

Alternatives to Traditional Transportation Fuels 1994

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Greenhouse Gas Emissions

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Listing of Commonly Used Acronyms

ATF	alternative transportation fuels
C	Celsius
CCM	Community Climate Model
CF ₃ COOH	trifluoroacetic acid
CFC	chlorofluorocarbon
CH ₃ Br	methyl bromide
CH ₄	methane
cm	centimeter
CNG	compressed natural gas
CnHm	nonmethane hydrocarbon
CO ₂	carbon dioxide
CO	carbon monoxide
EIA	Energy Information Administration
EPACT	Energy Policy Act of 1992
EPUB	EIA Electronic Publishing System
F	Fahrenheit
GCM	General Circulation Models
GHG	greenhouse gas
GWP	global warming potential
HCFC	hydrochlorofluorocarbon
H ₂ O	water vapor
LPG	liquefied petroleum gas
µm	micrometer
nm	nanometer
NMHC	nonmethane hydrocarbons
NO _x	nitrogen oxides
N ₂ O	nitrous oxide
O ₃	ozone
PFC	perfluorocarbon
UV	ultraviolet
VMT	vehicle mile traveled
W/m ²	watts per square meter

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Executive Summary

This report provides information on greenhouse gases (GHGs) as required by Section 503 a(4) and b(3) of the Energy Policy Act of 1992 (EPACT). Although EPACT is principally concerned with improving energy efficiency and curbing U.S. dependence on foreign oil, the requirement to estimate greenhouse gases reflects a desire that energy security not be promoted at the expense of the environment. EPACT was developed around the time (1992) that President Bush and other world leaders met in Rio de Janeiro to sign the "Framework Convention for Climate Change." This document committed developed nations to stabilizing emissions of greenhouse gases at 1990 levels.

Section 503 requires the Secretary of Energy, in consultation with the Administrator of the Energy Information Administration (EIA), to estimate GHG emissions resulting from the use of the subset of replacement fuels¹ known as "alternative transportation fuels."² Further, EPACT requires an examination of GHG emissions over the entire fuel cycle rather than only those produced from combustion. EIA has decided to use the "Delucchi" fuel cycle³ approach because it offers the best framework for adhering to the EPACT requirements for estimating GHG emissions from alternative transportation fuels, using gasoline as a

comparison.⁴ For a discussion of the Delucchi approach and EIA's prior work in the area, consult *Alternatives to Traditional Transportation Fuels: An Overview*,⁵ *Alternatives to Traditional Transportation Fuels 1993*,⁶ and *Alternatives to Traditional Transportation Fuels 1994: Volume I*.⁷

The Earth's average temperature has been increasing for the past few centuries, leading to concern about a variety of related issues (e.g., average ocean levels). One possible cause of the temperature rise is the amount of "greenhouse gases" that mankind is emitting into the atmosphere. Basically, greenhouse gases are those that trap heat emanating from the Earth's surface. Without these gases, this heat would otherwise escape from the atmosphere. Some level of greenhouse gases is necessary; without them the Earth's average temperature would be nearly 0°F.⁸ A major human activity responsible for increased greenhouse gases in the atmosphere is fuel combustion. Water vapor and carbon dioxide, both greenhouse gases, are the principal products produced from burning hydrocarbon fuel.

Concern about possible effects of greenhouse gases heightens when future trends in transportation fuel consumption are examined. Motor vehicle greenhouse

¹Replacement fuels include alternative fuels as well as other fuels. As defined in EPACT, "the term 'replacement fuel' means the portion of any motor fuel that is methanol, ethanol, or other alcohols, natural gas, liquefied petroleum gas, hydrogen, coal-derived liquid fuels, electricity (including electricity from solar energy), ethers, or any other fuel the Secretary of Energy determines, by rule, is substantially not petroleum and would yield substantial energy security benefits and substantial environmental benefits."

²As defined in EPACT, "the term 'alternative fuel' means methanol, denatured ethanol, and other alcohols; mixtures containing 85 percent or more (or such other percentage, but not less than 70 percent, as determined by the Secretary of Energy, by rule, to provide for requirements relating to cold-start, safety, or vehicle functions) by volume of methanol, denatured ethanol, and other alcohols with gasoline or other fuels; natural gas; liquefied petroleum gas; hydrogen; coal-derived liquefied fuels; fuels (other than alcohol) derived from biological materials; electricity (including electricity from solar energy); and any other fuel the Secretary determines, by rule, is substantially not petroleum and would yield substantial energy security benefits and substantial environmental benefits." Subsequent to the passage of EPACT, the Secretary of Energy determined that biodiesel, in neat form, was an alternative fuel.

³The fuel cycle of any transportation fuel includes several stages, such as recovery, processing, transportation, and end-use. See Argonne National Laboratory, Center for Transportation Research, *Emissions of Greenhouse Gases from the Use of Transportation Fuels and Electricity*, ANL/ESD/TM-22, prepared by Dr. Mark Delucchi, Vol. 1 (Argonne, IL, November 1991) and Vol. 2 (Argonne, IL, November 1993) and Energy Information Administration, *Alternatives to Traditional Transportation Fuels 1993*, DOE/EIA-0585/(93) (Washington, DC, June 1994), pp. 29-33, 49-53.

⁴Energy Information Administration, *Alternatives to Traditional Transportation Fuels: An Overview*, DOE/EIA-0580/O (Washington, DC, June 1994), and *Alternatives to Traditional Transportation Fuels 1993*, DOE/EIA-0585(93) (Washington, DC, January 1995).

⁵Energy Information Administration, *Alternatives to Traditional Transportation Fuels: An Overview*, pp. 93-101.

⁶Energy Information Administration, *Alternatives to Traditional Transportation Fuels 1993*, DOE/EIA-0585/(93) (Washington, DC, June 1994), pp. 29, 45.

⁷Energy Information Administration, *Alternatives to Traditional Transportation Fuels 1994: Volume I*, DOE/EIA-0585(94)/1 (Washington, DC, February 1996).

⁸Intergovernmental Panel on Climate Change, *The IPCC Scientific Assessment* (Cambridge, United Kingdom: Cambridge University Press, 1990), p. xxxvii.

gas emissions are projected to grow in the United States and throughout the world as a result of the increasing number of vehicles and vehicle miles traveled (VMT). VMT is expected to grow in the United States at double the rate of population growth and even faster in Africa and Asia. The transportation sector contributes about one-third of total carbon dioxide emissions in the United States and other countries that belong to the Organization for Economic Cooperation and Development.

Greenhouse gases considered by EIA are water vapor, carbon dioxide, methane, nonmethane hydrocarbons

(NMHC), carbon monoxide, nitrous oxide, nitrogen oxides,⁹ and ozone. Water vapor is the most abundant greenhouse gas, varying from roughly 0 to 4 percent of the Earth's atmosphere. Currently, however, water vapor from fuel combustion is not believed to have a significant impact on atmospheric water vapor concentrations. Next is carbon dioxide, followed by ozone, nitrous oxide, carbon monoxide, and nitrogen dioxide. The amount of each gas, except NMHC and ozone,¹⁰ is reported for conventional gasoline, methanol, ethanol, compressed natural gas (CNG), and liquefied petroleum gas (LPG, i.e., propane) (Table ES1).¹¹ GHG emissions are generally reported as moles per VMT

Table ES1. Total Fuel Cycle Greenhouse Gas Emissions From Gasoline and Alternative Transportation Fuels

Greenhouse Gas	Gasoline	Methanol From Natural Gas	Ethanol From Corn	Compressed Natural Gas	Liquefied Petroleum Gas
Unweighted Quantities (millimoles per VMT)					
Carbon Dioxide (CO ₂)	7,900	8,700	7,400	5,640	6,000
Water Vapor (H ₂ O)	7,750	16,230	17,280	10,930	8,180
Methane (CH ₄)	22.0	34.6	39.30	91.3	17.2
Nitrous Oxide (N ₂ O)	1.7	1.7	9.30	1.6	1.6
Nitrogen Oxides (NO _x)	26.5	36.2	58.30	24.2	22.9
Carbon Monoxide (CO)	330.4	327.1	258.25	324.2	325.0
Weighted Quantities (moles CO ₂ equivalent per VMT)					
Carbon Dioxide (CO ₂)	7.90	8.70	7.40	5.64	6.00
Water Vapor (H ₂ O) ^a	NA	NA	NA	NA	NA
Methane (CH ₄)	0.22	0.35	0.39	0.91	0.17
Nitrous Oxide (N ₂ O)	0.54	0.54	2.98	0.54	0.54
Nitrogen Oxides (NO _x)	1.06	1.45	2.33	0.97	0.92
Carbon Monoxide (CO)	0.99	0.98	0.78	0.97	0.98
Total^b	10.71	12.02	13.88	9.03	8.61

^aGlobal warming potential value for water vapor has not been determined by the Intergovernmental Panel on Climate Change.

^bTotal weighted greenhouse gas (GHG) emissions do not include contributions from water vapor.

CO₂ = Carbon dioxide.

NA = Not applicable because the Intergovernmental Panel on Climate Change has not issued a global warming potential for water vapor.

VMT = Vehicle mile traveled.

For notes and sources, see Table 1 on page 3.

⁹Nitrogen oxides represent a family of gases, generically written as NO_x.

¹⁰Data are not currently available for NMHC and ozone.

¹¹Emissions from electric vehicles occur largely in manufacturing and recycling batteries. This information will be available in a subsequent report.

throughout this report instead of the traditional grams per VMT.¹² The raw quantity of each greenhouse gas (“unweighted”) is reported, in terms of the amount emitted into the atmosphere per VMT. In addition, a “weighted” quantity is shown for each gas except water vapor. This represents the equivalent amount of carbon dioxide that would have to be emitted in order to have the same heat-absorbing capability as the unweighted amount of each gas.

Total “weighted” emissions of alternative transportation fuels do not vary by more than 20 percent from those of gasoline. Because of the uncertainties in estimating the “weighting factors” (i.e., the global warming potential (GWP)¹³ of each gas, compared with carbon dioxide), the fuel-specific variations shown in weighted emissions may not be significant. Alcohol fuels show greater weighted emissions than conventional gasoline, while the gaseous fuels show less. Weighted estimates for water vapor are not presented because the Intergovernmental Panel on Climate Change has not established a definitive GWP factor for water vapor.

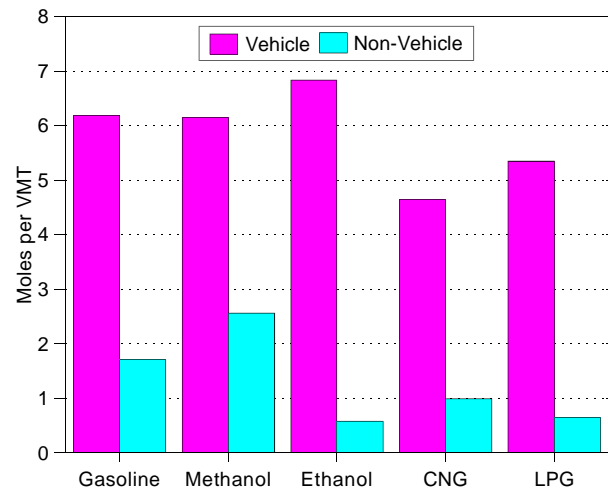
These results represent emissions from the total fuel cycle—from resource recovery through energy transformation (e.g., refining) through end-use consumption. Emission estimates for each portion of the fuel cycle are shown in the report. Notable facts involving total fuel cycle emissions include the following:

- CNG produces the lowest level of carbon dioxide emission across the total fuel cycle, followed by LPG and ethanol from corn.
- CNG produces the largest methane emissions.

- Ethanol from corn produces the largest nitrous oxide emissions across the total fuel cycle.

Except for methanol, the “vehicle” (end-use) portion of the fuel cycle accounts for at least 80 percent of total fuel cycle carbon dioxide emissions (Figure ES1). This suggests that examining actions to reduce greenhouse gases as a direct result of vehicle use is justified.

Figure ES1. Carbon Dioxide Emissions per Vehicle Mile Traveled in Vehicle and Non-Vehicle Stages of the Fuel Cycle for Various Fuels



CNG = Compressed natural gas.

LPG = Liquefied petroleum gas.

VMT = Vehicle mile traveled.

For notes and sources, see Figure 1 on page 2.

¹²One mole of a gas is equal to the amount of substance that contains as many elementary units (6.023×10^{23} molecules or atoms) as there are atoms in 12 grams of carbon-12. Normally, emissions are reported in grams per VMT. However, reporting in moles is preferable because greenhouse gas heat absorption is directly related to the number of molecules of a gas, i.e., its volume.

¹³The actual concept here is the ability of gases to absorb infrared (heat) energy radiated from the Earth's surface. The more common term, “global warming potential,” is used to refer to this concept. Strictly speaking, however, global warming potential includes other factors.

1. Introduction

This report addresses the Energy Information Administration's (EIA's) efforts to fulfill its reporting obligations under Section 503 (a)(4) and (b)(3) of the Energy Policy Act of 1992 (EPACT)¹ regarding alternative transportation fuels² and replacement fuels³. These provisions authorize EIA to collect and report information on greenhouse gases emitted by use of replacement fuels, which is the subject of this publication. The full text of Section 503 is as follows:

Section 503. Replacement Fuel Demand Estimates and Supply Information

- (a) ESTIMATES—Not later than October 1, 1993,⁴ and annually thereafter, the Secretary [of Energy], in consultation with the [EIA] Administrator, the Secretary of Transportation, and other appropriate State and Federal officials, shall estimate for the following calendar year—
 - (1) the number of each type of alternative fueled vehicle likely to be in use in the United States;
 - (2) the probable geographic distribution of such vehicles;
 - (3) the amount and distribution of each type of replacement fuels; and
 - (4) the greenhouse gas emissions likely to result from replacement fuel use.
- (b) INFORMATION—Beginning on October 1, 1994,⁵ the Secretary shall annually require—
 - (1) fuel suppliers to report to the Secretary on the amount of each type of replacement fuel that such supplier—

- (A) has supplied in the previous calendar year; and
 - (B) plans to supply the following calendar year;
- (2) suppliers of alternative fueled vehicles to report to the Secretary on the number of each type of alternative fueled vehicle that such supplier—
 - (A) has made available in the previous calendar year; and
 - (B) plans to make available for the following calendar year; and
 - (3) [fuel suppliers] to provide the Secretary information necessary to determine the greenhouse gas emissions from the replacement fuels used, taking into account the entire fuel cycle.
- (c) PROTECTION OF INFORMATION.—Information provided to the Secretary under subsection (b) shall be subject to applicable provisions of law protecting the confidentiality of trade secrets and business and financial information, including section 1905 of Title 18, United States Code.

In 1994, EIA implemented its first EPACT data collection program and released the required information in *Alternatives to Traditional Transportation Fuels: An Overview* (DOE/EIA-0585/O). In 1995, the agency published *Alternatives to Traditional Transportation Fuels 1993* (DOE/EIA-0585/93). Also in 1995, EIA delivered its analysis of the greenhouse gases (GHGs) from alternative transportation fuel use in a presentation at an international conference on the emissions inventory

¹Public Law 102-486, Section 503, 42 U.S.C. 13253, "Energy Policy Act of 1992" (Enacted October 24, 1992).

²Replacement fuels include alternative fuels as well as other fuels. As defined in EPACT, "the term 'replacement fuel' means the portion of any motor fuel that is methanol, ethanol, or other alcohols, natural gas, liquefied petroleum gas, hydrogen, coal-derived liquid fuels, electricity (including electricity from solar energy); ethers, or any other fuel the Secretary of Energy determines, by rule, is substantially not petroleum and would yield substantial energy security benefits and substantial environmental benefits."

³As defined in EPACT, "the term 'alternative fuel' means methanol, denatured ethanol, and other alcohols; mixtures containing 85 percent or more (or such other percentage, but not less than 70 percent, as determined by the Secretary of Energy, by rule, to provide for requirements relating to cold-start, safety, or vehicle functions) by volume of methanol, denatured ethanol, and other alcohols with gasoline or other fuels; natural gas; liquefied petroleum gas; hydrogen; coal-derived liquefied fuels; fuels (other than alcohol) derived from biological materials; electricity (including electricity from solar energy), and any other fuel the Secretary determines, by rule, is substantially not petroleum and would yield substantial energy security benefits and substantial environmental benefits. Subsequent to the passage of EPACT, the Secretary of Energy determined that biodiesel, in neat form, was an alternative fuel.

⁴The date, October 1, 1993, was subsequently modified to October 1, 1994.

⁵The date applicable to Section 503 (b) (2) was changed from October 1, 1994, to December 31, 1995, and the date for other data collection activities was modified to December 31, 1995.

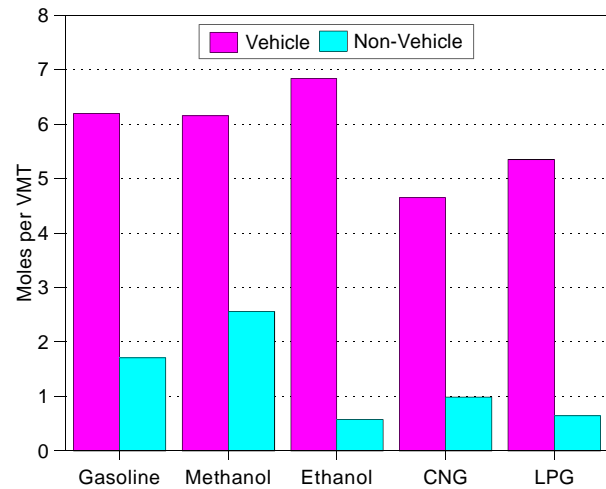
sponsored by the U.S. Environmental Protection Agency in Raleigh, North Carolina.⁶ In February 1996, Volume 1 of *Alternatives to Traditional Transportation Fuels 1994* (DOE/EIA-0585/94) presented data on alternative-fueled vehicles and alternative transportation fuels (ATFs). EIA had previously released the required information by placing data tables on the EIA Electronic Publishing System (EPUB). Now, Volume 2 of that report compiles the greenhouse gas emission results, based on information currently available.

Section 503 (a)(4) and (b)(3) require estimations of GHG emissions resulting from alternative transportation fuels that take the entire fuel cycle into account. After reviewing numerous studies, EIA decided that an approach proposed by Dr. Mark Delucchi⁷ was best suited to supply the required information. This model is reasonably comprehensive and detailed in its methodology for estimating transportation fuel GHG emissions. EIA continues to modify it to provide all required emissions information for each alternative fuel.⁸

Global warming due to anthropogenic (i.e., human-based) GHGs is a controversial issue. EIA, therefore, considers it important to increase public understanding of this complex topic as well as to satisfy the reporting requirements of EPACT Section 503. Chapter 2 gives an overview of the greenhouse effect.

Using available data, Chapter 3 presents EIA's analysis of total fuel cycle emissions of GHGs for gasoline, compressed natural gas (CNG), liquefied petroleum gas (LPG) from oil and gas, methanol from natural gas, and ethanol from corn. EIA's analysis produced several major conclusions. One was that while CNG produces the lowest level of carbon dioxide emissions across the total fuel cycle (followed closely by LPG and ethanol from corn), it produces the largest methane emissions across the total fuel cycle (Figure 1 and Table 1). In addition, there are probably minimal, if any, reductions in weighted GHG emissions from alternative transportation fuels for the entire fuel cycle, except for LPG

Figure 1. Carbon Dioxide Emissions per Vehicle Mile Traveled in Vehicle and Non-Vehicle Stages of the Fuel Cycle for Various Fuels



CNG = Compressed natural gas.
LPG = Liquefied petroleum gas.
VMT = Vehicle mile traveled.

Note: One mole of a gas is equal to the amount of substance that contains as many elementary units (6.023×10^{23} molecules or atoms) as there are atoms in 12 grams of carbon-12. Normally, emissions are reported in grams per VMT. However, reporting in moles is preferable because greenhouse gas heat absorption is directly related to the number of molecules of a gas.

Sources: Derived from greenhouse gas emissions spreadsheet provided to the Energy Information Administration, July 1994. The spreadsheet is an unpublished revision of Argonne National Laboratory, Center for Transportation Research, *Emissions of Greenhouse Gases from the Use of Transportation Fuels and Electricity*, ANL/ESD/TM-22, prepared by Dr. Mark Delucchi, Vol. 1 (Argonne, IL, November 1991) and Vol. 2 (Argonne, IL, November 1993). Also see Energy Information Administration, *Alternatives to Traditional Transportation Fuels 1993*, EIA/DOE-0585(93) (Washington, DC, January 1995); and Decision Analysis Corporation, "Measurement of Emissions: Greenhouse Gas Estimates for Alternative Transportation Fuels," unpublished final report prepared for the Energy Information Administration (Vienna, VA, December 1995).

⁶V. Senthil and P. Warnken, "Estimating Greenhouse Gas Emissions from Replacement Fuels: Fulfilling the Energy Policy Mandate," *The Emissions Inventory*, 1995, pp. 98-107.

⁷Argonne National Laboratory, *Emissions of Greenhouse Gases from the Use of Transportation Fuels and Electricity*, ANL/ESD/TM-22, Vol. I (Argonne, IL, November 1991) and Vol. II (Argonne, IL, November 1993).

⁸Mark A. Delucchi, "Revisions to the Greenhouse Gas Emissions Model Used in *Emissions of Greenhouse Gases from the Use of Transportation Fuels and Electricity*, ANL/ESD/TM-22, November 1991," draft report submitted to the Energy Information Administration in June 1996. Also, see Energy Information Administration, *Alternatives to Traditional Transportation Fuels: An Overview*, pp. 25-29, and Energy Information Administration, *Alternatives to Traditional Transportation Fuels 1993*, DOE/EIA-0585/(93) (Washington, DC, June 1994), pp. 49-53, and Decision Analysis Corp., "Measurement of Emissions: Greenhouse Gas Estimates for Alternative Transportation Fuels," unpublished final report prepared for the Energy Information Administration (Vienna, VA, December, 1995), and V. Senthil and P. Warnken, "Estimating Greenhouse Gas Emissions from Replacement Fuels: Fulfilling the Energy Policy Mandate," *The Emissions Inventory*, 1995, pp. 98-107.

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Methane (CH ₄)	22.0	34.6	39.30	91.3	17.2
Nitrous Oxide (N ₂ O)	1.7	1.7	9.30	1.6	1.6
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Carbon Monoxide (CO)	330.4	327.1	258.25	324.2	325.0
Weighted Quantities					
Carbon Dioxide (CO ₂)	7.90	8.70	7.40	5.64	6.00
Water Vapor (H ₂ O) ^a	NA	NA	NA	NA	NA
Methane (CH ₄)	0.22	0.35	0.39	0.91	0.17
Nitrous Oxide (N ₂ O)	0.54	0.54	2.98	0.54	0.54
Nitrogen Oxides (NO _x)	1.06	1.45	2.33	0.97	0.92
Carbon Monoxide (CO)	0.99	0.98	0.78	0.97	0.98
Total^b	10.71	12.02	13.88	9.03	8.61

^aGlobal warming potential value for water vapor has not been determined by the Intergovernmental Panel on Climate Change.

^bTotal weighted greenhouse gas (GHG) emissions do not include contributions from water vapor.

NA = Not applicable because the Intergovernmental Panel on Climate Change has not issued a global warming potential for water vapor.

Notes: • **Unweighted** GHG emissions are in millimoles per vehicle mile traveled (VMT). One mole of a gas is equal to the amount of substance that contains as many elementary units (6.023 x 10²³ molecules or atoms) as there are atoms in 12 grams of carbon-12. Normally, emissions are reported in grams per VMT. However, reporting in moles is preferable because greenhouse gas heat absorption is directly related to the number of molecules of a gas. **Weighted** GHG emissions are shown in moles of CO₂ equivalent per VMT equal to the unweighted quantity multiplied by the global warming potential per mole of each gas, relative to carbon dioxide. • Gasoline refers to conventional unleaded gasoline in this report. • VMT estimate derived assuming a vehicle with gasoline efficiency of 30 miles per gallon. • Emissions from vehicle manufacturing are not included. • Nitrogen oxides include primarily nitric oxide and nitrogen dioxide.

Sources: **Unweighted:** Derived from greenhouse gas emissions spreadsheet provided to the Energy Information Administration, July 1994. The spreadsheet is an unpublished revision of a report from the Argonne National Laboratory, Center for Transportation Research, *Emissions of Greenhouse Gases from the Use of Transportation Fuels and Electricity*, ANL/ESD/TM-22, prepared by Dr. Mark Delucchi, Vol. 1 (Argonne, IL, November 1991) and Vol. 2 (Argonne, IL, November 1993). Also see Energy Information Administration, *Alternatives to Traditional Transportation Fuels 1993*, EIA/DOE-0585(93) (Washington, DC, January 1995); and Decision Analysis Corp., "Measurement of Emissions: Greenhouse Gas Estimates for Alternative Transportation Fuels," unpublished final report prepared for the Energy Information Administration (Vienna, VA, December, 1995). **Weighted:** High global warming potential values per mole (relative contribution in 100 years) found in Table 5 are used. Global warming potential values for nitrogen oxides and carbon monoxide of 40 and 3 per mole, respectively, are found in Argonne National Laboratory Center for Transportation Research, "Development and Use of GREET Model to Estimate Fuel Cycle Energy Use and Emissions of Various Transportation Technologies and Fuels," ANLIESD-31, prepared by Michael Q. Wang (Argonne, IL, March 1996), and Decision Analysis Corp., "Measurement of Emissions: Greenhouse Gas Estimates for Alternative Transportation Fuels," unpublished final report prepared for the Energy Information Administration (Vienna, VA, December 1995).

if water vapor is taken into account.⁹ However, it is currently believed that water vapor produced from surface sources such as the transportation fuel cycle, makes a minimal impact on atmospheric water vapor concentrations. EIA also concluded that ethanol from corn produces the largest nitrous oxide emissions across the total fuel cycle (Table 1).

Appendix A contains an overview of global warming, including GWP, radiative forcing, albedo, and vertical mixing concepts. It also discusses the present status of global climate models and community climate models,

which include the latest findings on clouds' unexpected four-fold absorption of short-wave radiation.

Appendix B discusses the factors involved in ozone stability in the atmosphere.

Appendix C discusses the combustion chemistry of alternative and traditional transportation fuels. Appendix D describes the spectral overlaps of greenhouse gases and their significance in terms of the greenhouse effect and global warming.

⁹The results in Table 1 imply that weighted greenhouse gas emissions (including water vapor) from gasoline will be less than for all ATF's, except LPG, if water vapor's GWP is less than 4.8. If water vapor's GWP is greater than 0.55, total weighted greenhouse gas emissions for CNG and alcohol fuels will be less than for gasoline. Although a GWP *per se* for water vapor has yet to be determined, researchers have calculated similar properties to GWP (i.e., "positive feedback" and "direct radiative forcing") which leads to speculation that water vapor's GWP lies between 0.5 and 3.0. For further details, see Decision Analysis Corporation, *Measurement of Emissions: Greenhouse Gas Estimates for Alternative Transportation Fuels*, unpublished final report prepared for the Energy Information Administration (Vienna, VA, December 1995). For information on water vapor positive feedback, see V. Ramanathan and A. Raval, "Observational Determination of the Greenhouse Effect," *Nature* 342 (1989):758-761 and D. Lubin, "The Role of Tropical Super Greenhouse Effect in Heating the Ocean's Surface," *Science* 265 (1994): 224-227 and R.D. Cess, "Gauging Water Vapor Feedback," *Nature* 342 (1989): 736-737.

2. The Greenhouse Effect and Greenhouse Gases: An Overview

The term “greenhouse effect” was coined by the 19th century scientist Jean Fourier. The greenhouse effect occurs when GHGs allow sunlight to reach the Earth's surface but absorb or scatter most of the heat emanating from the Earth's surface, thus retaining heat in the atmosphere. Without the natural greenhouse effect, the average temperature would be about -18°C , or -0.4°F .^{10,11} Although the terms “greenhouse effect” and “global warming” are used due to their familiarity, the concept at issue here is actually “infrared absorptivity” of greenhouse gases.¹²

Scientists have been concerned with the greenhouse effect regarding not only the quality of life on Earth, but also its effect on other planets. Twenty-six million miles from Earth, in an orbit much closer to the Sun, Venus spins through space with a furnace-like surface temperature of more than 800°F (426.5°C), which is much hotter than its proximity to the Sun would explain. Scientists used to believe that Venus fell victim to the greenhouse effect because 96 percent of its atmosphere is carbon dioxide, with nitrogen accounting for almost all the remainder.¹³ It is now generally agreed within the planetary atmospheres community that carbon dioxide alone would lead to an average temperature of less than 25°C . The primary reason that Venus is warmer than this is the presence of sulfuric acid cloud cover over the entire planet, extending from about 50 kilometers to 70 kilometers from the surface.

Unlike Venus, Earth is blessed with an atmosphere rich in nitrogen and oxygen. Dry air near Earth's surface currently contains 78.08 percent nitrogen, 20.95 percent oxygen, 0.93 percent argon, 0.0353 percent carbon dioxide, and trace amounts of methane, nitrous oxide,

carbon monoxide, ozone, hydrogen, helium, neon, ammonia, hydrogen sulfide, and sulfur dioxide (Table 2).^{14,15} Water can vary roughly from 0 percent to 4 percent of the atmosphere (by volume) depending on location, altitude, and atmospheric conditions, with the global average being around 3 percent.

The Earth's atmosphere has been transformed slowly, as human activity has pumped into it billions of tons of greenhouse gases (GHGs) such as carbon dioxide, water vapor, and large amounts of other gases that absorb the heat energy emitted from Earth's surface, not to mention the addition of anthropogenic heat (i.e., direct heat generated by human activities) from burning of fossil fuels, including transportation fuels, and operation of almost all equipment.

The principal force driving Earth's weather and climate change comes from the Sun. Although the Earth receives only about one two-billionth of the energy emitted by the Sun, it is this energy that heats the Earth, drives ocean currents, and creates weather patterns. The heat output of the Sun has varied by about one-third since life on Earth began, and continues to vary during the solar cycles. Despite this change, global temperatures have remained in a narrow range suitable for life. It appears that some form of climate regulation is in operation.

During the past decade or so, people have become concerned with how human activity may be affecting the world's climate. This concern has focused largely on anthropogenic GHGs—that is, GHGs generated by human activity such as the combustion of fuel for transportation. Anthropogenic¹⁶ GHGs intensify the natural greenhouse effect because they absorb infrared

¹⁰Intergovernmental Panel on Climate Change, *The IPCC Scientific Assessment* (Cambridge, United Kingdom: Cambridge University Press, 1990), p. xxxvii.

¹¹The radiative greenhouse effect alone would lead to temperatures of 77°C . However, non-radiative processes, such as evaporation and convection, cool the Earth, leading to its average temperature of 15°C .

¹²Infrared absorptivity is a dimensionless quantity equal to the ratio of the absorbed infrared radiation to the infrared radiation incident on a given surface.

¹³*Encyclopedia of Science and Technology*, 5th Ed. (New York: McGraw Hill Book Co., 1982), p. 381.

¹⁴R.P. Wayne, *Chemistry of Atmospheres* (Oxford, United Kingdom: Clarendon Press, 1991).

¹⁵D.L. Hartmann, *Global Physical Climatology* (New York: Academic Press, 1994), p. 8.

¹⁶Human activity is sometimes referred to as “anthropogenic” activity.

Table 2. Composition of the Atmosphere

Constituent	Fraction by Volume in Dry Air	Total Amount	
		moles	grams
Nitrogen	78.08%	1.38×10^{20}	3.87×10^{21}
Oxygen	20.95%	3.7×10^{19}	1.19×10^{21}
Argon	0.934%	1.65×10^{19}	6.59×10^{19}
Water Vapor	variable	9.4×10^{17}	1.7×10^{18}
Carbon Dioxide	353 ppmv	6.27×10^{16}	2.76×10^{18}
Neon	^a 18.18 ppmv	3.2×10^{15}	6.48×10^{16}
Helium	^a 5.24 ppmv	9.28×10^{14}	3.71×10^{15}
Methane	^a 1.72 ppbv	3.1×10^{14}	4.9×10^{15}
Krypton	^a 1.14 ppmv	2.0×10^{14}	1.69×10^{16}
Hydrogen	^a 500 ppbv	9.0×10^{13}	1.8×10^{14}
Ozone	^a variable	6.88×10^{13}	3.3×10^{15}
Nitrous Oxide	^a 310 ppbv	5.2×10^{13}	2.3×10^{15}
Carbon Monoxide	^a 120 ppbv	2.1×10^{13}	5.9×10^{14}
Xenon	^a 87 ppbv	1.54×10^{13}	2.02×10^{15}
Ammonia	^a 100 ppbv	1.76×10^{12}	3.0×10^{13}
Nitrogen Dioxide	^a 1 pptv	1.76×10^{11}	8.1×10^{12}
CFC-12	^a 480 pptv	8.3×10^{10}	1.0×10^{13}
CFC-11	^a 280 pptv	4.95×10^{10}	6.8×10^{12}
Sulfur Dioxide	^a 200 pptv	3.59×10^{10}	2.3×10^{12}
Hydrogen Sulfide	^a 200 pptv	3.5×10^{10}	1.2×10^{12}

^aValues of trace constituents valid in 1990.

CFC-12 = CCl₂F₂.

CFC-11 = CCl₃F.

ppmv = Parts per million by volume. ppbv = Parts per billion by volume. pptv = Parts per trillion by volume.

Note: One mole of a gas is equal to the amount of a substance that contains as many elementary units (6.023×10^{23} molecules or atoms) as there are atoms in 12 grams of carbon-12.

Source: D.C. Hartmann, *Global Physical Climatology* (San Diego: Academic Press, 1994), p. 8.

radiation emitted from the Earth's surface, increasing the heat trapped inside the atmosphere (Figure 2). GHGs occur naturally in the atmosphere, and they are essential to life on Earth in its present form. The concern is that human activity may be increasing the concentration of atmospheric GHGs enough to alter the climate worldwide.

Most of the radiation reaching the Earth's surface and atmosphere is visible and infrared light. About 70 percent of the radiation reaching the Earth's atmosphere and surface is absorbed. The Earth's atmosphere and surface reflect the remainder. Molecules always emit lower energy than they absorb. Therefore, when the visible light of solar radiation is absorbed, it is emitted as long wavelength infrared heat waves. Part of the total heat emitted as a result of visible and infrared light absorption is absorbed by GHG molecules and

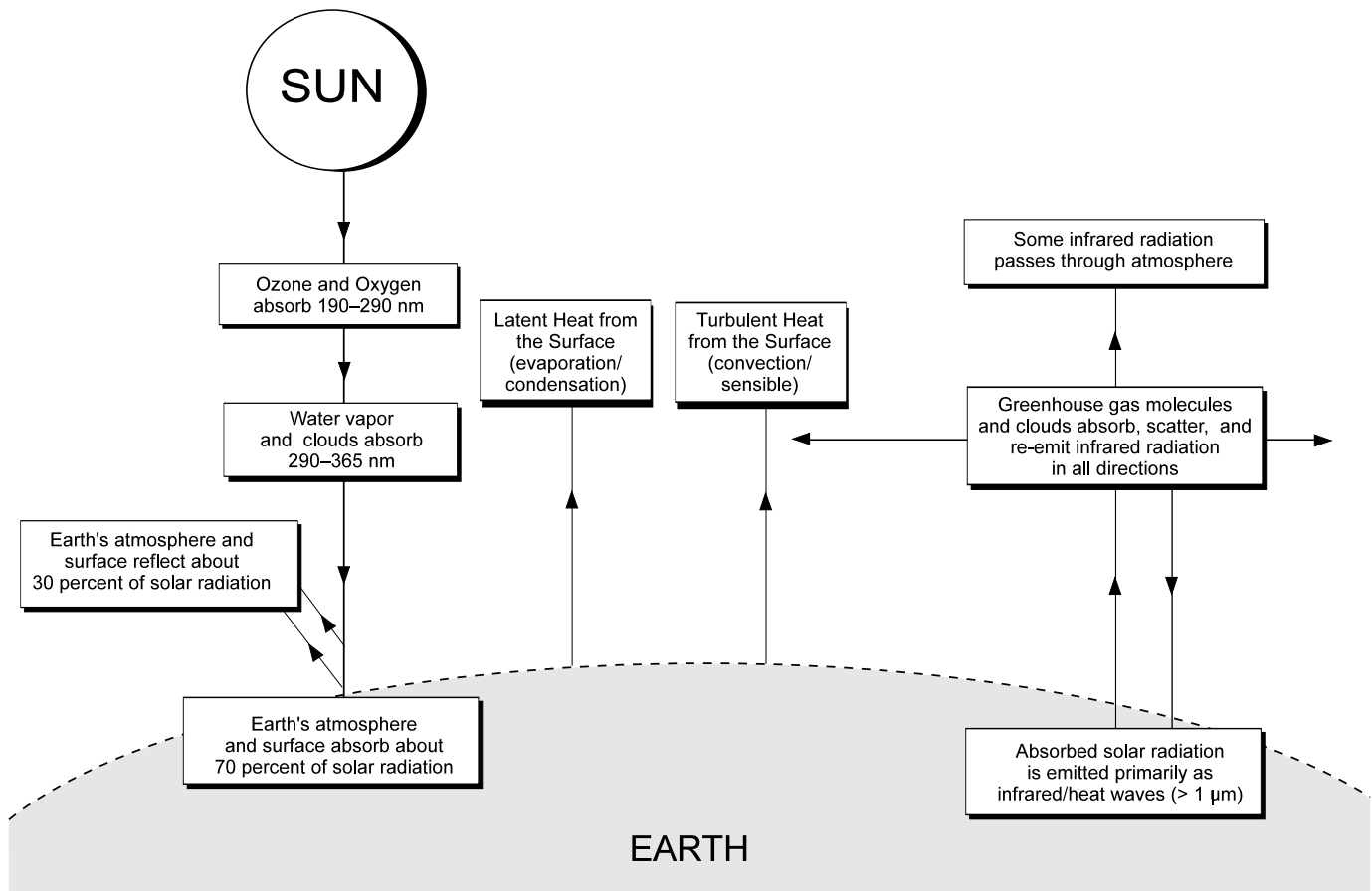
clouds and re-emitted in all directions. Some of the re-emitted radiation is absorbed by the surface. The remainder of the total heat escapes through the atmosphere and into space (Figure 2).

The major GHGs are water vapor (H₂O), carbon dioxide (CO₂), methane (CH₄), nitrous oxide₂ (N₂O), fluorocarbons,¹⁷ and ozone (O₃). Of these, carbon dioxide is the most commonly discussed. However, water vapor is the most important GHG due to its abundance (it represents about 3 percent of the gases in the Earth's atmosphere). Carbon dioxide and water vapor are the two major products of all hydrocarbon fuel combustion.

Water vapor is the predominant absorber of incoming solar radiation and a major contributor to the natural greenhouse effect. Scientists at the National Oceanic and Atmospheric Administration have reported that the

¹⁷Chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs), and perfluorocarbons (PFCs) are not directly related to the internal combustion engine operations.

Figure 2. The Greenhouse Effect (Simplified Diagram)



Note: Atmospheric gases and Earth's surface absorb solar radiation of different wavelengths, measured in nanometers (nm), and emit infrared radiation, measured in micrometers (μm).

Source: Energy Information Administration, Office of Coal, Nuclear, Electric and Alternate Fuels, Renewable Energy Branch (Washington, DC, 1996).

atmospheric water vapor content in the stratosphere at mid-latitudes in the northern hemisphere has been increasing over the last 14 years.¹⁸ Water vapor in the stratosphere can harm the ozone layer by stimulating the formation of polar clouds, which help pollutants such as oxides of nitrogen and halocarbons destroy ozone. At the tropopause, a rather distinct boundary between the troposphere and the stratosphere located at an altitude fluctuating around 15 kilometers, there is a sharp change in the concentration of water vapor (that is, the variation in concentration within the strato-

sphere is minimal) (Table 3). Lindzen and others¹⁹ argue that water vapor between 2 kilometers (800 millibars) and 16 kilometers from Earth's surface (the tropopause) is the primary determinant of the greenhouse effect. However, Shine and others²⁰ argue that water vapor concentration in the lower troposphere is an equally important contributor to the greenhouse effect. Currently, it is believed that the impact of anthropogenic water vapor from the surface sources such as fuel combustion is minimal on the atmospheric water vapor concentrations.

¹⁸S.J. Oltmans and D.J. Hoffman, "Increase in Lower-stratospheric Water Vapor at a Mid-latitude Northern Hemisphere Site from 1981-1994" *Nature* 374 (1995):146-149.

¹⁹R.S. Lindzen, "Some Coolness Concerning Global Warming," *Bulletin of the American Meteorological Society* 71 (1990):288-299, and D.G. Sun and R.S. Lindzen, "Distribution of Tropical Tropospheric Water Vapor," *Journal of Atmospheric Science* 50 (1993):1643-1660.

²⁰K.P. Shine and A. Sinha, "Sensitivity of the Earth's Climate to Height-Dependent Changes in the Water Vapor Mixing Ratio," *Nature* 354 (1991):382-384, and D. Lubin, "The Role of Tropical Super Greenhouse Effect in Healing the Ocean Surface," *Science* 265 (1994):224-227.

Table 3. Atmospheric Water Vapor Concentrations, 1981-1994

Altitude (kilometers)	Concentration (parts per million)	Average Annual Increase (percent)
10 – 12	59.20	1.03
12 – 14	11.88	0.49
14 – 16	4.66	0.54
16 – 18	3.87	0.73
18 – 20	3.85	0.84
20 – 22	4.07	0.54
22 – 24	4.21	0.38
24 – 26	4.29	0.34

Source: S.J. Oltmans and D.J. Hoffman, "Increase in Lower-Stratospheric Water Vapor at Mid-Latitude Northern Hemisphere Site from 1981–1994," *Nature*, 374 (1995): 146-149.

Methane (CH₄) is a product of organic decay. The largest natural source of methane is the world's wetlands, although it is also the major constituent of natural gas and a potent GHG. Although methane occurs in the atmosphere in one two-hundredth of the quantity of carbon dioxide, it has 5–10 times the heat-trapping potential per molecule.^{21,22} Methane is increasing in the atmosphere at an annual rate of 1 percent, double the rate of increase for carbon dioxide. Activities that release methane are rice-paddy agriculture, waste treatment, biomass burning, livestock production, and venting during natural gas and coal exploration and production activities. Methane is also released during the transport of natural gas.

Approximately 90 percent of atmospheric methane is chemically destroyed in the troposphere. Chemical destruction of methane through oxidation occurs by hydroxyl radicals. Although the concentration of hydroxyl radicals is very small (0.04 parts per trillion by volume),²³ they are the main oxidants of atmospheric methane, carbon monoxide,²⁴ oxides of nitrogen, and non-methane hydrocarbons. Atmospheric hydroxyl radicals are produced by dissociation of water vapor and reaction between water vapor and other trace gases in the atmosphere. These reactions are controlled by pressure, temperature, atmospheric pH, altitude, and reactants concentration.

Nitrous oxide (N₂O) is also a powerful GHG. It stays in the atmosphere for 150–180 years, eventually floating up into the stratosphere where it helps destroy the ozone layer. Its concentration is increasing by 0.2 percent to 0.3 percent per year. Its main source is the tropics, but roughly 20 percent of nitrous oxide emissions result from manufacturing and using chemical fertilizers and from burning fossil fuels. The increased use of emission control devices like catalytic converters in internal combustion engines contributes further to these emissions. The use of fertilizers in growing corn for ethanol is the major component of the ethanol fuel cycle's high nitrous oxide emission.

Although chlorofluorocarbons (CFCs) are not products of engine combustion, these chemicals are associated with vehicle activity because they result from the production and use of air cooling devices. Automotive CFCs are being phased out of new models. Concentrations of CFCs are rising approximately 0.5 percent per year, and these chemicals typically persist in the atmosphere from 75 to 180 years. CFCs are 20,000 times more potent than carbon dioxide in trapping Earth's thermal radiation. However, some scientists believe that CFCs might have countervailing effects that cause cooling, so on balance, the effect of CFCs is not clear.

Ozone is not produced directly from the combustion of transportation fuels; however, combustion products like NO_x, hydrocarbons, and water vapor play a major role in its formation. Ozone is a beneficial GHG in the stratosphere and a harmful pollutant in the troposphere. Ozone survives anywhere from a few hours to a few days in the upper troposphere and for only an hour in the stratosphere²⁵ (see Appendix B for a discussion of ozone's stability). Thinning the stratospheric ozone layer increases the amount of harmful UV-C radiation reaching the Earth's surface. This will not only increase UV-induced diseases, but also aid the production of ozone in the troposphere. It is beneficial when ozone stays in the stratosphere because ozone shields the Earth's surface from harmful ultraviolet rays of the Sun. Because of its oxidizing power, ozone is hazardous to health. Therefore, ozone is classified as a criteria pollutant in the troposphere. Throughout the atmosphere, however, ozone acts as a greenhouse gas.

²¹On a 100-year basis. See Table 5.

²²U.S. *Climate Action Report*, Submission of the United States of America Under the United Nations Framework Convention on Climate Change, 1994, p. 8.

²³R.D. Prinn and others, "Global Average Concentration and Trend for Hydroxyl Radicals Deduced from ALE/GAGE Trichloroethane Data for 1978-1990," *Journal of Geophysical Research* 97 (1992):2445-2461.

²⁴B. Weinstock, "Carbon Monoxide: Residence Time in the Atmosphere," *Science* 166:224-225, and World Meteorological Organization, *Scientific Assessment of Ozone Depletion*, (Geneva, Switzerland, 1991).

²⁵As ozone is transported to the lower stratosphere and to high latitudes, it lasts many months (possibly years) and is stored there until destroyed or transported down into the troposphere.

Greenhouse gases have the ability to absorb infrared radiation (radiation with a wavelength of 1 micrometer or more) and also have, in general, longer residence times in the atmosphere than criteria pollutants. Although some compounds (e.g., carbon monoxide,

oxides of nitrogen [except nitrous oxide], and non-methane volatile organic compounds) have properties of greenhouse gases in terms of absorption of infrared radiation, they are also called criteria pollutants because they are hazardous to health.

3. Greenhouse Gases Emitted From Transportation Uses

In the United States, transportation is a multimodal system of highway, mass transit, air, rail, waterborne, and pipeline transport. Light trucks²⁶ are becoming a greater proportion of the surface transportation fleet, accounting for almost 40 percent of new vehicle purchases. These vehicles, as well as conventional automobiles (collectively known “light-duty” vehicles), are the basis in this report for GHG emissions resulting from fuel combustion.

In 1990, highway travel accounted for 85 percent of total passenger miles traveled, air travel for 11 percent, and rail and bus travel for 4 percent. In addition, more than 3.1 trillion ton-miles of freight are moved in the United States each year. A 50-percent increase in vehicle miles traveled since 1969 has been partly offset by a 34 percent decrease (equivalent to an increase in efficiency of 7 miles per gallon) in the amount of fuel consumed per mile. Fossil fuels account for approximately 85 percent of U.S. energy consumed, with the remaining 15 percent coming from renewable and other energy sources.²⁷

Motor vehicle greenhouse gas (GHG) emissions are projected to grow in the United States and throughout the world as the result of increasing vehicle miles traveled (VMT). EIA projects a 1.4 percent VMT growth per year from 1994 to 2015 in the U.S. compared with a 5.5 percent growth rate between 1980 and 1990.²⁸ The 1990 Nationwide Personal Transportation Survey (NPTS)²⁹ suggests that vehicle miles traveled will increase at a rate about double the population growth. The greatest growth in vehicle miles traveled is expected to come from non-work-related trips and increases in commuting distances, which are associated with suburban sprawl. These trends are occurring not only in the United States but also in all major cities around

the world and promise to continue even if economic growth is minimal. Moreover, the rate of increase in vehicle ownership in Asia and Africa is greater than in the United States and elsewhere (Table 4). Removing the 55 mile-per-hour speed limit will also add to GHG emissions' growth.

Table 4. Worldwide Vehicle Ownership Trends
(Vehicles per Person)

Area	1980	1990	Percent Change
Africa	0.013	0.021	61.5
Asia	0.019	0.033	73.7
United States	0.588	0.769	30.8
South America . . .	0.067	0.083	23.9
Europe	0.217	0.278	28.0

Source: Decision Analysis Corporation, *Measurement of Emissions: Greenhouse Gas Estimates for Alternative Transportation Fuels*, unpublished final report prepared for the Energy Information Administration (Vienna, VA, December 1995).

The transportation sector contributes about one-third of total carbon dioxide emissions in the United States and other countries that belong to the Organization for Economic Cooperation and Development.³⁰ Annual worldwide carbon dioxide produced from motor vehicle use is estimated at around 0.32 trillion moles (14 trillion grams), or about 20 percent of total carbon dioxide production.³¹

GHGs contribute to the greenhouse effect through different amplification rates (effectivenesses) over varying time periods (Table 5). These total effects are referred to as “weighted,” or the GWP of each GHG.

²⁶Light trucks include certain automobiles (e.g., minivans) and trucks having a gross vehicle weight rating of less than 8,500 pounds.

²⁷Energy Information Administration, *Renewable Energy Annual 1995*, DOE/EIA-0603(95) (Washington, DC, December 1995), p. 9.

²⁸Energy Information Administration, *Annual Energy Outlook 1996*, DOE/EIA-0383(96) (Washington, DC, January 1996), p. 24.

²⁹Oak Ridge National Laboratory, *1990 NPTS Data Book* (Oak Ridge, TN, 1993), pp. 1-2, was used for non-U.S. countries.

³⁰*U.S. Climate Action Report*, Submission of the United States of America Under the United Nations Framework Convention on Climate Change, 1994, p. 8.

³¹Argonne National Laboratory, *Emissions of Greenhouse Gases from the Use of Transportation Fuels and Electricity*, ANL/ESD/TM-22, Vol. I (Argonne, IL, November 1991) and Vol. II (Argonne, IL, November 1993).

Table 5. Greenhouse Gases and Their Potential Contribution to Global Warming

Greenhouse Gas	Relative Effectiveness ^a		Decay Time ^b (years)	Relative Contribution ^c in 100 Years	
	per Kilogram	per Mole		per Kilogram	per Mole
Carbon Dioxide (CO ₂)	1	1	120–500 ^d	1	1
Methane (CH ₄)	70	25	7–14.5	15–30	5–10
Nitrous Oxide (N ₂ O)	210	210	120	320	320
Ozone (O ₃)	1,800	2,000	0.01	3	4
CFC-11	4,000	12,000	50	4,000	11,000
CFC-12	6,000	15,000	102	8,500	21,250

^aThe greenhouse effectiveness of a gas in the atmosphere depends, in part, on its concentration. As the atmospheric concentration of a gas increases, the effectiveness of additional gas decreases. The relative effectiveness means the effectiveness of a greenhouse gas relative to carbon dioxide. The relative effectiveness refers to global warming potential (GWP) of a greenhouse gas relative to carbon dioxide GWP.

^bThe decay time is a rough measure of how long the greenhouse gas remains in the atmosphere. If the decay time is 150 years, one-half of the initial amount remains in the atmosphere after 150 years.

^cThe relative contribution is the accumulated greenhouse effect as the integral of the greenhouse effect over time, when each gas is undergoing an exponential decrease, while at the same time being added to by continuing industrial emissions.

^dH. Rhode, "A Comparison of the Contribution of Various Gases to the Greenhouse Effect," *Science* 248 (1990):1217–1219. U.S. Department of Energy, *A Primer on Greenhouse Gases*, DOE/NBB-0083 (Washington, DC, March 1988).

CFC-11 = CCl₃F.

CFC-12 = CCl₂F₂.

Note: Global warming potential for water vapors is not available.

Sources: David M. Gates, *Climate Change and Its Biological Consequences* (Sunderland, MA: Sinauer Associates Publishers, Inc. 1993), p. 9; Energy Information Administration, *Emissions of Greenhouse Gases in the United States 1987–1994*, DOE/EIA-0573(87–94) (Washington, DC, October 1995), p. 6.

One of the main reasons for weighting GHGs is that each gas absorbs radiation at a different energy level, with a different coefficient of absorption, and has a different residence time, or decay time, in the atmosphere. Although weighting is the best way to estimate the actual effect of various GHGs, the assumptions needed to arrive at GWP values for some GHGs (e.g., methane and nitrogen oxides) are at best very approximate. Recent data on atmospheric methyl chloroform concentrations indicate that hydroxyl radical (OH*) concentrations are about 20 percent greater than previously estimated, and the revision of these data leads to the projection of a shorter atmospheric methane lifetime than previously estimated.^{32,33} These findings suggest that the actual greenhouse effects for methane, nonmethane hydrocarbons, and oxides of nitrogen are probably lower than the values presently used because the residence times for these GHGs were developed based on lower estimates of hydroxyl radical concentration in the atmosphere.

The two most important variables in calculating the GWP of a greenhouse gas are its "instantaneous radiative forcing" and atmospheric residence time (see Appendix A for details). Radiative forcing values greatly depend not only on GHG concentrations (including absorption bands overlap and reactivity of GHGs), but also on the vertical (altitude) and horizontal distribution of GHGs (see Appendix D for details about the overlap of the absorption bands of GHGs). Except for carbon dioxide, all other major GHG vertical and horizontal (i.e., altitude and surface area, respectively) distribution profiles vary greatly. The radiative forcing may be a function of horizontal and vertical distribution of greenhouse gases, leading to variable GWPs at different locations. The variable GWP values will actually be very useful in estimating or forecasting regional impacts of GHGs.

The estimates presented in Table 1 show both unweighted and weighted GHG emissions,³⁴ while

³²R.G. Prinn and others, "Atmospheric Trends and Lifetimes of Methyl Chloroform and Global Hydroxyl Radical Concentration," *Science* 269 (1995):187-192.

³³A.R. Ravishankara and D.L. Albritton, "Methyl Chloroform and the Atmosphere," *Science* 269 (1995):183-184.

³⁴Assuming current vehicle fuel combustion technology.

Tables 7 through 12 show only unweighted emissions. (To obtain weighted estimates, apply the GWPs from Table 5.) The unweighted estimate measures contributions from all GHGs simply as moles and grams of emissions for the fuel consumed per VMT. The unweighted estimate is a good place to begin GHG analysis, particularly because the GWPs of methane, nitrogen oxides, and water vapor are subject to considerable uncertainty and require scientific investigation beyond the scope of the Energy Information Administration (EIA).

Greenhouse Gas Emissions From Alternative Transportation Fuels and Gasoline

EIA began its effort to estimate GHG emissions from replacement fuels in 1993 by examining existing literature on the subject and developing information specific to alternative transportation fuels (ATFs) across the fuel cycle.³⁵ In general, this work paralleled the framework established by Delucchi.³⁶ Estimates of GHGs are not based upon actual measurements from operating vehicles, but rather on the simplified chemistry of hydrocarbon combustion in automotive engines as formalized in the U.S. Environmental Protection Agency (EPA) "Mobile 5a" emission model.³⁷ A brief overview of the combustion chemistry of alternative and traditional transportation fuels is presented in Appendix C.

EIA uses the Decision Analysis Corporation (DAC) emissions model³⁸ for the estimation of greenhouse gases emitted from the end-use of alternative and traditional transportation fuels because the Mobile 5a model does not provide fully for alternative transportation fuels. EIA then combines this result with its previous estimates³⁹ based on Delucchi's model to obtain the emissions from the remaining stages of the total fuel cycle. The DAC emissions model first calculates theoretical amounts of CO₂ and water emitted

from vehicles per million Btu of fuel consumption, assuming perfect combustion. Carbon dioxide and water emissions per million Btu are then converted to emissions in grams and/or moles⁴⁰ per VMT based on assumptions about miles per gallon, relative efficiencies of different fuels, and the density of gasoline. EIA then estimates criteria pollutant emissions in grams and/or moles per VMT for the different alternative fuels, based on the average emission rate observed in an alternate transportation fuel vehicles database.⁴¹ Criteria pollutants from gasoline are provided in the model. Evaporative emissions obtained from EPA's Mobile 5a model for different liquid fuels are then added to arrive at total vehicle emission estimates.⁴² The DAC emissions model then adjusts the theoretical water and carbon dioxide emissions to account for all criteria pollutants and evaporative emissions.

Carbon dioxide and water vapor account for more than 97 percent of alternative and traditional transportation fuel combustion products (Tables 6, 7, and 8). Water vapor production from gasoline-fueled vehicle combustion is of the same magnitude as carbon dioxide; that is, they are roughly equimolar combustion products, each totaling approximately 17.34×10^{12} moles per year in the world and 5.63×10^{12} moles per year in the United States.⁴³

Table 7 and Figure 3 show the total carbon dioxide emissions per VMT for the entire fuel cycle for different fuels. For the entire fuel cycle, CNG produces the lowest carbon dioxide emissions, or 5.64 moles (248.2 grams) per VMT, closely followed by liquefied petroleum gas (LPG) at 6 moles (263.5 grams) per VMT. Compressed natural gas (CNG) and LPG follow similar trends in the vehicle stage. Alcohol fuels emit less carbon dioxide in the vehicle stage than gasoline. Total carbon dioxide emissions for the fuel cycle from corn-based ethanol is smaller than from gasoline. Ethanol from corn produces the lowest amount of carbon dioxide emissions in the pre-vehicle stage at 0.56 moles (24.4 grams) per VMT due to the sequestration carbon

³⁵Energy Information Administration, *Annual Report to Congress 1994*, DOE/EIA-0173(94) (Washington, DC, April 1995), p. 7.

³⁶Argonne National Laboratory, *Emissions of Greenhouse Gases from the Use of Transportation Fuels and Electricity*, ANL/ESD/TM-22, Vol. I (Argonne, IL, November 1991) and Vol. II (Argonne, IL, November 1993).

³⁷The "Mobile 5a" calculates most emissions, uses regulatory maxima for others, and uses measured values for the remainder (e.g., carbon monoxide).

³⁸*Ibid.*

³⁹Energy Information Administration, *Alternatives to Traditional Transportation Fuels 1993*, DOE/EIA-0585/(93) (Washington, DC, June 1994), pp. 29-36.

⁴⁰One mole of a gas is equal to the amount of substance that contains as many elementary units (6.023×10^{23} molecules or atoms) as there are atoms in 12 grams of carbon-12. Normally, emissions are reported in grams per VMT. However, reporting in moles is preferable because greenhouse gas heat absorption is directly related to the number of molecules of a gas.

⁴¹Decision Analysis Corporation, *Measurement of Emissions: Greenhouse Gas Estimates for Alternative Transportation Fuels*.

⁴²Evaporative emissions occur when a portion of the liquid fuels vaporizes as opposed to being combusted.

⁴³There are 188 million vehicles in the United States and 582 million vehicles in the world (from the *1992 Motor Vehicle Manufacturers Association Fact Book*). Average consumption is approximately 619 gallons per vehicle annually.

Table 6. Gasoline Exhaust Products per Vehicle Mile Traveled
(Grams and Moles)

Exhaust Product	Emissions			
	Grams	Percent of Total	Moles	Percent of Total
Carbon Dioxide (CO ₂)	272.38	69.38	6.19	49.01
Water Vapor (H ₂ O)	109.42	27.88	6.08	48.14
Methane (CH ₄)	0.08	0.02	<0.01	0.07
Nitrogen Oxides (NO _x) and Nitrous Oxide (N ₂ O) . .	0.87	0.22	0.02	0.16
Carbon Monoxide (CO)	9.00	2.29	0.32	2.53
Nonmethane Hydrocarbons (C _n H _m)	0.86	0.21	0.01	0.09

Notes: Gasoline refers to unleaded gasoline in this report. Estimates are based on the Environmental Protection Agency's Mobile 5a model for emissions produced by hydrocarbon combustion in automotive engines. Nitrogen oxides include primarily nitric oxide and nitrogen dioxide. One mole of a gas is equal to the amount of substance that contains as many elementary units (6.023 x 10²³ molecules or atoms) as there are atoms in 12 grams of carbon-12. Normally, emissions are reported in grams per vehicle mile traveled. However, reporting in moles is preferable because greenhouse gas heat absorption is directly related to the number of molecules of a gas.

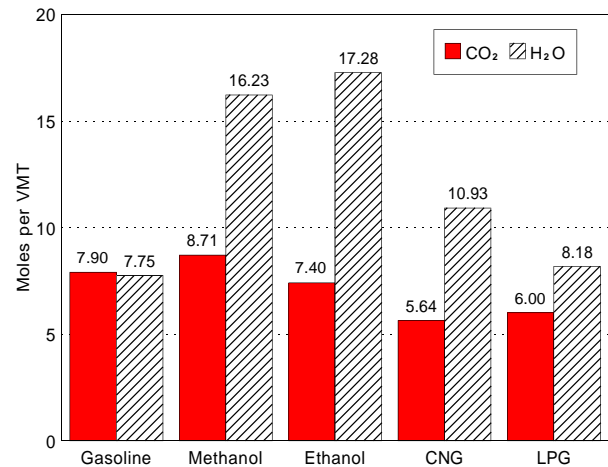
Source: Decision Analysis Corporation, "Measurement of Emissions: Greenhouse Gas Estimates for Alternative Transportation Fuels," unpublished final report prepared for the Energy Information Administration (Vienna, VA, December 1995).

dioxide credit of 6.8 moles (299.1 grams), followed by LPG at 0.65 moles (28.1 grams) and CNG at 0.99 moles (43.5 grams).

Total fuel cycle water vapor emissions are the lowest for gasoline at 7.75 moles (139.5 grams) followed by LPG at 8.18 moles (147.3 grams) and CNG at 10.93 moles (196.8 grams) (Table 8 and Figure 3). Currently, however, water vapor from fuel combustion is not believed to have a significant impact on atmospheric water vapor concentrations.

All other emissions are best represented by millimoles (one-thousandth of a mole) and milligrams (one-thousandth of a gram) rather than moles and grams. LPG emits the least methane, 17.2 millimoles (271 milligrams) per VMT, followed by gasoline at 22 millimoles (349 milligrams) per VMT (Table 9, Figure 4). CNG tops the list for methane emissions, producing 56.3 millimoles (900 milligrams) per VMT in the vehicle stage and 35 millimoles (559 milligrams) per VMT in other stages. Corn-based ethanol emits the largest amount of nitrous oxide, 9.3 millimoles (410 milligrams) per VMT, largely due to fertilizer use (7.41 millimoles or 327 milligrams per VMT) (Table 10 and Figure 4). Because actual measurements of nitrous oxide in the vehicle stage vary greatly, the regulatory maximum of 1.6 millimoles (70 milligrams) per VMT is used to calculate nitrous oxide emissions.

Figure 3. Total Fuel Cycle Carbon Dioxide and Water Vapor Emissions per Vehicle Mile Traveled for Five Selected Fuels



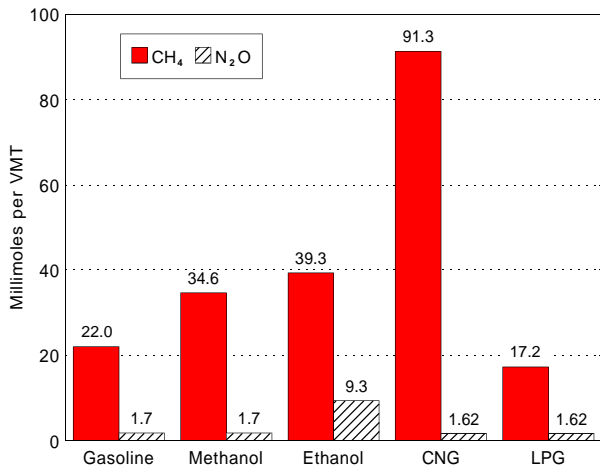
CNG = Compressed natural gas. CO₂ = Carbon dioxide. H₂O = Water vapor. LPG = Liquefied petroleum gases. VMT = Vehicle mile traveled.

Source: Tables 7 and 8.

Table 11 shows the carbon monoxide emissions for the various fuels as being identical—321.4 millimoles (9,000 milligrams) per VMT in the vehicle stage.⁴⁴ The reason is that the value shown is the regulatory maximum set

⁴⁴Although some data indicate that CNG emits lower levels of carbon monoxide than gasoline, the regulatory maximum is used for all the fuels considered in this report.

Figure 4. Total Fuel Cycle Methane and Nitrous Oxide Emissions per Vehicle Mile Traveled for Five Selected Fuels



CH₄ = Methane. CNG = Compressed natural gas. LPG = Liquefied petroleum gases. N₂O = Nitrous oxide. VMT = Vehicle mile traveled.

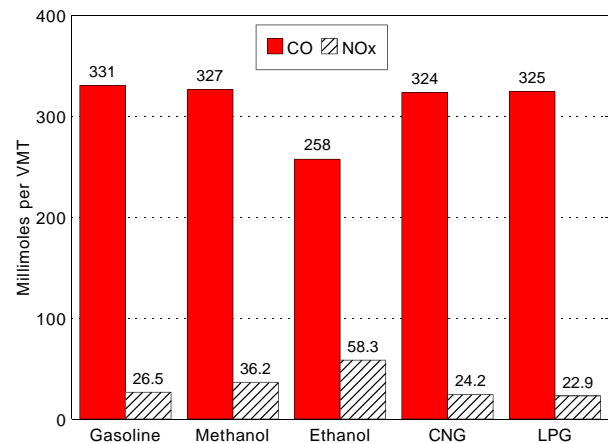
Source: Tables 9 and 10.

within the model with a value of 321.4 millimoles (9,000 milligrams) per VMT. These emissions are not measured values due to the huge range of values reported in the alternative-fueled vehicles (AFVs) database. Ethanol has the lowest total fuel cycle carbon monoxide emissions at 258.3 millimoles (7,232 milligrams) per VMT (Figure 5).

Total fuel cycle nitric oxide and nitrogen dioxide emissions for LPG and CNG are lowest at 22.9 millimoles (870 milligrams) and 24.2 millimoles (919 milligrams), respectively, per VMT, mainly because the vehicle stage uses the regulatory maximum value of 21.1 millimoles (800 milligrams) per VMT (Table 12 and Figure 5). Ethanol from corn emits the most nitrogen oxides—37.2 millimoles (1,417 milligrams) per VMT—due to large releases during the corn-growing and fuel production (fermentation) processes. At 1.8 millimoles (70 milligrams) per VMT, LPG emits the least nitrogen oxides prior to the vehicle stage of the fuel cycle.

An evaluation of available data on total fuel cycle emissions for five fuel types (namely, gasoline, CNG,

Figure 5. Total Fuel Cycle Carbon Monoxide and Nitrogen Oxide Emissions per Vehicle Mile Traveled for Five Selected Fuels



CNG = Compressed natural gas. CO = Carbon monoxide. LPG = Liquefied petroleum gases. NO_x = Nitrogen oxide. VMT = Vehicle mile traveled.

Source: Tables 11 and 12.

LPG from oil and gas, methanol from natural gas, and ethanol from corn) and combustion chemistry results in certain conclusions with respect to existing information on GHGs in the transportation sector. First, ATFs would produce minimal, if any, weighted GHG reductions if water vapor were taken into account. For a variety of reasons, however, most current analyses of GHGs do not include water vapor as a greenhouse gas in analyzing fuel emissions. For instance, some analysts question whether the marginal addition of water vapor from fuels, except emissions from high-flying aircraft,⁴⁵ has a measurable impact, compared with the impact of “background” levels of water vapor in the atmosphere. The relation between surface sources and atmospheric concentrations of water vapor is complicated and indirect. Second, CNG produces the lowest level of carbon dioxide emissions across the total fuel cycle, followed by LPG and ethanol from corn. Third, CNG produces the largest methane emissions across the total fuel cycle. Finally, ethanol from corn produces the largest nitrous oxide emissions across the total fuel cycle.

⁴⁵D.W. Fahey and others, “Emission Measurements of the Concorde Supersonic Aircraft in the Lower Stratosphere,” *Science* 270 (1995):70-74.

Table 7. Fuel Cycle Carbon Dioxide Emissions per Vehicle Mile Traveled
(Grams and Moles)

Fuel Cycle Stage	Gasoline		Methanol From Natural Gas		Ethanol From Corn		Compressed Natural Gas		LPG From Oil and Gas	
	Grams/VMT	Moles/VMT	Grams/VMT	Moles/VMT	Grams/VMT	Moles/VMT	Grams/VMT	Moles/VMT	Grams/VMT	Moles/VMT
CO ₂ From Natural Gas Wells	0.0 . . .	0.00	6.3	0.14	0.0	0.00	4.5	0.10	2.9	0.07
Gas Leaks and Flares ^a	. . . 3.5 . . .	0.08	0.0	0.00	0.0	0.00	0.0	0.00	0.9	0.02
Fertilizer Manufacture 0.0 . . .	0.00	0.0	0.00	57.0	1.30	0.0	0.00	0.0	0.00
N ₂ O, NO _x , CO ₂ From Fertilizer	0.0 . . .	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00
Feedstock Recovery 10.0 . . .	0.23	15.9	0.36	10.8	0.25	6.2	0.14	6.4	0.15
Feedstock Transmission	. . 8.7 . . .	0.20	4.8	0.11	13.7	0.31	0.0	0.00	2.2	0.05
Fuel Production 47.8 . . .	1.09	62.5	1.42	226.1	5.14	5.4	0.12	10.0	0.23
Sequestration ^b 0.0 . . .	0.00	0.0	0.00	-299.1	-6.80	0.0	0.00	0.0	0.00
Fuel Distribution 4.9 . . .	0.11	23.2	0.53	15.9	0.36	8.7	0.20	5.7	0.13
Compression or Liquefaction	0.0 . . .	0.00	0.0	0.00	0.0	0.00	18.7	0.43	0.0	0.00
Subtotal 74.9 . . .	1.71	112.7	2.56	24.4	0.56	43.5	0.99	28.1	0.65
Vehicle ^{c,d,e} 272.4 . . .	6.19	270.4	6.15	301.1	6.84	204.7	4.65	235.4	5.35
Total 347.3 . . .	7.90	383.1	8.71	325.5	7.40	248.2	5.64	263.5	6.00

^aAssumes that flared gas is burned completely to CO₂ and water vapor with no methane, nonmethane, organic components, or carbon monoxide.

^bSequestration refers to the fixation process of greenhouse gases emitted (e.g., carbon dioxide and water vapors are sequestered through photosynthesis).

^cDecision Analysis Corporation, "Measurement of Emissions: Greenhouse Gas Estimates for Alternative Transportation Fuels," unpublished final report prepared for the Energy Information Administration (Vienna, VA, December 1995).

^dGreenhouse gas (GHG) emission values from vehicle end-use are revised.

^eThe total GHG emission values are revised because vehicle end-use values are revised.

CO₂ = Carbon dioxide.

LPG = Liquefied petroleum gases.

N₂O = Nitrous oxide.

NO_x = Nitrogen oxides.

VMT = Vehicle mile traveled.

Notes: Gasoline refers to unleaded gasoline in this report. • Table was derived using a vehicle with gasoline efficiency of 30 miles per gallon. • Emissions from manufacturing the vehicles are not included. • Nitrogen oxides include primarily nitric oxide and nitrogen dioxide. One mole of a gas is equal to the amount of substance that contains as many elementary units (6.023 x 10²³ molecules or atoms) as there are atoms in 12 grams of carbon-12. Normally, emissions are reported in grams per VMT. However, reporting in moles is preferable because GHG heat absorption is directly related to the number of molecules of a gas.

Sources: Derived from GHG emissions spreadsheet provided to the Energy Information Administration, July 1994. Spreadsheet is an unpublished revision of Argonne National Laboratory, Center for Transportation Research, *Emissions of Greenhouse Gases From the Use of Transportation Fuels and Electricity*, ANL/ESD/TM-22, prepared by Dr. Mark Delucchi, Vol. 1 (Argonne, IL, November 1991) and Vol. 2 (Argonne, IL, November 1993). Also see Energy Information Administration, *Alternatives to Traditional Transportation Fuels 1993*, EIA/DOE-0585(93) (Washington, DC, January 1995).

Table 8. Fuel Cycle Water Vapor Emissions per Vehicle Mile Traveled
(Grams and Moles)

Fuel Cycle Stage	Gasoline		Methanol From Natural Gas		Ethanol From Corn		Compressed Natural Gas		LPG From Oil and Gas	
	Grams/VMT	Moles/VMT	Grams/VMT	Moles/VMT	Grams/VMT	Moles/VMT	Grams/VMT	Moles/VMT	Grams/VMT	Moles/VMT
CO ₂ From Natural Gas Wells	0.0	0.00	2.5	0.14	0.0	0.00	1.8	0.10	1.2	0.70
Gas Leaks and Flares ^a	1.4	0.08	0.0	0.00	0.0	0.00	0.0	0.00	0.4	0.02
Fertilizer Manufacture	0.0	0.00	0.0	0.00	22.9	1.27	0.0	0.00	0.0	0.00
N ₂ O, NO _x , CO ₂ From Fertilizer	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00
Feedstock Recovery	4.0	0.22	6.4	0.36	4.3	0.24	2.5	0.14	2.6	0.14
Feedstock Transmission	3.5	0.19	1.9	0.11	5.5	0.31	0.0	0.00	0.9	0.05
Fuel Production	19.2	1.07	25.1	1.39	90.8	5.04	2.2	0.12	4.0	0.22
Sequestration ^b	0.0	0.00	0.0	0.00	-120.1	-6.67	0.0	0.00	0.0	0.00
Fuel Distribution	2.0	0.11	9.3	1.29	6.4	0.36	3.5	0.19	2.0	0.13
Compression or Liquefaction	0.0	0.00	0.0	0.00	0.0	0.00	7.5	0.42	0.0	0.00
Subtotal	30.1	1.67	45.2	3.29	9.8	0.55	17.5	0.97	11.1	0.63
Vehicle ^{c,d,e}	109.4	6.08	232.9	12.94	301.1	16.73	179.3	9.96	135.9	7.55
Total	139.5	7.75	278.1	16.23	310.9	17.28	196.8	10.93	147.0	8.18

^aAssumes that flared gas is burned completely to CO₂ and water vapor with no methane, nonmethane, organic compounds, carbon monoxide, NO_x, or N₂O.

^bSequestration refers to the fixation process of greenhouse gases (GHGs) emitted (e.g., carbon dioxide and water vapors are sequestered through photosynthesis). Water vapor sequestration through photosynthesis is the only process considered in this report. There are other processes that may merit consideration.

^cDecision Analysis Corporation, "Measurement of Emissions: Greenhouse Gas Estimates for Alternative Transportation Fuels," unpublished final report prepared for the Energy Information Administration (Vienna, VA, December 1995).

^dGreenhouse gas (GHG) emission values from vehicle end-use are revised.

^eThe total GHG emission values are revised because vehicle end-use values are revised.

CO₂ = Carbon dioxide.

LPG = Liquefied petroleum gases.

N₂O = Nitrous oxide.

NO_x = Nitrogen oxides.

VMT = Vehicle mile traveled.

Notes: Gasoline refers to unleaded gasoline in this report. • Table was derived using a vehicle with gasoline efficiency of 30 miles per gallon. • Emissions from manufacturing the vehicles are not included. • Nitrogen oxides include primarily nitric oxide and nitrogen dioxide. One mole of a gas is equal to the amount of substance that contains as many elementary units (6.023 x 10²³ molecules or atoms) as there are atoms in 12 grams of carbon-12. Normally, emissions are reported in grams per VMT. However, reporting in moles is preferable because GHG heat absorption is directly related to the number of molecules of a gas.

Sources: Derived from GHG emissions spreadsheet provided to the Energy Information Administration, July 1994. Spreadsheet is an unpublished revision of Argonne National Laboratory, Center for Transportation Research, *Emissions of Greenhouse Gases From the Use of Transportation Fuels and Electricity*, ANL/ESD/TM-22, prepared by Dr. Mark Deluchi, Vol. 1 (Argonne, IL, November 1991) and Vol. 2 (Argonne, IL, November 1993). Also see Energy Information Administration, *Alternatives to Traditional Transportation Fuels 1993*, EIA/DOE-0585(93) (Washington, DC, January 1995).

Table 9. Fuel Cycle Methane Emissions per Vehicle Mile Traveled
(Milligrams and Millimoles)

Fuel Cycle Stage	Gasoline		Methanol From Natural Gas		Ethanol From Corn		Compressed Natural Gas		LPG From Oil and Gas	
	mg/VMT	mmol/VMT	mg/VMT	mmol/VMT	mg/VMT	mmol/VMT	mg/VMT	mmol/VMT	mg/VMT	mmol/VMT
CO ₂ From Natural Gas Wells	0	0.0	0	0.0	0	0.0	0	0.0	0	0.0
Gas Leaks and Flares ^a	178	11.1	367	22.9	0	0.0	490	30.6	169	10.6
Fertilizer Manufacture	0	0.0	0	0.0	100	6.3	0	0.0	0	0.0
N ₂ O, NO _x , CO ₂ From Fertilizer	0	0.0	0	0.0	0	0.0	0	0.0	0	0.0
Feedstock Recovery	16	1.0	3	0.2	0	0.0	1	0.1	5	0.3
Feedstock Transmission	9	0.6	30	1.9	16	1.0	0	0.0	2	0.1
Fuel Production	62	3.9	37	2.3	405	25.3	1	0.1	7	0.4
Sequestration	0	0.0	0	0.0	0	0.0	0	0.0	0	0.0
Fuel Distribution	4	0.0	30	1.9	20	1.3	40	2.5	7	0.4
Compression or Liquefaction	0	0.0	0	0.0	0	0.0	27	1.7	0	0.0
Subtotal	269	16.6	467	29.2	541	33.9	559	35.0	190	11.8
Vehicle ^{b,c,d}	80	5.4	80	5.4	80	5.4	900	56.3	80	5.4
Total	349	22.0	547	34.6	621	39.3	1,459	91.3	270	17.2

^a Assumes that flared gas is burned completely to CO₂ and H₂O with no methane, nonmethane organic compounds, carbon monoxide, NO, or N₂O.

^b Decision Analysis Corporation, "Measurement of Emissions: Greenhouse Gas Estimates for Alternative Transportation Fuels," unpublished final report prepared for the Energy Information Administration (Vienna, VA, December 1995).

^c Greenhouse gas (GHG) emission values from vehicle end-use are revised.

^d The total GHG emission values are revised because vehicle end-use values are revised.

CO₂ = Carbon dioxide.

LPG = Liquefied petroleum gases.

mg = Milligrams.

mmol = Millimoles.

N₂O = Nitrous Oxide.

NO_x = Nitrogen Oxides.

VMT = Vehicle mile traveled.

Notes: Gasoline refers to unleaded gasoline in this report. • Table was derived using a vehicle with gasoline efficiency of 30 miles per gallon. • Emissions from manufacturing the vehicles are not included. • Nitrogen oxides include primarily nitric oxide and nitrogen dioxide. One mole of a gas is equal to the amount of substance that contains as many elementary units (6.023 x 10²³ molecules or atoms) as there are atoms in 12 grams of carbon-12. Normally, emissions are reported in grams per VMT. However, reporting in moles is preferable because GHG heat absorption is directly related to the number of molecules of a gas.

Sources: Derived from GHG emissions spreadsheet provided to the Energy Information Administration, July 1994. Spreadsheet is an unpublished revision of Argonne National Laboratory, Center for Transportation Research, *Emissions of Greenhouse Gases From the Use of Transportation Fuels and Electricity*, ANL/ESD/TM-22, prepared by Dr. Mark Delucchi, Vol. 1 (Argonne, IL, November 1991) and Vol. 2 (Argonne, IL, November 1993). Also see Energy Information Administration, *Alternatives to Traditional Transportation Fuels 1993*, EIA/DOE-0585(93) (Washington, DC, January 1995).

Table 10. Fuel Cycle Nitrous Oxide Emissions per Vehicle Mile Traveled
(Milligrams and Millimoles)

Fuel Cycle Stage	Gasoline		Methanol From Natural Gas		Ethanol From Corn		Compressed Natural Gas		LPG From Oil and Gas	
	mg/VMT	mmol/VMT	mg/VMT	mmol/VMT	mg/VMT	mmol/VMT	mg/VMT	mmol/VMT	mg/VMT	mmol/VMT
CO ₂ From Natural Gas Wells	0.	0.0	0	0.00	0	0	0	0.00	0	0.00
Gas Leaks and Flares ^a	. . . 0.	0.0	0	0.00	0	0	0	0.00	0	0.00
Fertilizer Manufacture 0.	0.0	0	0.00	2	0.05	0	0.00	0	0.00
N ₂ O, NO _x , CO ₂ From Fertilizer	0	0.0	0	0.00	327	7.41	0	0.00	0	0.00
Feedstock Recovery 0.	0.0	1	0.02	0	0.00	0	0.00	0	0.00
Feedstock Transmission	. . 0.	0.0	0	0.00	1	0.02	0	0.00	0	0.00
Fuel Production 4.	0.1	3	0.07	10	0.20	0	0.00	0	0.00
Sequestration 0.	0.0	0	0.00	0	0.00	0	0.00	0	0.00
Fuel Distribution 0.	0.0	1	0.01	1	0.02	0	0.00	1	0.02
Compression or Liquefaction	0.0	0	0.00	0	0.00	1	0.02	0	0.00
Subtotal 4.	0.1	5	0.10	341	7.70	1	0.02	1	0.02
Vehicle ^{b,c,d} 70.	1.6	70	1.60	70	1.60	70	1.60	70	1.60
Total 74.	1.7	75	1.70	411	9.30	71	1.62	71	1.62

^aAssumes that flared gas is burned completely to CO₂ and water vapor with no methane, nonmethane organic compounds, carbon monoxide, N₂O, or N₂O.

^bDecision Analysis Corporation, "Measurement of Emissions: Greenhouse Gas Estimates for Alternative Transportation Fuels," unpublished final report prepared for the Energy Information Administration (Vienna, VA, December 1995).

^cGreenhouse gas (GHG) emission values from vehicle end-use are revised.

^dThe total GHG emission values are revised because vehicle end-use values are revised.

CO₂ = Carbon dioxide.

LPG = Liquefied petroleum gases.

mg = Milligrams.

mmol = Millimoles.

N₂O = Nitrous oxide.

NO_x = Nitrogen oxides.

VMT = Vehicle mile traveled.

Notes: Gasoline refers to unleaded gasoline in this report. • Table was derived using a vehicle with gasoline efficiency of 30 miles per gallon. • Emissions from manufacturing the vehicles are not included. • Nitrogen oxides include primarily nitric oxide and nitrogen dioxide. One mole of a gas is equal to the amount of substance that contains as many elementary units (6.023 x 10²³ molecules or atoms) as there are atoms in 12 grams of carbon-12. Normally, emissions are reported in grams per VMT. However, reporting in moles is preferable because GHG heat absorption is directly related to the number of molecules of a gas.

Sources: Derived from a GHG emissions spreadsheet provided to the Energy Information Administration, July 1994. Spreadsheet is an unpublished revision of Argonne National Laboratory, Center for Transportation Research, *Emissions of Greenhouse Gases From the Use of Transportation Fuels and Electricity*, ANL/ESD/TM-22, prepared by Dr. Mark Delucchi, Vol. 1 (Argonne, IL, November 1991) and Vol. 2 (Argonne, IL, November 1993). Also see Energy Information Administration, *Alternatives to Traditional Transportation Fuels 1993*, EIA/DOE-0585(93) (Washington, DC, January 1995).

Table 11. Fuel Cycle Carbon Monoxide Emissions per Vehicle Mile Traveled
(Milligrams and Millimoles)

Fuel Cycle Stage	Gasoline		Methanol From Natural Gas		Ethanol From Corn		Compressed Natural Gas		LPG From Oil and Gas	
	mg/VMT	mmol/VMT	mg/VMT	mmol/VMT	mg/VMT	mmol/VMT	mg/VMT	mmol/VMT	mg/VMT	mmol/VMT
CO ₂ From Natural Gas Wells	.0...	0.0	0	0.0	0	0.0	0	0.0	0	0
Gas Leaks and Flares ^a0...	0.0	0	0.0	0	0.0	0	0.0	0	0
Fertilizer Manufacture0...	0.0	0	0.0	119	4.3	0	0.0	0	0
N ₂ O, NO _x , CO ₂ From Fertilizer	0...	0.0	0	0.0	0	0.0	0	0.0	0	0
Feedstock Recovery138...	4.9	65	2.3	-2,211	-79.0	43	1.5	62	2.2
Feedstock Transmission	...21...	0.8	17	0.6	52	1.9	0	0.0	5	0.2
Fuel Production75...	2.7	9	0.3	218	7.8	2	0.1	14	0.5
Sequestration0...	0.0	0	0.0	0	0.0	0	0.0	0	0.0
Fuel Distribution16...	.6	69	2.5	54	1.9	25	0.9	19	0.7
Compression or Liquefaction	.0...	0.0	0	0.0	0	0.0	7	0.3	0	0.0
Subtotal250...	9.0	160	5.7	-1,768	-63.2	77	2.8	100	3.6
Vehicle ^{b,c,d}9,000...	321.4	9,000	321.4	9,000	321.4	9,000	321.4	9,000	321.4
Total9,250...	330.4	9,160	327.1	7,232	258.3	9,077	324.2	9,100	325.0

^a Assumes that flared gas is burned completely to CO₂ and H₂O with no methane, nonmethane organic compounds, carbon monoxide, NO_x, or N₂O.

^b Decision Analysis Corporation, "Measurement of Emissions: Greenhouse Gas Estimates for Alternative Transportation Fuels," unpublished final report prepared for the Energy Information Administration (Vienna, VA, December 1995).

^c Greenhouse gas (GHG) emission values from vehicle end-use are revised.

^d The total GHG emission values are revised because vehicle end-use values are revised.

CO₂ = Carbon dioxide.

LPG = Liquefied petroleum gases.

mg = Milligrams.

mmol = Millimoles.

N₂O = Nitrous oxide.

NO_x = Nitrogen oxides.

VMT = Vehicle mile traveled.

Notes: Gasoline refers to unleaded gasoline in this report. • Table was derived using a vehicle with gasoline efficiency of 30 miles per gallon. • Emissions from manufacturing the vehicles are not included. • Nitrogen oxides include primarily nitric oxide and nitrogen dioxide. One mole of a gas is equal to the amount of substance that contains as many elementary units (6.023 x 10²³ molecules or atoms) as there are atoms in 12 grams of carbon-12. Normally, emissions are reported in grams per VMT. However, reporting in moles is preferable because GHG heat absorption is directly related to the number of molecules of a gas.

Sources: Derived from GHG emissions spreadsheet provided to the Energy Information Administration, July 1994. Spreadsheet is an unpublished revision of Argonne National Laboratory, Center for Transportation Research, *Emissions of Greenhouse Gases From the Use of Transportation Fuels and Electricity*, ANL/ESD/TM-22, prepared by Dr. Mark Delucchi, Vol. 1 (Argonne, IL, November 1991) and Vol. 2 (Argonne, IL, November 1993). Also see Energy Information Administration, *Alternatives to Traditional Transportation Fuels 1993*, EIA/DOE-0585(93) (Washington, DC, January 1995).

Table 12. Fuel Cycle Nitrogen Oxides Emissions per Vehicle Mile Traveled
(Milligrams and Millimoles)

Fuel Cycle Stage	Gasoline		Methanol From Natural Gas		Ethanol From Corn		Compressed Natural Gas		LPG From Oil and Gas	
	mg/VMT	mmol/VMT	mg/VMT	mmol/VMT	mg/VMT	mmol/VMT	mg/VMT	mmol/VMT	mg/VMT	mmol/VMT
CO ₂ From Natural Gas Wells	.0...	0.0	0	0.0	0	0.0	0	0.0	0	0.0
Gas Leaks and Flares ^a0...	0.0	0	0.0	0	0.0	0	0.0	0	0.0
Fertilizer Manufacture0...	0.0	0	0.0	476	12.5	0	0.0	0	0.0
N ₂ O, NO _x , CO ₂ From Fertilizer	0...	0.0	0	0.0	210	5.5	0	0.0	0	0.0
Feedstock Recovery38...	1.0	26	0.7	45	1.2	13	0.3	18	0.5
Feedstock Transmission	...52...	1.4	37	1.0	57	1.5	0	0.0	13	0.3
Fuel Production90...	2.4	380	10.0	560	14.7	6	0.2	16	0.4
Sequestration0...	0.0	0	0.0	0	0.0	0	0.0	0	0.0
Fuel Distribution22...	0.6	130	3.4	70	1.8	54	1.4	23	0.6
Compression or Liquefaction	.0...	0.0	0	0.0	0	0.0	45	1.2	0	0.0
Subtotal 202 ...	5.4	573	15.1	1,418	37.2	118	3.1	70	1.8
Vehicle ^{b,c,d}800...	21.1	800	21.1	800	21.1	800	21.1	800	21.1
Total 1,002 ...	26.5	1,373	36.2	2,218	58.3	918	24.2	870	22.9

^a Assumes that flared gas is burned completely to CO₂ and H₂O with no methane, nonmethane organic compounds, carbon monoxide, NO_x, or N₂O.

^b Decision Analysis Corporation, "Measurement of Emissions: Greenhouse Gas Estimates for Alternative Transportation Fuels," unpublished final report prepared for the Energy Information Administration (Vienna, VA, December 1995).

^c Greenhouse gas (GHG) emission values from vehicle end-use are revised.

^d The total GHG emission values are revised because vehicle end-use values are revised.

CO₂ = Carbon dioxide.

LPG = Liquefied petroleum gases.

mg = Milligrams.

mmol = Millimoles.

N₂O = Nitrous oxide.

NO_x = Nitrogen oxides.

VMT = Vehicle mile traveled.

Notes: Gasoline refers to unleaded gasoline in this report. • Table was derived using a vehicle with gasoline efficiency of 30 miles per gallon. • Emissions from manufacturing the vehicles are not included. • Nitrogen oxides include primarily nitric oxide and nitrogen dioxide. One mole of a gas is equal to the amount of substance that contains as many elementary units (6.023 x 10²³ molecules or atoms) as there are atoms in 12 grams of carbon-12. Normally, emissions are reported in grams per VMT. However, reporting in moles is preferable because GHG heat absorption is directly related to the number of molecules of a gas.

Sources: Derived from GHG emissions spreadsheet provided to the Energy Information Administration, July 1994. Spreadsheet is an unpublished revision of Argonne National Laboratory, Center for Transportation Research, *Emissions of Greenhouse Gases From the Use of Transportation Fuels and Electricity*, ANL/ESD/TM-22, prepared by Dr. Mark Delucchi, Vol. 1 (Argonne, IL, November 1991) and Vol. 2 (Argonne, IL, November 1993). Also see Energy Information Administration, *Alternatives to Traditional Transportation Fuels 1993*, EIA/DOE-0585(93) (Washington, DC, January 1995).

Appendix A

The Chemistry and Physics of Global Warming: An Overview

The regulating factor for global climate change depends on a fundamental principle, the First Law of Thermodynamics, also known as the Law of Conservation of Energy. Mathematically this can be represented as follows:

$$dQ = dU - dW \quad ,$$

where dQ = heat added to the system, dU = change in the internal energy of the system, and dW = work extracted. Heat can be transported to and from a system in three ways.⁴⁶ This law states that the total amount of energy added should be equal to the amount of energy removed from a stable system to keep the system stable. Energy cannot be gained or lost in a stable system; it can only change forms. Such a system is said to follow an "Energy Balance Model." To maintain stability, the Earth-ocean-atmosphere system absorbs energy from the Sun, radiates it in the form of infrared (heat) energy, and transports it in the form of both latent and sensible heat flux. Several natural events (volcanic eruptions, forest fires, fluctuating intensity of solar radiation, varying cloud cover, and others) and human activities (fuel combustion, aerosol production, industrial and land use practices that release or remove heat-trapping greenhouse gases, and others) can affect the balance between the absorption and emission of radiation.

The absorption of light by fluids (here, greenhouse gases [GHGs]) can be measured by the following simple relation:

$$A = \log_{10} (1/T) = \epsilon cd \quad ,$$

where A is the *absorbance* or optical density of the solute (here, a GHG), ϵ (liters per mole per centimeter)

is the *molar extinction coefficient* of the GHG at the wavelength of measurement, c (moles per liters) is the concentration of the GHG, d is the optical pathlength in centimeters, and T is the *transmittance*.⁴⁷ When a molecule absorbs light, it normally goes from the ground state to an excited or "hot" state. The hot molecule can release its excess energy primarily in three ways: chemical reaction, quenching, and emission. Because greenhouse gases are fairly stable, chemical reaction is not a common pathway for releasing the excess energy. Excited or hot greenhouse molecules release excess energy mostly through emission and quenching. Quenching is the process of transferring excess energy to other molecules in a ground state, thereby increasing the temperature of the other molecules. The other hot molecules can also emit excess energy in the form of radiation.

At the top of the atmosphere, the shortwave energy flux received from the Sun is about 1,368 watts per square meter (W/m^2).⁴⁸ Because of its spherical shape, at any instant the Earth receives on average half the incident solar flux, that is, $684 W/m^2$. Due to the Earth's rotation, the average radiative flux received over a day-night cycle is half of this value, that is, $342 W/m^2$, approximately $105 W/m^2$ of which is reflected by the Earth's surface and the atmosphere. According to measurements made from satellites, the outgoing longwave, or infrared, radiation is $237 W/m^2$. Approximately $169 W/m^2$ of solar radiation is absorbed by the Earth's oceanic and land surfaces and $68 W/m^2$ by the atmosphere. About $90 W/m^2$ of latent heat flux and $16 W/m^2$ of turbulent heat flux are estimated to leave the surface and enter the atmosphere. These latent and turbulent heat fluxes do not necessarily become part of the infrared radiation emitted by the surface and the atmosphere. This relatively shortwave radiation either

⁴⁶In *radiation* no mass is exchanged, and no medium is required. Pure radiant energy moves at the speed of light. In *conduction* no mass is exchanged, but a medium is required to transfer heat by diffusion. In *convection* mass is exchanged. Energy may be exchanged without a net movement of mass.

⁴⁷For a rigorous approach, use "The Lambert-Bouguet-Beer Law Approach" found in D.L. Hartmann, *Global Physical Climatology* (New York: Academic Press, 1994).

⁴⁸National Aeronautics and Space Administration, *The Detection of Climate Change Due to the Enhanced Greenhouse Effect* (Columbia, MD, July 1991).

can be absorbed by water (including clouds), ozone, and/or oxygen, or it can be simply added to the outgoing reflected solar radiation in the global energy balance model.^{49,50}

Radiation from the Sun varies greatly in energy, from high-energy gamma rays to low-energy microwaves (Table A1). Shortwave ultraviolet (UV) radiation includes wavelengths from 160 billionths of a meter (nanometers or nm) to the threshold of visible light at 400 nm. In wavelengths longer than one millionth of a meter (micrometer or μm), energy takes the form of heat. These wavelengths are grouped into the infrared and microwave bands. The spectrum of sunlight from the zenith at the surface of the Earth (Figure A1) reflects dips in the ultraviolet (290–365 nm)⁵¹ and red to infrared (650–1100 nm)⁵² regions, which are due to absorption by water vapor.

Most of the high-energy radiation from the Sun—for example, gamma rays—does not pass through the mesosphere.⁵³ In the stratosphere,⁵⁴ ozone and oxygen absorb virtually all ultraviolet (UV) light in band C (wavelengths of from 100 to 280 nanometers [nm]), the UV light with the shortest wavelengths and highest energy (see Figure 2 on page 7). All cellular constituents, including all the proteins (such as deoxyribonucleic acid [DNA] and ribonucleic acid [RNA]), absorb UV-C. Without the stratospheric ozone layer, all living things in the biosphere would suffer enormously from UV-induced diseases, including radiation-induced alterations/mutations of genetic fingerprints (DNA and RNA) and ocular diseases. In the stratosphere, oxygen uses this energy to produce ozone, and ozone absorbs most of the UV light in band B (280 to 320 nm), preventing it from reaching the surface of the Earth. Still further down, in the troposphere,⁵⁵ water vapor and clouds absorb on average more than 60 percent of the

Table A1. Electromagnetic Spectrum

Spectral Band	Wavelength Range	Photon Energy (electronvolts)
Microwave	0.1 – 100 cm	0.000001 – 0.001
Infrared - C	3.0 – 1,000 μm	0.001 – 0.4
Infrared - B	1.4 – 3.0 μm	0.4 – 0.9
Infrared - A	0.76 – 1.4 μm	0.9 – 1.6
Visible	400 – 760 nm	1.6 – 3.1
Ultraviolet - A	320 – 400 nm	3.1 – 3.9
Ultraviolet - B	280 – 320 nm	3.9 – 4.4
Ultraviolet - C	100 – 280 nm	4.4 – 12.4
Vacuum Ultraviolet	10 – 100 nm	12.4 – 124
X-rays	0.1 – 10 nm	100 – 100,000
Gamma (γ)-rays	0.0001 – 0.1 nm	10,000 – 10,000,000

cm = Centimeter.

μm = Micrometer.

nm = Nanometer.

Notes: 100 cm = 1 meter; 1 million μm = 1 meter; 1 thousand nm = 1 μm ; 1 billion nm = 1 meter.

Source: L.I. Grossweiner, *The Science of Photobiology*, ed. K.C. Smith (New York: Plenum Press, 1989), pp. 1-77.

⁴⁹V. Ramanathan and others, "Climate and the Earth's Radiation Budget," *Physics Today* 42 (1989):22-33.

⁵⁰V. Ramanathan and others, "Cloud Radiative Forcing and Climate: Results from the Earth Radiation Budget Experiment," *Science* 243 (1989):57-63.

⁵¹L.I. Grossweiner, *The Science of Photobiology*, ed. K.C. Smith (New York: Plenum Press, 1989), pp. 1-77.

⁵²R.B. Withrow and A.P. Withrow, *Radiation Biology, Volume 3*, Chapter 3, ed. A. Hollander (New York: McGraw-Hill, 1956).

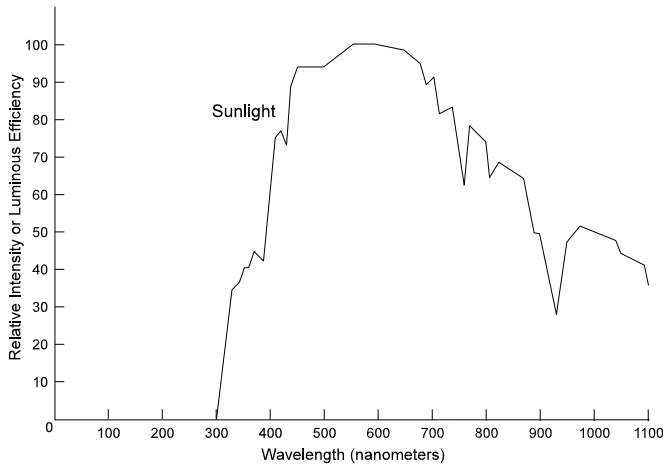
⁵³The mesosphere is the coldest region of the atmosphere extending from the stratopause (50 kilometers) to about 90 kilometers from the Earth's surface.

⁵⁴The stratosphere is the region of the upper atmosphere extending from the tropopause (8 to 15 kilometers altitude) to about 50 kilometers. The thermal structure is determined by its radiation balance and is generally very stable with low humidity.

⁵⁵The troposphere is the inner layer of the atmosphere below about 15 kilometers within which there is normally a steady decrease of temperature with increasing altitude. Its thermal structure is caused primarily by the heating of the Earth's surface by solar radiation, followed by heat transfer by turbulent mixing and convection. Nearly all clouds are formed and weather conditions manifest within this region.

remaining incoming radiation with wavelengths between 290 and 365 nm. Because the water vapor content varies from 0 to 4 percent, the amount of radiation with wavelengths between 290 and 365 nm and between 650 and 1100 nm reaching the Earth's surface also varies (Figure A1).

Figure A1. The Spectrum of Sunlight From the Zenith at the Surface of Earth



Source: R.B. Withrow and A.P. Withrow, *Radiation Biology, Volume 3* (New York: McGraw-Hill, 1965), Chapter 3, and *The Science of Photobiology*, 2nd ed., L.I. Grossweiner, "Photo-physics," ed. K.C. Smith (New York: Plenum Press, 1989).

What happens after the GHG molecules absorb infrared radiation? The hot molecules release their energy, usually at lower energy (longer wavelength) radiation than the energy previously absorbed. The molecules cannot absorb energy emitted by other molecules of their own kind. Methane molecules, for example, cannot absorb radiation emitted by other methane molecules. This constraint limits how often GHG molecules can absorb emitted infrared radiation. Frequency of absorption also depends on how long the hot GHG molecules take to emit or otherwise release the excess energy.

Emission of radiative heat from excited greenhouse molecules to some extent is independent of surroundings. Transport of the heat emitted, however, can be facilitated by wind patterns and sensible heat flux. The absorption coefficients of some of the greenhouse gases are temperature dependent.⁵⁶

Albedo is defined as the ratio of energy incident to energy reflected. It exercises a tremendous influence on absorption, reflection, and emission of radiation in the Earth-ocean-atmosphere system. Snow or white clouds have relatively high albedo values due to their reflective surfaces, whereas water has a low albedo value.

Vertical mixing of atmospheric constituents occurs in the troposphere because of the turbulence that characterizes the region. Temperature inversions and mountains surrounding cities inhibit this mixing. However, in the upper atmosphere, this process is mostly controlled by *molecular diffusion* (that is, conduction of heat by collisions of atoms and molecules), which depends solely on molecular size, and by *thermal diffusion*, which depends on the temperature gradient between hot molecules and their surroundings.

Assuming steady incident radiation, the radiating power of a GHG molecule depends largely on the absorption coefficients for that GHG, which determine how much of the available radiation it absorbs in each of the wavelength ranges where it absorbs radiation. Other important factors are the concentration of the gas and its residence time, or decay time, in the atmosphere. The residence time of GHGs depends mostly on two factors, namely reactivity of GHGs and the GHG sinks in the biosphere. Plants and trees, for example, store carbon and thus serve as sinks for carbon dioxide.

The radiating power of a GHG is usually expressed as its global warming potential (GWP). The decay time or residence time for carbon dioxide ranges from around 150 to about 500 years.^{57,58} Without carbon dioxide absorbers (sinks), the carbon dioxide residence time would be only 3.9 years, which is precisely its exchange rate. The lifetime of the hydrological cycle is estimated to be approximately 2 to 4 weeks. The replacement time for deep ocean water is believed to be on the order of a thousand years,⁵⁹ and the replacement time for deep ice in the Arctic may be on the order of tens of thousands of years. Most of the GWPs found in scientific literature are expressed in relation to the carbon dioxide GWP. The GWP of a GHG is expressed in the following relationship:⁶⁰

$$) = \frac{a_i}{a_j} \cdot \frac{\tau_i}{\tau_j} \cdot \frac{(1 - \exp(-t/\tau_i))}{(1 - \exp(-t/\tau_j))} \cdot GWP$$

⁵⁶A. Nolle and others, "Temperature Dependent UV Absorption Spectra of Carbonyl Chloro-fluoride," *Geophysical Research Letter* 20 (1993):707-710.

⁵⁷H. Rhode, "A Comparison of the Contribution of Various Gases to the Greenhouse Effect," *Science* 248 (1990):1217-1219.

⁵⁸U.S. Department of Energy, *A Primer on Greenhouse Gases*, DOE/NBB-0083 (Washington, DC, March 1988).

⁵⁹Intergovernmental Panel on Climate Change, *The IPCC Scientific Assessment* (Cambridge, United Kingdom: Cambridge University Press, 1990), pp. 179-180.

⁶⁰A.S. Grossman and D.J. Wuebbles, "Global Warming Potential for SF₆," *UCRL Report*, ID# 112944 (1992), pp. 1-3.

where τ_i and τ_j are the residence times of the GHG of interest, i , and the reference GHG, j (usually carbon dioxide), respectively, in years; a_i and a_j are the instantaneous radiative forcings of GHGs per unit mass due to a unit increase in the concentration of GHG of interest i and the reference GHG j , respectively;⁶¹ t is the integration time in years; and $GWP(C_i)$ and $GWP(C_j)$ are the GWPs of the GHG of interest i and the reference GHG j , respectively, at a given concentration C remaining at time t after their release.

This relation can be further simplified by defining the GWP for carbon dioxide as a reference GHG with a value of 1 (see Table 5 on page 12). This equation was derived by assuming that the concentration of a greenhouse gas is independent of altitude, and other factors. GWP calculations assume homogeneous mixing of GHGs in the troposphere. Homogeneity must be defined in terms of an appropriate scale, because given a sufficiently fine scale, all matter is heterogeneous in view of its atomic and molecular constitution.⁶² Moreover, according to the United Nations' Intergovernmental Panel on Climate Change (IPCC), carbon dioxide equivalency (GWP) values are generally within the range of plus or minus 35 percent. GWPs obtained for GHGs, therefore, are very rough approximations and their reliability varies greatly.

Radiative forcing is defined as a **change** in average net radiation at the boundary between troposphere and stratosphere (known as the tropopause). A positive radiative forcing tends on average to warm the surface;

there is a net heat flow from troposphere to stratosphere. A negative forcing on average tends to cool the surface; there is a net heat flow from stratosphere to troposphere. The global average radiative forcing is based on the assumption that the vertical irradiance gradient is significant at the tropopause and that the horizontal irradiance gradient along the tropopause and both the regional horizontal irradiance gradient and vertical irradiance gradient in the troposphere and stratosphere are not significant. Radiative forcing (also known as climate forcing), therefore, is an empirical tool designed for policy makers. Possibly policy makers would find the carbon dioxide equivalency or GWP values more useful when coupled with cost and other economic variables. Table A2 provides an explanation for some units for commonly used measures to describe energy.

Another important piece in the global warming maze is the tropospheric **lapse rate**. The lapse rate is mathematically defined by

$$\Gamma \equiv - \frac{\partial T}{\partial z} ,$$

where Γ = tropospheric lapse rate, ∂T = change in temperature (T), and ∂z = change in altitude (z). This indicates the rate of cooling with height, and the decrease in temperature with increase in altitude in the troposphere. The global average tropospheric lapse rate is 6.5°C per kilometer. The lapse rate varies with altitude, season, and latitude.

Table A2. Radiometric Units

Radiometric Quantity	Concept	SI Unit
Radiant energy (Q)	Quantity of light	Joule (J)
Radiant flux (F)	Power	Watt (W)
Radiant energy density (W) . .	Energy content per unit volume	Joule per cubic meter
Radiant irradiance (E)	Flux per unit area incident on a small plane surface	Watt per square meter
Radiant intensity (I)	Flux emitted into a unit solid angle	Watt per steradian ^a
Radiant radiance (L)	Flux in a given direction per unit solid angle per unit area normal to the direction of propagation	Watt per square meter-steradian
Radiant exposure (Q)	Energy per unit area incident on one side of a small-plane area	Joule per square meter

^aA steradian is a unit of measure equal to the solid angle subtended at the center of a sphere by an area equal to the radius squared on the surface of the sphere.

Source: L.I. Grossweiner, *Photophysics—The Science of Photobiology*, 2nd ed., ed. K.C. Smith (New York: Plenum Press, 1989), pp. 1–77.

⁶¹The radiative forcing is expressed as a change in the flux of energy in watts per square meter.

⁶²K.C. Cho and R.A. Greenkorn, *Thermodynamics of Fluids* (New York: Marcel Dekker, 1975), p. 2.

At present, the most accurate models for projecting the impact of the greenhouse effect are General Circulation Models (GCMs). GCMs attempt to take into account the entire climate system over an extended period of time, including the roles of the oceans, the atmosphere, the biosphere, the polar regions, and other important features. GCMs usually treat the atmosphere and the ocean as fluids, calculating how various factors such as the concentration of carbon dioxide interact with atmosphere and oceans to generate the entire climate system.⁶³ Both proponents and critics of global warming models agree that GCMs have well-documented inadequacies that significantly impair their capacity to project global warming. Most GCMs, for example, cannot predict cloud formation well.

Based on preliminary data from satellite measurements, Ramanathan and his colleagues concluded that clouds appear to cool Earth's climate, possibly offsetting the atmospheric greenhouse effect.^{64,65} This observation supports the theory that sulfur dioxide creates "cool clouds." That is, sulfur dioxide emissions not only acidify rain, but also combine with water to form "aerosols" that brighten the clouds, increase their albedo, and thus enhance the reflection of radiation away from Earth. Some scientists advocate considering sulfur dioxide effects together with carbon dioxide effects on evaporation and hence on cloud cover and convection. As carbon dioxide speeds up the hydro-

logical cycle, increased convection in turn increases clouds and cooling.

Recently, some models like the Community Climate Model (CCM) have incorporated clouds into climate calculations, including clouds' radiative properties and their effects on the global energy balance. Recent satellite observations indicate that clouds absorb four times more shortwave radiation (from 25 W/m² to 30 W/m²) than indicated by previous model simulations. This absorption of shortwave radiation occurs in addition to reflection of solar radiation and absorption of infrared radiation emitted by the Earth's surface and the atmosphere. The enhanced cloud absorption observed may lead to an important reinterpretation of the energetics of the models. Increased water vapor in the atmosphere increases the number of cirrus-anvil clouds, which effectively absorb shortwave radiation, thus reducing the emission of infrared radiation.^{66,67,68} The observations may be due to aggregation phenomena of water molecules in the crystalline phase. As is very common for a large number of compounds, the spectra either broaden or shift to shorter wavelengths as aggregation increases. Most current infrared spectra of water available in the literature are for water in the vapor phase. Infrared spectral characteristics of ice crystals and liquid mist should be explored to understand the behavior of cirrus-anvil clouds fully.

⁶³The interaction is radiative for the atmosphere and chemical for the oceans.

⁶⁴V. Ramanathan and A. Raval, "Observational Determination of the Greenhouse Effect," *Nature* 342 (1989):758-761.

⁶⁵V. Ramanathan and W. Collins, "Thermodynamic Regulation of Ocean Warming by Cirrus Clouds Deduced from Observations of 1987 El Nino," *Nature* 351 (1991):27-32.

⁶⁶V. Ramanathan and others, "Warm Pool Heat Budget and Shortwave Cloud Forcing: A Missing Physics," *Science* 267 (1995):499-503.

⁶⁷R.D. Cess and others, "Absorption of Solar Radiation by Clouds: Observations Versus Models," *Science* 267 (1995): 496-499 and Y Baskin, "Under the Clouds," *Discover* (September 1995), pp. 62-69.

⁶⁸D. Lubin, "The Role of Tropical Super Greenhouse Effect in Healing the Ocean Surface," *Science* 265 (1994):224-227.

Appendix B

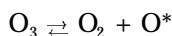
Stability of Ozone

Biological processes influence both the generation and the destruction of ozone. Ozone formation is an endothermic process, one that requires energy to initiate the reaction:



where ΔH = the heat of reaction.

In other words, reactions involving ozone decomposition are thermodynamically favorable:



where O^* is a reactive oxygen atom that reacts readily with water, methane, and nitrous oxide as follows:



where OH^* , CH_3^* , and NO^* are hydroxyl, methyl, and nitric oxide radicals,^{69,70} respectively. The enthalpy, that is, ΔH , or the value of the heat of the reaction, demonstrates why nitrous oxide is a far better ozone scavenger than methane and water vapor. The rate of forward reaction, or ozone decomposition to a molecular oxygen and reactive oxygen atom, is several orders greater than the backward reaction, or ozone formation from molecular oxygen and reactive oxygen atoms.⁷¹

Hydrocarbons and/or oxygenated hydrocarbons readily react with ozone in the troposphere, producing alkyl and hydroxyl radicals. It has recently been reported that airborne measurements showed very high concentrations of oxygenated hydrocarbons in the global troposphere. This surprisingly abundant presence of such oxygenated hydrocarbons (acetone, ethanol, methanol, and acetaldehyde), which may affect the "ozone cycle" may be due to land-use change, biomass burning, and alcohol-based biofuel use.⁷²

Halogenated hydrocarbons such as chlorofluorocarbons (CFCs) produce very reactive halogen atoms during photolysis. These halogen atoms are excellent ozone scavengers. Each CFC molecule can destroy 10 thousand molecules of ozone or more by chain reaction during its lifetime. Hydrochlorofluorocarbons (HCFCs) and perfluorocarbons (PFCs) are preferred alternatives to CFCs because they are roughly 10 times less destructive to ozone. According to a new study, CFC alternatives pose a potential risk of accumulating trifluoroacetic acid (CF_3COOH), a breakdown product, in certain wetlands.⁷³

Unlike CFCs, atmospheric methyl bromide (CH_3Br), another halogenated hydrocarbon, is not entirely anthropogenic in origin. About one-third comes from automobile emissions from leaded gasoline and fumigation. Atmospheric methyl bromide is the chief source of stratospheric bromine. Each bromine atom is roughly 50 times more destructive than a chlorine atom, which is responsible for 20 to 25 percent of the "Antarctic Ozone Hole."⁷⁴

⁶⁹D.D. Davis and others, "A Photostationary State Analysis of the NO_2 -NO System Based on Airborne Observations from the Subtropical/Tropical North and South Atlantic," *Journal of Geophysical Research* 98 (1993):23,501-23,523.

⁷⁰C.A. Cantrell and others, "Branching Ratios for the Singlet Oxygen and Nitrous Oxide Reaction," *Journal of Geophysical Research* 99 (1994):3739-3743.

⁷¹Lefevre and others, "Chemistry of the 1991-1992 Stratospheric Winter: Three Dimensional Model Simulations," *Journal of Geophysical Research* 99 (1994):8183-8195.

⁷²H.B. Singh, M. Kanakidou, P.J. Crutzen, and D.J. Jacob, "High Concentrations and Photochemical Fate of Oxygenated Hydrocarbons in the Global Troposphere," *Nature* 378 (1995):50-53.

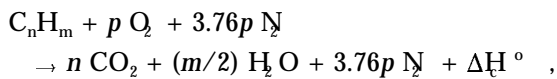
⁷³S.E. Schwarzbach, "CFC Alternatives Under a Cloud," *Nature* 376 (1995):297-298.

⁷⁴J.H. Butler, "Methyl Bromide Under Scrutiny," *Nature* 376 (1995):469-470.

Appendix C

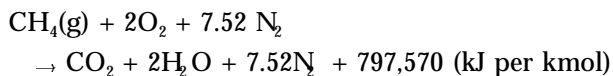
Combustion Chemistry of Alternative and Traditional Transportation Fuels

Hydrocarbon fuel combustion under ideal conditions would produce carbon dioxide and water as the only products.

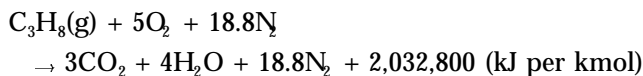


where n and m are positive integers, p is a positive number, and ΔH_c° is the heat of combustion, or "enthalpy," under ideal conditions. The specific reactions for four alternative fuels under ideal conditions are given below:⁷⁵

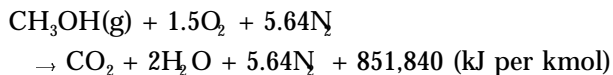
Compressed Natural Gas:



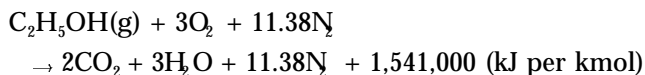
Liquefied Petroleum Gas:



Methanol:

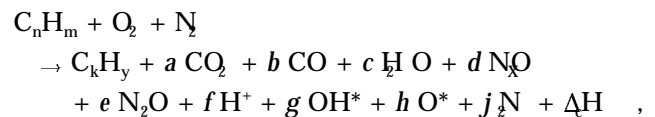


Ethanol:



However, hydrocarbon fuels combustion under actual (non-ideal) combustion conditions produces several

intermediate products in addition to carbon dioxide and water. This is the general combustion reaction for any hydrocarbon fuel under non-ideal conditions:



where C_kH_y = unburned or partially burned hydrocarbon fuel, CO_2 = carbon dioxide, H_2O = water, CO = carbon monoxide, NO_x = oxides of nitrogen ($x = 1-3$), N_2O = nitrous oxide, OH^\cdot = hydroxyl radical, O^\cdot = oxygen radical and/or singlet oxygen, H^\cdot = hydrogen ion, ΔH_c = heat of combustion⁷⁶ (or enthalpy) under actual (non-ideal) conditions, and the coefficients a , b , c , d , e , f , g , h , and j vary with fuels and operating conditions. The heat of combustion is also referred to either as the "lower heating value" (with "gaseous" water as one of the products) or as the "higher heating value" (with "liquid" water as one of the products).

Combustion in internal combustion engines is a very complex chain reaction system that leads to hundreds of intermediate products, byproducts, and end products.⁷⁷ In internal combustion engines, the products in the exhaust are determined by a large number of parameters, including fuel to air ratio, compression ratio, fuel composition, internal design, operating condition of the cylinder and combustion chamber, and exhaust inflation. For methane, propane, and methanol fuels, the number of identified reaction products in the exhaust are 25, 41, and 84, respectively.

⁷⁵A.S. Campbell, *Thermodynamic Analysis of Combustion Engines* (New York: John Wiley & Sons, 1992), Table E.4, p. 357.

⁷⁶The heat of combustion can be measured either at constant pressure using a constant flow calorimeter or at constant volume using a batch calorimeter.

⁷⁷Decision Analysis Corporation, *Measurement of Emissions: Greenhouse Gas Estimates for Alternative Transportation Fuels*, unpublished final report prepared for the Energy Information Administration (Vienna, VA, December 1995).

Appendix D

Greenhouse Gas Spectral Overlaps and Their Significance

One of the difficulties in measuring the GWP of GHGs is that GHGs absorb infrared radiation at a variety of wavelengths.^{78,79,80,81,82,83,84,85,86,87} Some GHGs have common absorption bands. Table D1 shows how the GHGs absorption bands overlap. Water is the sole absorber in the windows from 0.5 micrometers (μm) to 2.0 μm and from 5.0 μm to 7.0 μm , ozone in the 8.0- μm window, carbon dioxide in the 14.7- μm to 16.5- μm window, and nitrous oxide in the 16.5- μm to 46.0- μm window. However, in some regions absorption frequencies of various GHGs overlap; water, carbon dioxide, and carbon monoxide absorption bands overlap in the 2.0- μm to 3.0- μm region; water and methane absorption bands overlap in the 3.0- μm to 4.0- μm region; carbon dioxide and carbon monoxide absorption bands overlap in the 4.0- μm to 5.0- μm window; nitrous oxide and methane absorption bands overlap in the 7.0- μm to 8.0- μm region; and carbon dioxide, ozone, and methane absorption bands overlap in the 13.7- μm to 14.7- μm region. Methane does not have a separate and distinct absorption window for itself like other GHGs.

Current global warming calculations and some climate models include infrared absorption characteristics of GHGs to a moderate extent.^{88,89,90} The infrared absorption spectrum of atmospheric greenhouse gases is very complex. The monochromaticity (radiation of one wavelength) of most of its absorption bands of individual GHGs is lost due to pressure, temperature, aggregation, emission, and other factors. Mathematical and statistical models are used to deconvolute the polychromatic (radiation of more than one wavelength) infrared absorption spectrum of atmospheric GHGs, and this brings a certain amount of uncertainty into the data. In addition, uncertainty in the proper treatment of the water vapor continuum in the infrared spectrum of atmospheric GHGs still poses a challenge for line-by-line models to provide an absolute reference for evaluating less detailed model calculations.⁹¹ The infrared absorption spectrum of atmospheric GHGs may also depend on latitude/longitude and altitude locations since GHG distributions other than carbon dioxide are not uniform.

⁷⁸J. Schirmer and others, "K-shell Excitation of the Water, Ammonia, and Methane Molecules Using High-resolution Photoabsorption Spectroscopy," *Physical Review A* 47 (1993):1136-1147.

⁷⁹B.E. Priloglou and others, "On the Atmospheric Water Vapor Transmission Function for Solar Radiation Models," *Solar Energy* 53 (1994):445-453.

⁸⁰S. Elliott and others, *Kinetics Programs for Simulations of Tropospheric Photochemistry on the Global Scale*, Report No. LA-12539-MS, (Los Alamos, NM: Los Alamos National Laboratory, August 1993).

⁸¹D.P. Kratz and others, "Infrared Radiation Parameterizations for the Minor CO₂ Bands for Several CFC Bands in the Window Region," *Journal of Climate*, 6 (1993):1269-1281.

⁸²M.D. Di Rosa and R.K. Hanson, "Collision-broadening and -shift of NO Absorption Lines by H₂O, O₂, and NO at 295 K," *Journal of Molecular Spectroscopy* 164 (1994):97-117.

⁸³J. Heidberg and others, "Polarized FTIR—Spectra of C₆₀ Layers and the Adsorbates of CO and CQ on C₆₀," *Journal of Electron Spectroscopy and Related Phenomena* 64/65 (1993):883-892.

⁸⁴P.J. Medvez and K.M. Nichols, "Experimental Determination of Line Strengths for Selected Carbon Monoxide and Carbon Dioxide Absorption Lines at Temperatures Between 295 and 1250°K," *Applied Spectroscopy* 48 (1994):1442-1450.

⁸⁵Sadtler Research Laboratories, *Infrared Spectra of Organic Compounds* (1979), pp. 51, 585.

⁸⁶Snell-Ettré, *Encyclopedia of Industrial Chemical Analysis*, Vol. 8 (1966), p. 252.

⁸⁷N.V. Sidgwick, *The Chemical Elements and their Compounds*, Vol. 11 (Oxford, UK: Clarendon Press, 1950), pp. 859-863.

⁸⁸D.P. Kratz and others, "Infrared Parameterizations for the Minor CO₂ Bands and for Several CFC Bands in the Window Region," *Journal of Climate* 6 (1993):1269-1281.

⁸⁹R.G. Ellingson and others, "The Intercomparison of Radiation Codes in Climate Models (ICRCCM): Long Wave Results," *Journal of Geophysical Research* 96 (1991):8929-8953.

⁹⁰M.D. Chou and others, "Infrared Radiation Parameterizations in Numerical Climate Models," *Journal of Climate* 4 (1991):424-437.

⁹¹R.G. Ellingson and others, "The Intercomparison of Radiation Codes in Climate Models (ICRCCM): Long Wave Results," *Journal of Geophysical Research* 96 (1991):8929-8953.

Partly because the infrared absorption bands of the various components of the atmosphere overlap, the contributions from individual absorbers do not add linearly. Clouds trap only 14 percent of the radiation with all other major species present, but would trap 50 percent if all other absorbers were removed⁹² (Table D2 and Figure D1). Carbon dioxide adds 12 percent to radiation trapping, which is less than the contribution from either water vapor or clouds. By itself, however, carbon dioxide is capable of trapping three times as much radiation as it actually does in the Earth's atmosphere. Freidenreich and colleagues⁹³ have reported the overlap of carbon dioxide and water absorption bands in the infrared region. Given the present composition of the atmosphere, the contribution to the total heating rate in the troposphere is around 5 percent from carbon dioxide and around 95 percent from water vapor. In the stratosphere, the contribution is about 80 percent from carbon dioxide and about 20 percent from water vapor. It is important to remember, however, that it is currently believed that the impact of water vapor produced

from surface sources such as fuel combustion on the atmospheric water vapor concentrations is minimal.

Table D2. Efficiency of Heat Trapping by Greenhouse Gases and Clouds

Species Removed	Percentage Heat Trapped	Percentage Heat Not Trapped
All ^a	0	100
H ₂ O, CO ₂ , O ₃	50	50
H ₂ O	64	36
Clouds	86	14
CO ₂	88	12
O ₃	97	3
None	100	0

CO₂ = Carbon dioxide. H₂O = Water vapor. O₃ = Ozone.
^aIncludes clouds.

Source: V. Ramanathan and J.A. Coakley, Jr., "Climate Modeling Through Radiative-Convective Models," *Review of Geophysics & Space Physics* 16 (1978):465.

Table D1. Overlap of Absorption Bands of Greenhouse Gases (Micrometers)

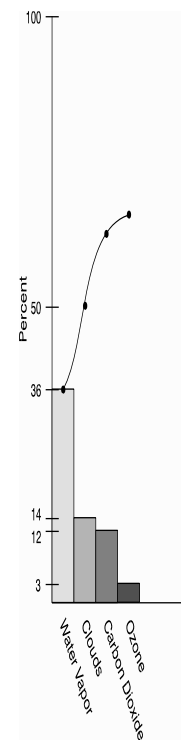
Greenhouse Gases	Greenhouse Gases' Absorption Bands
H ₂ O	0.5 – 2.0
H ₂ O, CO, and CO ₂	2.0 – 3.0
H ₂ O and CH ₄	3.0 – 4.0
CO and CO ₂	4.0 – 5.0
H ₂ O	5.0 – 7.0
N ₂ O and CH ₄	7.0 – 8.0
O ₃	8.0 – 10.0
CO ₂ , CH ₄ , and O ₃	13.7 – 14.7
CO ₂	14.7 – 16.5
N ₂ O	16.5 – 46.0

CH₄ = Methane. CO = Carbon monoxide. CO₂ = Carbon dioxide. H₂O = Water vapor. N₂O = Nitrous oxide. O₃ = Ozone.

Notes: Carbon dioxide absorbs infrared radiation at wavelengths of 2.69 micrometers (μm), 2.76 μm, 4.25 μm, 14 μm, and 15 μm. Carbon monoxide absorbs at 2.3 μm, and 4.7 μm. Water vapor absorbs at 0.6 μm, 0.72 μm, 0.82 μm, 0.94 μm, 1.10 μm, 1.38 μm, 1.87 μm, 2.70 μm, 3.20 μm, and 6.30 μm. Methane absorbs at 3.4 μm, 7.4 μm, 7.58 μm, and 7.87 μm. Nitrous oxide absorbs at 7.83 μm, 16.98 μm, and 44.9 μm. Ozone absorbs at 9.0 μm, 9.6 μm, and 14.2 μm.

Sources: Snell-Ettre, *Encyclopedia of Industrial Chemical Analysis*, Vol. 8, p. 252; and N.V. Sidgewick, *The Chemical Elements and Their Compounds*, Vol. 11 (Oxford, United Kingdom: Clarendon Press, 1950), pp. 859–863.

Figure D1. Pareto Diagram of the Heat Trapping Efficiency of Greenhouse Gases and Clouds in the Atmosphere



Note: The curve was obtained by adding the values for water vapor, clouds, carbon dioxide, and ozone.

Source: Table D2.

⁹²V. Ramanathan and J.A. Coakley, Jr., "Climate Modeling Through Radiative-Convective Models," *Review of Geophysics and Space Physics* 16 (1978):465.
⁹³S.M. Freidenreich and V. Ramaswamy, "Solar Radiation Absorption by Carbon Dioxide, Overlap with Water, and a Parameterization for General Circulation Models," *Journal of Geophysical Research* 98 (1993):7255-7264.