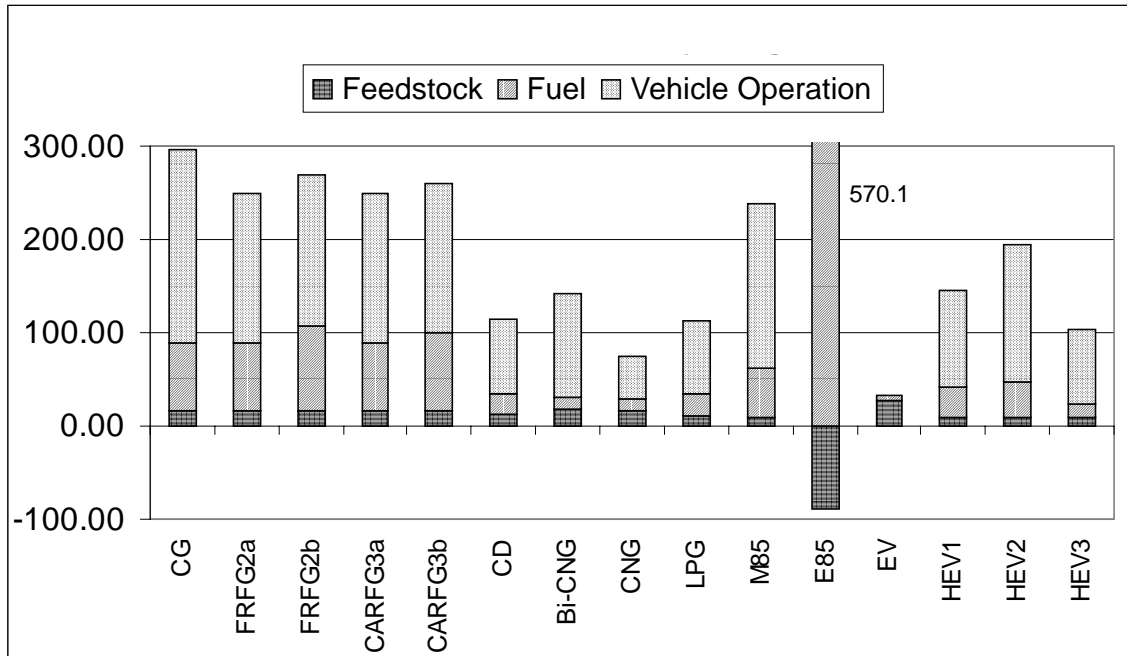Glassman (1996) contains more information on these and other combustion reactions.

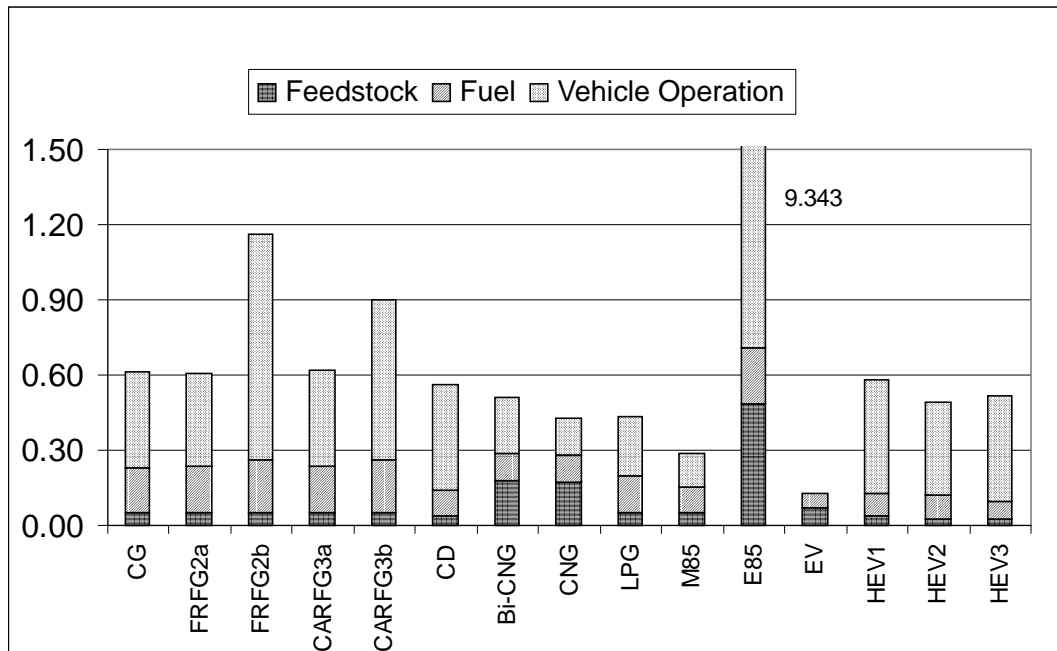**Figure 5.1 VOC Apportionment by Fuel-Cycle Stage (mg/mi)**

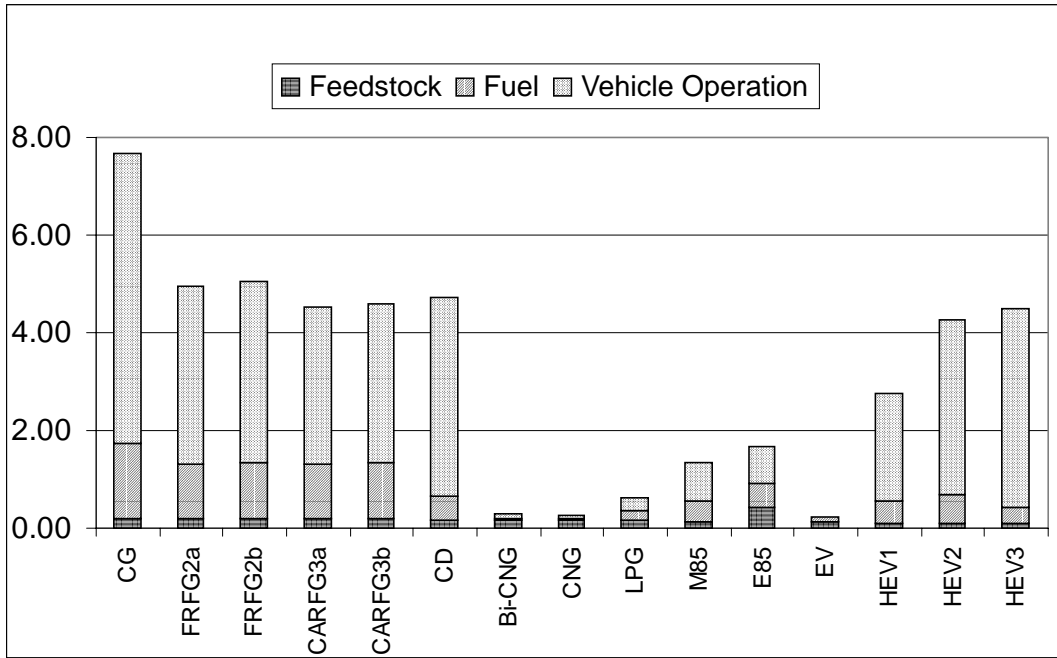**Figure 5.2 Acetaldehyde Apportionment by Fuel-Cycle Stage (mg/mi)**

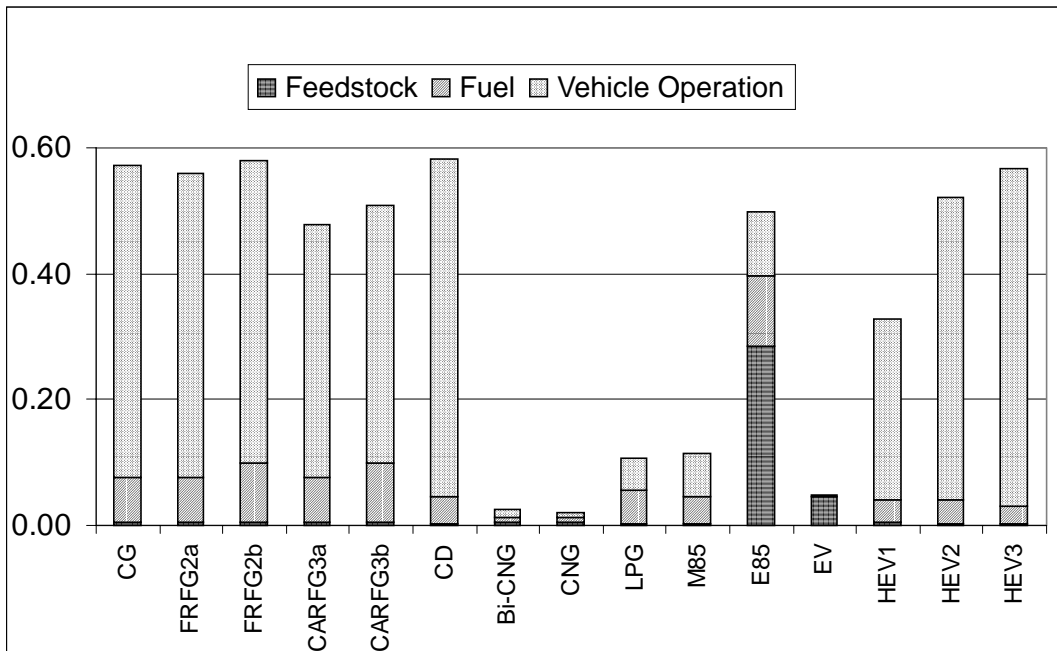**Figure 5.3 Benzene Apportionment by Fuel-Cycle Stage (mg/mi)**

Figure 5.4 Butadiene Apportionment by Fuel-Cycle Stage (mg/mi)

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Figure 5.5 reveals that vehicle operation contributes the highest levels of formaldehyde emissions for most fuels. This finding is especially true for the alcohol fuels (M85 and E85) and for CNG. On the basis of combustion chemistry, such levels of aldehydes are expected from the combustion of alcohol fuels and NG; aldehydes tend to be one of the primary combustion products of these fuels (Glassman 1996) (see footnote 23). However, formaldehyde emissions from M85, E85, and CNG vehicles are still below the 15-mg/mi emission standard established in EPA's Tier II regulations (EPA 1999c).

Formaldehyde emissions are also important during the fuel processing stage for several of the conventional fuels (CG, FRFG2, and CARFG3). These emissions are caused primarily by the refining process. Very few formaldehyde emissions occur in the feedstock stage of the fuel cycle.

5.2 Comparative Fuel-Cycle Emissions for Conventional and Alternative Fuel Vehicles

This section presents per-mile fuel-cycle emissions results for each of the fuels analyzed. We used the GREET model discussed in Wang (1999a) to calculate the per-mile toxic emissions for each fuel and vehicle technology. The model determines VOC emissions for each stage of the total fuel cycle. The VOC values were multiplied by the T/VOC fractions presented in Section 3 to calculate toxic emissions for each stage of the fuel cycle.[24] A summary of the results is provided in Table 5.1.

Figures 5.6 through 5.12 depict per-mile fuel-cycle emissions for each fuel type relative to CG. These figures can be used to better understand the potential impact that reformulated and alternative fuels will have on toxic emissions. The graphs show both total emissions and emissions expected to occur in urban areas. The reader is cautioned, however, that these emissions estimates do not necessarily characterize the relative *risk* posed by these toxic pollutants. Emissions estimates must be combined with appropriate exposure and dose-response assessments to compare the relative risks of the fuels.

As shown in Figure 5.6, urban VOC emissions are lower for all fuels relative to CG. The gaseous fuels demonstrate reductions in excess of 60%, while the alcohol fuels offer close to 20% fewer urban VOC emissions. Even the conventional, reformulated fuels show reductions in urban VOC emissions of about 20%. These urban emissions are largely a function of lower downstream VOC emissions.

We see similar results for total emissions (which include many nonurban, fuel production-related processes), with one striking exception — E85 vehicles. Total VOC emissions for E85 vehicles are much higher (over 60%) relative to CG. These emissions are caused by the high VOC levels associated with ethanol fuel production and distribution (see Table 5.1). However, because these emissions are likely to occur outside of urban centers, their overall health and environmental consequences are debatable.

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[24] Note that in some cases, particularly noncombustion process-related emissions, T/VOC fractions were not used. Instead air toxic emissions factors, usually in units of mg/10^6 Btu, were calculated and applied to total fuel throughput (in 10^6 Btu). This approach is discussed in Section 3.
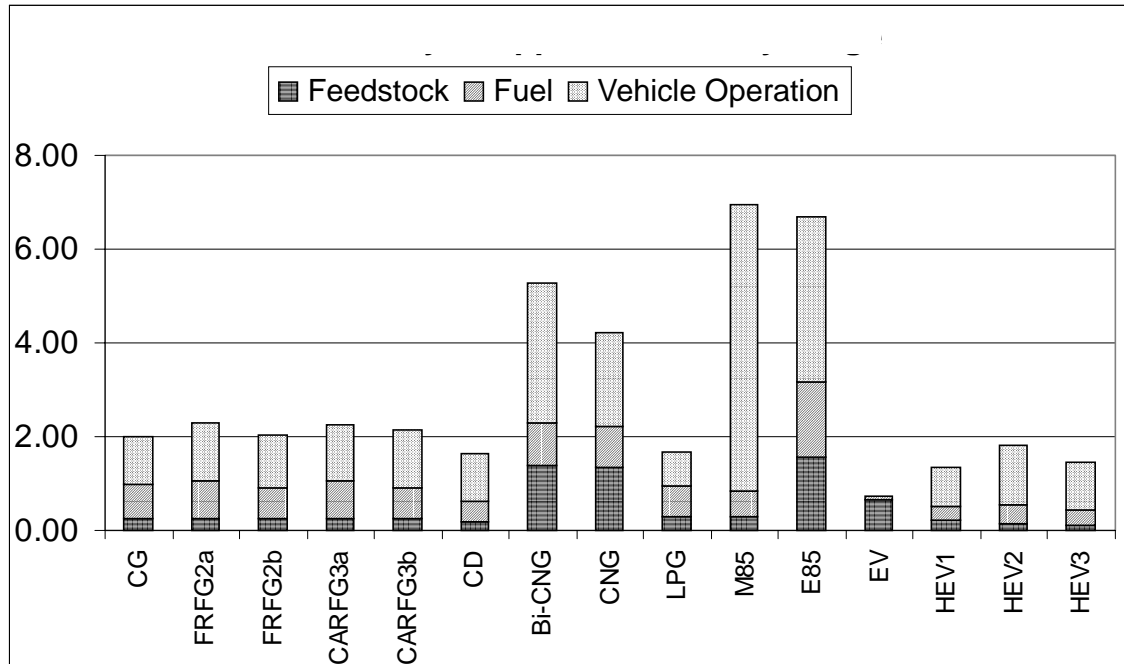
Figure 5.5 Formaldehyde Apportionment by Fuel-Cycle Stage (mg/mi)

Figure 5.7 depicts changes in per-mile fuel-cycle acetaldehyde emissions relative to CG. The most substantial increase comes from E85 vehicles (1,946% increase in total emissions and 1,431% increase in urban emissions). The high acetaldehyde tailpipe emissions generated by E85 vehicles are well documented (see footnote 23). As discussed in Section 4 and shown in Table 5.1, downstream emissions from ethanol-fueled vehicles are almost 20 times higher than for CG-fueled vehicles. The feedstock stage emissions of acetaldehyde are also 10 times greater for E85 than for CG, primarily because of the high upstream VOC emissions for ethanol.

CARFG3b and FRFG2b also exhibit higher acetaldehyde emissions, primarily because of the production and combustion of the ethanol oxygenate in these fuels. As expected, the ethanol oxygenate causes a significant increase in acetaldehyde emissions relative to gasoline, especially in urban environments, where vehicle tailpipe emissions dominate.

The gaseous fuels demonstrate reductions in acetaldehyde emissions of almost 50% — although their T/VOC fractions for acetaldehyde are higher than those for CG, their total VOC emissions are lower and cancel out the higher fractions. Vehicles fueled by M85 also exhibit low acetaldehyde emissions relative to gasoline. Because of the relative elimination of VOCs in the entire fuel cycle, EVs show the largest acetaldehyde reductions of all the alternatives.

Acetaldehyde emissions represent only *primary* emissions. Secondary acetaldehyde may form through reactions of various VOCs in the atmosphere. So secondary acetaldehyde emissions will likely be smaller for fuels that release fewer VOCs.
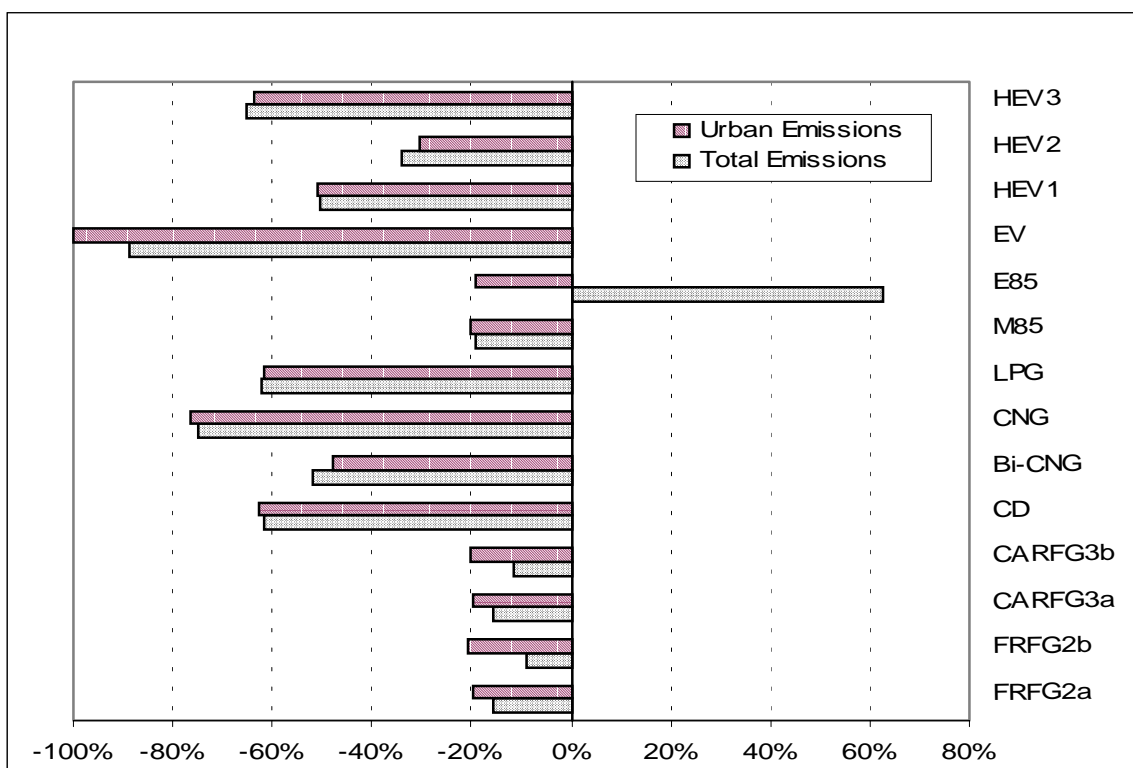
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Figure 5.6 Changes in Fuel-Cycle VOC Emissions for Alternative Fuel Vehicles Relative to Conventional Gasoline Vehicles

Unlike formaldehyde emissions, tailpipe acetaldehyde emissions will not be regulated under EPA's Tier II regulations (EPA 1999c). Although we may expect to see decreases in formaldehyde emissions as the Tier II regulations become effective, we may not see similar reductions for acetaldehyde unless EPA begins to regulate acetaldehyde.

Figure 5.8 depicts the per-mile fuel-cycle benzene emissions of various alternative fuels relative to CG. All fuels demonstrate significantly lower emissions; EVs, LPG vehicles, and CNG vehicles achieve close to a 100% reduction.

The alcohol fuels demonstrate benzene emission reductions of over 85% in the urban environment, mostly because of the low levels of benzene in these fuels. The RFGs show reductions between 38–45%, also because of a much lower percentage of benzene than CG.

As shown in Figure 5.9, urban butadiene emissions are much lower for all the alternatives relative to CG, except for CD. As discussed in Section 4, diesel fuels have T/VOC fractions for butadiene that are almost twice as high as those for CG primarily because diesel fuel contains more high molecular-weight polynuclear aromatic hydrocarbons (PAHs) than gasoline. These
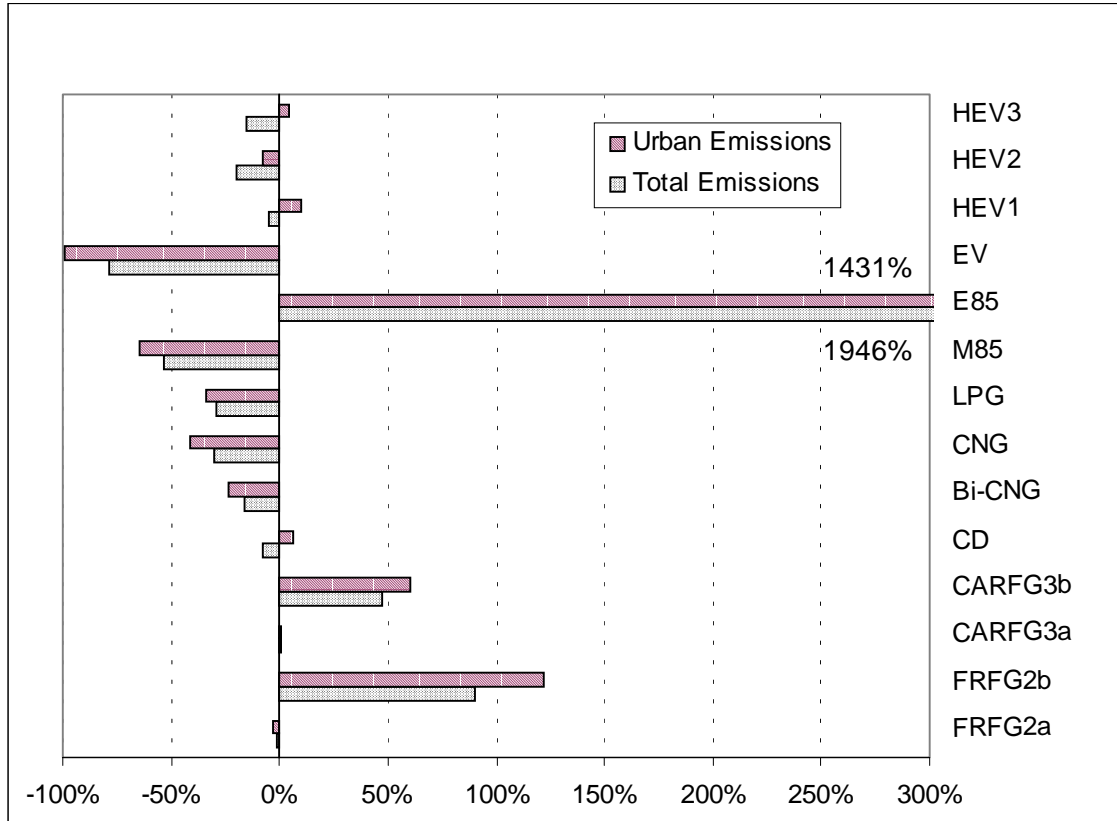
Figure 5.7 Changes in Fuel-Cycle Acetaldehyde Emissions for Alternative Fuel Vehicles Relative to Conventional Gasoline Vehicles

heavier PAH compounds found in diesel provide an abundant source for intermediate cyclic compounds such as benzene, which ultimately react to form butadiene (Coffman 2000; Glassman 1996).

Because of the virtual elimination of butadiene in the vehicle operations stage of the fuel cycle for gaseous fuels, there are significant butadiene emissions reductions for LPG and CNG vehicles. The alcohol fuels also achieve decreases of 70–85%. (Note the differences between *urban* and *total* butadiene emissions for E85 vehicles. The graph indicates that most of the butadiene emissions for E85 occur in the nonurban fuel production stages of the fuel cycle.)

As Figure 5.10 shows, formaldehyde emissions demonstrate significant variation depending on the fuel selected. The first noticeable difference is the extremely large increase in formaldehyde for M85 vehicles (424% higher than for CG). E85 vehicles and CNG vehicles also exhibit large increases relative to CG.

These emissions differences are primarily attributable to downstream formaldehyde emissions, as discussed in Section 4. Formaldehyde emissions from vehicle operation are up to
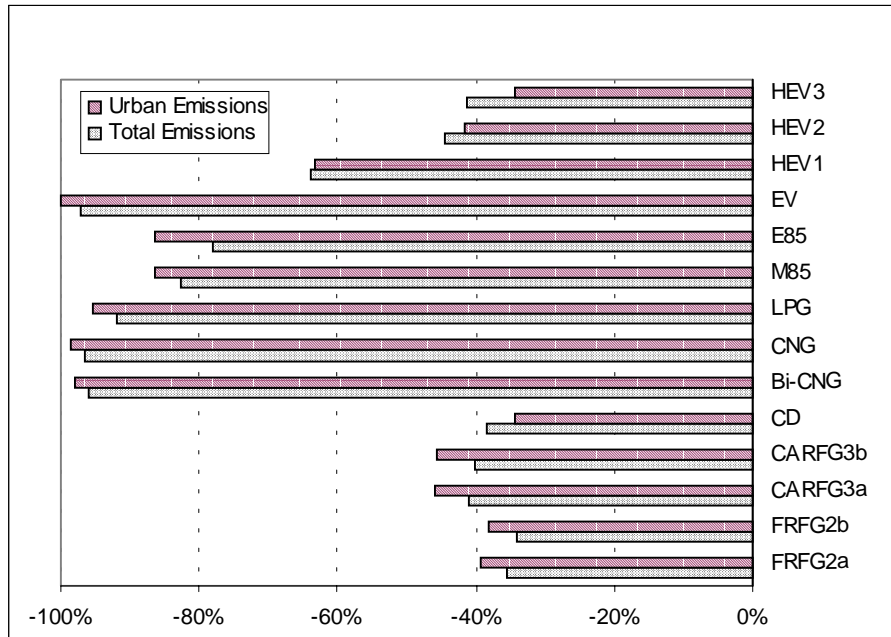
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Figure 5.8 Changes in Fuel-Cycle Benzene Emissions for Alternative Fuel Vehicles Relative to Conventional Gasoline Vehicles
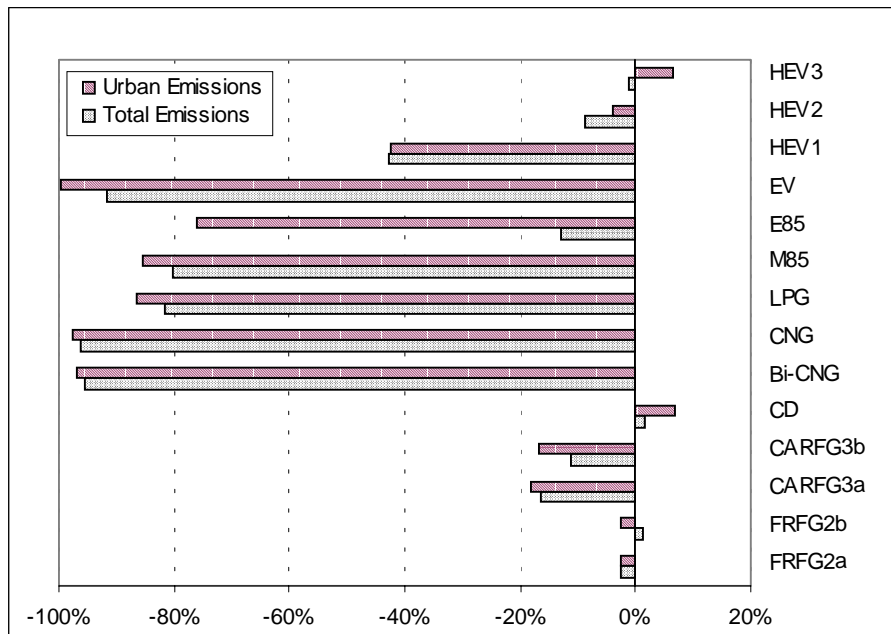

Figure 5.9 Changes in Fuel-Cycle Butadiene Emissions for Alternative Fuel Vehicles Relative to Conventional Gasoline Vehicles
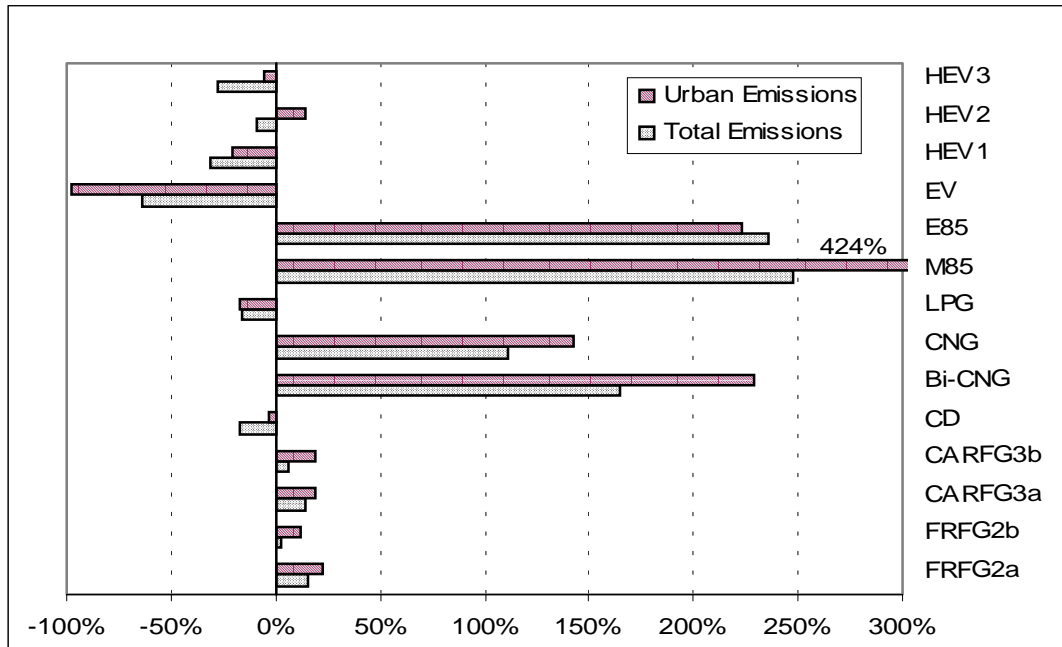
Figure 5.10 Changes in Fuel-Cycle Formaldehyde Emissions for Alternative Fuel Vehicles Relative to Conventional Gasoline Vehicles

ten times higher for alcohol- and NG-fueled vehicles than for CG-fueled vehicles because of the normal combustion products of alcohol fuels and NG (see footnote 23 and Glassman [1996] for more information). Even the RFG fuels demonstrate higher formaldehyde emissions because of a combination of the fuel production process and the combustion products of their oxygenate additives (ethanol and MTBE).

Formaldehyde emissions in this case are *primary* emissions and do not include formaldehyde formed as a secondary pollutant in the atmosphere because of VOCs emitted from these vehicles. As discussed in Section 2, EPA has estimated that up to 40% of formaldehyde in the atmosphere may be attributable to secondary formaldehyde formation. Because CG vehicles have higher urban VOC emissions than vehicles fueled by alternative fuels (see Figure 5.6), we would expect secondary formaldehyde emissions from CG-fueled vehicles to be higher than those from these alternatives. In future phases of this study, we will attempt to include secondary formaldehyde formation in the emissions estimates.

Despite the relatively higher formaldehyde tailpipe emissions from the alcohol fuels, the values depicted here and listed in Table 5.1 are still within EPA's proposed Tier II tailpipe emissions standards for formaldehyde (EPA 1999c).

Figures 5.11 and 5.12 show each fuel's combined emissions of the four air toxics relative to CG, employing the metric described in the introduction to Section 5. This metric normalizes the emissions of each toxic compound by using the benzene CURE value as the normalization
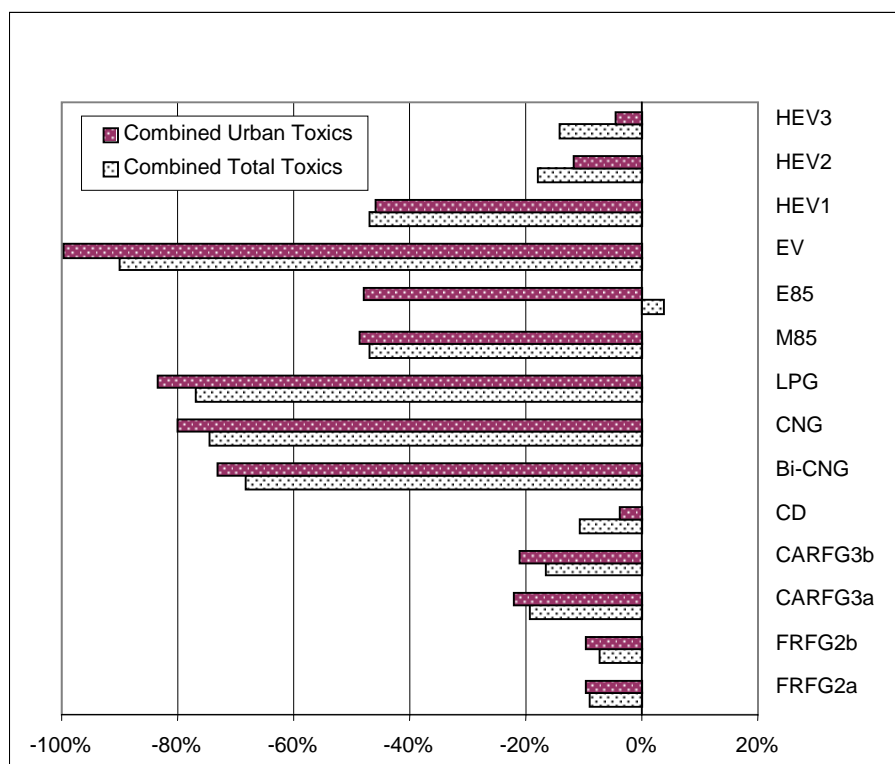
Figure 5.11 Changes in Combined Air Toxics Emissions for Alternative Fuel Vehicles Relative to Conventional Gasoline Vehicles (benzene-equivalent using EPA CURE)

parameter. Toxic emissions values are modified by multiplying by a factor equal to the emission's CURE divided by the benzene CURE. These values are then added for each fuel and compared to the CG value. This new "benzene-equivalent" combined emissions value can be used to evaluate overall toxic emissions from various fuels adjusted for their toxicity.

The calculated values do not necessarily represent the relative risk of each of the fuels. To determine risk levels, researchers would need to address concentrations, toxicity, and exposure. Certainly, issues of atmospheric lifetimes, atmospheric chemistry, and exposure pathways, among others, would be important considerations in conducting such an analysis. Such comprehensive risk analysis is beyond the scope of this study.

The combined air toxic metric calculated here does account for the fact that toxic pollutants are not equal; some fuels that emit slightly larger amounts of very toxic substances (such as butadiene) may have a toxic impact that is much larger than fuels that emit a relatively larger amount of less toxic substances (such as acetaldehyde).

Figure 5.11 uses CURE values derived from EPA to calculate the "combined air toxics emissions" value; Figure 5.12 uses CURE values derived from CARB (EPA 1993 and 2000;
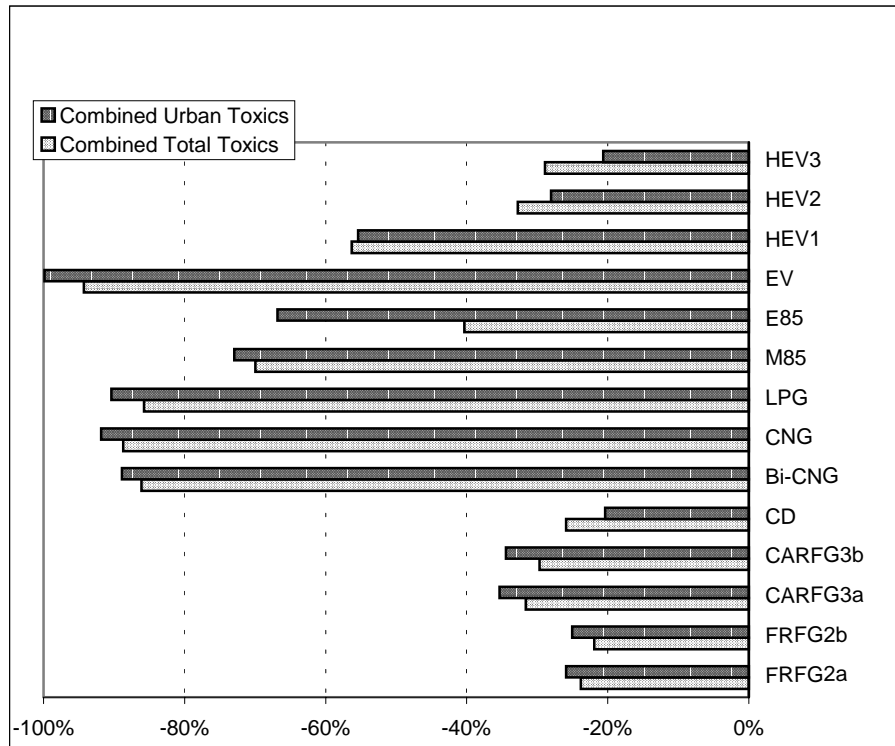
Figure 5.12 Changes in Combined Air Toxics Emissions for Alternative Fuel Vehicles Relative to Conventional Gasoline Vehicles (benzene-equivalent using CARB CURE)

CARB 1997a). As shown in Table 2.2 and in the list below, the EPA and CARB CURE values differ:

	EPA CURE	CARB CURE
Acetaldehyde	2.2×10^{-6}	2.7×10^{-6}
Benzene	8.3×10^{-6}	2.9×10^{-5}
Butadiene	2.8×10^{-4}	1.7×10^{-4}
Formaldehyde	1.3×10^{-5}	6.0×10^{-6}

In both the EPA and CARB cases, butadiene is identified as the most toxic pollutant. Butadiene is approximately one hundred times more toxic than acetaldehyde and 10–30 times more toxic than benzene or formaldehyde. Thus, the "combined toxic emissions" value will be heavily affected by a fuel's relative butadiene emissions.

CURE values for acetaldehyde and butadiene are very similar in the EPA and CARB references. However, CARB assigns a benzene CURE value that is about three times higher than EPA's value. On the other hand, EPA has a formaldehyde CURE that is more than two times

higher than CARB's. Thus, the differences we see in Figures 5.11 and 5.12 are largely attributable to a particular fuel's relative benzene and formaldehyde emissions.

Figure 5.11 shows that all the fuels that we studied are less toxic than CG when considering urban emissions. In fact, the gaseous fuels demonstrate an 80% reduction in their "combined air toxic emissions" value compared to CG. Alcohol fuels also do well, because their higher acetaldehyde emissions are offset by their much lower butadiene emissions compared to CG. Only E85 shows any increase relative to CG, and that increase is for "total" emissions, which include many of the emissions that occur during the nonurban upstream stages of the fuel cycle.

Figure 5.12 shows similar results using the CARB CURE values. In this figure, the fuels we studied demonstrate even higher reductions compared to gasoline than in Figure 5.11, primarily because the CARB CURE values for formaldehyde and benzene are different than the EPA values. The CARB scenario (Figure 5.12) weighs benzene emissions more heavily than the EPA scenario (Figure 5.11). The CARB scenario also weighs formaldehyde emissions less heavily than the EPA scenario. So fuels that have lower benzene emissions compared to gasoline (all do) also have lower "combined air toxics emissions" values using the CARB CURE. Formaldehyde emissions, such as those generated by the alcohol fuels and NG, are not weighed nearly as heavily. For example, M85, shown as having an approximately 50% relative reduction in combined toxic emissions in Figure 5.11, has an almost 70% reduction in Figure 5.12. We also see the total emissions from E85 change from a 5% increase in Figure 5.11 to an approximately 40% decrease in Figure 5.12. This result demonstrates the importance of the toxicity of each individual pollutant in assessing the overall air toxic effects of each fuel.

5.3 Sensitivity Analysis for Upstream Butadiene Emissions

In the original analysis, we treated butadiene emissions from some upstream technologies as zero because no emissions data were available (see Section 3). Although we estimated in such cases that the actual value of butadiene is probably close to zero (because some tests give a value of "NA" when concentrations are lower than the detectable test limit), our treatment may slightly underestimate upstream butadiene emissions.

To determine how sensitive our final results are to this "zero-butadiene" assumption, we conducted a sensitivity analysis. For technologies without available butadiene emission factors, we determined the maximum possible value (MPV) that could be expected from that particular emissions event. We conducted the analysis with these positive butadiene emission factors and compared the new results with our original results.

We derived the following MPVs for technologies with "NA" butadiene emission factors:

- NG boilers: the available BU/VOC fractions for NG combustors are turbines = 0.02%, internal combustion engines = 0.02%, and dedicated and bi-fuel CNG vehicles = 0.05 %. Because all of these values are lower than 0.1%, we used 0.1% as the MPV for NG boilers.

- NG flares: same as the NG boiler MPV.

- Diesel boilers: the BU/VOC fraction for residual oil boilers is 1.5%. We assumed this value for the diesel boiler MPV.

- LPG boilers: same as the NG boiler MPV.

- Coal boilers: 1% BU/VOC fraction.

- Wood boilers: 1% BU/VOC fraction.

Our results indicate that total butadiene emissions vary only slightly under the MPV assumptions. Most changes (measured as differences in total per-mile emissions) are less than 5%, except for bi-fuel and dedicated CNG vehicles, which demonstrate 13% and 16% increases, respectively. These increases are driven by upstream emissions changes, which increase by less than 10% for all fuels, except bi-fuel and dedicated CNG vehicles, which have upstream increases of about 40%.

On the basis of this sensitivity analysis, we are confident that the lack of butadiene data for some upstream processes had little effect on the relative total emissions values obtained in the original analysis, except in the case of upstream emissions for CNG vehicles. We will continue to upgrade the analysis as new butadiene data become available.

Section 6
Summary and Conclusions

Our analysis revealed that, in most cases, alternative fuels and technologies — particularly the gaseous fuels and EVs/HEVs — offer significant reductions of both total and urban air toxics emissions. The air toxics emissions were not only significantly lower than those of CG-fueled vehicles, but also much lower than emissions from vehicles fueled by the new RFGs that will penetrate the U.S. market over the coming decade.

The alcohol fuels were shown to have higher aldehyde (formaldehyde and acetaldehyde) emissions than CG. For M85, this result was largely attributable to downstream (i.e., vehicle operation) stages of the fuel cycle. For E85, these emissions occurred in both the downstream and upstream (i.e., feedstock and fuel production) stages of the fuel cycle. The higher aldehyde emissions from the alcohol fuels were largely offset by lower benzene and butadiene emissions. Therefore, when the four air pollutants studied here are considered in light of their individual toxicity, all alternatives, including the alcohol fuels, demonstrate emissions benefits relative to CG.

Several issues still need to be resolved. First, acquisition of upstream data has been difficult. EPA has not monitored or developed inventories for some of the air toxics sources considered in the upstream process. We must therefore generate estimates on the basis of our own assumptions or seek data from industries that may be reluctant to release this information. Continuing efforts are needed to enhance the data quantity and quality for upstream processes.

The second issue, related to the first, applies to downstream activities. Although there are a large number of studies on toxic emissions for near-term conventional fuels, the same wealth of information is not available for long-term alternative transportation fuels or advanced vehicle technologies. However, as more data are collected and analyzed at sites such as NAFDC, the accuracy of downstream emissions predictions could improve.

The final issue involves the recoding of GREET. Calculations in this report were conducted using a modified version of GREET; the modified version contains additional worksheets in which GREET's fuel-cycle VOC values were applied to our estimated T/VOC fractions. These calculations need to be coded so they are transparent in GREET, and the standard output of GREET must be modified to include air toxics estimates. In addition, GREET must be programmed to easily accept new parameter inputs (e.g., T/VOC fractions) that might affect air toxics results.

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