APPENDIX F: EMISSIONS OF NITROUS OXIDE AND METHANE FROM ALTERNATIVE FUELS FOR MOTOR VEHICLES AND ELECTRICITY-GENERATING PLANTS IN THE U.S.

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An Appendix to the Report "A Lifecycle Emissions Model (LEM): Lifecycle Emissions from Transportation Fuels, Motor Vehicles, Transportation Modes, Electricity Use, Heating and Cooking Fuels, and Materials"

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ABSTRACT

This appendix provides a database of estimates of emissions of two important but often not well-characterized GHG emissions related to energy use: CH_4 and N_2O. The appendix focuses on emissions of CH_4 and N_2O from motor vehicles and power plants because unlike emissions of CO_2 from combustion processes, which are relatively easy to estimate, emissions of CH_4 and N_2O are a function of many complex aspects of combustion dynamics and of the type of emission control systems used. They therefore cannot be derived easily and instead must be determined through the use of published emission factors for each combination of fuel, end-use technology, combustion conditions, and emission control system. Furthermore, emissions of CH_4 and N_2O may be particularly important with regard to the relative CO_2-equivalent GHG emissions from the use of alternative transportation fuels, in comparison with the use of conventional fuels. In addition to providing a database of emission estimates, we develop emission factors for N_2O and CH_4 emissions from conventional vehicles, in order to supplement recent EPA and IPCC estimates, and we estimate the relative emissions of N_2O and CH_4 from different alternative fuel passenger cars, light-duty trucks, and heavy-duty vehicles.

1 INTRODUCTION

The use of energy accounts for a major fraction of all anthropogenic emissions of greenhouse gases (GHGs) (IPCC, 1996a) . In most industrialized countries, transportation fuel and electricity use produces a major fraction of all energy-related emissions. In the U.S., for example, emissions of carbon dioxide (CO_2) from the production and use of motor-vehicle fuels account for as much as 30% of CO_2 emissions from the use of all fossil fuels (DeLuchi, 1991) . The production and use of fuels for transportation and electricity also results in emissions of other greenhouse gases, including methane (CH_4) and nitrous oxide (N_2O). In light of this, and in the face of growing concern about global climate change, analysts have been evaluating long-term energy policies for their potential impact on global climate (OTA, 1990; EIA, 1991a; Victor, 1992; IEA, 1997; EIA, 1998b; EIA, 1999) . The “Climate Change Action Plan” proposed by President Clinton and Vice President Gore in 1993 calls on the “National Economic Council, the Office on Environmental Policy, and the Office of Science and Technology Policy to co-chair a process...”to develop measures to significantly reduce greenhouse gas emissions from personal motor vehicles, including cars and light trucks” (Clinton and Gore, 1993, p. 30) . More recently, specific GHG emission reduction goals, known as the Kyoto Protocol, were established during a meeting in Kyoto, Japan, in December, 1997. The international agreement reached at this summit meeting calls for the U.S. to reduce GHG emissions by 7%, relative to 1990 levels, between 2008 and 2012 (Douville, et al., 1998) .

Emission reduction strategies based on alternative fuels, for motor vehicles and for power plants, may play an important role in efforts to meet the Kyoto Summit emission-reduction targets. For example, promising strategies for powering motor vehicles with reduced GHG emissions include expanded use of natural gas as a fuel and as a feedstock for methanol and hydrogen fuel production, biomass as a feedstock for methanol and ethanol fuel production, and solar, wind, and natural gas-produced electricity for battery EVs (Ogden, et al., 1994; Delucchi, 1997) . Already, vehicles powered by compressed natural gas, propane, methanol-based fuel blends, and electricity are beginning to be used in urban areas to improve air quality.[1] In the future, the combination of these low-carbon fuels with emerging internal-combustion engine / electric hybrid and fuel cell / electric hybrid drivetrain technologies offers the potential for significant reductions in per-mile GHG emissions from motor vehicles. Possible strategies for reducing GHG emissions from power plants include expanded use of natural gas combined-cycle power plants, methods of reducing N_2O emissions from coal-fired plants, and continued development of photovoltaic, solar thermal, and wind power systems (these latter options are not assessed in detail here, but they offer

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[1] As of mid-year 1998, 204,274 alternative fuel vehicles had been introduced into major urban areas in the U.S. (U.S. DOE, 1998).

the potential of electricity production with near zero GHG emissions). To evaluate such alternative-energy strategies for their potential impact on global climate, one needs to know the amount of each GHG emitted, and the effect of each GHG on global climate. The purpose of this appendix is to provide a partial database of estimates of motor-vehicle and electricity-plant emissions of the two most important GHGs after CO_2: CH_4 and N_2O.

We focus on CH_4 and N_2O because, for many energy-use technologies –(and particularly alternative-fuel vehicles), emissions of CH_4 and especially N_2O are not well characterized, whereas emissions of CO_2 from fuel combustion are relatively easy to estimate. CO_2 emissions can be approximated as the carbon content of the fuel multiplied by 3.664 (the ratio of the molecular mass of CO_2 to the molecular mass of carbon), on the assumption that virtually all of the carbon in fuel oxidizes to CO_2 (for data and discussions pertaining to estimating CO_2 emissions from energy use see Grubb, 1989; Marland and Pippin, 1990; IEA, 1991; OECD, 1991; EIA, 1995b; IPCC, 1997; EIA, 1998a; U.S. EPA, 1999) . In contrast, combustion emissions of CH_4 and N_2O are a function of many complex aspects of combustion dynamics (such as temperature, pressure, and air-to-fuel ratio) and of the type of emission control systems used, and, hence, cannot be derived from one or two basic characteristics of a fuel. Instead, one must rely ultimately on measured emissions for each combination of fuel, end-use technology, combustion conditions, and emission control system. Likewise, non-combustion emissions of CH_4 and N_2O (for example, gas flared at oil fields), cannot be derived from basic fuel properties, and instead must be measured and estimated source-by-source. And as shown in Table F-1, emissions of CH_4 and especially N_2O can contribute significantly to total CO_2-equivalent emissions of GHGs over the lifecycle of alternative transportation fuels and technologies.

Although the U. S. Environmental Protection Agency (EPA) (1998; 1999) , the U. S. Energy Information Administration (EIA) (1998a) , and the IPCC (1997) provide CH_4 and N_2O emission factors for the purpose of estimating GHG emission inventories, in many instances the databases and documentation are sparse. More importantly for our purposes, none have GHG emission factors for motor vehicles using nonpetroleum fuels. The EIA acknowledges the shortcomings in the underlying emission factors:

> [A]ll emissions inventories have inherent limitations in their accuracy and comparability. The first problem is the absence of any directly measured or reported information on greenhouse gas emissions, and the consequent necessity to infer emissions from available information. In the case of carbon dioxide, emissions are calculated by multiplying reported energy consumption by the estimated carbon content of fossil fuels. This is a fairly reliable estimate; both energy statistics and estimates of carbon content are probably accurate within a few percent. For methane and nitrous oxide, however, emissions are generally inferred by extrapolating experiments conducted on a small number of samples across a large, national,

sometimes heterogeneous population. As a result, methane and nitrous oxide emissions estimates are much more uncertain than carbon dioxide emissions estimates, and they are more prone to large revisions as additional information becomes available (EIA, 1995b, p. 1-2) . Emissions estimates for nitrous oxide from motor vehicles, in particular, have been the subject of controversy. The U.S. EPA Office of Mobile Sources commented recently that the contribution of N_2O from mobile sources to the total estimate of nitrous oxide emissions in the U.S. jumped from 0.5% in the EPA GHG-emissions inventory published in 1997, to 3.0% percent in the draft *Inventory of U.S. Greenhouse Gas Emissions and Sinks 1990-1996* (U.S. EPA, 1998) . The Office of Mobile Sources notes that this increase was due to much higher N_2O emissions factors -- the ones, in fact, suggested by the latest IPCC (1997) *Guidelines* for U. S. emissions inventories -- rather than from a significant increase in VMT. They recommended the use of a revised, much lower set of N_2O emissions factors (Michaels, 1998), which the EPA (1999) and the EIA (1998a) adopted in their latest emission inventories.

Thus, GHG emissions factors are still somewhat controversial, even for conventional vehicles and fuels. As noted above, there are even fewer data available on emissions of GHGs from the use of alternative fuel, and no single source that reports what few data exist. For example, the revised IPCC (1997) *Guidelines* on emissions of GHGs reports that N_2O emission factors for alternative-fuel vehicles are “not available”. (We do present some limited data, below.) The IPCC (1997) does report CH_4 factors for alternative fuels, but does not discuss the source or quality of the factors.

We do not consider chlorofluorocarbons (CFCs), aerosols, or the so-called “indirect” GHGs (carbon monoxide [CO], nonmethane hydrocarbons [NMHCs], and nitrogen oxides [NO_x]), which do not cause direct radiative forcing themselves, but do affect the concentration of other direct-forcing gases such as ozone and methane. All of these gases except CO appear to have minor CO_2-equivalent effects in most fuelcycles (Table F-1), and all of them are adequately covered in national emission-factor guidelines and emission inventories, such as the U.S. EPA's "AP-42" database (U.S. EPA, 1998) and the U. S. National Emission Data System (NEDS) (U.S. EPA, 1997; U.S. EPA, 1998) , developed for the purpose of estimating urban air pollution. By now, there also is substantial information on emissions of these pollutants from alternative-fuel vehicles (AFVs) (e.g., OECD, 1993; NREL, 1996; Whalen, et al., 1996; Delucchi, 1999) . Although CFCs and their replacements tend to have high CO_2-equivalent effects, and thereby do contribute significantly to fuelcycle GHG emissions, they are being phased out, and there is already an extensive literature on their impacts and inventories. (Also, with regard to transportation fuel cycles, CFCs only appear in air-conditioning systems and thus are not a basis for differentiating the use of various types of AFVs.)

2 NITROUS OXIDE EMISSIONS

2.1 NITROUS OXIDE FROM MOTOR VEHICLES

N_2O is emitted directly from motor vehicles. N_2O emissions from catalyst-equipped gasoline light-duty vehicles (LDVs) depend significantly on the type and temperature of catalyst, rather than total NO_x levels or fuel nitrogen content, because gasoline contains relatively little nitrogen, and fuel NO_x and fuel N_2O emissions from autos are low. The high temperatures and pressures of the internal- combustion engine are sufficient to form NO_x thermally, but evidently are inefficient for production of N_2O (Hao, et al., 1987) . As a result, cars without catalytic converters produce essentially no net N_2O (Table F-2). On the other hand, Weiss and Craig (1976) predicted N_2O exhaust concentrations of up to 400 ppmv from autos with platinum reduction catalysts only, according to the reactions:

$6NO + 4NH_3 \rightarrow 5N_2O + 6H_2O$ and eq. F-1
$2NO + H_2 \rightarrow N_2O + H_2O$

Seinfeld (in Pierotti and Rasmussen, 1976) suggests that N_2O production in 3-way catalysts (those that oxidize HC and CO to H_2O and CO_2, and reduce NO to N) may occur by a different route:

$NH_3 + 2O_2 \rightarrow N_2O + 3H_2O$ eq. F-2

Alternatively, the NO can be reduced by CO, rather than H_2 (Prigent and Soete, 1989; Ryan and Srivastava, 1989; Dasch, 1992) :

$2NO + CO \rightarrow N_2O + CO_2$ eq. F-3

N_2O formed in this last way also may be reduced back to N_2 (Dasch, 1992) , via:

$N_2O + CO \rightarrow N_2 + CO_2$ eq. F-4

Feijen-Jeurissen et al. (2001) provide a good discussion of N_2O emissions from motor vehicles.

2.1.1 N_2O emissions and catalysts

Prigent and De Soete (1989) conclude that the N_2O is formed at relatively low catalyst temperatures; at higher temperatures, the N_2O itself is destroyed. They show a graph in which N_2O formation, via reduction by CO over a metal catalyst, peaks at 120 ppmv at 500 K and drops to zero on either side, at 400 K and 650 K. Prigent (in Ryan and Srivastava, 1989) shows N_2O formation across a 3-way platinum-rhodium catalyst peaks at 180 ppmv at about a 635 K catalyst inlet temperature (which implies a slightly cooler temperature across the catalyst). Odaka, et al. (1997) examined N_2O formation across different types of catalysts, and found that catalysts using different noble metals exhibit different N_2O formation characteristics. Fresh and aged Pt/Rh catalysts exhibited peak N_2O formation at about 573 K, while a fresh Pd catalyst exhibited peak formation at about 473 K, and a fresh Pd/Rh catalyst exhibited peak formation about 523 K. The peak N_2O formation zone for the Pd and Pd/Rh catalysts shifted with age, such that the peak for the aged catalysts occurred at about 623 K. (Jimenez, et al., 1997) .

The dependence of N_2O formation on temperature causes higher emissions from a cold-start test than a hot-start test, and relatively high emissions during catalyst light-off (Prigent and Soete, 1989; Jimenez, et al., 1997; Feijen-Jeurissen et al., 2001). For example, Lindskog (in Ryan and Srivastava, 1989) found that after a cold start the concentration of N_2O in the exhaust pipe downstream of the catalyst is two times higher than the concentration before the catalyst. This has important implications: electrically heated catalysts, which might be used to reduce cold-start HC emissions, probably would reduce N_2O emissions too.

Although lower *catalyst* temperatures almost certainly increase N_2O emissions (Ryan and Srivastava, 1989; Dasch, 1992), colder ambient temperatures may increase or decrease N_2O emissions (see note j, Table F-2). This occurs because once the vehicle's engine is warm, the temperature of the catalyst is not directly related to the air temperature, but rather is determined by the temperature of the exhaust gases, which are determined by engine load and combustion conditions.

2.1.2 N_2O emissions and fuel characteristics

The data in Table F-2 show that some of the lowest N_2O emissions among gasoline vehicles have been observed in California (the Jimenez et al., 1997 data), while higher emissions have generally been observed among vehicles operated in other states. Some of the highest emissions reported in Table F-2 are for a set of vehicles that were tested in Canada, with average emissions of well over 100 mg/mi (the Ballantyne, et al., 1994 data). One explanation for these differences has recently been suggested by Michaels (1998). The vehicles tested in Canada were tested using fuel that contained 700 ppm sulfur, which is more than twice the typical level in U.S. gasoline, and several times the level found in the reformulated gasoline that is currently used in California. In tests conducted at the National Vehicle and Fuel Emissions Laboratory, the U.S. EPA found that N_2O emissions were substantially higher when vehicles were operated using a fuel with a sulfur content of 285 ppm than they were when the vehicles were operated on Indolene, a fuel with a sulfur content of only 24 ppm. For example, one vehicle produced 54 mg/mi of N_2O using the standard 285 ppm sulfur fuel, and 39 mg/mi of N_2O when Indolene was used. Also, a high emitting vehicle that produced 227 mg/mi of N_2O on the 285 ppm sulfur fuel produced only 115 mg/mi of N_2O on Indolene. The EPA found that increasing the sulfur content of Indolene was by far the most influential variable, among the fuel characteristics studied, in reducing the catalytic reduction of NOx, and the agency suspects that this also increases production of N_2O (Michaels, 1998) .

In summary, fuel sulfur content appears to be an important variable for N_2O production (Feijen-Jeurissen et al., 2001). The Ballantyne, et al. (1994) data may not be applicable to situations in which lower sulfur fuels are used, because high levels of fuel sulfur seem to decrease the effectiveness of NOx conversion and result in higher emissions of N_2O. See Section 2.2 of this appendix for further discussion of the relationship between N_2O emissions and the presence of fuel sulfur compounds.

2.1.3 N_2O emissions and drive cycle

The type of drive cycle appears to influence N_2O as well, probably because it affects the temperature across the catalyst. N_2O emissions are consistently lower in the highway driving cycle, when the catalyst is warmed up, than in the FTP (Table F-2; Dasch, 1992; Feijen-Jeurissen et al., 2001, report the same for European test cycles).

Based on tests of four gasoline vehicles and one diesel vehicle, Sasake and Kameoka (1992) show that, for gasoline LDVs, N_2O emissions decrease with higher vehicle speeds (over the range from 60 km/hr to 100 km/hr) and higher incline gradients. While variations in vehicle speed and incline gradient had no significant effect on N_2O emissions from the diesel vehicle tested, one new gasoline vehicle equipped with a 3-way catalyst demonstrated a reduction in N_2O emissions from 2.6 mg/mi to 0.3 mg/mi with an increase in vehicle speed from 37 mph to 62 mph. This same vehicle produced 1.3 mg/mi of N_2O when operated at 37 mph on a 2% incline gradient, and only 0.6 mg/km of N_2O on a 4% gradient. Over the Japanese "11-step" driving cycle (which includes a cold start), a vehicle with a 1000 km odometer reading produced 26.7 mg/mi of N_2O.

One significant complication to the analysis of N_2O emissions from motor vehicles is that the FTP, the drive cycle used in many N_2O emission tests, overestimates average trip length (and hence underestimates the fraction of total trip mileage in cold-start mode in real driving), but also underestimates average vehicle speed (German, 1995; U.S. EPA, 1995d). In the real world as compared to the FTP, N_2O emissions will be higher on account of the additional cold starts, but lower on account of the higher speeds. The net effect of these two factors is not clear.

2.1.4 N_2O emissions and catalyst age

Relatively few studies have investigated the potential effect of catalyst age on N_2O emissions, but most of the available data suggest that N_2O emissions can increase significantly as catalyst age accumulates. Based on a study of eight new or laboratory aged catalysts, De Soete (1993) reports that N_2O emissions from vehicles equipped with catalysts aged to an equivalent of about 15,000 miles of use are on average 3.9 times higher than emissions from vehicles equipped with new catalysts, when tested on the European Extra Urban Driving Cycle (EUDC -- a high speed driving cycle with a top speed of 120 km/hr). On the Economic Commission for Europe (ECE) hot-start cycle, average N_2O emissions from the aged catalyst equipped vehicles were 4.4 times higher than those from the new catalyst vehicles. On the ECE 15-04 driving cycle, which includes a cold-start, N_2O emissions from the aged catalyst vehicles were 2.1 times higher than those from the new catalyst vehicles.

Sasake and Kameoka (1992) found that older vehicles produced much higher N_2O emissions than newer vehicles with similar emission control equipment. While this study was not controlled in such a way as to isolate the effect of catalyst age, the oldest vehicle tested (which had an odometer reading of 52,000 km) produced several times the N_2O emissions of the newest vehicle (with only 1,000 km of use). The exact magnitude of the emissions difference between the two vehicles varied by driving cycle, but averaged across the three Japanese driving cycles studied the older vehicle produced 8.4 times the N_2O emissions of the new vehicle.

A 1989 study by Lindskog (in De Soete, 1993) reports that N_2O emissions from a vehicle with a catalyst aged 15,000 km were 1.3 times (Swedish cold-start driving cycle) and 1.5 times (Swedish hot-start driving cycle) higher than emissions with a new catalyst. Prigent and De Soete (also in De Soete, 1993) report similar findings, with emissions increases of 1.5 times on both the ECE 15-04 (cold start) and EUDC (hot start) cycles, for vehicles using a catalyst bench aged for 150 hours relative to a new catalyst. Also, a recent study of nine "clean fleet" vans operating on reformulated gasoline in Los

Angeles revealed that emissions of N_2O at 15,000 miles were on average 1.9 times higher than emissions at 5,000 miles, and that N_2O emissions at 25,000 miles were on average 2.8 times higher than emissions at 5,000 miles (Battelle, 1995) .

More recently, Jimenez, et al. (1997) conducted a study of actual, on-road N_2O emissions from vehicles in El Segundo, California in November, 1996. Using a remote sensing approach based on an Aerodyne Research Tunable Diode Laser (TILDAS) instrument, Jimenez, et al. took a total of 1386 measurements of different vehicles and found a wide variation in N_2O emissions, with a mean of 5.0 ppm and a standard deviation of 24.3 ppm. Including a systematic bias evident in the data and other sources of uncertainty, the authors place the mean rate of emissions at 4.3 to 8.5 ppm. Using an average fuel economy estimate of 17.4 mpg, and the 5.0 ppm figure, Jimenez, et al. calculated an overall mean emission rate of 19.3 mg N_2O / mile (Jimenez, et al., 1997) . Although this value is considerably lower than that reported in most other studies, it is important to note that these on-road data are measurements of vehicles with hot catalysts, and that "cold start" emissions -- probably the largest source of N_2O -- are therefore not included.

Jimenez, et al. also present a breakdown in vehicle N_2O emissions by vehicle vintage. They showed that non-3-way catalyst equipped vehicles, older than model year 1982, produced very little N_2O emissions. The oldest vehicles with three-way catalysts, those of vintages from 1982 to 1988, produced the highest level of N_2O emissions, with values as high as 15 ppm. The emissions from newer catalyst vehicles, 1989 and newer, tended to be close to the reported mean value of 5 ppm (Jimenez, et al., 1997) . Hence, these data show clearly that catalyst-equipped vehicles produce higher N_2O emissions than earlier non-catalyst vehicles, and that, for catalyst-equipped vehicles, emissions of N_2O are substantially higher for older (1982-89) vehicles than for newer (1990-97) ones. This latter effect could be due to either a model year effect (i.e., older vehicles produce more N2O than newer vehicles, both when new and when old) or a catalyst aging effect, but there were no major changes to emission control technology from 1982 until 1994, when the EPA's Tier 1 standards became implemented. Therefore, it is more likely that the higher emission levels observed for older vehicles are the result of the catalyst aging effect.

Finally, in a laboratory study of N_2O formation across different types of new and aged catalysts, Odaka, et al. (1997) found that N_2O formation characteristics changed when the new catalysts were artificially aged to an equivalent of 30,000 miles. They found that both the type of metal used in the catalyst and the quantity of metal used were significant variables. For Pt/Rh catalysts with high metal contents (1.25 g/L Pt and 0.25 g/L Rh), relatively minor changes were apparent upon aging. The peak level of N_2O formation was constant at about 160 ppmv (at about 573 K), and the profile shifted only slightly upon aging such that formation levels were slightly lower at temperatures below 523 K, slightly higher at 523-573 K, slightly lower at 573 to 673 K, and somewhat higher at higher temperatures. For Pt/Rh catalysts with lower metals contents of 0.8 g/L Pt and 0.16 g/L Rh, peak N_2O formation increased dramatically with aging, with the peak (at about 573 K) rising from about 50 ppmv to over 150 ppmv in the aged catalyst. In contrast, a Pd catalyst with a content of 3.0 g/L exhibited no change in peak N_2O formation levels with aging, but the peak shifted from occurring at about 200° C in the fresh catalyst to about 623 K in the aged catalyst. Higher formation levels were observed across a wide temperature range of from 573 to 673 K. Finally, a Pd/Rh catalyst with metals contents of 1.0 g/L Pd and 0.2 g/L Rh exhibited both shifts upon aging, with an increase in peak formation of from about 75 ppmv at 523 K, to about 175 ppmv at 623 K (Jimenez, et al., 1997) .

These studies are not sufficient to provide a complete understanding of the effect of catalyst age on N_2O emissions, but they do suggest that N_2O emissions increase with catalyst age.[2] Vehicle running emissions of N_2O would seem to increase substantially over the life of the vehicle, such that after a vehicle is about eight years old, its N_2O emissions rise to a point that is likely to be three to four times higher than those when new. Based on what has been learned from laboratory studies, this effect can be readily explained with the understanding that peak N_2O formation occurs at higher temperatures with aged catalysts. While the peak quantity of N_2O formed over aged catalysts may or may not be higher at these higher temperatures than the peak for newer catalysts at lower temperatures, actual vehicle emissions are higher for vehicles with aged catalysts because a greater proportion of the driving cycle occurs in the "window" of relatively high temperature and N_2O formation (De Soete, 1993; Jimenez, et al., 1997) .

2.1.5 N_2O emissions and failure of emission-control equipment

The failure of emission controls can increase or decrease N_2O emissions. If the EGR system is disconnected, emissions increase substantially (see note d, Table F-2). However, if the oxygen sensor is disabled, N_2O emissions are apparently eliminated (see note k, Table F-2).

2.1.6 N_2O emissions and future emission controls

Electrically heated or close-coupled catalysts, which might be used to meet the new NMHC tailpipe emission standards, will reduce the amount of time that the catalyst is cold, and so will reduce N_2O emissions (Feijen-Jeurissen et al., 2001). Also, the possible N_2O formation mechanism, $2NO + CO \dashrightarrow N_2O + CO_2$, indicates that when CO emissions are reduced, N_2O emissions may be reduced. Finally, as the sulfur content of gasoline and diesel fuel is reduced, N_2O emissions may be reduced (Feijen-Jeurissen

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[2] The EPA (Michaels, 1998) believes that the “aging effect” happens very early, but does not give evidence to support this.

et al., 2001). For these reasons, it is likely that emissions from future vehicles will be lower than the vehicles summarized in Table F-2.

2.1.7 N_2O emissions and fuel consumption

The IPCC *Guidelines* (1997) state that, in the absence of g / mi emissions data for a particular class of vehicles (e.g., heavy-duty gasoline vehicles with advanced controls), emissions can be estimated by multiplying the kg / mi fuel consumption of the vehicle class in question by a fuel-and-technology specific g-N_2O / kg-fuel factor, derived from data on emissions and fuel consumption for a similar vehicle class (e.g., light-duty gasoline vehicles with advanced controls). The EPA adopts this procedure in its own analysis, justifying it on the grounds that they found that light trucks emit more than passenger cars (Michaels, 1998).

The IPCC (1997) justifies its recommendation on the grounds that “emissions and fuel consumption tend to vary in parallel (vehicles and operating modes causing high emission rates tend to result in high fuel consumption, and vice versa)” (p. 1.66). However, we note that while it probably is true that emissions and fuel consumption tend to move in the same direction with respect to *some* (but not necessarily *all*) vehicle and operating characteristics, there is little reason to believe that this relationship is one of strict proportionality (such that if fuel consumption per mile doubles, emissions per mile double as well), which is what the IPCC and the EPA assume. The relationship between fuel economy and emissions depends in complex ways on vehicle engine technology, vehicle age, emission control technology, driving conditions, and emission standards. Certainly, for the regulated air pollutants (CO, NMHCs, and NO_x), the relationship is not one of proportionality, mainly because the regulated pollutants are subject to a g / mi standard that is not proportional vehicle fuel economy (DeLuchi, et al., 1994; Khazzoom, 1995; Harrington, 1997) . However, in the case of unregulated pollutants such as N_2O (and CH_4), which by definition are not subject to a g / mi standard, the matter is more complicated. Theory and the scant available data do not provide definitive answers.

Our data (Table F-2) do not include fuel consumption. However, when we examine emissions versus vehicle size, for a particular type of fuel and emission control technology, we do not find any striking evidence that emissions are proportional to fuel economy. Nonetheless, it does not seem unreasonable to assume that, all else equal, there is some positive relationship between fuel consumption and emissions. The increasing proportion of light-duty trucks in the U.S. motor vehicle fleet highlights the need to collect additional data on N_2O emissions from these vehicles, and to confirm that emissions are in fact approximately proportional to fuel consumption, given certain fuel specification and catalyst type and age conditions.

2.1.8 N_2O emissions and NOx/N_2O ratios

Table F-2 includes some data on the NOx / N_2O ratios (in terms of grams per mile) that correspond to the N_2O emissions measurements shown. In theory, a correlation might be expected between NOx / N_2O ratios and N_2O emission levels, because higher NOx emissions might by associated with higher N_2O emissions: high engine-out NOx may increase the amount of N available for N_2O formation, and reduced catalyst efficiency (and hence high tailpipe NOx) might increase N_2O formation (Feijen-Jeurissen et al., 2001). In general, the data in Table F-2 show that for gasoline LDVs, higher NOx / N_2O ratios seem to be correlated with lower N_2O emission levels. However, for other vehicles types, such as diesel vehicles, NOx / N_2O ratios can be much higher than for even uncontrolled gasoline vehicles, and N_2O emissions are apparently only somewhat lower. Thus, there is weak evidence for a general correlation between NOx / N_2O ratios and N_2O emissions, but no firm conclusions can be drawn from the available information due to incomplete data and the confounding factors of engine type, emission control type, and catalyst age (Feijen-Jeurissen et al., 2001). (See Section 2.2.2 for a discussion of NOx and N_2O emissions from stationary power plants).

2.1.9 Gasoline LDV N_2O emissions summary

The discussion above, and the data presented in Table F-2, suggest that N_2O emissions are a function of the type of emission control equipment (N_2O emissions from cars with 3-way catalysts are uniformly higher than from cars without catalysts), drive cycle, vehicle speed (N_2O emissions are relatively high from vehicles operated over test cycles that include a cold-start), catalyst age (emissions tend to increase as the catalyst ages), and other factors. Table F-3 summarizes our assumptions, along with those of the IPCC (1997) and EPA (1999).

The data of Table F-2 indicate that low-mileage 1980s / early 1990s model-year (Tier 0) passenger cars with 3-way catalytic converters, or 3-way catalytic converters plus oxidation catalysts, emit 20 to 100 mg / mi of N_2O, with an average of about 50 mg / mi. Low-mileage mid-1990s model-year (Tier 1) cars with advanced 3-way catalytic converters also emit about 50 mg / mi of N_2O. Passenger cars with aged catalysts produce somewhat higher emissions, and the available data show a somewhat greater increase in emissions with catalyst age for Tier 0 vehicles than for Tier 1 vehicles[3]. Figure F-1 (below) presents the N_2O emissions data from Table F-2 for Tier 0 and Tier 1 gasoline light-duty passenger automobiles with different odometer readings, along with regression lines fitted to the test data (excluding the Ballantyne et al. "high sulfur fuel" data, and using the average of the U.S. EPA emissions estimates for vehicle operation with and without the air conditioner on). Also shown is the U.S.

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[3] Although more data on high-mileage vehicles would be useful to further support this conclusion.

emission factor suggested by the IPCC (1997) and used by the U.S. EPA in its March 1998 draft emissions inventory (U.S. EPA, 1998) , and the revised Tier 0 and Tier 1 emission factors suggested by the Office of Mobile Sources (OMS) of the U.S. EPA (Michaels, 1998) and used in the latest EPA (1999) and EIA (1998a) emissions inventories. Based on the regression analyses shown in Figure F-1, we specify an N_2O emission-factor model for Tier 0 and Tier 1 gasoline light-duty passenger automobiles (LDAs) as:

$$EM_{T0/T1} = ZM_{T0/T1} + DA \cdot \frac{MI}{1000} \qquad \text{eq. F-5}$$

where:

$EM_{T0/T1}$ = N_2O emissions from Tier 0 or Tier 1 gasoline LDAs (g / mi).
$ZM_{T0/T1}$ = zero-mile N_2O emissions (0.0299 g / mi for Tier 0 vehicles and 0.0422 g / mi for Tier 1 vehicles).
DA = the deterioration rate in emissions with vehicle mile (0.00136 g / mi per 1000 miles for Tier 0 vehicles and 0.00016 g / mi per 1000 miles for Tier 1 vehicles).
MI = total mileage on the vehicle (miles).

Figure F-1 shows that the revised EPA / OMS emission factor agrees much better with the available data than does the IPCC emission factor. However, on our Tier 0 trend line the emission rate at the mid life of a vehicle (around 70,000 miles) lies above the revised EPA / OMS Tier 0 emission rate. This suggests that the EPA / OMS factor for Tier-0 vehicles may be conservative.

Similarly , Figure F-2 shows emission data, regression lines, and EPA emission factors for gasoline light-duty trucks (LDTs). Low-mileage Tier 0 and Tier 1 LDTs generally emit about 20 to 140 mg / mi of N_2O, although one Tier 0 vehicle tested emitted about 250 mg / mi with a mileage of only 5,000 miles. The data suggest that the deterioration rate for Tier 0 vehicles may be substantially higher than for Tier 1 vehicles, but again more data for high-mileage vehicles are needed to further support this conclusion. Based on the regression analyses shown in the figure, we specify an N_2O emission-factor model for Tier 0 and Tier 1 gasoline LDTs as:

$$EM_{T0/T1} = ZM_{T0/T1} + DA \cdot \frac{MI}{1000} \qquad \text{eq. F-6}$$

where:

$EM_{T0/T1}$ = N_2O emissions from Tier 0 or Tier 1 gasoline LDTs (g / mi)
$ZM_{T0/T1}$ = zero-mile N_2O emissions (0.0843 g / mi for Tier 0 vehicles and 0.0725 g / mi for Tier 1 vehicles)
DA = the deterioration rate in emissions with vehicle mile (0.0028 g / mi per 1000 miles for Tier 0 vehicles and 0.00054 g / mi per 1000 miles for Tier 1 vehicles)
MI = total mileage on the vehicle (miles)

Again, the U. S. emission factor suggested in the IPCC *Guidelines* appears to be too high. On the other hand, the revised emission factors suggested by EPA (Michaels, 1998) might be too low, as for the most part, they lie below the trend lines that we plot from the available data (Figure F-2). However, our Tier-0 trend line is influenced strongly by the very high emissions of one of the three vehicles tested, and the upward slope of our Tier-1 trend line might not be real. Although we do use our trend lines as the basis of our own estimates, we emphasize that there is a good deal of uncertainty here.

2.1.10 N_2O emissions from gasoline HDVs, and diesel LDVs and HDVs

There are few data on N_2O emissions from diesel LDVs and heavy-duty vehicles (HDVs), and very few data on N_2O emissions from gasoline HDVs or vehicles with advanced emission control systems. Table F-2 reports the data that we have found. Table F-3 summarizes the IPCC (1997) and EPA (1999) estimates.

The IPCC (1997) estimates separate N_2O emission factors for U.S. and European vehicles. They use the Deitzmann, et al. (1980) data to estimate N_2O factors for diesel HDVs in the U.S., and unspecified data (we speculate that it is the “Diesel LDV” data of our Table F-2) to estimate N_2O emission factors for diesel LDVs in Europe. For diesel HDVs in Europe, diesel LDVs in the U. S., and gasoline HDVs in Europe and the U.S., the IPCC (1997) apparently estimates N_2O emissions by multiplying the kg / mi fuel consumption of each vehicle class by a fuel-specific emission factor, in g-N_2O / kg-fuel, derived from emissions and fuel consumption data available for similar vehicle classes (see section 2.1.7). Neither the IPCC (1997) nor the EPA (Michaels, 1998) report the Dietzmann, et al. (1981) data for gasoline HDVs (Table F-2).

The IPCC (1997) -- and by following them, the EPA (Michaels, 1998) -- resort to extrapolating by fuel consumption in part because they apparently do not have data for gasoline HDVs, or report the details of the data for diesel LDVs. We prefer to examine all of the available data as a whole. Upon first inspection, the N_2O emissions from diesel HDVs, diesel LDVs, and gasoline HDVs appear similar. However, the N_2O emissions from the two low-mileage diesel HDVs were less than the emissions from the high-mileage diesel HDVs, and less than the emissions from the gasoline HDVs, which had low mileage. This might suggest that emissions increase with HDV mileage, and that for a given vehicle vintage (the gasoline and diesel vehicles in the Dietzmann, et al. tests were of the same vintage) and age, diesel HDVs emit less than do gasoline HDVs. However, it is not clear why emissions should increase with age for vehicles without catalytic converters, or what properties of gasoline engines might make them emit more N_2O than diesel engines.

It is difficult to interpret the few data on N_2O emissions from diesel LDVs (Table F-2). Comparing the Euro 1, 2, and 3 diesel vehicles with the Euro 1, 2, and 3 gasoline vehicles from the same testing program (Feijen-Jeurissen et al., 2001), we find that Euro 1 and Euro 2 diesel LDVs emitted much less N_2O than Euro 1 and Euro 2 gasoline LDVs, but that Euro 3 diesel LDVs emitted slightly more than did Euro 3 gasoline LDVs. However, the diesel LDVs had an oxidation catalyst whereas the gasoline LDVs had a 3-way catalyst, and other data from Table F-2 suggest that vehicles with oxidation catalysts emit more N_2O than vehicles with 3-way catalysts. Thus, our tentative conclusion is that N_2O emissions are affected by the drive cycle, the emission control system, and the sulfur content of the fuel, but not by *other* (inherent) differences between diesel and gasoline vehicles.

Clearly, it is difficult to draw any firm conclusions from the available data. We think it most reasonable to assume that diesel engines emit roughly the same amount of N_2O as do gasoline engines given a similar emission control system, engine size, drive cycle, and fuel sulfur content. This indicates a factor of 10-50 mg/mi for diesel LDAs, and 40-60 mg/mi for diesel HDVs. We are unable to estimate a factor for gasoline HDVs with 3-way catalysts.

Feijen-Jeurissen et al. (2001) discuss the effect of HDV emission-control strategies on N_2O emissions. They note that oxidation catalysts, catalytic particulate traps, and selective catalytic reduction "deNOx" systems have platinum catalysts that can in principle produce N_2O. In their own tests, they measured significant N_2O production across a catalyzed particulate filter. Thus, the new emission controls being developed for HDDVs may increase N_2O emissions from HDDVs.

2.1.11 N_2O emissions from alternative-fuel vehicles (AFVs)

Based on the preceding analysis, one would expect that N_2O emissions from AFVs would be related to the operating temperature and composition of the catalytic-converter emission-control system. Virtually all AFVs built or converted to date use stock gasoline-vehicle catalytic control systems (or systems very similar to gasoline systems), and emit about as much N_2O as do gasoline vehicles. Advanced catalytic-control systems made specifically for AFVs may affect N_2O emissions. Such catalysts are being developed for methanol and compressed natural gas (CNG) vehicles. However, there are so few advanced, optimized AFVs, and even fewer optimized emission control systems, that at present it is impossible to estimate N_2O emissions from fully optimized AFVs.

Tests by Ford Motor Company (1988a) on two flexible-fuel Escorts and two flexible-fuel Crown Victoria vehicles (flexible-fuel vehicles can use any mixture of methanol and gasoline) show no striking relationship between N_2O emissions and the methanol content of the fuel (Table F-2, and other emission results not shown here). The data suggest that N_2O emissions increase with the age of the catalyst, but there are so few data that one cannot draw a firm conclusion. As shown in Table F-2, the emission rates from the FFVs spanned the range of emissions typically measured from gasoline LDVs. The Escort emitted over 100 mg/mi, and the Crown Victoria 10-15 mg/mi. Because of this, and because N_2O emissions were not affected by the amount of methanol or gasoline fuel, it is likely that methanol vehicles -- both flexible-fuel and dedicated -- emit about the same amount of N_2O as gasoline LDVs with similar emission controls.

The few data available (Table F-2) also do not provide a basis for assuming that ethanol and liquified petroleum gas (LPG) vehicles emit appreciably different levels of N_2O than do gasoline vehicles. However, some CNG vehicles appear to emit less, perhaps because their low levels of engine-out CO lead to lower levels of N_2O formation (see Equation F-3). A recent study of 36 gasoline, LPG, methanol, and CNG vans produced by Chevrolet, Dodge, and Ford demonstrates (see Table F-2) that emissions of N_2O from all four vehicle types are comparable (Battelle, 1995) -- except that the Dodge CNG vans, which were among the first CNG vehicles produced with catalyst systems tailored for CNG exhaust, emitted significantly less N_2O than the other vehicles. These vehicles produced only 9 mg/mi of N_2O on average when new, but emissions clearly increased with catalyst age to the point where, at 15,000 miles, an average emission rate of 39 mg/mi of N_2O was measured. Based on these data, a reasonable approximation would be to assume that the N_2O emission factor for advanced CNG vehicles is about 75% of the factor for Tier 1 gasoline vehicles. More emission tests would be useful, however, to measure N_2O emissions from CNG passenger cars, to assess the relative deterioration rates for CNG vehicles and gasoline vehicles, and to determine how representative the Battelle (1995) data are.

Feijen-Jeurissen et al. (2001) tested three LPG vehicles configured to meet “Euro 2” emission standards, over the European Test Cycle (ECE-15) (Table F-2). The vehicles had the same emissions as Euro 2 gasoline vehicles.

There do not appear to be any data at present on emissions of N_2O from alternative-fuel HDVs. In the absence of data, it might be reasonable to assume that the ratio of N_2O emissions from advanced alternative-fuel HDVs to N_2O emissions from advanced gasoline HDVs is the same as the ratio for advanced LDVs.

Table F-3 shows our assumptions regarding emissions of N_2O from various types of AFVs. The IPCC and the EPA do not estimate N_2O emissions from AFVs.

2.2 N_2O EMISSIONS FROM POWER PLANTS

Power plants also emit N_2O. Although the power plant combustion chemistry of N_2O is quite complex, several general trends are apparent. Higher N_2O emissions are generally associated with lower combustion temperatures, higher rank fuels, lower ratios of fuel oxygen to fuel nitrogen, higher levels of excess air, and higher fuel carbon contents (Kramlich and Linak, 1994) . The exact mechanisms responsible for these relationships are still not fully understood, and in fact are somewhat controversial. Explanations for the temperature dependence of N_2O formation include lower catalytic decomposition activity at lower temperatures, lower availability of NCO[4] at higher temperatures due to oxidation to NO, and higher rates of removal of N_2O through reaction with atomic hydrogen at higher temperatures (Kramlich and Linak, 1994) . The dependence of N_2O formation on the other variables listed above is less strong than the dependence on temperature, and competing explanations are at least as controversial. Very likely, several mechanisms are, to greater or lesser degrees, responsible for these relationships. Table F-4 shows emissions of NO and N_2O as a function of type of fuel, type of combustion, combustion temperature, sulfur content, and sampling protocol.

Early tests, especially those by Hao, et al. (1987), indicated that coal-fired power plants emitted relatively large amounts of N_2O. Weiss and Craig (1976) and Pierotti and Rasmussen (1976) also measured relatively large amounts of N_2O from fossil-fuel-fired power plants. However, more recent research has shown that these earlier, high N_2O values obtained for power plants are artifacts of the N_2O sampling method. Muzio and Kramlich (1988) report that "the storage of moist combustion products containing SO_2 and NO for periods as short as 2 hours can lead to the formation of several hundreds of parts-per-million of N_2O in the sample containers where none originally existed" (p. 1369). Drying the stored flue gas reduced but did not eliminate this artifactual in-sample N_2O formation; removing the sulfur eliminated it. The presence of sulfur in the sample flue gas increased the concentration of N_2O by two orders of magnitude, from less than 5 to several hundred ppm. The mechanism for this

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[4] NCO is formed through reactions involving the decomposition of cyano species such as HCN and HNCO. It is needed for one important route of N_2O formation where the combination of NCO and NO forms N_2O and CO.

artifactual formation of N_2O is now believed to involve the dissolution of NO_2 and SO_2 into condensed water, which then produces N_2O through a complex series of additional liquid-phase reactions (Kramlich and Linak, 1994) . The effects of moisture, sulfur, and storage time on N_2O formation are illustrated in Table F-4 Importantly, there appears to be an "activation" level of SO_2. In one experiment, the concentration of N_2O in the sample remained quite low, about 15 ppm or less, with less than 600 ppm SO_2 in the furnace. At 1000 ppm SO_2, the concentration of N_2O had jumped to about 260 ppm (Muzio and Kramlich, 1988) . This suggests that a low-sulfur fuel will not produce enough SO_2 to cause the artifactual, in-sample formation of N_2O.[5]

Artifactual formation of N_2O can be avoided by measuring the concentration of N_2O in the flue gas in real time, without storing the sample (called “on-line” sampling), by storing the flue-gas samples for only a very short time before analyzing it, or by removing sulfur and water from stored flue-gas samples. Tests done in this way consistently find that the concentration of N_2O from high-temperature combustion systems is fairly low, typically less than 5 ppm, even for coal-fired plants. At this level, N_2O emissions from power plants contribute on the order of 1% of fuel-cycle CO_2-equivalent emissions from the use of electricity. However, it is possible that N_2O is formed in the atmosphere indirectly from direct NO emissions, possibly by the same mechanism that causes N_2O to form ingrab samples. For example, the primary reaction responsible for artifactual N_2O formation,

$$2NO + SO_2 \overset{H_2O}{\text{-->}} N_2O + SO_3 \qquad \text{eq. F-7}$$

might occur in the plumes of power plants and produce N_2O. However, Sloan and Laird (1990) point out that the concentration of the reactants in plumes is much less than in the flue gas samples which generate artifactual formation -- and the reaction in the samples is already quite slow -- so that in plumes in the atmosphere, the reaction likely will be much to slow to generate much N_2O. Kokkinos (1990) agrees with this assessment. Linak, et al. (1990) cite previous research that suggests that such indirect N_2O formation is unlikely, but they believe that additional research is needed.

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[5] The discovery of the artifactual formation of N_2O, and the implication that direct N_2O emissions may not be as high as previously thought, is consistent with "a priori" expectations, based on combustion kinetics and experiments, about how much N_2O should be formed. In fact, explaining the earlier, higher levels was proving to be something of a problem, since N_2O formed early in the flame zone should be destroyed rapidly before it reaches the exhaust (Lyon, et al., 1989).

Other artifactual formation routes may exist. Prigent and De Soete (1989) have demonstrated that with combustion in the presence of sulfur (in the form of $CaSO_4$, as might result from emission control devices), the concentration of N_2O dropped with increasing temperature up to about 1200 K, then increased to a maximum of about 4 ppm at 1275 K, and then declined again. This demonstration of N_2O formation at high temperatures may re-establish the possibility of significant N_2O formation from the combustion of fossil fuels.

De Soete also suggests that in fluidized-bed combustors, N_2O may be formed from reduction of NO and the oxidation of reduced sulfur compounds, via a path similar to that suspected of generating artifactual N_2O at room temperature in samples with sulfur and NO:

$$2NO + CaSO_3 \rightarrow N_2O + CaSO_4 \qquad \text{eq. F-8}$$

The particular sulfur compound he investigated, $CaSO_4$, is reduced (and thus "prepared", in a sense, for oxidation by NO), by CO and C, above 1200 K. Above about 1400 K, N_2O is destroyed. With other sulfur compounds, or different concentrations of oxygen, N_2O formation as a function of temperature may be different.

Thus, in summary, it seems likely that stack gas becomes too dilute too quickly to permit significant formation of N_2O via reactions involving sulfur species.

2.2.1 Fluidized-bed combustion

Modeling and experimental results indicate that fluidized-bed combustors, which operate at lower temperatures than utility boilers, and so produce less NO_x, may produce considerably more N_2O than boilers (Amand and Andersson, 1989; Ryan and Srivastava, 1989; Kokkinos, 1990; Makansi, 1991; Lu, et al., 1992; Mann, et al., 1992) . Indeed, tests of fluidized-bed combustion that use on-line sampling or are otherwise free of artifactual N_2O formation, indicate substantially higher N_2O emissions than from higher-temperature combustion processes (Amand and Leckner, 1991; Mann, Collings, et al., 1992) . N_2O emissions from fluidized-bed combustors are a function of the type of fuel (coal produces more N_2O than does natural gas), the operating temperature (lower temperatures produce more N_2O), the excess air level (more excess air is associated with higher N_2O emissions), char particle size for coal combustion (N_2O emissions peak with particle sizes of about 1 mm), and gas residence time within and after the fixed bed (N_2O yield increases and then plateaus with increased residence time) (Lu, et al., 1992; Mann, Collings, et al., 1992; Miettinen, et al., 1995) . Mann, et al. (1992) conclude that N_2O emissions from fluidized-bed combustors typically are between 30 and 120 ppm, and De Soete (1993) reports a range from 30 to 150 ppm with

3% oxygen. The data shown in Table F-4 confirm that these ranges encompass most data collected to date.

Fluidized-bed combustion is used at one stage in the production of gasoline. When the fluidized-bed catalytic cracker, which breaks the large hydrocarbon molecules of crude oil into the smaller molecules of gasoline, becomes coated with coke residue from the crude oil, the coke is burned off the catalysts by fluidized bed combustion (called in this case "regeneration") (Cooper and Emanuelsson, 1992). Hence, this step in the refining process may produce non-trivial amounts of N_2O (Lyon, et al., 1989) . The one test of which we are aware measured 3-26 ppm N_2O and about 400 ppm NO from a fluidized-bed catalytic cracker with a zeolite catalyst, in a modern Swedish refinery (Cooper and Emanuelsson, 1992) . This concentration is lower than the N_2O concentration measured in other fluidized-bed combustors (Table F-4). The authors speculate that this is due to differences in catalysts. The N_2O concentrations measured from the catalytic cracker indicate an emission rate of 0.6 to 5.0 grams N_2O per barrel of oil (Cooper and Emanuelsson, 1992). Given 0.32 barrels per day of catalytic cracking capacity per 1.00 barrel per day of crude-oil distillation capacity in the U.S as of January 1, 1990 (Thrash, 1990) , 29.66 quads of petroleum products produced by U.S. refineries in 1988 (DeLuchi, 1991), and 4.848 billion barrels of crude oil input to refineries in 1988 (EIA, 1989b) , we calculate that, if the Swedish emission rates are representative, 0.03 to 0.3 grams of N_2O were emitted from catalytic crackers for every 10^6 Btu of petroleum product produced in the U.S. in 1988. Assuming that other areas of refineries produce some N_2O as well, we calculate a refinery-wide emission rate of 0.50 g / 10^6 BTU-product. The CO_2-equivalent of this (about 180 g-CO_2 equivalent / g / 10^6 BTU-product) is about 0.3% of the CO_2 released from burning 10^6 BTU of gasoline product.

2.2.2 NOx emission controls and N_2O emissions

Some NO_x control strategies may increase N_2O emissions, while others may reduce them, but in general the effects are small. Laboratory investigations have shown that the sum of fuel-N conversion to N_2O and NO is quite constant over a range of temperatures in fluidized-bed combustors, despite the strong variations in the formation of each species with temperature (Pels, et al., 1995) . Thus, to the extent that NO_x emissions or N_2O emissions can be reduced through temperature control measures alone, one tends to be reduced at the expense of the other, at least so far as regards fuel nitrogen.[6] This fact has lead to the investigation of other measures than temperature control to reduce NO_x and N_2O emissions.

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[6] Fuel nitrogen is an increasingly important source of N_2O formation as fuel rank increases (Kramlich and Linak, 1994).

Linak, et al. (1990) report that combustion modifications to control NO_x emissions either did not have a significant effect on N_2O emissions, or else slightly increased them (Table F-4). Nimmo, et al. (1991) found that combustion-air staging in low-NO_x fuel-oil burners changed the concentration of N_2O as a function of distance from the fuel injector (and apparently slightly increased the concentration of N_2O in the flue gas), but that in both staged-and unstaged burners the final flue-gas concentration was less than 2 ppm. Lu, et al. (1992) report that combustion air staging slightly increased the concentration of N_2O from pressurized fluidized-bed combustors. Kokkinos (1990) noted that urea injection into an oil-fired boiler may have increased N_2O emissions, and Lu, et al. (1992) found that NH_3 injection into a pressurized fluidized-bed combustor definitely did increase N_2O (Table F-4). However, Sloan and Laird (1990) found no significant difference in N_2O emissions between low-NO_x and conventional burners (Table F-4). Also, the use of selective catalytic reduction (SCR) appears to slightly reduce N_2O emissions (Ryan and Srivastava, 1989) .

The relatively high emission rate of N_2O from fluidized-bed combustion has attracted recent attention, and research efforts have examined various methods of reducing these emissions. Two primary N_2O emission reduction strategies have been investigated: "afterburning," whereby the temperature of the cyclone is increased by the addition of extra fuel in the upper part of the combustion chamber, and "reversed air staging," which involves supplying more air than usual to the bottom part of the combustion chamber and less to the top part (Lyngfelt, et al., 1996) . Both of these methods seek to reduce N_2O emission by selectively altering combustion conditions in the upper and lower parts of the combustion chamber. Conditions in the upper part are most important to N_2O formation, because any N_2O formed in the lower part is readily destroyed, while conditions in the both the upper and lower parts control NO formation and sulfur capture (Lyngfelt, et al., 1996) . Experimental results suggest that afterburning can decrease N_2O emissions by up to 90%, and can also slightly reduce CO emissions, with the cost of increased fuel use and the construction of efficient afterburners. Reversed air staging can reduce N_2O emissions by up to 75%, without significant effects on other emissions, with the only cost being slightly higher power consumption (Lyngfelt, et al., 1996) . These two methods could be combined, presumably resulting in even more dramatic N_2O emission reductions. At present, though, there are no standards for N_2O emissions, and hence no reason for anyone to adopt these controls.

Shimizu, et al. (1992) found that the addition of limestone to control SO_x emissions in a bubbling fluidized-bed coal combustor caused a slight decrease in N_2O emissions if single-stage air feed was used, and had no effect on N_2O if staged air feed was used. Amand and Andersson (1989) found that injecting ammonia into the combustion zone of circulating fluidized-bed combustor did not affect N_2O emissions.

2.2.3 N_2O and CH_4 emission factors for utility boilers

The most recent supplements to AP-42 include N_2O and CH_4 emission factors for utility boilers, differentiated by type of fuel and firing configuration (U.S. EPA, 1998) . The IPCC (1997) summarizes the AP-42 emission factors in its “detailed” emission inventory guidelines. In its “simple” guidelines, the IPCC (1997) uses its judgment to “average” across fuel and boiler varieties and establish generic emission factors for the use of coal, oil, or gas, in what it refers to as the “energy industry” (also presented in EPA (1999)). The AP-42 emission factors for fuel combustion by electric utilities, the IPCC “generic” emission factors, and our assumptions, are shown in Table F-5.

The AP-42 N_2O emission factors appear to be consistent with the N_2O emission tests summarized here. In Table F-5, the IPCC (1997) generic factors for oil use in the “energy industry” differ from the AP-42 factors for utility boilers burning fuel oil (which is what we show in Table F-5) because the IPCC (1997) apparently includes and gives great weight to the emission factors for large diesel engines, whose factors are, according to AP-42, quite a bit higher than the factors for fuel-oil boilers, and which we exclude from the AP-42 estimates shown in Table F-5.

Our assumptions for coal, oil, and NG utility power plants are based on the AP-42 emissions factors. In the case of N_2O from coal-fired plants, we have allowed for the possibility of elevated emissions from the few fluidized-bed combustion plants. In the case of N_2O from NG-fired plants, we use the average of the factors for controlled and uncontrolled burners.

2.3 N_2O EMISSIONS FROM OTHER COMBUSTION SOURCES

The data on N_2O emissions from trains, ships, NG pipeline compressors, farm equipment, loaders, petroleum refineries, well equipment, methanol plants, and other miscellaneous sources are very scarce (the most recent supplements to AP-42 do include some N_2O emission factors). Consequently, for most sources, the best approach is probably to assume that N_2O emissions depend only on the kind of fuel burned, so that, for example, the N_2O emission rate, in $g/10^6$ Btu, from a ship burning residual fuel oil is the same as the known rate from a power plant burning residual fuel oil.

3 METHANE EMISSIONS

3.1 METHANE FROM MOTOR VEHICLES

Methane is emitted from gasoline, diesel, methanol, ethanol, LPG, and natural gas internal-combustion-engine vehicles. Methane emissions are a function of the type of fuel used, the design and tuning of the engine, the type of emission control system, the age of the vehicle, and other factors. Table F-6 is a compilation of reported measurements of CH_4 emissions from petroleum- and alternative-fuel vehicles (AFVs), along with the relevant key attributes of the vehicles.

It is important to note that although methane emissions *per se* are not regulated in the U.S., the systems used to control emissions of NMHCs and total hydrocarbons (THCs) do to some extent control CH_4 emissions. However, since CH_4 is difficult to oxidize catalytically, control systems do not have the same effectiveness in controlling CH_4 emissions as they do in controlling NMHCs. Thus, whereas controlled NMHC emissions can be an order of magnitude less than uncontrolled emissions, CH_4 emissions from vehicles with HC controls might be about 3 times less than CH_4 emissions from vehicles with no controls. The EPA's study for its MOBILE3 model found that vehicles without a catalytic converter emit 0.3 g/mi CH_4, compared with 0.1 g/mi for vehicles equipped with a catalytic converter. Thus, methane emissions are a larger fraction of total HC emissions from new, tightly controlled cars than from old, high-emitting cars.

The EPA's model of emission factors for mobile sources, called "MOBILE5" (a revised version, MOBILE6, is now available), reports THC and NMHC emissions for gasoline and diesel vehicles.[7] The difference between the two is the CH_4 emission rate. Because the THC and NMHC emission factors in MOBILE are derived from tests of 1000s of gasoline light-duty vehicles (Guensler, et al., 1991) , the EPA/MOBILE5 estimates of CH_4 emissions from gasoline LDAs and LDTs (see Tables F-3 and F-6), while certainly not perfect (we discuss this briefly below), have historically been the best available. However, it is unclear to what extent tests of post-1995 vintage (Tier 1) LDVs have been included in the database used in the MOBILE estimates. Based on

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[7] The MOBILE model estimates emissions from a fleet of gasoline or diesel vehicles of a particular size class, in a designated year. In essence, the fleet-average emission rate in year T is calculated as $?_{MY} E_{MY,T} \cdot MF_{MY,T}$, where $E_{MY,T}$ is g/mi emissions from vehicle model year MY in year T, and $MF_{MY,T}$ is model-year MY's fraction of total fleet miles of travel in year T. The model-year emission rate, in turn, is calculated on the basis of a "zero-mile" emission rate when the vehicle is new, and the rate at which emissions increase ("deteriorate") as the vehicle ages. The EPA refers to these underlying estimates of zero-mile emissions and deterioration rates in order to estimate CH_4 emissions from specific technology (model-year) classes of gasoline LDVs (Table F-3.) Documentation for a previous version of the model, MOBILE4, can be found in EPA (1991b).

recent tests of a few vehicle types, these Tier 1 vehicles appear to emit substantially less CH_4 than Tier 0 vehicles (see Table F-6). For this reason, we use the data in Table F-6 to estimate our own CH_4 emission rates for Tier 1 LDAs and LDTs, as well as Tier 0 vehicles (see Section 3.1.1). Also, as discussed below, the MOBILE5 emissions data for HDVs apparently are much poorer than the data for LDVs. However, in the absence of significant data with which to estimate new emission rates, we adopt the MOBILE5 estimates of CH_4 emissions from gasoline and diesel HDVs.

Given that there are many CH_4 emissions tests for gasoline LDVs, but comparatively few for alternative-fuel LDVs, and assuming that emissions relative to gasoline vary less than do absolute emissions, it is better to estimate CH_4 emissions from AFVs relative to emissions from gasoline vehicles. Therefore, in Table F-6, under "Gasoline LDVs," we show for the most part CH_4 emissions data from gasoline vehicles that are paired with an alternative-fuel vehicle in another section of Table F-6.

3.1.1 CH_4 emissions from gasoline LDVs

The EPA / MOBILE estimates, and the few other test data shown in Table F-6, indicate that gasoline LDVs with 3-way catalytic converters emit between 0.02 and 0.2 g / mi CH_4, with values for recent model-year cars centering around 0.08-0.10 g / mi. The emissions database used by EPA to develop an early version of the emissions model, MOBILE3, indicates that gasoline LDVs emit 0.1 g / mi at low-altitude (Chun, 1988; U.S. EPA, 1991b) . MOBILE5, the previous version of the EPA mobile-source emission-factor model, estimates that the LDV fleet will emit 0.12 g / mi in the year 1990, 0.06 g / mi in the year 2000, and 0.04 g / mi in the year 2020 (Table F-6). The model projects a decline in emissions because beginning in 1994 vehicles had to meet the lower NMHC emission standards called for in the Clean Air Act Amendments of 1990 (U.S. EPA, 1991a) , and the technology used to control NMHC emissions to some extent also controls CH_4 emissions.

One would expect methane emissions to increase somewhat as the engine and the emission-control system age and deteriorate. The data of Table F-6 suggest that for most fuels -- nonpetroleum fuels as well as petroleum fuels -- CH_4 emissions increase with the age of the catalyst. On the other hand, the EPA's (1991b) analysis for MOBILE3 indicated that CH_4 emissions from pre-1985 gasoline vehicles did not deteriorate with age. The few tests that couple modern vehicles and fuels (i.e. 1992 vans using reformulated gasoline) show emission levels of about 0.05 g / mi when new, rising to about 0.15 g / mi with significant catalyst age. Older three-way catalyst equipped vehicles exhibit somewhat higher rates, ranging from perhaps 0.1 g / mi when new to 0.3 g / mi or more when older. We note that there are virtually no data on methane emissions from very old vehicles.

Methane emissions, like NMHC emissions, appear to be higher at lower ambient temperatures (Stump, et al., 1989; 1990) . This is to be expected because before the engine is warmed up the temperature of the fuel going into the engine is close to the ambient temperature, and at lower temperatures a liquid fuel does not vaporize as completely, and hence does not burn as completely. If CH_4 emissions are related to temperature, such that lower combustion and exhaust temperatures increase methane emissions, then one would expect that methane emissions also would be related to the driving cycle, which can affect engine and exhaust temperatures. This expectation is borne out by recent measurements that show that g/mi CH_4 emissions are higher during cold-start mode (which is measured in "bag 1" of the Federal Test Procedure, or FTP) than during other driving modes (measured in "bag 2" and "bag 3" of the FTP), and higher over the whole FTP drive cycle than over a high-speed, high-power cycle called the REP05 (Auto/Oil, 1996) . Because of deficiencies in the MOBILE emissions model, discussed next, these two "drive-cycle" effects -- higher emissions in FTP bag-1 than in other bags, and higher emissions over the FTP than the REP05 cycle -- suggest that MOBILE's estimates of methane emissions might be in error.

One deficiency in the MOBILE model is that the model overestimates average trip lengths and hence underestimates the average fraction of time spent in the cold-start mode, when emissions are highest (German, 1995; U.S. EPA, 1995d) . Because of this, MOBILE tends to underestimate drive-cycle CH_4 emissions. But the MOBILE model also in effect assumes that vehicles drive slower and accelerate less rapidly than they actually do (Ross, et al., 1995) . Because of this, MOBILE tends to overestimate CH_4 emissions, which as noted above are lower in high-speed, high-power driving. Thus, these two effects tend to offset one another, and the net effect is unclear.

It is worth noting that data on the fuel economy of the vehicles in Table F-6 (not shown in Table F-6) indicate that CH_4 emissions are not proportional to fuel consumption. This is not surprising, because as discussed above tailpipe emissions in general are not proportional to fuel consumption.

On the basis of the data of Table F-6, we estimate CH_4 emissions for Tier 0 and Tier 1 gasoline LDAs. As with N_2O emissions from gasoline LDVs, CH_4 emissions also seem to increase somewhat as a function of catalyst age. However, there are few data for high-mileage LDVs, particularly for Tier 1 LDAs and LDTs, and this makes the estimation of deterioration rates difficult. When regression analyses are performed on the available data, emission trend lines slope upward, but with very low associated coefficient of determination (r-squared) values. Given the general lack of data on CH_4 emissions from high-mileage vehicles, we are reluctant to base emission factors on such regression analysis. Instead, we prefer to calculate average emission rates based on the data in Table F-6, as well as to estimate approximate emission trends with increasing catalyst age for Tier 1 vehicles. Based on the data shown in Table F-6, average CH_4 emissions from Tier 0 LDAs are approximately 0.043 g/mi, and average CH_4 emissions from Tier 1 LDAs are approximately 0.019 g/mi.

These average emission rates compare to IPCC and EPA values of 0.05 g/mi for Tier 1 LDAs (see Table F-3), meaning that they indicate somewhat lower emissions than the EPA estimates. We note that while the average emissions estimate for Tier 0 LDAs is based on emissions tests from a range of different vehicle types, the estimate for Tier 1 vehicles is based on two sets of recent data that encompass tests on only two vehicle types: the Ford Crown Victoria and the Mercury Marquis. Emissions tests on a broader array of Tier 1 vehicle types are needed to determine whether Tier 1 LDA CH_4 emissions really are consistently as low as about 0.02 g / mi, as shown in the recent tests documented in Table F-6, or if at least some vehicle types produce levels of emissions closer to the 0.05 g / mi estimated by the EPA.

Given the likely increase in emissions with catalyst age, these average emission rates may therefore underestimate emissions from high-mileage vehicles. Thus, we also estimate an approximate emissions function for Tier 1 LDAs, as our "best guess" estimate. Once again, additional emissions data will be necessary to better substantiate an emissions function for CH_4 emissions from Tier 1 LDAs. The emissions function for CH_4 emissions from Tier 1 LDAs is as follows:

$$EM_{\mathrm{T1}} = ZM_{\mathrm{T1}} + DA \cdot \frac{MI}{1000} \qquad \text{eq. F-9}$$

where:

EM_{T1} = CH_4 emissions from Tier 1 gasoline LDAs (g / mi)
ZM_{T1} = zero-mile CH_4 emissions (0.01 g / mi)
DA = the deterioration rate in emissions with vehicle mile (0.0002 g / mi per 1000 miles)
MI = total mileage on the vehicle (miles)

Similarly, we estimate average CH_4 emissions for Tier 0 and Tier 1 gasoline LDTs, also on the basis of data in Table F-6. The average CH_4 emissions from Tier 0 LDTs are approximately 0.087 g / mi, and average CH_4 emissions from Tier 1 LDTs are approximately 0.049 g / mi. These emission values compare with the EPA estimated value of 0.06 g / mi for Tier 1 LDTs (see Table F-3). Once again, these emissions estimates may somewhat underestimate emissions from high-mileage LDTs due to the possible increase in emissions with catalyst age. Thus, we also estimate an approximate emissions function for Tier 1 LDTs, as our "best guess" estimate. This function is as follows:

$$EM_{\mathrm{T1}} = ZM_{\mathrm{T1}} + DA \cdot \frac{MI}{1000} \qquad \text{eq. F-10}$$

where:

EM_{T1} = CH_4 emissions from Tier 1 gasoline LDTs (g / mi)

ZM_{T1} = zero-mile CH_4 emissions (0.03 g / mi)
DA = the deterioration rate in emissions with vehicle mile (0.0004 g / mi per 1000 miles)
MI = total mileage on the vehicle (miles)

Figure F-3 plots representative CH_4 emission data for LDV passenger cars and trucks, and shows the average emission values for Tier 0 vehicles and "best guess" emissions functions for Tier 1 vehicles, along with the EPA / IPCC recommended values.

3.1.2 CH_4 emissions from natural-gas LDVs

Because CH_4 is the primary component of natural gas, one would expect that vehicles using natural gas would emit considerably more CH_4 than gasoline LDVs. The data of Table F-6 confirm this, showing that CH_4 emissions from natural-gas vehicles (NGVs) range from 0.6 to 4 g / mi for dual-fuel vehicles (which carry and use two fuels, gasoline and natural gas), and between 0.13 and 3 g / mi for dedicated vehicles (which carry and use only natural gas).

Most of the NGVs of Table F-6 are retrofitted or rebuilt gasoline vehicles. Only some of the vehicles (three 1992 Dodge 5.2 liter V8 vans, eight 1996 Ford Crown Victoria vehicles, a 1995 Dodge Ram van, and a 1994 GMC Pickup) were completely designed and built for maximum performance and lowest emissions on natural gas (Battelle, 1995; GRI, 1998) . The much lower emissions of these optimized vehicles, relative to older NGVs and similar model but non-optimized NGV vehicles, suggest that CH_4 emissions from future, advanced NGVs will likely be under 0.5 g / mi for new vehicles, and perhaps around 1.0 g / mi for vehicles with some catalyst age. The need to meet relatively tight NMHC standards, such as the “ultra-low-emission-vehicle” (ULEV) standard promulgated by the California Air Resources Board (*California Code of Regulations*, Title 13, Section 1960.1) also may reduce CH_4 emissions somewhat, although the need to meet tight NO_X standards might require a fuel-rich air / fuel mixture (to allow the reduction catalyst to reduce NO_X emissions), which would tend to increase emissions of unburned fuel.

The cleanest NGVs tested to date have exceptionally low emissions. Methane emissions from the 1992 Dodge vans averaged 0.44 g / mi averaged over three vehicles, and as low as 0.28 g / mi in one test (Battelle, 1995) . The 1995 Dodge van and 1994 GMC pickup had similar emission levels, in the 0.4 to 0.5 g / mi range. The relatively new 1996 Ford Crown Victoria had even lower emissions of 0.134 g / mi when tested over the FTP-75 test procedure, but seven other 1996 Crown Victoria vehicles, with an average of about 60,000 miles of use, had substantially higher emissions, averaging 0.595 g / mi (GRI, 1998; NREL, 1998) .

Methane emissions from NGVs, like methane emissions from gasoline vehicles, increase with the age of the catalyst. This is best shown by the Battelle (1995) data from tests of nine 1992 CNG vans from three manufacturers. This is one of the few controlled studies with repeated tests of the same vehicles at different mileage intervals, and the data collected show a consistent increase in emissions from 5,000 to 15,000 miles and from 15,000 to 25,000 miles. The increase in emissions with catalyst age is also apparent from test data for new and used Ford Crown Victoria NGVs, as discussed above. Unfortunately, no data are available yet regarding emissions at very high mileage.

Whereas ambient temperature does influence CH_4 emissions from gasoline LDVs, it does not strongly influence CH_4 emissions from NGVs (Gabele, et al., 1990a) , mainly because CH_4 is a gas at all ambient temperatures and hence does not have to be vaporized -- a process that is dependent on temperature. Nevertheless, the recent tests by the Auto/Oil Program (1996) show that CH_4 emissions from NGVs depend on the drive cycle, in the same way as do CH_4 emissions from gasoline vehicles. CH_4 emissions are somewhat higher in "bag 1" of the FTP than in the other bags, and considerably higher over the whole FTP cycle than over the high-speed, high-power REP05 cycle (Table F-6).

One might expect that CH_4 emissions from NGVs would be related to the methane content of the natural gas. However, tests by the Auto/Oil Program (1996) suggest that there is no strong relationship between CH_4 content and CH_4 emissions:

Methane content of natural gas	86%	90%	94%	97%
Methane emissions from vehicles (REP05 cycle/FTP cycle)	0.47/0.91	0.50/0.93	0.48/0.96	0.49/0.92

With regard to the potential for abating CH_4 emissions from NGVs with exhaust catalysts, palladium/alumina catalysts would appear to be the most active. However, traces of sulfur in the exhaust of even 1 ppm can severely reduce the oxidation activity for all alkanes, and especially for methane (GRI, 1997b) .

In summary, the data of Table F-6, and considerations discussed above, suggest that CH_4 emissions from NGVs, like CH_4 emissions from gasoline vehicles, decrease with model year (later models emit less) and increase with vehicle mileage, and generally are about an order of magnitude higher than CH_4 emissions from gasoline vehicles of similar technology and age. The data in Table F-6 show that CH_4 emissions from NGV passenger cars are about 4 to 10 times the CH_4 emissions from Tier 0 gasoline passenger cars, and perhaps 5 to 40 times the CH_4 emissions from Tier 1 gasoline passenger cars. Based on the average emissions of Tier 1 gasoline and CNG LDAs, it is reasonable to assume that CH_4 emissions from CNG LDAs are about 20 times the emissions of Tier 1 gasoline LDAs. CH_4 emissions from NGV LDTs are about 5-10 times the emissions from comparable gasoline LDTs. Emissions from uncontrolled NGVs appear to be about 10 times emissions from uncontrolled gasoline vehicles.

3.1.3 CH_4 emissions from methanol LDVs

Methanol LDVs vehicles definitely emit less CH_4 than do comparable gasoline vehicles. For example, Table F-6 shows that dedicated methanol vehicles generally emit less CH_4 than do dedicated gasoline vehicles of the same model. Also, CH_4 emissions from "flexible-fuel vehicles" (FFVs), which can use any mixture of gasoline and methanol, tend to decrease when the gasoline content of the fuel mixture is decreased (Ford Motor Company, 1988a; Williams, et al., 1990; Gabele, 1990b; CARB, 1991) . Furthermore, the upper end of reported CH_4 emissions from methanol LDVs is not as high as the upper end for gasoline LDVs. Taken together, the data suggest that dedicated M100 vehicles emit about half as much CH_4 as dedicated gasoline vehicles, and M85 vehicles (which use a mixture of 85% methanol and 15% gasoline) about two-thirds as much. Data plots of emissions of methanol dedicated and dual fuel LDVs as a function of catalyst age show slowly rising emissions with increased age, but with very few data points from older vehicles. Based on these data, it is reasonable to assume that CH_4 emissions from gasoline / methanol mixtures are equal to the M100 emission rate (which appears to be about 50% of the gasoline emission rate) multiplied by the methanol fraction, plus the gasoline emission rate multiplied by the gasoline fraction of the mixture. (The IPCC [1997] estimate in Table F-3 is consistent with this assumption.)

3.1.4 CH_4 emissions from ethanol LDVs

There have been only a handful of recent emission tests of late-model ethanol, LPG, and hydrogen vehicles. The California Air Resources Board (CARB) (1991) has tested one of its Crown Victoria FFVs -- which are designed to run on any mixture of alcohol and gasoline, but are optimized for *methanol* and gasoline -- on 85% and 95% ethanol (Table F-6). As shown, the FFV emitted a relatively large amount of CH_4 when it was run on ethanol -- about 2-3 times more CH_4 on E85 than on M85, and about 30% more than on indolene. However, as noted above, the vehicle was not designed to burn ethanol, and CARB is not confident of the results.

Kelly, et al. (1996b) report on FTP tests of 21 1992 / 1993 Chevrolet Lumina variable-fuel ethanol vehicles. As in the CARB results, CH_4 emissions increased with ethanol content, such that CH_4 emissions with 50% ethanol were 37% higher than CH_4 emissions on pure RFG, and that CH_4 emissions with 85% ethanol were 67% higher than with RFG and 24% higher than with 50% ethanol (Table F-6). The CH_4 emission rate when operating on pure RFG was similar to the emission rate from a standard, single-fuel Lumina, of about 0.04 g / mile of CH_4. These results are significant because they support that CARB test of a single vehicle, and show that FFVs running on ethanol have very different CH_4 emission characteristics than FFVs running on methanol. The results show that CH_4 emissions tend to increase with ethanol content, which is the reverse of what occurs with methanol.

Baudino, et al. (1993) also tested Luminas optimized for ethanol fuel, and got similar results: on indolene, the vehicles emitted 0.033 g/mi CH_4; on E85, the vehicles emitted 0.052 g/mi (Table F-6).Thus, the few available data are consistent, and suggest that ethanol vehicles emit more methane than comparable gasoline vehicles.

Based on these data, we assume that CH_4 emissions from gasoline/ethanol mixtures are equal to the E100 emission rate (which appears to be about 150% of the gasoline emission rate) multiplied by the ethanol fraction, plus the gasoline emission rate multiplied by the gasoline fraction of the mixture.

3.1.5 CH_4 emissions from liquefied petroleum gas (LPG) LDVs

The data of Table F-6 indicate that LPG vehicles emit about as much CH_4 as gasoline vehicles. This is not entirely unexpected, because the species profile of HC emissions from any vehicle tends to reflect the HC composition of the fuel,[8] and LPG is mostly propane (C_3H_8), which is similar in many respects to the main components of gasoline (e.g., octane, C_8H_{18}). Although LPG, like natural gas, is a gaseous fuel, it does not contain CH_4, and hence would not be expected to produce as much CH_4 as does natural gas (which typically is at least 90% CH_4). Similarly, LPG is not an alcohol and does not have the properties responsible for the relatively low CH_4 emissions of methanol vehicles or the relatively high CH_4 emissions of ethanol vehicles. Thus, it is probably reasonable to assume that most LPG vehicles emit as much methane as comparable gasoline vehicles. The IPCC (1997) CH_4 emission factor for LPG LDVs, shown in Table F-3, is consistent with this assumption.

3.1.6 CH_4 emissions from hydrogen LDVs

Theoretically, hydrogen internal-combustion engine vehicles could emit small amounts of CH_4 from the combustion of lubricating oil. However, CARB (1989) found no CH_4 in the oil-related HCs from a hydrogen truck, even though the vehicle burned an unexpectedly large amount of oil. Therefore, one probably can assume that hydrogen vehicles do not emit any CH_4.

3.1.7 CH_4 emissions from heavy-duty vehicles (HDVs)

Table F-6 shows the results of several emission tests of gasoline and diesel-fueled HDVs, and compares the results with the CH_4 emissions estimated by MOBILE5. Compared to the test results reported here, the MOBILE5 data indicate

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[8] The main component of the organic emission from any vehicle is unburned fuel: gasoline components from gasoline vehicles, methane from NGVs, methanol from methanol vehicles, propane from LPG vehicles, and so on.

higher CH_4 emissions from diesel HDVs, and lower CH_4 emissions from gasoline HDVs. We believe that the EPA's MOBILE5 estimates are based on more vehicle tests than are cited in Table F-6 here. According to Guensler, et al. (1991) , in general the heavy-duty emission factors in EPA's MOBILE model are based on tests of 9 in-use medium heavy-duty diesel engines, 13 in-use heavy-heavy-duty diesel engines, and 18 heavy-duty gasoline engines, in 1983 and 1984 (p. 40). However, we do not know whether the EPA actually measured methane emissions from all or even any of these engines; it is possible that they applied assumed CH_4 fractions to measured total hydrocarbon emissions. Beyond that, Guensler, et al. (1991) point out various deficiencies in the EPA's 1983/1984 testing program. Finally, it is not clear how the EPA (1999) derived estimates of CH_4 emissions for advanced heavy-duty vehicles (Table F-3), given that the available test data pertain to engines of a relatively old vintage.

Clearly, we need more test data. In the meantime, we tentatively favor the EPA/MOBILE5 estimates over the few test data in Table F-6.

Table F-6 also shows CH_4 emissions from methanol and natural-gas HDVs. In order to meet the stringent 1994 NO_X emission standard for HDVs, natural-gas HDVs either will use lean-burn engines, or three-way catalytic converters. According to the few tests conducted so far (Table F-6), such vehicles probably will emit between 2 and 6 g/mi CH_4 (the IPCC [1997] suggests a similar range [Table F-3]), or something on the order of 30 times the CH_4 emissions from advanced diesel HDVs.

Unfortunately, the few CH_4 emissions data for methanol HDVs cover a wide range, from near zero to over 1 g/mi. Because there are so few emissions results for methanol HDVs, and because what few there are do not agree, it might be better to ignore the data and assume instead that, just as methanol LDVs emit less CH_4 than gasoline LDVs, methanol HDVs emit less CH_4 than do gasoline HDVs, or about as much as diesel HDVs.

The one recent test of an advanced LPG HDV reported very low emissions, on the order of those from an advanced diesel vehicle (Table F-6), which does not seem unreasonable. Therefore, the IPCC (1997) estimate (Table F-3) might be too high.

There are no data on CH_4 emissions from ethanol or hydrogen HDVs. In the absence of data, it might be reasonable to assume that the ratio of CH_4 emissions from ethanol HDVs to CH_4 emissions from methanol HDVs is the same as the ratio for LDVs: namely, about 3.0. We adopt this assumption here. Hydrogen HDVs presumably do not emit appreciable amounts of CH_4.

3.2 CH_4 EMISSIONS FROM POWER PLANTS

See section 2.2.3 and Table F-5. Our estimates for CH_4 emissions from power plants are also based on the EPA AP-42 database.

4 CONCLUSIONS

Despite the international concern about emissions of GHGs from motor vehicles and power plants, and the Kyoto Protocol establishing non-binding emission reduction targets, there still are significant knowledge gaps regarding emissions of important non-CO_2 GHGs from motor vehicle and stationary power plant fuelcycles. These non-CO_2 GHGs include most notably CH_4 and N_2O, which are released in significant quantities through combustion and (in the case of N_2O) emission-control processes. Unlike emissions of CO_2, emissions of CH_4 and N_2O are determined by the complex interaction of fuels, combustion system types, control technologies, and combustion and catalyst temperatures, and they cannot be simply estimated based on fuel carbon or fuel/air nitrogen compositions. This Appendix has compiled a database of CH_4 and N_2O emission measurements from conventional gasoline and alternative-fuel LDAs, LDTs, and HDVs, as well as utility boilers and combustion turbines. Analyses of these emission data have then been used to supplement the CH_4 and N_2O emissions estimates and guidelines reported by the EPA and IPCC.

Major findings include that emissions of N_2O from conventional gasoline LDAs and LDTs that are equipped with Tier 1 emission controls are much lower than currently suggested by the IPCC guidelines (IPCC, 1997) , but are perhaps somewhat higher than suggested in recent EPA revisions, particularly for high-mileage vehicles. On the other hand, recent (although limited) data suggest that emissions of CH_4 from Tier 1 gasoline LDAs may be somewhat lower than currently estimated by EPA. Emissions of CH_4 and N_2O from diesel vehicles and AFVs vary considerably depending on fuel type. Diesel vehicles appear to emit the same order of magnitude of N_2O as gasoline vehicles, although the data (though sparse) indicate the possibility of somewhat lower emissions for diesel vehicles. Advanced CNG vehicles appear to emit about 75% as much N_2O as gasoline vehicles, while the available data suggest that ethanol and LPG vehicles emit similar levels of N_2O as gasoline vehicles. CNG LDAs emit about an order of magnitude more CH_4 than early 1990s vintage Tier 0 gasoline LDAs, and about 20 times more CH_4 than Tier 1 gasoline LDAs. Meanwhile, CNG LDTs emit about 6 to 10 times more CH_4 than comparable gasoline LDTs. Interestingly, methanol LDVs emit considerably less CH_4 than gasoline LDVs, with M100 vehicles emitting about half as much, and flexible-fuel methanol vehicles emitting somewhere in between 50% and 100% of the gasoline LDV rate depending on the fuel mix. On the other hand, ethanol LDVs emit about 50% more CH_4 than gasoline vehicles. LPG LDVs appear to emit about the same amount of CH_4 as gasoline vehicles, and hydrogen vehicles emit no CH_4. Finally, emissions of CH_4 from methanol, CNG, LPG, ethanol, and hydrogen HDVs appear to be about 50%, 3000%, 100%, 300%, and 0% those of diesel HDVs, respectively.

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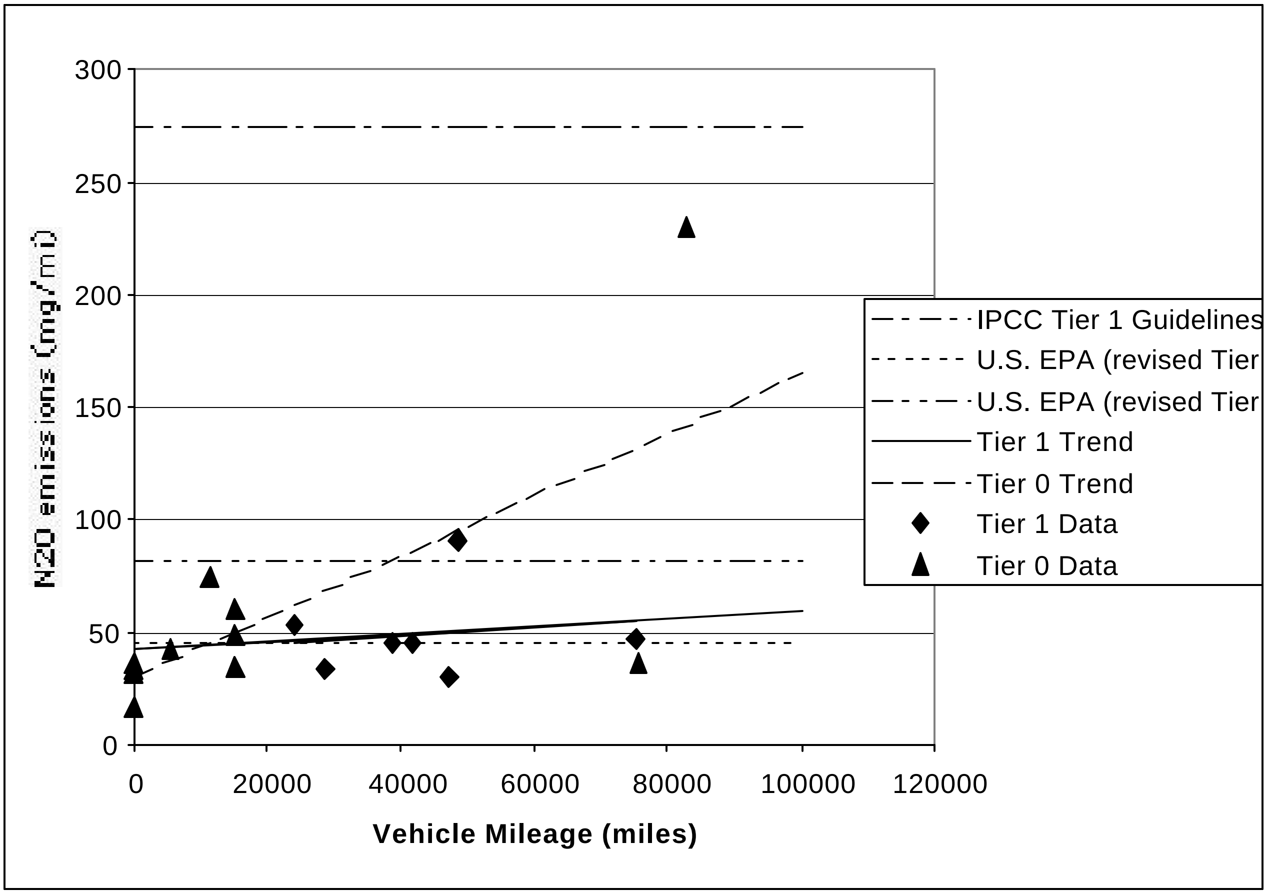
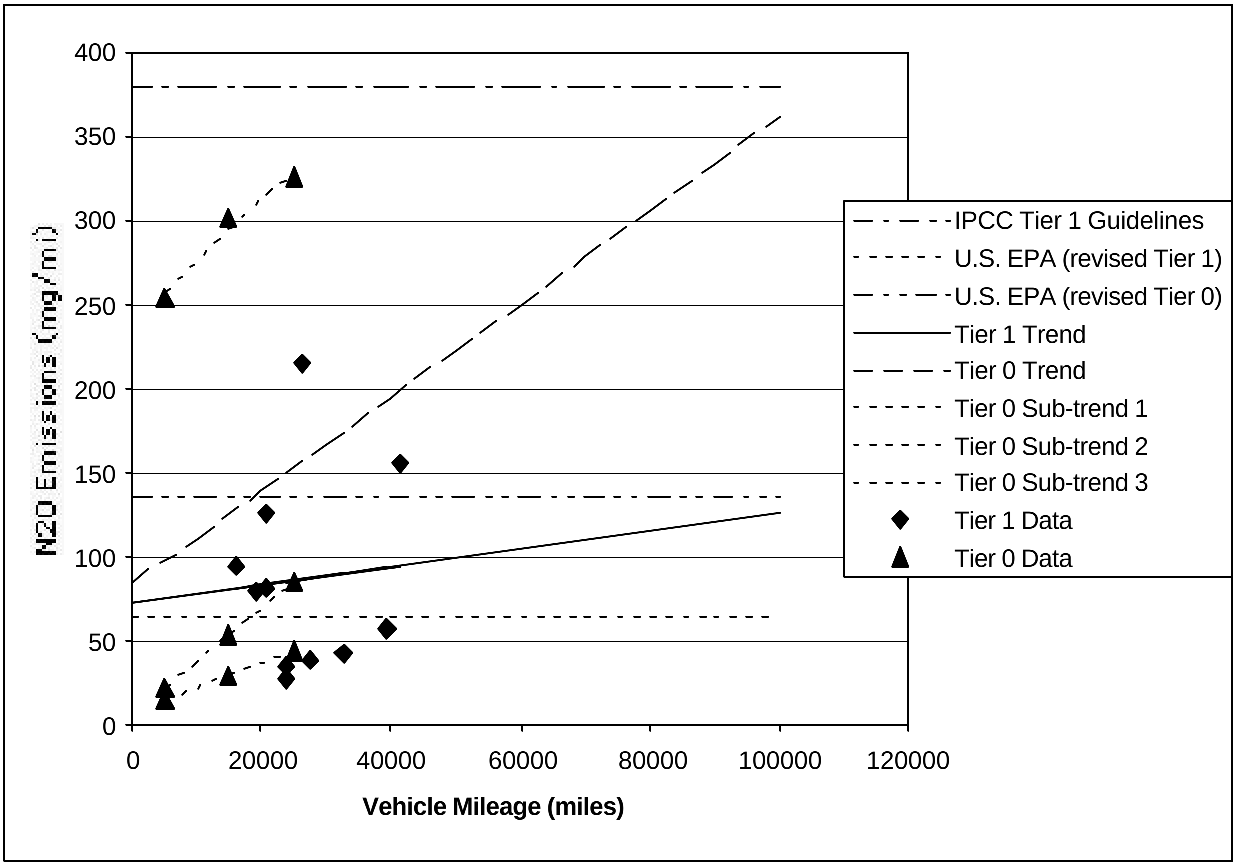
FIGURE F-1: GASOLINE LIGHT-DUTY PASSENGER AUTOMOBILE N_2O EMISSION DATA



Note:

TIER 0 VEHICLES ARE ASSUMED TO BE THOSE WITH VINTAGES PRIOR TO 1995, WHILE TIER 1 VEHICLES ARE MODEL YEAR 1995 AND LATER, BASED ON THE EPA ESTIMATE THAT 80% OF MODEL YEAR 1995 VEHICLES WERE EQUIPPED WITH TIER 1 EMISSION CONTROLS (MICHAELS, 1998).

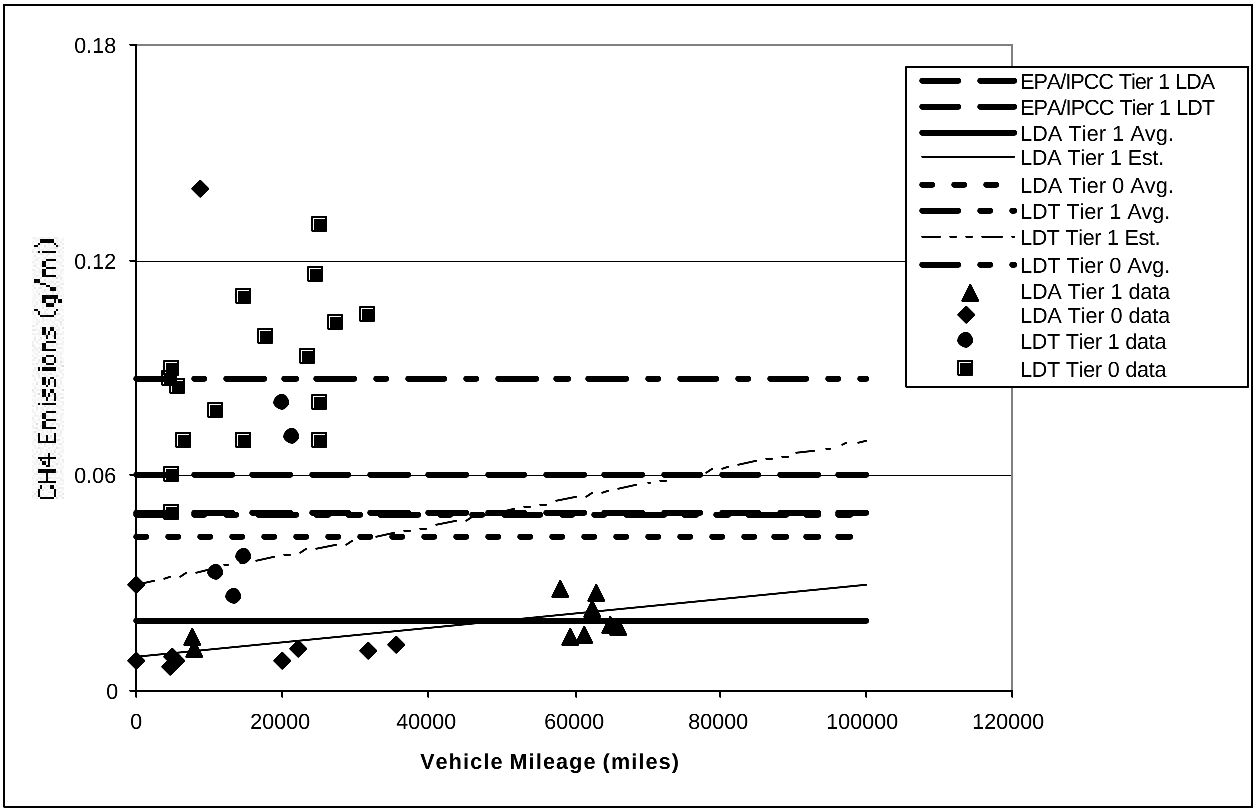
Figure F-2: Gasoline Light-Duty Truck N_2O Emission Data and Trends



Note:

TIER 0 VEHICLES ARE ASSUMED TO BE THOSE WITH VINTAGES PRIOR TO 1995, WHILE TIER 1 VEHICLES ARE MODEL YEAR 1995 AND LATER, BASED ON THE EPA ESTIMATE THAT 80% OF MODEL YEAR 1995 VEHICLES WERE EQUIPPED WITH TIER 1 EMISSION CONTROLS (MICHAELS, 1998).

FIGURE F-3: GASOLINE LIGHT-DUTY PASSENGER AUTOMOBILE AND TRUCK CH4 EMISSION DATA AND ESTIMATED EMISSION FACTORS



Note:

Tier 0 vehicles are assumed to be those with vintages prior to 1995, while Tier 1 vehicles are model year 1995 and later, based on the EPA estimate that 80% of model year 1995 vehicles were equipped with Tier 1 emission controls (Michaels, 1998).

TABLE F-1: THE PERCENTAGE CONTRIBUTION OF INDIVIDUAL GHGS TO LIFECYCLE CO_2 -EQUIVALENT EMISSIONS FOR ALTERNATIVE TRANSPORTATION FUELS FOR LIGHT-DUTY VEHICLES

A. INTERNAL-COMBUSTION-ENGINE VEHICLES USING FOSSIL FUELS

Fuel --> *Feedstock -->*	**conv. gasoline** *oil*	**reform. gasoline** *oil*	**low-S Diesel** *oil*	**85% MeOH** *NG*	**comp. NG** *NG*	**comp. H_2** *NG*	**LPG** *NG, oil*
vehicular CO_2	46%	47%	53%	42%	40%	1%	50%
lifecycle CO_2	76%	77%	82%	77%	67%	92%	76%
CH_4	3%	3%	3%	5%	17%	7%	4%
N2O	12%	12%	10%	12%	11%	1%	14%
CO	9%	7%	6%	6%	6%	2%	6%
NMOC	1%	1%	0%	1%	0%	0%	0%
NO_2	-1%	-1%	-2%	-1%	-1%	-1%	-1%
SO_2	-1%	-1%	-1%	-1%	-1%	-2%	-1%
PM	-0%	-0%	-1%	-0%	-0%	-0%	-0%
HFC-134a	1%	1%	2%	1%	1%	2%	1%

B. INTERNAL-COMBUSTION-ENGINE VEHICLES USING BIOMASS-DERIVED FUELS

Fuel --> *Feedstock -->*	**90% EtOH** *corn*	**90% EtOH** *wood, grass*	**85% MeOH** *wood*
vehicular CO_2	6%	14%	23%
lifecycle CO_2	66%	43%	58%
CH_4	5%	7%	4%
N2O	24%	36%	26%
CO	6%	14%	13%
NMOC	1%	2%	1%
NO_2	-1%	-2%	-2%
SO_2	-2%	-2%	-2%

PM	-1%	-1%	-1%
HFC-134a	1%	3%	2%

C. ELECTRIC-DRIVE VEHICLES (BATTERY-POWERED AND FUEL-CELL POWERED)

Power source --> Fuel --> *Feedstock -->*	**Battery** grid power *64% coal*	**Fuel cell** 100 % MeOH *NG*	**Fuel cell** comp. H_2 *water/nuclear*	**Fuel cell** comp. H_2 *NG*
vehicular CO_2	0%	44%	1%	1%
lifecycle CO_2	99%	92%	94%	92%
CH_4	4%	6%	4%	6%
N2O	1%	1%	1%	1%
CO	0%	0%	0%	0%
NMOC	0%	0%	0%	0%
NO_2	-0%	-0%	-1%	-0%
SO_2	-4%	-1%	-3%	-2%
PM	-0%	-0%	-1%	-0%
HFC-134a	1%	2%	5%	3%

Source: The lifecycle energy use and emissions model documented in Delucchi (1999) . The model uses the CH_4 and N_2O emission factors presented here.

Notes: conv. = conventional; reform = reformulated; low-S = low-sulfur; MeOH = methanol, comp. = compressed; NG = natural gas, H_2 = hydrogen, LPG = liquefied petroleum gas; EtOH = ethanol.

For each GHG *i*, the percentage shown is equal to: $\frac{LCE_i \cdot CEF_i}{\sum_i LCE_i \cdot CEF_i} \cdot 100$,

where LCE_i = lifecycle (or, in the case of "vehicular CO_2", vehicular) emissions of GHG *i* and CEFi = the CO_2-equivalency factor for GHG *i*.

The "lifecycle" here includes all emissions from the vehicles, upstream fuel and feedstock production and distribution activities, the manufacture of vehicles, and the lifecycle of materials used in vehicles. Lifecycle CO_2 includes vehicular CO_2, plus CO_2 from other stages of the vehicle and fuel lifecycle. The "CO_2 equivalent" mass of a non-CO_2 GHG is the mass amount of the gas that would have the same time-integrated effect, on climate or on some measure of the welfare impact of climate change, as would one mass unit of CO_2 emitted at the same time.

The CO_2-equivalency factors used in the model runs that produced these results are:

NMHC	CH4	CO	N2O	NO2	SO2	PM	HFC-134a
4.0+CO_2	20.1	4.06	355.0	-2.4	-14.2	-5.2	2,000

In the case of NMHCs, the “CO_2” in “4.0 +CO_2” is the effect of oxidizing the NMHC to CO_2, which varies with the C content of the NMHCs. Note that in the case of CO, almost half of the CEF is due to the relatively rapid oxidation of CO to CO_2.

TABLE F-2: N_2O EMISSIONS FROM MOTOR VEHICLES

Type of vehicle	Emission control equipment	Odometer (miles)	N_2O Emissions (mg / mi)	Ratio, NO_x / N_2O[a]	Reference
Gasoline LDV	*no cat. converter*				
NS	none	NS	0[b]	NS	Pierotti and Rasmussen (1976)
NS	none	NS	20	NS	Robertson (1991)
1974 Chevy Impala	none	62,700	16 (15)[c]	179	Warner-Selph & Harvey (1990)
1977 AMC Pacer	none; AP	NS	5[d]	400	Urban and Garbe (1979)
1977 Volvo	lean operation	200	0	--	Bradow and Stump (1987)
NS	unspecified cat.	NS	up to 21	NS	Pierotti and Rasmussen (1976)
NS	unspecified cat.	NS	200	NS	Robertson (1991)
	ox. cat.				
1977 Mercury Marquis	OC, AP	81,700	10 (13)[c]	167	Warner-Selph & Harvey (1990)
1978 Olds Cutlass	OC, EGR	NS	18[d]	45	Urban and Garbe (1979)
1978 Olds Cutlass	OC	NS	23[e]	NS	EPA unpublished data
1977 Olds Cutlass	OC	NS	47[e]	NS	EPA unpublished data
1978 Malibu	OC, AP	NS	8[d]	86	Urban and Garbe (1979)
1978 Malibu	OC, no AP	NS	66[d]	18	Urban and Garbe (1979)
1978 Granada	OC, AP	NS	34[d]	58	Urban and Garbe (1979)
1978 Mustang	OC, no AP	NS	43	38	Urban and Garbe (1979)
NS 660 cc	OC, EGR	300	1.4, 0.3, 1.0, 0.3, 0.3[f]	NS	Sasaki and Kameoka (1992)
	3-wy plus ox. cat.				
8 1978 and 2 1979 cars	7 w / OC, 3 w / 3WY	38,000-68,000	74 / 57[g]	28 / 29[g]	Smith and Carey (1982)
1978 Ford Pinto	3WY, OC, EGR	low	12-128[h]	9-29[h]	Urban and Garbe (1980)
1978 Ford Pinto	3WY, OC, EGR	0-15,000	34-35[i]	19-26[i]	Smith and Black (1980)
1979 Mercury Marquis	3WY, OC, EGR	low	17-141[h]	6-238[h]	Urban and Garbe (1980)
1979 Mercury Marquis	3WY, OC, EGR	0-15,000	36-60[i]	27-35[i]	Smith and Black (1980)
1980 Chevrolet Caprice	3WY, OC, EGR	low	63, 69[j]	16, 17[j]	Braddock (1981)
1978 Ford Pinto	3WY, OC, EGR	low	84, 84[j]	12, 11[j]	Braddock (1981)
1977 Volvo	3WY	200	64[k]	14	Bradow and Stump (1987)
1978 Saab	3WY	low	5-37	10-31	Urban and Garbe (1980)
1978 Saab	3WY	0-15,000	16-35[i]	10-34	Smith and Black (1980)

TABLE F-2 (CONT'D): N_2O EMISSIONS FROM MOTOR VEHICLES

Type of vehicle	Emission control equipment	Odometer (miles)	N_2O Emissions (mg/mi)	Ratio, NO_x / N_2O[a]	Reference
Gasoline LDV (cont'd)	*3-wy cat.*				
1978 Pontiac Sunbird	3WY, EGR	low	6-44	21-44	Urban and Garbe (1980)
1978 Pontiac Sunbird	3WY, EGR	0-15,000	32-48[i]	20-40	Smith and Black (1980)
1980 Buick Century	3WY, EGR	low	101, 137[j]	8, 10[j]	Braddock (1981)
1980 Lincoln Continental	3WY, EGR	low	72, 37[j]	24, 38[j]	Braddock (1981)
1983 Buick Regal	3WY, AP	83,000	231 (239)[c]	8	Warner-Selph & Harvey (1990)
2.2 liter Renault	3WY, EFI	NS	50-55[l]	NS	Prigent and De Soete (1989)
1989-1990 U. S. cars	3WY	NS	13-78 [42][m]	5-29[n]	Dasch (1992)
1990 Chevy Lumina van	3WY	NS	89	NS	Dasch (1992)
1990 Chevy Lumina	3WY, TBI	5,300	42 (45)[c]	6	Warner-Selph & Harvey (1990)
1990 Ford Probe	3WY, MPFI	11,500	74 (86)[c]	15	Warner-Selph & Harvey (1990)
Ford Taurus	3WY	low	46	24	Ford (1988b)
Ford Topaz	3WY	low	43	27	Ford (1988b)
1986 Ford Tempo	3 WY, EGR, EVP	47,643	211, 136[o]	NS	Ballantyne, et al. (1994)
1986 Oldsmobile Calais	3 WY, EGR, EVP	50,108	120, n/a[o]	NS	Ballantyne, et al. (1994)
1987 Chrysler Lebaron	3 WY, EGR, EVP	73,440	192, 66[o]	NS	Ballantyne, et al. (1994)
1987 Toyota Pickup	3 WY, EGR, EVP	35,034	93, 30[o]	NS	Ballantyne, et al. (1994)
1988 Ford Taurus Wag.	3 WY, EGR, EVP	57,484	114, 53[o]	NS	Ballantyne, et al. (1994)
1989 Honda Accord	3 WY, EGR, EVP	54,108	72, 44[o]	NS	Ballantyne, et al. (1994)
1989 Honda Civic	3 WY, EVP	66,697	88, 46[o]	NS	Ballantyne, et al. (1994)
1989 Volkswagen GTI	3 WY, EVP	58,522	85, 66[o]	NS	Ballantyne, et al. (1994)
1990 Mazda 323	3 WY, EVP	21,095	126, 46[o]	NS	Ballantyne, et al. (1994)
1992 Honda Civic LX	3 WY, EVP	2,403	75, 25[o]	NS	Ballantyne, et al. (1994)
1992 Suzuki Swift	3 WY, EVP	2,299	21, 11[o]	NS	Ballantyne, et al. (1994)
1992 Pontiac Sunbird	3 WY, EGR, EVP	2,290	126, 65[o]	NS	Ballantyne, et al. (1994)
1992 Chevrolet Pickup	3 WY, EGR, EVP	2,367	264, 47[o]	NS	Ballantyne, et al. (1994)
1992 Chevrolet Astro	3 WY, EGR, EVP	2,251	209, 70[o]	NS	Ballantyne, et al. (1994)
1989 Volvo 740	3 WY	NS	72, 13, 271[p]	NS	Jobson, et al. (1994)
NS 1800 cc	3 WY, EGR	600	26.7, 22.1, 47.0, 13.8, 2.7[q]	NS	Sasaki and Kameoka (1992)
NS 1500 cc	3 WY, EGR	20,000	34.3, 7.4, 54.7, 20.6, 12.2[q]	NS	Sasaki and Kameoka (1992)
NS 2000 cc	3 WY, EGR	32,000	197, 116.6, 77.9, 17.4, 25.1[q]	NS	Sasaki and Kameoka (1992)

TABLE F-2 (CONT'D): N_2O EMISSIONS FROM MOTOR VEHICLES

Type of vehicle	Emission control equipment	Odometer (miles)	N_2O Emissions (mg/mi)	Ratio, NO_x / N_2O[a]	Reference
Gasoline LDV (cont'd)	*3-wy cat.*				
3 1992 Ford 4.9 liter vans	3 WY	5,000, 15,000, 25,000	14, 30, 44[r] (RFG)	NS	Battelle (1995)
3 1992 Dodge 5.2 liter vans	3 WY	5,000, 15,000, 25,000	22, 54, 86[r] (RFG)	NS	Battelle (1995)
3 1992 Chevy 4.3 liter vans	3 WY	5,000, 15,000, 25,000	254, 301, 326[r] (RFG)	NS	Battelle (1995)
1386 California vehicles	3 WY, EGR	NS	mean 19.3 (16.6 to 32.8)	0.56	Jimenez, et al. (1997)
12 Tier 1 passenger vehicles	3 WY	24,000-75,000	mean 46.3 (24 to 124)	NS	Michaels (1998)
5 Tier 1 light trucks/SUVs	3 WY	16,000-75,000	mean 108.9 (80 to 167)	NS	Michaels (1998)
24 Euro 1 LDVs	3 WY	30,000 –110,000	43	see note y	Feijen-Jeurissen et al. (2001) [y]
6 Euro 2 LDVs	3 WY	5,000 – 50,000	21	see note y	Feijen-Jeurissen et al. (2001) [y]
2 Euro 3 LDVs	3 WY	2,000 – 15,000	11	see note y	Feijen-Jeurissen et al. (2001) [y]
Effect of Catalyst Age on Gasoline LDVs					
NS 2200 cc	3 WY	new	37.7, 26.6, 15.7[s]	3.5, 0.94, 2.87[s]	De Soete (1993)
NS 2200 cc	3 WY	15,000	77.5, 104.5, 69.2[s]	3.25, 1.28, 1.54[s]	De Soete (1993)
NS 2300 cc	3 WY	new	392.8, 265.6[t]	NS	Lindskog (1989) in De Soete (1993)
NS 2300 cc	3 WY	9,300	502.3, 397.7[t]	NS	Lindskog (1989) in De Soete (1993)
NS 2100 cc	3 WY	new	34.9, 22.2[u]	NS	Prigent and De Soete (1992)
NS 2100 cc	3 WY	150 hours	52.8, 32.2[u]	NS	Prigent and De Soete (1992)
3 1992 Ford 4.9 liter vans	3 WY	5,000, 15,000, 25,000	14, 30, 44[r]	NS	Battelle (1995)
3 1992 Dodge 5.2 liter vans	3 WY	5,000, 15,000, 25,000	22, 54, 86[r]	NS	Battelle (1995)
3 1992 Chevy 5.7 liter vans	3 WY	5,000, 15,000, 25,000	254, 301, 326[r]	NS	Battelle (1995)
32 gasoline LDVs	3 WY	see Feijen-Jeurissen et al. (2001) above	see Feijen-Jeurissen et al. (2001) above	see note y	Feijen-Jeurissen et al. (2001) [y]
Diesel LDV					
1.9 liter Citroen	NS	NS	50-58[l]	NS	Prigent and De Soete (1989)
NS	NS	NS	50	NS	Robertson (1991)
NS 1800 cc	EGR	17,500	10.5, 10.8, 13.7, 10.8, 7.9[q]	NS	Sasaki and Kameoka (1992)
1 unspecified LDV	no cat.	NS	0	see note y	Feijen-Jeurissen et al. (2001) [y]
2 Euro 1 LDVs	OC	NS	3	see note y	Feijen-Jeurissen et al. (2001) [y]
4 Euro 2 LDVs	OC	NS	7	see note y	Feijen-Jeurissen et al. (2001) [y]
2 Euro 3 LDVs	OC	NS	13	see note y	Feijen-Jeurissen et al. (2001) [y]

TABLE F-2 (CONT'D): N_2O EMISSIONS FROM MOTOR VEHICLES

Type of vehicle	Emission control equipment	Odometer (miles)	N_2O Emissions (mg / mi)	Ratio, NO_x / N_2O[a]	Reference
Gasoline HDV					
1979 Ford	NS	11,000	96	133	Dietzmann, et al. (1981)
1979 Int'l Harvester	NS	15,000	48	272	Dietzmann, et al. (1981)
Diesel HDV					
1977 DDT 2-stroke	NS	60,000	68-85[v]	494-571	Dietzmann, et al. (1980)
1979 Caterpillar 4-stroke	NS	7,000	22-35[v]	545-785	Dietzmann, et al. (1980)
1979 Mack 4-stroke	NS	69,000	50-58[v]	500-565	Dietzmann, et al. (1980)
1979 Cummins 4-stroke	NS	26,000	35-47[v]	517-773	Dietzmann, et al. (1980)
Diesel truck engine	NS	NS	2000	NS	Robertson (1991)
Flexible-fuel methanol/gasoline vehicles					
Ford Escort-1	3 WY	4,000[w]	61 M100; 105 M85 / I; 99 I	4.3 M100; 4.1 M85 / I; 4.4 I	Ford (1988a)[x]
Ford Escort-2	3 WY	50,000[w]	119 M100; 111 M85 / I; 147 I	4.6 M100; 5.9 M85 / I; 5.6 I	Ford (1988a)[x]
Ford Escort-2	no catalyst	NS	-3 M100; -2 M85 / I	--	Ford (1988a)[x]
Ford Crown Victoria-1	3 WY	0 / 8,000 / 16,000[w]	6 / 17 / 16 M85 / G	90 / 34 / 53 M85 / G	Ford (1988a)[x]
Ford Crown Victoria-2	no catalyst	NS	0 M100; 3 M85 / G	--	Ford (1988a)[x]
Ford Crown Victoria-2	3 WY	3,000[w]	14 M100; 12 M85 / G	37 M100; 59 M85 / G	Ford (1988a)[x]
3 Ford 4.9 liter 6-cyl. vans	3 WY	5,000, 15,000, 25,000	61 M85, 65 M85, 70 M85[r]	NS	Battelle (1995)
CNG vehicles					
3 1992 Ford 4.9 liter vans	3 WY	5,000, 15,000, 25,000	26, 36, 44[r]	NS	Battelle (1995)
3 1992 Dodge 5.2 liter vans	3 WY, CNG opt.	5,000, 15,000, 25,000	9, 24, 39[r]	NS	Battelle (1995)
3 1992 Chevy 5.7 liter vans	3 WY, Engelhard CNG	5,000, 15,000, 25,000	47, 50, 54[r]	NS	Battelle (1995)
Propane vehicles					
3 1992 Ford 4.9 liter vans	3 WY	5,000, 15,000, 25,000	99, 74, 68[r]	NS	Battelle (1995)
3 1992 Chevy 5.7 liter vans	3 WY	5,000, 15,000, 25,000	69, 87, 101[r]	NS	Battelle (1995)
3 Euro 2 LDVs	3 WY	NS	20	NS	Feijen-Jeurissen et al. (2001)[y]

Notes: See Dasch (1992) for a similar table.

EPA testing protocol requires that all vehicular emissions be corrected for background concentration (i.e., that the ambient concentration be subtracted from total measured emissions). We therefore assume that all reported emissions are net of background, unless it is clear that they are not (as in Weiss & Craig, Pierotti & Rasmussen). LDV = light-duty vehicle; HDV = heavy-duty vehicle; 3WY = three-way catalytic converter; OC = oxidation catalytic converter; AP = air pump; EGR = exhaust gas recirculation; EFI = electronic fuel injection; TBI = throttle-body fuel injection; MPFI = multipoint fuel injection; NS = not specified; FTP = Federal Test Procedure; NYCC = New York City Cycle; HFET = Highway Fuel Economy Test; RFG = reformulated gasoline.

All LDVs except those not identified (noted as “NS” under “vehicle” column) were tested over the FTP. All HDVs except the “diesel truck engine” (Robertson, 1991) were tested over the chassis version of the 1983 Heavy Duty Transient Cycle (HDTC).

^ The same vehicle as the one immediately above (i.e., not a different vehicle of the same model). Vehicles of the same description but not marked with “^” are the same model but different vehicles.

[a] This is the ratio of g/mi emissions, not the ratio of ppm, except as noted.

[b] A gross concentration of 0.1-0.2 ppm was measured in the exhaust. The background N_2O is 0.3 ppm.

[c] The emission value in parentheses is the result when the vehicle was run on gasoline containing 16.4% MTBE.

[d] The mg/mi figure shown is the reported average of several tests with the emission control system functioning properly. Disabling the EGR increased N_2O emissions by a factor of 1.5-3.0. (Prigent and de Soete [1989] also found that N_2O emissions increased when EGR was disconnected). Other malfunctions were relatively unimportant.

[e] The emission rates reported in test cycles other than the FTP were similar to the FTP emission rates.

[f] The five numbers represent, respectively, results for the Japanese "11-step" driving cycle (with cold start), the Japanese "10-step" driving cycle, urban driving cycle at 10 km/hr, urban driving cycle at 20 km/hr, and urban driving cycle at 50 km/hr. Tests were performed using a chassis dynamometer, sample collection in a heated (393 K) steel tank, and gas chromatography analysis at 543 K.

g The first number is the average for the 10 cars as received; the second number is the average after the cars were tuned up. The 10 vehicles were: a 1978 Buick Regal (OC, EGR), 2 1979 Mercury Marquis (3WY, EGR, AP); a 1978 Ford Granada (OC, EGR, AP); a 1978 Volvo 245 DL (3WY); a 1978 Oldsmobile Cutlass (OC); a 1978 Chevrolet Malibu (OC, EGR, AP); a 1978 Chevrolet Monte Carlo (OC, EGR); a 1978 Ford Fiesta (OC, EGR, AP); and a 1978 Chrysler New Yorker (OC, EGR). The Malibu was the only vehicle that had been previously tested (Urban and Garbe, 1979; the model with the air pump [AP]); most of the others were the same model as previously tested vehicles (see entries in this table), but not the same actual vehicle.

h The vehicles were tested with a variety of malfunctions, including: a disabled oxygen sensor, disabled EGR, 12% misfire, and high oil consumption. The very high emissions from the Pinto and the Marquis were the result of a disabled EGR system.

i The first emission number is at zero miles; the second is at 15,000 miles. Emissions were consistently higher in the NYCC and lower in the HFET than in the FTP. N_2O emissions did not vary appreciably with the type of gasoline.

j The first number is the result when the FTP was run at normal temperature (78° or 81° F); the second number is the result at low temperature (55°, 58°, 60°, or 61° F). Laurikko and Nylund (1993) found that N_2O emissions were higher in a +20°C cold-start test (FTP) than in a -20°C cold-start test.

k When the oxygen sensor was disconnected, N2O emissions disappeared.

l The SO_2 content of the gas was reported to be 12 ppm for undiluted samples, and ten times less for diluted samples. This is well below what appears to be the concentration that actuates artifactual N_2O formation.

m The number in the brackets is the average value.

n This range includes the NO_x/N_2O ratios measured for the 1978 Pontiac Sunbird, the 1978 Saab, the 1980 Lincoln Continental, and the 1980 Buick Century.

o The first number is the composite result from the three phases of the Urban Dynamometer Driving Schedule (UDDS). The second number is the result from the Highway Fuel Consumption Test (HWFCT). These emission tests were conducted in Canada using a fuel with a high sulfur content of approximately 700 ppm. If tested with a lower sulfur content fuel, the measured emissions would probably be lower.

p The three numbers represent, respectively, tests taken over the FTP75 cycle with no catalyst, a new catalyst, and a "severely deteriorated" catalyst.

q The five numbers represent, respectively, results for the Japanese "11-step" driving cycle (with cold start), the Japanese "10-step" driving cycle, urban driving cycle at 10 km/hr, urban driving cycle at 20 km/hr, and urban driving cycle at 50 km/hr. Tests were performed using a chassis dynamometer, sample collection in a heated (393 K) steel tank, and gas chromatography analysis at 543 K.

r Tests were performed using an on-line FTIR analyzer. The three numbers correspond to the three vehicle mileage figures listed, and each number is a mean value for tests of three different vans by each manufacturer. Note that the Dodge CNG vans are among the first to use a catalyst system designed and optimized for CNG vehicles.

s The three numbers represent, respectively, tests performed on the ECE 15-04 Driving Cycle (with cold start), the European Urban Driving Cycle (EUDC), and the ECE Driving Cycle. As in note a, the ratio of NOx to N_20 is based on mass and not ppm.

t The emissions data have been converted from units of grams of N_20 per kilometer. The first number represents emissions based on the Swedish driving cycle with cold start, and the second number represents emissions on the Swedish driving cycle with hot start.

u The emissions data have been converted from units of grams of N_20 per kilometer. The first number represents emissions based on the ECE 15 (cold start) driving cycle and the second number represents emissions based on the EUDC.

v Emissions varied with the quality of the diesel fuel used.

w Miles accumulated on the catalytic converter.

x Ford reported detailed speculated FTIR data for two flexible-fuel Escorts and two flexible-fuel Crown Victoria, at different methanol/gasoline mixtures, and with different catalysts and catalyst ages. The Escort was tested on indolene, the Crown Victoria on gasoline.

y Emissions were measured over a European test cycle, the ECE-15, which consists of 800 seconds of urban driving after a cold start (the UDC, or Urban Drive Cycle) and then 400 seconds of higher-power driving (the EUDC, or Extra-Urban Drive Cycle). The official ECE-15 emissions are a weighted average (composite) of the emissions from the two portions; formally, they are equal to: (UDC x D1 + EUDC x D2)/TD, where UDC is g/km emissions in the UDC portion, D1 is the length of the UDC, EUCD is g/km emissions in the EUDC portion, D2 is the length of the EUCD, and TD is the total distance (D1+D2 = 11 km). Feijen-Jeurissen et al. (2001) report the composite ECE-15 emissions for the Euro 1, Euro 2, and Euro 3 gasoline vehicles, but for the LPG and diesel LDVs they report only the UDC and EUCD results. For these vehicles, we estimate the composite ECE-15 values by assuming that D1=4.2 km and D2=6.8 km, values which are consistent with the data of Feijen-Jeurissen et al. (2001).

Euro 1, Euro 2, and Euro 3 are progressively more stringent emission standard established by the European Community; they correspond roughly to 1983, 1994, and 2004 Federal emission standards in the U. S.

Feijen-Jeurissen et al. (2001) plot N_20 versus mileage and N_20 versus NOx, but do not analyze the relationships formally or provide the actual data values. The plots show a great deal of scatter, but perhaps indicate a very weak positive correlation between N_20 and mileage and N_20 and NOx.

TABLE F-3: SUMMARY OF IPCC, EPA, AND AUTHOR N_2O AND CH_4 EMISSION FACTORS FOR U.S. MOTOR VEHICLES (G/MI)

	N_2O			CH_4		
	IPCC (1997)[a]	*EPA (1999)*	*this paper*[b]	*IPCC (1997)*[a,c]	*EPA (1999)*[c]	*this paper*[b]
gasoline LDAs, Tier 1[d]	0.27	0.05	0.05[e]	0.05	0.05	0.024[e]
gasoline LDAs, no controls	0.03	0.02	0-0.02	0.21-0.23	0.22	use EPA
gasoline LDTs, Tier 1[d]	0.38	0.06	0.11[f]	0.05-0.06	0.06	0.058[f]
gasoline LDTs, no controls	0.04	0.02	use LDA	0.21-0.23	0.22	use EPA
gasoline HDVs, Tier 0[g]	0.98	0.28	n.e.[h]	0.11-0.13	0.12	use EPA
gasoline HDVs, no controls	0.09	0.04	0.05-0.1[h]	0.40-0.47	0.43	use EPA
diesel LDAs	0.01-0.02	0.02[i]	0.01-0.06	0.02	0.02	use EPA
diesel LDTs	0.04-0.10	0.03[i]	use LDA	0.02	0.02	use EPA
diesel HDVs	0.04-0.05	0.05[i]	0.02-0.09	0.06-0.10	0.06-0.10[j]	use EPA
methanol LDVs, advanced	n.e.	n.e.	1.0·GLDV	0.03	n.e.	0.5·GLDV
methanol HDVs, advanced	n.e.	n.e.	1.0·GHDV	0.16	n.e.	1.0·DHDV
CNG LDVs, advanced	n.e.	n.e.	0.75·GLDV	1.1	n.e.	20·GLDV[k]
CNG LDVs, no controls	n.e.	n.e.	n.e.	5.6	n.e.	10·GLDV
CNG HDVs, advanced	n.e.	n.e.	0.75·GHDV	4.8-6.4[l]	n.e.	30·DHDV
CNG HDVs, no controls	n.e.	n.e.	n.e.	16	n.e.	n.e.
LPG LDVs, advanced	n.e.	n.e.	1.0·GLDV	0.05	n.e.	1.0·GLDV
LPG LDVs, no controls	n.e.	n.e.	1.0·GLDV	0.29	n.e.	1.0·GLDV
LPG HDVs, advanced	n.e.	n.e.	1.0·GHDV	0.24[m]	n.e.	1.0·DHDV
LPG HDVs, no controls	n.e.	n.e.	n.e.	0.64[m]	n.e.	n.e.
ethanol LDVs	n.e.	n.e.	1.0·GLDV	n.e.	n.e.	1.5·GLDV
ethanol HDVs	n.e.	n.e.	n.e.	n.e.	n.e.	3.0·DHDV
hydrogen LDVs	n.e.	n.e.	n.e.	n.e.	n.e.	0.0
hydrogen HDVs	n.e.	n.e.	n.e.	n.e.	n.e.	0.0

Notes:

LDA = light-duty passenger auto; LDT = light-duty truck; LDV = light-duty vehicle (passenger auto or truck) HDV = heavy-duty vehicle; GLDV = gasoline light-duty vehicle; GHDV = gasoline heavy-duty vehicle; DHDV = diesel heavy-duty vehicle; CNG = compressed natural gas; LPG = liquefied petroleum gases; n.e. = not estimated. Note that for alternative-fuel vehicles, we do not distinguish LDT from LDA emissions factors, and instead use a generic LDV emission factor.

[a] The IPCC reports emission factors for Spring or Fall, Summer, Winter, and year-round average. We show their year-round average factors.

[b] Our estimates our based on our analysis of the data complied in Tables F-2 and F-6, as discussed in the text.

[c] Both the IPCC and the EPA get their CH_4 emission factors from the EPA's MOBILE5 model; hence the agreement between the two sources.

[d] The EPA (Michaels, 1998) defines "Tier 1"controls to be "advanced" 3-way catalysts, as distinguished from "early" 3-way catalysts, which are identified as Tier-0 controls. The IPCC (1997) distinguishes between "early 3-way catalyst" and "3-way catalyst control," for gasoline LDAs and LDTs. We assume that the IPCC "3-way catalyst control" corresponds to the EPA's "Tier 1", and that the IPCC "early 3-way catalyst" corresponds to the EPA's "Tier 0".

[e] From equation F-5 (N_2O), with MI = 70,000 mile (about the midlife of a light-duty passenger auto), or equation F-10 (CH_4).

[f] From equation F-6 (N_2O), with MI = 75,000 mile (about the midlife of a light-duty truck), or equation F-11 (CH_4).

[g] In the EPA inventory, "Tier 0" is the most stringent control category for gasoline HDVs. In the IPCC inventory, "3-way catalyst control" is the most stringent control category for gasoline HDVs.

[h] The two gasoline HDVs reported in Table F-2 are of the1979 model year, which presumably was more like an uncontrolled vehicle than a Tier-0 vehicle.

[i] For diesel vehicles, the EPA adopts the IPCC's recommended emission factors for European vehicles, and not the recommendations for U. S. diesels (which are shown in this table), on the grounds that Europeans have "greater experience" with diesels (Michaels, 1998). However, as discussed in the text here, the IPCC (1997) apparently

has *no* data on N_2O emissions from European diesel HDVs or European diesel LDTs, and very limited data (probably the same data summarized in Table F-2 here) on emissions from European diesel LDAs (see p. 1.79 of IPCC). Moreover, the IPCC does have data on N_2O emissions from U. S. diesel HDVs -- the same data summarized in Table F-2 here -- and uses those data to estimate the U. S. diesel emission factors shown here. Our own approach, as discussed in the text, is to use all of the available data.

[j] The EPA (1999) uses 0.06 g / mi for "advanced" vehicles, 0.08 g / mi for "moderately" controlled vehicles, and 0.10 g / mi for "uncontrolled" vehicles. These estimates appear to be lower than the estimates from MOBILE4 and MOBILE5 (see Table F-6).

[k] But see the text and Table F-6 for details.

[l] The lower figure is for an advanced stoichiometric engine (to be compared with gasoline, according to the IPCC); the higher figure is for an advanced lean-burn engine (to be compared with diesel, according to the IPCC).

[m] The IPCC factors are for a stoichiometric engine, and according to the IPCC are to be “compared with gasoline” (p. 1.87).

TABLE F-4: N_2O EMISSIONS FROM COMBUSTION SYSTEMS

Combustor type	Fuel	Sampling method	Temp. (K)	NO_x (ppm)[a]	N_2O (ppm)	Reference
Coal combustion						
6 full-scale utility boilers	medium-S bituminous coal	on-line GC	NS	386-559	<4	Linak, et al. (1990)
29 kW DF tunnel furnace	4 bituminous coals	on-line GC	NS	553-753	2.2-4.2	Linak, et al. (1990)
Coal furnace	bituminous coal	on-line GC	NS	216-1121	1.28-4.45	Linak, et al. (1990)
7 175-700 MW, LNB	coal (S removed from gas)	tedlar bags, S removed	NS	NS	0.5	Yokoyama, et al. (1991)
171 MW CF drum boiler	bituminous coal, 0.6% S	on-line GC	NS	386	3.3	Ryan and Srivastava (1989)
50 kW coal combustor	coal	on-line IR	NS	2000	30	Ryan and Srivastava (1989)
~450 MW WF boiler	coal	on-line ND IR	NS	625-735	11-16[b]	Sloan and Laird (1990)
490 MW CF boiler, LNB	coal	on-line ND IR	NS	270-300	2-3[b]	Sloan and Laird (1990)
OF utility boiler	coal	on-line ND IR	NS	662-982	2-11	Kokkinos (1990)
TF utility boiler	coal	on-line ND IR	NS	325-498	1	Kokkinos (1990)
IGCC power plant	coal	on-line ND IR	NS	19	1	Kokkinos (1990)
500 MW CF boiler, LNB	coal	on-line IR	NS	NS	2.2-3.0	Laird and Sloan (1993)
500 MW CF boiler, LNB	coal	off-line GC[c]	NS	270-330	0.6-4.0	Laird and Sloan (1993)
500 MW CF boiler	coal	off-line GC[c]	NS	470-530	1.9-7.1	Laird and Sloan (1993)
500 MW CF boiler	coal	on-line IR	NS	470-530	7-13	Laird and Sloan (1993)
500 MW WF boiler	coal	off-line GC[c]	NS	512-538	0.2-1.4	Laird and Sloan (1993)
660 MW OF boiler, LNB	coal	on-line IR	NS	360-420	2.5-7.1	Laird and Sloan (1993)
660 MW OF boiler	coal	on-line IR	NS	640-740	3.7-4.3	Laird and Sloan (1993)
500 MW WF boiler, LNB	coal	off-line GC[c]	NS	390-450	1.6-2.6	Laird and Sloan (1993)
500 MW WF boiler	coal	off-line GC[c]	NS	690-750	4.2-5.4	Laird and Sloan (1993)
500 MW WF boiler, LNB	coal	off-line GC[c]	NS	390-450	0.2-1.2	Laird and Sloan (1993)

TABLE F-4 (CONT'D): N_2O EMISSIONS FROM COMBUSTION SYSTEMS

Combustor type	Fuel	Sampling method	Temp. (K)	NO_x (ppm)[a]	N_2O (ppm)	Reference
Fuel-oil combustion						
FF utility boiler	oil	on-line ND IR	NS	268	1	Kokkinos (1990)
21 156-1000 MW boilers	oil (S removed from gas)	tedlar bags, S removed	NS	NS	0.3	Yokoyama, et al. (1991)
733 kW boiler	#5 fuel oil (236 ppm S in gas)	on-line GC	NS	189 NO	1.3	Linak, et al. (1990)
733 kW boiler	#2 fuel oil (58 ppm S in gas)	on-line GC	NS	105 NO	0.30	Linak, et al. (1990)
588 kW boiler, LNB	#2 fuel oil (130 ppm S in gas)	on-line GC	NS	64 / 536 NO[d]	<0.24 / 0.27[d]	Linak, et al. (1990)
588 kW boiler, LNB	#5 fuel oil (270 ppm S in gas)	on-line GC	NS	60 / 682 NO[d]	0.26 / 0.73[d]	Linak, et al. (1990)
320 MW OF	#6 fuel oil, 3% S	on-line GC	NS	220-480	n.d.-1	Ryan and Srivastava (1989)
3 500 MW WF boilers	oil	off-line GC	NS	550-650	0.4-0.9	Laird and Sloan (1993)
Natural-gas combustion						
FF utility boiler	NG	on-line ND IR	NS	120	2	Kokkinos (1990)
Combustion turbine	NG	on-line ND IR	NS	19	4	Kokkinos (1990)
733 kW boiler	NG (0 ppm S in gas)	on-line GC	NS	62 NO	<0.24	Linak, et al. (1990)
588 kW boiler, LNB	NG (4-6 ppm S in gas)	on-line GC[c]	NS	50 / 638 NO[d]	<0.24 / 0.72[d]	Linak, et al. (1990)
15 175-1000 MW, LNB	LNG (S removed from gas)	tedlar bags, S removed	NS	NS	0.1	Yokoyama, et al. (1991)
35 MW turbine, no water inject.	NG	NS	NS	NS	0.5-1.9	De Soete (1993)
35 MW turbine, water injection	NG	NS	NS	NS	0.75-1.65	De Soete (1993)

TABLE F-4 (CONT'D): N_2O EMISSIONS FROM COMBUSTION SYSTEMS

Combustor type	Fuel	Sampling method	Temp. (K)	NO_x (ppm)[a]	N_2O (ppm)	Reference
Fluidized-bed combustion						
100-kW FBC	coal	on-line IR	NS	NS	100	Ryan and Srivastava (1989)
CFBC	coke	aluminum bags, stored dry	1180	32	124[e]	Amand and Anderson (1989)
CFBC	coke	aluminum bags, stored dry	1073	32	170[e]	Amand and Anderson (1989)
CFBC	NS	on-line ND IR	NS	NS	20-100	Kokkinos (1990)
CFBC	coal	NS	NS	NS	80-315	Makansi (1991)
1 MW CFBC	lignite coal, 0.7% S	on-line ND IR	1125 / 1020	NS	22 / 125[f,b]	Mann, et al. (1992)
1 MW CFBC	bituminous coal, 2.3% S	on-line ND IR	1200 / 1085	NS	50 / 265[f,b]	Mann, et al. (1992)
130 kW PFBC	peat, 0.2% S	on-line IR	1073 / 1123	140 / 175[f]	95 / 37[f]	Lu, et al. (1992)
130 kW PFBC	bituminous coal, 1.2% S	on-line IR	1073 / 1193	70 / 105[f]	59 / 4[f]	Lu, et al. (1992)
FBCC	petroleum	aluminum bags, S removed	923-1033	~400	3-4	Cooper and Emanuelsson (1992)
FBCC	petroleum	aluminum bags, dried	923-1033	~400	12-26	Cooper and Emanulesson (1992)
7 CFBCs 30-160 MW	coal	NS	850-910	NS	20-132	De Soete (1993)
bubbling FBC	coal, 0.4% S	on-line ND IR	1123	200-800	25-90	Shimizu, et al. (1992)
Effect of sulfur and temperature						
Fixed-bed laboratory reactor	graphite, no S	on-line GC	1000 / 1275	1000 / 1000 f	4 / 0[f]	De Soete (1989)
Fixed-bed laboratory reactor	graphite plus $CaSO_4$	on-line GC	1275	700	4	De Soete (1989)
Entrained-flow reactor	peat, 0.14% S	on-line IR	1000 / 1123	710 / 870	~380 / 125[g]	Aho and Rantanen (1989)
1 MW CFBC	lignite coal, 0.7% S	on-line ND IR	1125 / 1020	NS	22 / 125[f,b]	Mann, et al. (1992)
1 MW CFBC	bituminous coal, 2.3% S	on-line ND IR	200 / 1085	NS	50 / 265[f,b]	Mann, et al. (1992)
130 kW PFBC	peat, 0.2% S	on-line IR	1073 / 1123	140 / 175[f]	95 / 37[f]	Lu, et al. (1992)
130 kW PFBC	bituminous coal, 1.2% S	on-line IR	1073 / 1193	70 / 105[f]	59 / 4[f]	Lu, et al. (1992)

TABLE F-4 (CONT'D): N_2O EMISSIONS FROM COMBUSTION SYSTEMS

Combustor type	Fuel	Sampling method	Temp. (K)	NO_x (ppm)[a]	N_2O (ppm)	Reference
Effect of emission controls						
160-kW air-staged burner	oil (S removed from gas)	SS probes, S removed	NS	210 / 280[h]	< 2 / <2[h]	Nimmo, et al. (1991)
588-kW boiler, LNB	#2 fuel oil (130 ppm S in gas)	on-line GC	NS	64 / 536[d]	<0.24 / 0.27[d]	Linak, et al. (1990)
588-kW boiler, LNB	#5 fuel oil (270 ppm S in gas)	on-line GC	NS	60 / 682[d]	0.26 / 0.73[d]	Linak, et al. (1990)
588-kW boiler, LNB	NG (4-6 ppm S in gas)	on-line GC	NS	50 / 638[d]	<0.24 / 0.72[d]	Linak, et al. (1990)
130 kW PFBC w / air staging	peat, 0.2% S	on-line IR	NS	110 / 55[i]	70 / 90[i]	Lu ,et al. (1992)
130 kW PFBC w / air staging	bituminous coal, 1.2% S	on-line IR	NS	70 / 25[i]	59 / 72[i]	Lu, et al. (1992)
130 kW PFBC w / NH_3	peat , 0.2% S	on-line IR	NS	195 / 70[i]	60 / 90[i]	Lu, et al. (1992)
Front-fired boiler w / urea	oil	on-line ND IR	NS	117	23	Kokkinos (1990)
175-MW boiler w / SCR	coal (S removed from gas)	tedlar bag, S removed	NS	NS	1.9 / 1.3[j]	Yokoyama, et al. (1991)
700-MW boiler w / SCR	coal (S removed from gas)	tedlar bag, S removed	NS	NS	1.2 / 0.7[j]	Yokoyama, et al. (1991)
175-MW boiler w / FGD	coal (S removed from gas)	tedlar bag, S removed	NS	NS	1.5 / 1.4[j]	Yokoyama, et al. (1991)
Effect of sample storage:						
29-kW DF tunnel furnace	bituminous coal	SS container wet, 0 / 1 / 4 / 150 hrs	NS	757	~5 / 145 / 155 / 180[k]	Linak, et al. (1990)
29-kW DF tunnel furnace	bituminous coal	SS container dry, 0 / 1 / 4 / 140 hrs	NS	757	~5 / 5 / 5 / 15[k]	Linak, et al. (1990)
165-MW utility boiler	bituminous coal, medium-S	SS container wet, 0 / 1 / 4 / 150 hrs	NS	354	~2 / 35 / 50 / 65[k]	Linak, et al. (1990)
450-MW WF boiler	coal	plastic bag wet, 3 / 8 / 15 days	NS	735 / 725 / 645[b]	53 / 184 / 212[b]	Sloan and Laird (1990)
450-MW WF boiler	coal	plastic bag dry 3 / 15 days	NS	700,720 / 625[b]	12,18 / 15[b]	Sloan and Laird (1990)

Notes:

IGCC= integrated-gasification combined-cycle; LNB = low-NO_x burner; CFBC = circulating fluidized-bed combustor; FBC = fluidized-bed combustor; PFBC = pressurized fluidized-bed combustor; FBCC = fluidized-bed catalytic cracker; LNG = liquefied natural gas; DF = down-fired; TF = tangentially fired; OF = opposite-fired; CF = corner-fired; WF = wall-fired; FF = front-fired; SCR = selective catalytic reduction; S = sulfur; FGD = flue-gas desulfurization; GC = gas chromatograph; IR = infrared spectrometer; ND = non-dispersive; SS = stainless steel; MW= megawatt; ND = none detected; NS = not specified.

See Ryan and Srivastava (1989) for a tabulation of results obtained prior to 1989, and also (U.S. DOE, 1991) , Appendix B.

[a] Reported as NO in Cooper and Emanuelsson (1992); Nimmo et al. (1991); Linak et al. (1990), Aho and Rantanen (1989), and de Soete (1989), and as NO_x in the others.

[b] All gas concentrations were measured at 3% oxygen, dry. In all cases, N_2O emissions measured by on-line IR were between 11 and 17 ppm.

[c] Off-line gas chromatography analyses, using electron capture detection, were conducted using either 5.5 liter Saran (polyvinylidene chloride) or 10 liter polyethylene/aluminum gas sampling bags. GCs were installed on-site, and time from sampling to analysis was less than 10 minutes.

[d] The first emission result is with combustion air staging; the second result is without.

[e] The results were reported as 73 mg-N_2O/MJ-coke and 100 mg-N_2O/MJ-coke, with a conversion factor of 1.7 ppm/(mg/MJ).

[f] The first concentration number corresponds to the first temperature, the second to the second temperature.

[g] The first emission measurement is at the first temperature, the second is at the second temperature. The N_2O concentration was reported at 1073^oK, per 10% CO_2. They also reported the percentage of the nitrogen in the fuel that

was converted to N_2O at 1000, 1073, and 1123^oK. We estimated the N_2O ppm concentration at 1000 and 1123^oK by assuming that the ratio of ppmv concentrations at two temperatures is equal to the ratio of fuel conversion percentages at the same two temperatures.

[h] This is the NO concentration with / without combustion-air staging, with 3% excess oxygen (wet).

[i] The first result is without NH_3 injection or combustion-air staging; the second result is with NH_3 injection or combustion-air staging. Measured at 6% oxygen, dry. The emission results with NH_3 injection are at a 4:1 NH_3:NOx molar ratio; the emission results with combustion-air staging are at a secondary air level of 20 volume percent, and with 25% excess air in the case of peat, and 29% in the case of bituminous coal.

[j] The first number is the concentration before the SCR or FGD inlet; the second number is the concentration at the outlet.

[k] Emission measurements separated by slashes correspond to the different sample storage times (in hours), which also are separated by slashes. NO_x concentration shown is initial concentration. In the wet sample taken from the 29-kW tunnel furnace, the SO_2 concentration declined from 800 ppm at 0 hours to near zero after only 1 hour.

TABLE F-5: CH_4 AND N_2O EMISSION FACTORS FOR UTILITY BOILERS (G/10^6-BTU-FUEL)

	CH_4			N_2O		
	IPCC generic	*AP-42, utilities*	*assumed here*	*IPCC generic*	*AP-42, utilities*	*assumed here*
Coal	1.1	0.2 - 1.4[a]	0.9	1.5	0.7 - 2.1[a]	0.9
Oil	3.2	0.8	0.8	0.6	0.3	0.3
NG	1.1	1.0	1.0	0.1	0.3, 1.0[b]	0.6
wood	32	n.e.	0.04	4.2	n.e.	0.02

Sources: “IPCC generic”: In its “simple” guidelines, the IPCC (1997) uses its judgment to “average” across fuel and boiler varieties and establish generic emission factors for the use of coal, oil, or gas, in what it refers to as the “energy industry,” which includes much more than electric utilities. “AP-42, utilities”: the EPA’s (1998) emission factors specifically for electric-utility boilers. NG = natural gas.

[a] Depends on the type of fuel used and the firing configuration.

[b] The lower figure applies to low-NO_X combustion, the higher to uncontrolled boilers.

TABLE F-6: METHANE EMISSIONS FROM HIGHWAY VEHICLES

Type of vehicle	Emission control equipment	Odometer (miles)	CH_4 emissions (g/mi)	Reference
Gasoline LDVs				
Ford F250 truck (see CNG)*	none	4,000-9,000	0.20	BC Research (1986)
16 1975-'78 passenger cars	various	various	0.19-0.32	Sigsby, et al. (1987)
1978 Olds Cutlass[a]	OC, EGR	NS	0.06-0.08	Urban and Garbe (1979)
Chevy S-10 truck (see CNG)*	OC, EGR	4,000-9,000	0.02	BC Research (1986)
4 1978-'80 passenger cars[b]	3WY, EGR; 2 w / OC	low	0.09-0.39	Braddock (1981)
4 1978-'79 passenger cars[c]	3WY; 2 cars w / OC	low	0.03-0.11 [0.07]	Smith and Black (1980)
30 1979-'82 passenger cars	various	various	0.14-0.18	Sigsby, et al. (1987)
Dodge 600es truck*	3WY	4,000-9,000	0.04	BC Research (1986)
1981 Rabbit (see MeOH car)*	3WY	25,000	0.03	CARB (1985)
1981 Escort (see MeOH car)*	3WY	38,000	0.23	CARB (1985)
1984 Ford Mustang (see MeOH car)*	3WY	100	0.14[d]	Gabele, et al. (1985)
1984 Chev. Cavalier (see MeOH car)*	3WY	4500	0.04[d]	Gabele, et al. (1985)
9 1984-1987 4-cylinder passenger cars	various	3,000-62,000	0.08-0.15[e]	Stump, et al. (1989)
11 1985-1987 4-8 cylinder cars	various	7,000-64,000	0.13-0.20	Stump, et al. (1989)
3 1992 Ford 4.9 liter 6-cyl. vans (see CNG, MeOH, LPG)*	3 WY	5,000, 15,000, 25,000	0.09, 0.11, 0.13[f] (RFG) 0.11, 0.11, 0.12[f] (RF-A)	Battelle (1995)
3 1992 Dodge 5.2 liter V8 vans (see CNG)*	3 WY	5,000, 15,000, 25,000	0.05, 0.07, 0.08[f] (RFG) 0.08, 0.08, 0.08[f] (RF-A)	Battelle (1995)
3 1992 Chevrolet 4.3 liter V6 vans (see CNG, LPG)*	3 WY	5,000, 15,000, 25,000	0.06, 0.07, 0.07[f] (RFG) 0.05, 0.07, 0.08[f] (RF-A)	Battelle (1995)
1992 Chev. pickup, 1993 Ford Crown Victoria, 1992 Dodge wagon (see CNG)*	3 WY (one dual)	5,000 (but 3-WY aged to 50,000)	[0.06] FTP,[0.03] REP (RFG) [0.07] FTP,[0.04]REP (RF-A)	Auto / Oil (1996)
7 1996 Ford Crown Victorias (see CNG)*	3 WY	64,433; 65,909; 63,123; 59,424; 61,443; 62,255; 57, 994	0.0196; 0.0182; 0.0276; 0.0147; 0.0157; 0.0229; 0.0283 [0.021][h]	NREL (1998)
69 1993 Dodge Spirits (see MeOH)*	3 WY	3,455-35,784	[0.0113][h] RFG	Kelly, et al. (1996a)
18 1993 Ford Econoline vans (see MeOH)*	3 WY	4,653-31,911	[0.086][h] RFG	Kelly, et al. (1996a)

TABLE F-6 (CONT'D): METHANE EMISSIONS FROM HIGHWAY VEHICLES

Type of vehicle	Emission control equipment	Odometer (miles)	CH_4 emissions (g/mi)	Reference
Gasoline LDVs (cont'd)				
1996 Ford Crown Victoria (see CNG)*	3 WY	7,600	0.012 RF-A; 0.015 RFG	GRI (1997a)
1996 Mercury Grand Marquis	3 WY	8,200	0.011 RF-A; 0.012 RFG	GRI (1997a)
1995 Dodge Caravan (see CNG)*	3 WY	14,990	0.031 RF-A; 0.037 RFG	GRI (1997a)
1995 Dodge Caravan (see CNG)*	3 WY	10,980	0.030 RF-A; 0.033 RFG	GRI (1997a)
1995 Dodge Ram Van (see CNG)*	3 WY	20,070	0.080 RF-A; 0.080 RFG	GRI (1997a)
1995 Dodge Ram Van (see CNG)*	3 WY	21,660	0.070 RF-A; 0.071 RFG	GRI (1997a)
1995 Dodge Caravan (see CNG)*	cat., EGR	13,596	0.0264 RFG FTP, 0.0219 RFG REP	Black et al. (1998)
pre-1975 model years (MOBILE4)	*none*	*over life of car*	*0.31*	*U.S. EPA* (1991b) [g]
post-1991 model years (MOBILE4)	*3WY*	*over life of car*	*0.05*	*U.S. EPA* (1991b) [g]
gasoline LDV fleet average, 1990-2020 (MOBILE5)	*fleet average in year*	*fleet average*	*0.12-0.04*	*simulation runs of MOBILE5*[h]
Gasoline HDVs				
Ford truck	NS	11,000	2.13	Dietzmann, et al. (1981)
International Harvester truck	NS	15,000	0.28	Dietzmann, et al. (1981)
5 trucks, 1973-1980	NS	35,000-105,000	0.4-1.0	Black, et al. (1984)
pre-1979 model years (MOBILE4)	*NS*	*over life of truck*	*0.67*	*U.S. EPA (1991b)*[g]
1979-1986 model years (MOBILE4)	*NS*	*over life of truck*	*0.31*	*U.S. EPA (1991b)*[g]
post-1986 model years (MOBILE4)	*NS*	*over life of truck*	*0.18*	*U.S. EPA (1991b)*[g]
gasoline HDV, 1990-2020 (MOBILE5)	*fleet average in year*	*fleet average*	*0.28-0.18*	*MOBILE5*[h] *simulation*
Diesel HDVs				
1979 Caterpillar 4-stroke	NS	7,000	0.05	Dietzmann, et al. (1981)
1979 Mack 4-stroke	NS	69,000	~ 0	Dietzmann, et al. (1980)
1979 Cummins 4-stroke	NS	26,000	~ 0	Dietzmann, et al. (1980)
1977 DDT 2-stroke	NS	60,000	~ 0	Dietzmann, et al. (1980)
1992 DDC 6V-92TA DDEC II 2-stroke	NS	NS	1.4 [x]	(Swain, et al., 1998)
pre-1982 model years (MOBILE4)	*NS*	*over life of truck*	*0.15*	*U.S. EPA (1991b)*[g]
1982-1987 model years (MOBILE4)[g]	*NS*	*over life of truck*	*0.12*	*U.S. EPA (1991b)*[g]

TABLE F-6 (CONT'D): METHANE EMISSIONS FROM HIGHWAY VEHICLES

Type of vehicle	Emission control equipment	Odometer (miles)	CH_4 emissions (g/mi)	Reference
Diesel HDVs (Cont'd)				
post-1987 model years (MOBILE4)	*NS*	*over life of truck*	*0.10*	*U.S. EPA (1991b)*[g]
diesel HDV, 1990-2020 (MOBILE5)	*fleet average in year*	*fleet average*	*0.12-0.10*	*MOBILE5*[h] *simulation*
Natural gas dual-fuel LDVs				
Ford F250 truck	none	4,000-9,000	1.8-3.0[i]CNG; 0.20 G	BC Research (1986)
13 1977-1981 passenger cars	NS	NS	0.60-3.13 [1.44] CNG 0.02-0.18 [0.07] G	Aerospace (1982)[j]
1986 Chevrolet C30 van	OC, AP	120,000	7.31	Gabele, et al. (1990b)
1980 Diplomat	OC, EGR, AP	low	1.18 CNG; 0.11 I; 0.09 I	Peninga (1981)[k]
1979 Impala	OC, EGR, AP	low	0.67 CNG; 0.06 I; 0.06 I	Peninga (1981)[k]
Chevy S-10 truck	OC, EGR	4,000-9,000	1.7-2.5[i] CNG; 0.02 G	BC Research (1986)
Dodge 600es truck	3-WY	4,000-9,000	0.6-1.4[i] CNG; 0.02 G	BC Research (1986)
1985 Ford Ranger	3WY	NS	2.19-4.38	Overby & Regdon (1987)
1984 GM Delta 88	3WY, EGR	high	2.37-2.46[l] CNG; 0.08 G	Bruetsch (1988)
1986 Mercury Marquis	3WY?	NS	2.63-3.59	NGV Coalition (1989)
1986 Buick Park Avenue	3WY?	25,000	1.80	CARB (1989)
1987 Ford Crown Victoria	3WY, EGR	low	3.03-3.55[l] CNG; 0.11 G	Bruetsch (1988)
1987 GM Celebrity	3WY, EGR	low	1.41-1.50[l] CNG; 0.02 G	Bruetsch (1988)
1989 Buick LeSabre	3WY, EGR	2,500	1.51 CNG; 0.013 I	CARB (1991)
1990 Ford Taurus	3WY, EGR	1,500	1.82 CNG; 0.04 I	CARB (1991)
1990 Dodge Dynasty	3WY, EGR	4,100	1.75 CNG; 2.11 CH_4; 0.05 I	CARB (1991)
1991 Ford Taurus (Impco mixer)	3WY?	NS	1.23	CARB (1992)
1991 Ford Taurus (S & S mixer)	3WY?	NS	0.81	CARB (1992)
1990 Chevrolet Astrovan (truck)	3WY, EGR	11,000	2.08	CARB (1992)
1994 GMC 1500 Pickup	3 WY	4,750	0.52	GRI (1995)
Natural gas dedicated LDV:				
1983 Ford 3.8l V-6	none	low	0.9-2.5[m]	Swain, et al. (1983)
1984 Ford Ranger Pickup	OC, EGR	low	1.06	Adams (1985)

TABLE F-6 (CONT'D): METHANE EMISSIONS FROM HIGHWAY VEHICLES

Type of vehicle	Emission control equipment	Odometer (miles)	CH_4 emissions (g/mi)	Reference
Natural gas dedicated LDV: (cont'd)				
1984 Ford Ranger Pickup	OC, EGR	NS	1.17-1.31[l]	Bruetsch (1988)
1989 Dodge Ram Van	3WY / none[l]	4,000	1.47 / 1.49[m]	Gabele, et al. (1990a)
3 1992 Ford 4.9 liter 6-cyl. vans	3 WY	5,000; 15,000; 25,000	1.78; 2.64; 3.34[f]	Battelle (1995)
3 1992 Dodge 5.2 liter V8 vans	3 WY, CNG optimized	5,000; 15,000; 25,000	0.44; 0.74; 1.0[f]	Battelle (1995)
3 1992 Chevrolet 5.7 liter V8 vans	3WY, Engelhard CNG	5,000; 15,000; 25,000	1.69; 2.58; 3.29[f]	Battelle (1995)
1992 Chev. pickup, 1993 Ford Crown Victoria, 1992 Dodge wagon	3WY (one dual)	5,000 (but 3 WY aged to 50,000)	[0.92] FTP, [0.49] REP (CG1) [0.91] FTP, [0.47] REP (CG4) [avg. of 3 vehicles]	Auto / Oil (1996)
7 1996 Ford Crown Victorias	3 WY	63,035; 62,917; 60,246; 59,421; 58,664; 59,130; 56,924	0.854; 0.469; 0.405; 0.605; 0.470; 0.479; 0.887 [0.595][h]	NREL (1998)
1996 Ford Crown Victoria	3WY	low	0.134	GRI (1998)
1995 Dodge Ram Van	3WY	low	0.395	GRI (1998)
2 1996 Ford Crown Victorias	3WY	4,100; 6,000	0.124; 0.134	GRI (1997a)
2 1995 Dodge Caravans	3WY	5,590; 4,150	0.106; 0.072	GRI (1997a)
1994 Dodge Ram Van	3WY	24,570	0.434	GRI (1997a)
1996 Dodge Ram Van	3WY	3,000	0.284	GRI (1997a)
1994 Dodge Caravan	cat., EGR	5,030	0.1025 FTP, 0.0679 REP	Black et al. (1998)
Natural gas dual-fuel MDVs:				
1989 Ford Club Wagon	CC, EGR / air	13,000	2.81	CARB (1991)
1990 Ford F-350 XLT	CC, EGR / air	800	0.27 I	CARB (1991)
Natural gas HDVs:				
Diesel dual-fuel pilot	NS	NS	27.2[o]	BC Research (1987)
GMC 454 CID V-8 bus engine	3WY	low	0.6; 2.4[p]	Jones, et al. (1988)

TABLE F-6 (CONT'D): METHANE EMISSIONS FROM HIGHWAY VEHICLES

Type of vehicle	Emission control equipment	Odometer (miles)	CH_4 emissions (g/mi)	Reference
Natural gas HDVs: (Cont'd)				
GMC 454 CID V-8 bus engine	none	low	6.4[q]	Alson, et al. (1989)
Cummins L-10 lean-burn engine	none	NS	4.0[r]	Lawson (1988)
1992 DDC 6V-92TA DDEC II 2-stroke (high-pressure DI)	NS	NS	6.5[x]	Douville, et al. (1998)
Methanol dual-fuel LDVs:				
Ford Crown Victoria	no catalyst	NS	0.039 M100; 0.72 M85 / G	Ford (1988a)
Ford Crown Victoria	3WY	3,000 on catalyst	0.037 M100; 0.031 M85 / G	Ford (1988a)
Ford Escort	no catalyst	NS	0.031 M100; 0.034 M85 / I	Ford (1988a)
Ford Escort	3WY	5,000 on catalyst	0.020 M100; 0.025 M85 / I; 0.037 I	Ford (1988a)
7 1987 Ford Crown Victorias	3WY	0- 16,000	0.02-0.06 [0.04] M85 / G; 0.05-0.10 [0.07] M50 / 1; 0.08-0.15 [0.10] I	CARB (1988)
1987 FFV Ford Crown Victoria	2-CC, 2-UF, EGR	22,000	0.023 M100; 0.046M85 / I; 0.116 I; 0.145 E85 / I; 0.171 E95 / I	CARB (1991)
1987 FFV Ford Crown Victoria	2-CC, 2-UF, EGR	43,700	0.056 M85 / I; 0.139 E85 / I; 0.110 I	CARB (1991)
1987 FFV Ford Crown Victoria	2-CC, 2-UF, EGR	15,000	0.049 M85 / I; 0.084 M25 / I; 0.086 I	CARB (1991)
1987 FFV Ford Crown Victoria	2-CC, 2-UF, EGR	61,000	0.079 M85 / I; 0.0192 I	CARB (1991)
1988 VFV Chevrolet Corsica	3WY	4,000	0.003 M100; M50 / I	CARB (1988)
1988 VFV Chevrolet Corsica	3WY-HC	2,300	0.014 M85 / US	CARB (1991)
1988 VFV Chevrolet Corsica	3WY	4,500	0.010 M100; 0.029 M50 / I; 0.031 I	Gabele (1990b) [s]
2.5-liter GM VFV	3-WY?	NS	0.0024 M100; 0.036 G	Williams, et al. (1990)
1989 FFV Toyota Corolla	3WY, EGR	4,700-11,300	0.049 M85 / I; 0.183 I	CARB (1991)
1988 FFV Nissan Stanza	3WY, EGR	15,700	0.023 M85 / US; 0.027 US	CARB (1991)
1989 VFV Chevrolet Corsica	3WY, EGR	21,000	0.050 M85 / I; 0.064 M50 / I; 0.072 I	CARB (1991)
1990 GTMV Plymouth Voyager	3WY	1,900-3,200	0.028 M85 / US; 0.079 US	CARB (1991)
1990 FFV Plymouth Voyager	3WY	2,000-2,500	0.014 M85 / US; 0.046 US	CARB (1991)
1981 Rabbit	HCC[t]	NS	0.01 M100	Blair & Piotrowski (1988)
2 1981 VW Rabbits	3WY	4,500	0.01-0.02 M95	CARB (1985)
2 1981 VW Rabbits	3WY	22,000	0.02-0.03 M90	CARB (1985)
2 1981 VW Rabbits	3WY	56,000- 66,000	0.03-0.13 M85 / G	CARB (1988)

TABLE F-6 (CONT'D): METHANE EMISSIONS FROM HIGHWAY VEHICLES

Type of vehicle	Emission control equipment	Odometer (miles)	CH$_4$ emissions (g/mi)	Reference
Methanol dual fuel LDVs: (cont'd)				
2 1981 Ford Escort Wagons	3WY	5,000- 50,000	0.07 M90-95	CARB (1985)
1981 Ford Escort Wagon	3WY	85,000-115,000	0.09 M90	CARB (1985)
1982 Chevrolet Citation	3WY	30,000-40,000	0.03 M85-90	CARB (1985)
8 1983 Ford Escort Wagons	3WY	0- 20,000	0.01-0.14 [0.06][u] M90	CARB (1985)
1983 Pontiac Phoenix	3WY	2,400	0.02 M88	CARB (1983)
1983 Ford Escort	3WY	1,500	0.06 M90	Gabele, et al. (1985)
unspecified developmental vehicle	NS	NS	0.076 M100	Williams, et al. (1990)
1985 Toyota Camry	3WY	0-26,000	0.02 M85 / G	CARB (1988)
1985 Toyota Camry	none	0-26,000	0.02 M85 / G	CARB (1988)
1986 Toyota Carina	3WY	0- 9,000	0.02 M85 / G	CARB (1988)
2 1986 Ford Crown Victorias	3WY	2,500-15,000	0.037 M85 / I	CARB (1991)
2 1986 Ford Crown Victorias	3WY	29,000-49,000	0.057 M85 / I	CARB (1991)
1989 Toyota Corolla	2 CC, 2-UF, EGR	4,000-15,000	0.029 M85 / I	CARB (1991)
1990 DI turbo CI VW Jetta	pt. cat., EGR	2,300	0.07 M100	Bruetsch & Hellman (1991)
3 Ford 4.9 liter 6-cyl. vans	3WY	5,000; 15,000; 25,000	0.04 M85, 0.05 M85, 0.06 M85[f]	Battelle (1995)
71 1993 FFV Dodge Spirits	3WY	3,844-26,126	[0.018 M85; 0.024 M50; 0.024 RFG][h]	Kelly, et al. (1996a)
16 1992-93 FFV Ford Econoline vans (prototypes)	3WY	3,359-28,218	[0.034 M85; 0.058 M50; 0.063 RFG][h]	Kelly, et al. (1996a)
1993 FFV Ford Taurus	3WY, EGR	16,996	0.0248 M85 FTP, 0.0151 M85 REP, 0.0137 RFG FTP, 0.0340 RFG REP[y]	Black et al. (1998)
1993 FFV Chevy Lumina	3WY, EGR	17,700	0.1072 E85 FTP, 0.0505 E85 REP, 0.0249 RFG FTP, 0.0490 RFG REP[y]	Black et al. (1998)
1993 FFV Dodge Spirit	cat., EGR	24,039	0.0234 M85 FTP, 0.0465 M85 REP, 0.0393 RFG FTP, 0.0467 RFG REP[y]	Black et al. (1998)
Methanol HDVs:				
MAN spark-ignited 6-cyl. engine 1	OC	new?	0.002[v] M100	Ullman & Hare (1986)

TABLE F-6 (CONT'D): METHANE EMISSIONS FROM HIGHWAY VEHICLES

Type of vehicle	Emission control equipment	Odometer (miles)	CH_4 emissions (g/mi)	Reference
Methanol HDVs: (Cont'd)				
MAN spark-ignited 6-cyl. engine 2	OC	28,300	0.04; 0.12[w] M100	Ullman & Hare (1986)
DDAD 6V-92TA spark-assisted	2-stroke	8900	1.17; 0.72[w] M100	Ullman & Hare (1986)
LPG LDVs and HDV				
1988 Dual-fuel LPG Chev. 1500 truck	NS	14,000	0.046	CARB (1989)
1989 Dual-fuel LPG Oldsmobile 88	3WY, EGR	22,700	0.064 LPG; 0.047 US	CARB (1991)
1989 Dual-fuel LPG Pontiac 6000 LE	3WY, EGR	31,300	0.042 LPG; 0.037 I	CARB (1991)
1991 LPG Chevrolet Lumina	3WY	4,000	0.022 (FTP) 0.149 (NYCC)	Gabele (1992)
3 Ford 4.9 liter 6-cyl. LPG vans	3WY	5,000; 15,000; 25,000	0.12; 0.14; 0.16[f]	Battelle (1995)
3 Chevrolet 5.7 liter V8 LPG vans	3WY	5,000; 15,000; 25,000	0.09; 0.11; 0.13[f]	Battelle (1995)
1998 Cummins B5.9-195 LPG (5.9 liter, 195 horsepower HDV engine)	cat., auto. engine mgt., closed loop A/F ratio control	New	0.077-0.12[z] (EPA HDV transient cycle)	Ortech Corp. (1995)
Ethanol dual-fuel LDVs				
1987 FFV Ford Crown Victoria	2-CC, 2-UF, EGR	22,000	0.023 M100; 0.046M85/I; 0.116 I; 0.145 E85/I; 0.171 E95/I	CARB (1991)
1987 FFV Ford Crown Victoria	2-CC, 2-UF, EGR	43,700	0.056 M85/I; 0.139 E85/I; 0.110 I	CARB (1991)
3 1992 VFV ethanol Chevrolet Luminas	3WY	~5,000	0.052 E85/I; 0.033 I	Baudino, et al. (1993)
21 1992/93 VFV ethanol Chevrolet Luminas	3WY	8,000-30,000	0.37 E0 (RFG)[aa]; 0.050 E50; 0.62 E85 FTP	Kelly, et al. (1996b)
Hydrogen LDV				
1979 Hydrogen pick-up truck	NS	23,000	0.00	CARB (1989)

Notes:

NS = not specified; cat. = catalytic converter; 3WY = three-way catalytic converter (one that oxidizes CO and NMHCs, and reduces NO$_X$); OC = oxidation catalytic converter; HC = heated catalytic converter; CC = close-coupled catalytic converter; UF = under-floor catalytic converter; EGR = exhaust-gas recirculation; LDV = light-duty vehicle; HDV = heavy-duty vehicle; GTMV = gasoline-tolerant methanol vehicle, designed to run on methanol, but "tolerant" of gasoline; FFV = flexible-fuel vehicle; VFV = variable-fuel vehicle; NGV = natural gas vehicle; I =

indolene; US = U.S. average gasoline; DI = Direct injection; CI = compression ignition; VW = Volkswagon; CARB = California Air Resources Board; NYCC = New York City Cycle; HFET = Highway Fuel-Economy Test; REP = REP05, the EPA's high-speed, high-load driving cycle used to measure "off-cycle" emissions; RFG = reformulated gasoline; RF-A = industry average unleaded gasoline; CG1 = industry-average natural gas (94% methane); CG4 = natural gas with relatively low methane content (86%)

All emissions results for LDVs were obtained over the Federal Test Procedure (FTP), unless noted otherwise. All emissions results for HDVs were obtained from engine tests over the Heavy-Duty Transient Cycle (HDTC), unless otherwise noted. (The chassis version of the HDTC [Dietzmann et al., 1980] tests the whole chassis, not just the engine.) The EPA results are net of the background ambient concentration.

Emissions estimates in brackets [ ] are averages. Abbreviations following emissions (e.g., M85/I) indicate the fuel used in multi-fuel vehicles (85% methanol and the rest, 15%, indolene). Multiple gram/mile results separated by a semicolon are results for different fuels tested on the particular vehicle in the dual-fuel or multi-fuel configuration.

* See the results for the same kind of vehicle tested on an alternative fuel, in this Table. The 1981 Rabbit and the 1981 Escort (tested by CARB, 1985) are production-line gasoline vehicles, and should be compared to the 1981 dedicated methanol Rabbits and Escorts tested by CARB (1985). The 1984 Mustang and the 1984 Cavalier (tested by Gabele et al., 1985) also are production-line gasoline vehicles, and should be compared to the dedicated methanol Escort tested by Gabele et al. (1985; see footnote "f" to this Table). The trucks tested by BC Research (1986) are the same trucks tested as dual-fuel NGVs, except that the results shown under "gasoline LDVs" were obtained prior to the installation of the CNG dual-fuel conversion kit. The Auto/Oil (1996) program tested three dedicated OEM CNG vehicles (1992/93 model years) and their gasoline counterparts. As part of its "CleanFleet" demonstration program, Battelle (1995) tested 21 vans running on California Phase II reformulated gasoline, 20 vans running on M85, 21 vans running on CNG, 20 vans on LPG, two electric vans, and 27 "control" vans using unleaded gasoline as a baseline. At each site, alternative-fuel vehicles were paired with unmodified production versions -- controls -- of the vehicle.

^ The same vehicle as the one immediately above (i.e., not a different vehicle of the same model). Vehicles of the same description but not marked with a "^" are same models but different vehicles.

[a] Methane emissions were slightly higher when the engine malfunctioned. Emissions were much higher with rich idle: 0.52 g/mi.

[b] Emissions were around 0.10 g/mi for 3 of 4 vehicles, with summer fuel and at 78°F ambient temperature, but were over 0.20 g/mi with winter fuel and at 55°F ambient temperature.

c Methane missions varied moderately with type of gasoline, and generally increased slightly from 0 to 15,000 miles. Methane emissions in the NYCC were higher, and in the HFET lower, than in FTP.

d Methane emissions were measured for the Mustang only. We assume that CH_4 was the same % of HC exhaust from Cavalier as from Mustang. The Cavalier is more similar in weight and power to the Escort than is the Mustang.

e The range represents emissions at different ambient temperatures. Methane emissions were lowest at 21^{o}C, which is typical of FTP test conditions, and highest at the lowest temperature (-6.7^{o}C).

f Tests were performed on vehicles operated over the FTP, and using an on-line FTIR analyzer. The three numbers correspond to the three vehicle mileage figures listed, and each number is a mean value for tests of three different vans by each manufacturer. Note that the Dodge CNG vans are among the first to use a catalyst system designed and optimized for CNG vehicles.

g These are emission rates over the life of an individual model years, as opposed to the fleet-average emission rate in a designated year, which is shown below. As explained in a note in the text, the fleet-average emission rate in year T (between 1990 and 2020) is based on emissions from each model year. Notice that the fleet-average emission rate in 2020 is the same as the emission rate for the latest model years shown, because by 2020 the fleet will be composed entirely of post-1986 gasoline HDVs, post-1987 diesel HDVs, or post-1991 LDVs. (In the case of gasoline LDVs, MOBILE5 estimates a further decline in emissions with the post-1994 model year, because of the 1990 Clean Air Act Amendments.) The model-year emission rates shown here, from MOBILE4, can be compared with the technology-class estimates that the EPA (1999) extracted from MOBILE5, in Table F-3. The California Air Resources Board “EMFAC” model gives similar results (CARB, 1986) .

h Methane emissions are the difference between exhaust THC and exhaust NMHC.

i Emissions varied with the conversion kit.

j The researchers actually *measured* CH_4 emissions from one car only, a 1978 Ford Fairmont. They *assumed* that CH_4 was 80% of total HCs from the 1977-model-year NGVs, 87% from later year NGVs, and 12% from gasoline vehicles. The authors did not specify the driving test cycle over which emissions were measured. The emission results on gasoline are prior to conversion to dual-fuel operation.

[k] The first emission result on indolene (I) is for the stock, unmodified gasoline configuration; the second is for the dual-fuel configuration, optimized for CNG, but running on gasoline (indolene).

[l] The authors reported total HCs and 4 different ways of measuring NMHCs. The range shown here is their HC minus their high highest (of the four) calculated NMHC to their HC minus their lowest NMHC.

[m] Emissions varied with the spark advance and the air-to-fuel ratio. The test cycle was an approximation of the EPA-CVS (the FTP).

[n] The first emission result is for the FTP test, with the vehicle’s 3-way catalytic converter in place. The second is the for the FTP test but with no catalyst. Emissions did not vary appreciably with ambient temperature (20^{o} F to 105^{o} F). Methane emissions were 3 g/mi in the NYCC, and 0.90 g/mi in the HFET (with the 3-way catalyst in place).

[o] The result was reported in the original reference as 13 g/bhp-hr and 85-90% CH_4. We assumed 2.31 bhp-hr/mi (U.S. EPA, 1991b). The engine was tested over the SAE 13-mode test.

[p] We assume that CH_4 was 85% of the total reported HCs, and 2.31 bhp-hr/mi (U.S. EPA, 1991b). The first test result shown was obtained by the manufacturer; the second was obtained by the EPA (see also Parker, 1988) . In the tests reported by Jones et al. (1988) , the HDTC was modified to reflect transit bus applications. See also Alson et al. (1989) results for other EPA tests on the GMC engine.

[q] We assume 2.31 bhp-hr/mi (U.S. EPA, 1991b). The engine was tested over the HDTC.

[r] We assumed that CH_4 was 85% of the total reported HCs, and 2.31 bhp-hr/mi (U.S. EPA, 1991b). The emissions results were obtained over the SAE 13-mode test.

[s] Emissions were about twice as high at 40^{o} F. Emissions at 90^{o} F were similar to FTP (75^{o}) emissions.

[t] The vehicle was equipped with a resistively heated monolithic catalyst designed to reduce cold-start HC and HCHO emissions.

[u] New vehicles emitted about 0.03 g/mi; older vehicles emitted around 0.06 g/mi, and the average was around 0.06 g/mi. Three of the vehicles had electronic fuel injection.

[v] The authors reported 70 mg CH_4 in the cold-start transient test, 0 in the hot-start test, and about 9.3 kw-hr work in both tests. We used their formula to convert these to mg/hp-hr, and then assumed 2.31 bhp-hr/mi (U.S. EPA, 1991b). The engine was tested over the HDTC.

[w] The first value was emitted over bus transient cycle; the second over the central business district transient cycle.

[x] We assumed 4.64 bhp-hr/mi for diesel HDVs, to convert the data from g/bhp-hr to g/mi (Browning, 1998) .

[y] Results are averages of two or four tests.

[z] Emissions converted from 0.029 to 0.046 g/bhp-hr using 2.67 bhp-hr/mi. Engine uses lean burn technology, with an air fuel ration of 27:1 (versus a stoichiometric ratio of 17:1).

[aa] The standard gasoline Lumina emitted about 0.04 g/mi CH_4.