Light Duty Vehicle Methane and Nitrous Oxide Emissions

Greenhouse Gas Impacts

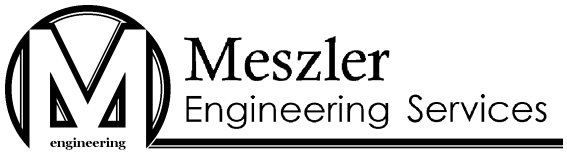
Final Report

Prepared for:

Northeast States Center for a Clean Air Future

101 Merrimac Street, 10th Floor
Boston, Massachusetts 02114

Prepared by:



906 Hamburg Drive
Abingdon, Maryland 21009
410-569-0599
www.meszler.com

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Notice

This report was prepared for incorporation into a larger study report commissioned by the Northeast States Center for a Clean Air Future (NESCCAF). As a result, section, table, and figure numbering is formatted for change and some references may be directed to sections of that larger report, which cannot be found herein. Unless otherwise stated, the opinions presented herein represent the views of the author and may not be consistent those of NESCCAF, its officers, or employees. Furthermore, although NESCCAF graciously funded the work leading to this report, any errors contained herein are attributable solely to the author.

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Q. Methane and Nitrous Oxide Emissions

Q.1 Introduction

In addition to CO_2 emissions, which are discussed throughout the other sections of this report, light duty vehicle GHG emissions also include methane (CH_4) and nitrous oxide (N_2O). Although emissions of these compounds are generally orders of magnitude lower than emissions of CO_2, the global warming potential (GWP[1]) of both CH_4 and N_2O is greater than that of CO_2. Methane is estimated to have a GWP 23 times that of CO_2, while the GWP of N_2O is estimated to be 296 times that of CO_2. [1] As a result, it may be important to consider these emissions in determining the overall GHG impact potential of light duty vehicles.

Naturally emitted methane, principally a product of vegetative decay and digestive processes, is estimated to comprise about 40 percent of total atmospheric methane. The principal anthropogenic (manmade) methane sources in the U.S. are landfills, agriculture, coal mining, and natural gas extraction and distribution, which together account for over 90 percent of manmade emissions. In contrast, highway vehicles and nonroad equipment are estimated to produce less than one percent of manmade methane. Since 1990, manmade methane emissions in the U.S. are estimated to have declined by about 15 percent, primarily due to recovery practices in the coal and landfill industries. [2]

Almost 60 percent of N_2O emissions result from natural processes, primarily bacterial breakdown of soil nitrogen, ocean upwelling, and stratospheric photo-dissociation and oxidation. Agricultural fertilization and solid waste denitrification are estimated to be responsible for the bulk of U.S. manmade N_2O emissions (about 70 percent), but nearly 20 percent are estimated to be produced by highway vehicles and nonroad equipment. Moreover, over 90 percent of the highway vehicle and nonroad equipment emissions share is estimated to be produced by light duty highway vehicles as a direct result of catalytic emissions conversion. Since 1990, manmade N_2O emissions in the U.S. are estimated to have remained mostly unchanged, although emissions from light duty vehicles have increased by about 30 percent (an increase offset by reductions in industrial and agricultural emissions). [2]

Methane emissions from vehicles represent a product of incomplete combustion.[2] Ideally, such emissions would be converted to CO_2 and water as they pass through the catalytic aftertreatment systems that are universally used on today's vehicles to meet existing criteria pollutant emission standards. However, as the simplest hydrocarbon, methane is less reactive than all other hydrocarbons and can pass through aftertreatment systems more easily than other hydrocarbon species. While catalyst system design can be tailored to more effectively convert CH_4, it is

[1] GWP indicates the global warming effectiveness of a compound relative to that of CO_2, so that the GWP of a compound indicates the estimated ratio of its impact on global warming to the impact of the same mass of CO_2.

[2] In the case of some automotive fuels, especially natural gas, methane comprises a substantial portion of the fuel itself. As a result, both incomplete combustion and fuel evaporation or venting can result in substantial methane emissions. Since this study focuses on gasoline and diesel vehicle emissions, methane-based fuels are not explicitly considered, but readers should recognize the increased methane emissions potential of such fuels.

important to recognize that this conversion will *not* result in the reduction of methane-based GHG emissions to zero. Since catalytic action will produce 2.75 grams of CO_2 for every gram of methane converted, the elimination of unburned methane through catalysis can achieve a considerable net reduction in GHG, but that reduction is capped at 88 percent.[3,4] Of course, this same cap exists for improving in-cylinder fuel combustion characteristics, as any "displaced" methane will lead to an increase in CO_2 emissions. Only reduced fuel use can provide a complete reduction in methane-based GHG emissions.

N_2O emissions result almost entirely from activity within the catalytic aftertreatment systems of vehicles. Several test programs have demonstrated that engine-out N_2O emissions are consistent with background N_2O concentrations within the limits of detectability (approximately 0.01 grams per mile). [3-6] N_2O appears to be associated with low temperature NO_x (oxides of nitrogen) reduction, being formed as an intermediary reaction product.[5] [3,4] Although the body of research on the specific formation chemistry of N_2O is considerably less than that of other automotive emission species, the low temperature reaction mechanism is quite consistent with observed experimental emissions data. As a result, it is widely believed that the control of vehicle N_2O emissions is a function of improved aftertreatment systems.

A detailed discussion of vehicle methane emissions and the potential for future reductions follows in Section Q.2. Section Q.3 presents a similar discussion for N_2O emissions. Finally, Section Q.4 presents a summary of associated conclusions.

Q.2 Methane Emissions

As indicated in Section Q.1, methane is emitted from light duty vehicles due to the incomplete combustion of fuel in the vehicle engine and the incomplete oxidation of engine-out methane in current catalytic aftertreatment systems. It is important to recognize, however, that current vehicles produce and emit substantially less methane than their older counterparts and, even in the absence of additional regulation, it is almost certain that future vehicles will exhibit even lower emission rates. Although there are currently no specific emission standards for methane, existing standards for non-methane organic compounds do effectively result in reduced methane emissions through the design and implementation of advanced combustion and catalyst technologies.

Emissions control of organic compounds has evolved over the years. While the latest (i.e., Tier 2 federal and LEV II California) standards are characterized in terms of non-methane organic gases (NMOG), other current (e.g., Tier 1 federal) and previous (e.g., Tier 0 federal) standards are, or have been, characterized in terms of non-methane hydrocarbons (NMHC) or total hydrocarbons (THC). While only THC standards explicitly require the control of CH_4 emissions, since by definition both NMHC and NMOG exclude CH_4, all have effectively reduced methane emissions since the technologies and control strategies implemented to reduce

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[3] $(x\ CH_4)\times(23\ GWP) \rightarrow (2.75x\ CO_2)\times(1\ GWP)$, so maximum reduction potential = $[(2.75x)/(23x)]-1 = 88$ percent.

[4] Conversion of one gram of CH_4 also produces 2.25 grams of water, which is the most prevalent GHG. However, the GWP of methane accounts for its indirect production of water. [1]

[5] $2NO + CO \rightarrow N_2O + CO_2$, which ideally is followed by $N_2O + CO \rightarrow N_2 + CO_2$.

NMHC also reduce the production and emission of methane. For example, engine technologies designed to reduce hydrocarbon emissions through improved combustion characteristics, reduce the full range of hydrocarbon emissions. Similarly, improved catalytic aftertreatment techniques that increase hydrocarbon conversion efficiency reduce both NMHC and methane emissions. While aftertreatment systems may preferentially oxidize NMHC due to its inherently higher reactivity, any improvement in oxidation efficiency will also increase the oxidation of methane. Therefore, even in the absence of explicit GHG-based limits, methane emissions should continue to decline as combustion and aftertreatment efficiencies are further improved.

Since methane emissions are measured as part of the standard vehicle certification process in the U.S., there is an extensive library of certification data that can be used to assess both the historic and current methane emission rates of light duty vehicles. Even so, a considerable degree of processing is required to assemble and analyze these data. For this study, a smaller 39 vehicle dataset developed by the California Air Resources Board (ARB) was utilized to estimate methane emission rates. [7] This ARB dataset was used for several reasons, including the following:

- The dataset represents emissions data for actual in-use vehicles and, therefore, provides an indication of actual in-use methane and N_2O emission rates.
- The dataset includes a wide range of vehicle model years, allowing a wide range of emissions levels to be analyzed.
- The dataset includes THC, NMHC, CH_4, NO_x, and N_2O emissions measurements for all 39 vehicles.

Generally, the ARB data was collected between 2000 and 2002 as part of the agency's 16th Vehicle Surveillance Program (VSP). Overall, the VSP, which is conducted periodically, is a much larger (than 39 vehicles) investigation of the in-use vehicle fleet, intended to evaluate such issues as the cost effectiveness of the state's vehicle emissions inspection program, in-use emissions deterioration rates, in-use evaporative emission rates, in-use speciation profiles, and alternative test cycles. This study looked at only a subset of the full VSP dataset, since N_2O emissions were not collected for all study vehicles. Moreover, only VSP data collected over the standard FTP-75 driving cycle were analyzed to avoid any potential confounding issues related to driving cycles. As indicated, these criteria constrain the overall dataset size to 39 vehicles.

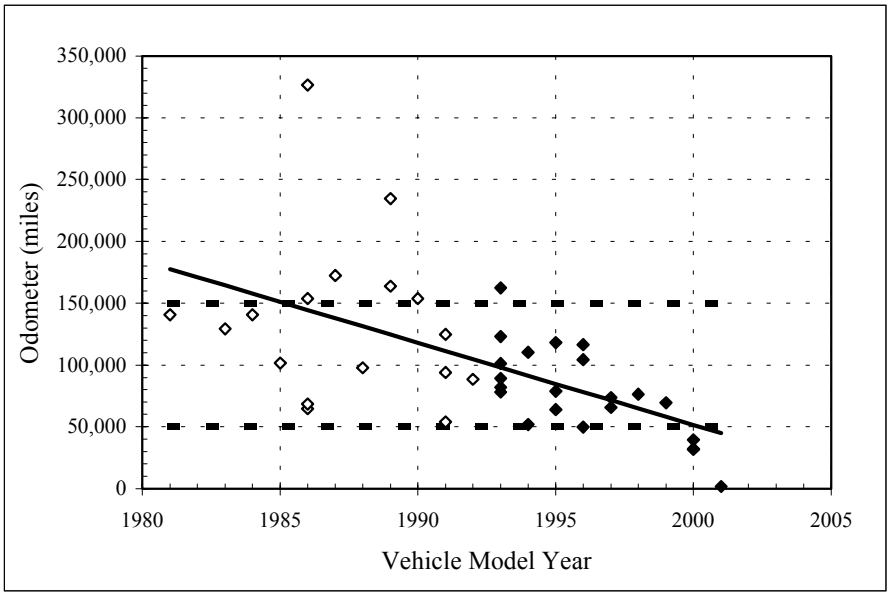
The vehicles included in the VSP are California-based light duty vehicles. Since federal and California vehicle emission standards have varied over the years (and continue to do so), this might be cause for variation in estimated emission rates from those expected in the rest of the U.S. However, it is expected that any such variation will be minor for several reasons. First, for pre-1993 vehicles, the differences between the federal and California hydrocarbon standards are minor. Second, much of the federal fleet now consists of vehicles certified to the National Low Emissions Vehicle (NLEV) standards, which are similar to the California Low Emission Vehicle (LEV) standards. Third, the estimated emission rate is determined as an average across vehicles and the variation between individual vehicles is at least as large as the variation between federal and California standards. Finally, the data are primarily used to derive emission rate ratios as opposed to absolute emission rates. These ratios are then applied to applicable federal

certification standards to develop expected federal emission rates, so that the absolute emission levels of the California data are primarily a reference point rather than a final emissions estimate.

Figure Q-1 and Table Q-1 provide an overview of the vehicle fleet represented in the VSP dataset used for this study. As indicated, vehicles span a 21 model year range of 1981 through 2001, with odometer readings ranging from 1,700 to 326,000 miles. Most of the 39 test vehicles (31) are passenger cars, but there are also 8 light duty trucks. Thus, trucks are underrepresented in the test sample. The test vehicles do, however, represent a wide range of engine sizes, with displacements ranging from one to five liters.

The relationship between measured methane and measured THC emission rates, as well as the relationship between measured methane and measured NMHC emission rates, was investigated. Figure Q-2 and Table Q-2 present the results of the THC analysis, while Figure Q-3 and Table Q-3 present the results of the NMHC analysis. As expected, statistically significant relations between both CH_4 and THC and CH_4 and NMHC were found (of course, a valid relation for either implies a valid relation for the other). As shown in Tables Q-2 and Q-3, valid relations exist for all three bags of the FTP, but the CH_4 fraction of HC increases in Bag 2. This is expected since Bag 2 reflects hot stabilized catalyst operation, wherein NMHC conversion efficiencies will be at their maximum. Although CH_4 conversion will also increase in Bag 2, efficiency will generally be below the peak efficiencies for NMHC due to the decreased reactivity of methane.

Figure Q-1. Mileage and Model Year of Vehicles in the ARB VSP Dataset

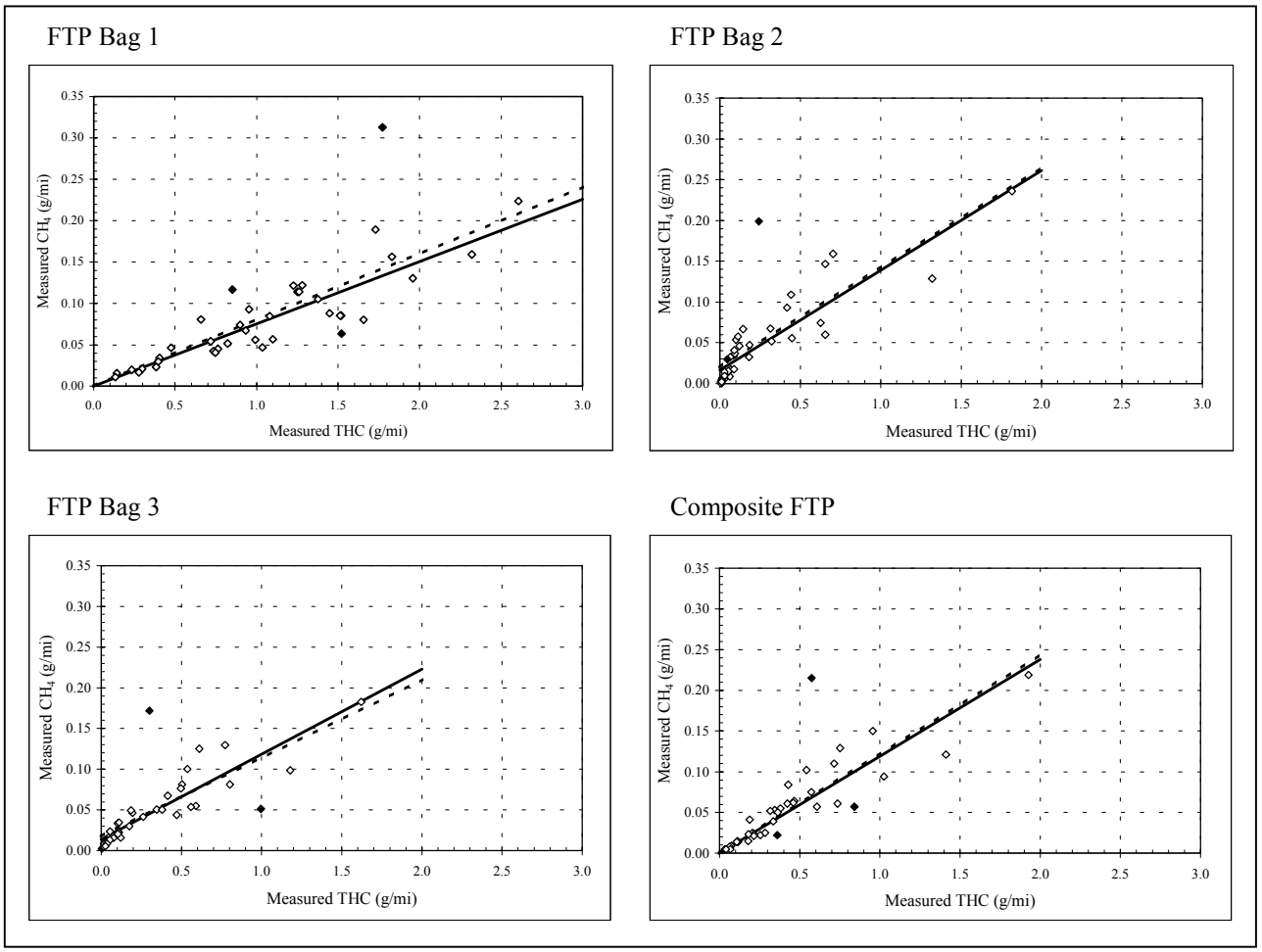


Note: Solid markers indicate data for 1993 and newer vehicles, open markers indicate data for 1992 and older vehicles. The sloping solid line is a simple linear trendline that is not used for any specific purpose other than to determine the general year-to-year rate of mileage change (6,640 miles). The dashed lines indicate the mileage bounds applied to a secondary data analysis described in detail below.

Table Q-1. Summary Descriptive Data for Vehicles in the ARB VSP Dataset

Model Year	Vehicle Make	Vehicle Model	Disp (liters)	Odometer (miles)	Vehicle Class
1981	Chevrolet	Van 20	5.0	140,642	MDV
1983	Chevrolet	Caprice Classic Station Wagon	5.0	129,370	PC
1984	Volvo	DL 4-Door	2.3	140,508	PC
1985	Chevrolet	Blazer	2.8	101,625	LDT1
1986	Saab	900	2.0	153,916	PC
1986	Cadillac	El Dorado Biarritz	4.1	64,505	PC
1986	Toyota	Camry LE	2.0	326,358	PC
1986	Mercury	Capri GS	3.8	68,251	PC
1987	Cadillac	El Dorado 2-Door	4.1	172,416	PC
1988	Toyota	Corolla FX	1.6	97,947	PC
1989	Chevrolet	Geo Metro LSi	1.0	163,882	PC
1989	Toyota	Tercel Hatchback	1.5	234,588	PC
1990	Nissan	Pathfinder XEV6	3.0	153,896	LDT2
1991	Pontiac	Transport	3.1	124,716	LDT2
1991	Chrysler	Lebaron LE	3.0	94,121	PC
1991	Cadillac	Sedan DeVille	4.9	53,804	PC
1992	Pontiac	Grand Am 4-Door	3.3	88,497	PC
1993	Cadillac	Sedan DeVille 4-Door	4.9	101,147	PC
1993	Mercury	Villager GS	3.0	123,070	LDT2
1993	Toyota	Corolla	1.6	162,332	PC
1993	Nissan	Sentra XE	1.6	78,016	PC
1993	Toyota	Camry LE 4-Door	2.2	89,252	PC
1993	Acura	Integra LS 3-Door	1.8	81,987	PC
1994	Ford	Taurus GL 4-Door	3.0	51,773	PC
1994	Toyota	Camry XLE	3.0	110,134	PC
1995	Chevrolet	Geo Prism LSi	1.6	118,082	PC
1995	Plymouth	Neon 4-Door	2.0	63,752	PC
1995	Toyota	Camry LE	2.2	78,773	PC
1996	Dodge	Ram 1500	5.2	116,400	MDV3
1996	Mazda	626 LX	2.0	104,185	PC
1996	Toyota	Camry LE	2.2	49,631	PC
1997	Ford	Expedition XLT	4.6	73,598	MDV3
1997	Mazda	Miata	1.8	65,733	PC
1998	Dodge	Neon 4-Door	2.0	76,375	PC
1999	Ford	Taurus SE	3.0	69,617	PC
2000	Volkswagen	GTI Turbo	1.8	31,959	PC
2000	Toyota	4Runner 2WD	2.7	39,252	LDT2
2000	Saturn	Saturn SL 4-Door	1.9	31,973	PC
2001	Ford	Taurus LS	3.0	1,724	PC

Figure Q-2. CH_4 Emission Rate Versus THC Emission Rate



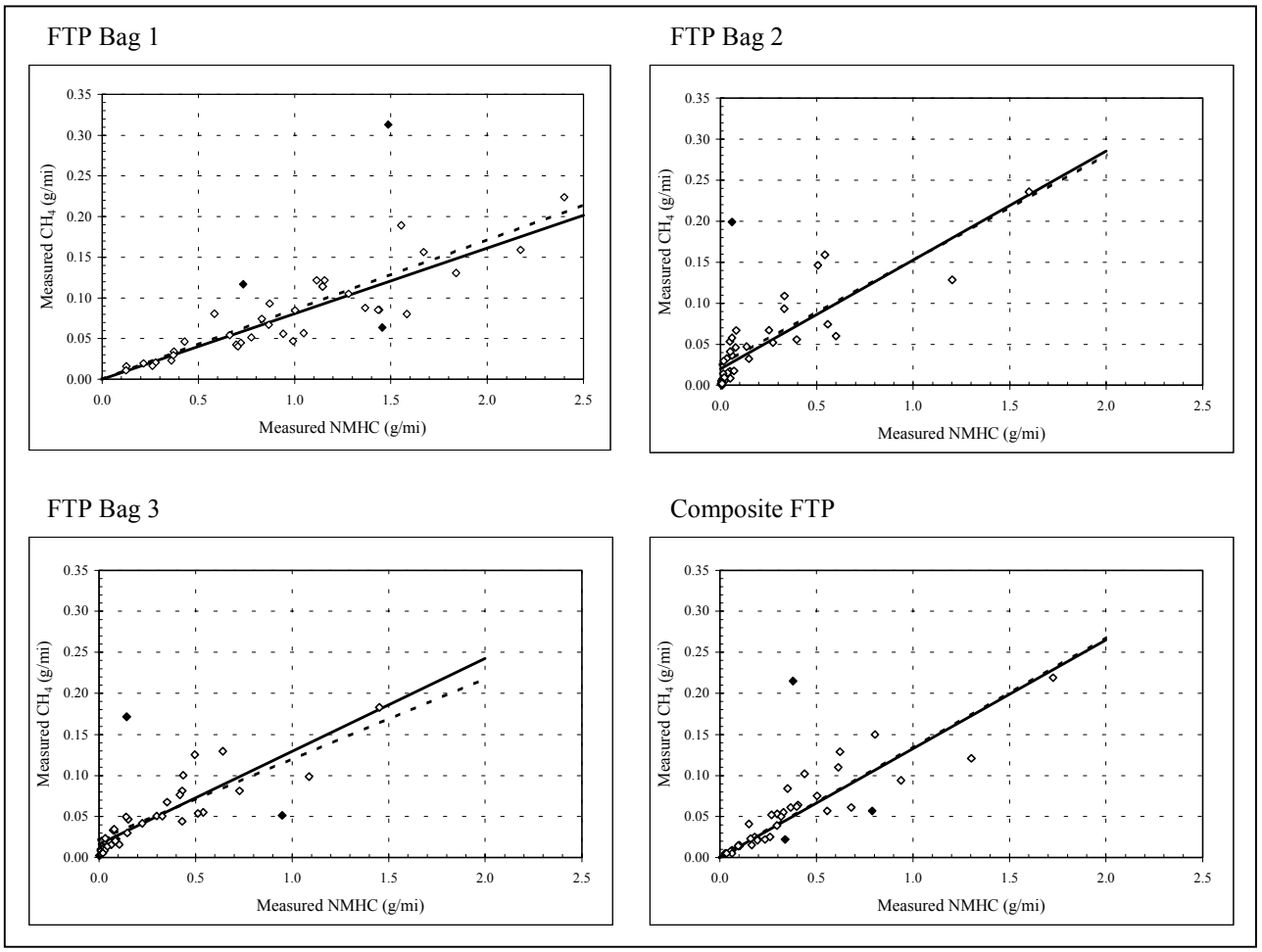
Note: The dotted and solid lines indicate regression-based relations. Dotted lines include all data, solid lines exclude outliers (defined as datapoints that vary from the average CH_4/THC or THC/CH_4 ratio by more than two standard deviations).

Table Q-2. Regression Statistics for CH_4 (g/mi) Versus THC (g/mi)

Statistic	All Data				Outliers (±2σ) Removed			
	Bag 1	Bag 2	Bag 3	Composite	Bag 1	Bag 2	Bag 3	Composite
Intercept	0.0000	0.0201	0.0175	0.0000	0.0000	0.0165	0.0137	0.0000
Slope	0.0803	0.1227	0.0963	0.1220	0.0753	0.1223	0.1047	0.1190
r^2	0.64	0.67	0.62	0.67	0.83	0.82	0.84	0.86
n (obs)	39	39	39	39	36	36	35	36

Slope and intercept statistics are selected at 95 percent confidence level.

Figure Q-3. CH_4 Emission Rate Versus NMHC Emission Rate



Note: The dotted and solid lines indicate regression-based relations. Dotted lines include all data, solid lines exclude outliers (defined as datapoints that vary from the average CH_4/NMHC or NMHC/CH_4 ratio by more than two standard deviations).

Table Q-3. Regression Statistics for CH_4 (g/mi) Versus NMHC (g/mi)

Statistic	All Data				Outliers (±2σ) Removed			
	Bag 1	Bag 2	Bag 3	Composite	Bag 1	Bag 2	Bag 3	Composite
Intercept	0.0000	0.0248	0.0213	0.0000	0.0000	0.0201	0.0160	0.0000
Slope	0.0857	0.1282	0.0986	0.1342	0.0806	0.1328	0.1132	0.1326
r^2	0.59	0.57	0.54	0.58	0.80	0.76	0.80	0.82
n (obs)	39	39	39	39	36	37	35	36

Slope and intercept statistics are selected at 95 percent confidence level.

As shown in Table Q-2, methane generally constitutes about 7.5 to 12 percent of THC emissions, with the smaller fractions being observed in Bags 1 and 3 of the FTP, during which the catalyst has not yet attained peak conversion conditions and NMHC emissions are highest.[6] Relative to NMHC, Table Q-3 shows that the methane emission rate generally ranges from 8 to 13 percent of that for NMHC. This is in good agreement with algebraic expectations, where a 10± percent increase in emissions fraction would be expected in moving the relationship base from THC to NMHC.[7] From a composite emissions standpoint,

$$CH_4 = 0.119\ (THC)$$

or

$$CH_4 = 0.133\ (NMHC)$$

Assuming the THC coefficient to be precise, the algebraic NMHC equivalent coefficient would be 0.135 (0.119/(1-0.119)). This varies from the regression-based coefficient by less than 2 percent, so the independent regression analysis results are quite consistent.

As indicated by the VSP data, as THC (and NMHC) is reduced, methane is also reduced in a proportional manner. Thus, as vehicle technology advances to meet stricter organic compound emission standards, it is reasonable to expect that methane emissions will also decline. However, since it could be possible to derive similar relationships from data for equivalently emitting vehicles tested at different mileage accumulations throughout their deterioration cycle, a secondary analysis was performed to ensure that this was not the case with the VSP data.

In this secondary analysis, the VSP data were split into two component datasets, one for 1992 and earlier vehicles (17 vehicles) and one for 1993 and newer vehicles (22 vehicles). This split was selected on the basis that organic compound emission standards generally shifted in stringency beginning in 1993 when the first Tier 1 vehicles were required to be sold in California. Light duty vehicles from model years 1981 through 1992 were certified to Tier 0 emission standards. Organic compound emission standards continued to evolve throughout the 1990s as differing numbers of LEV vehicles were sold, but the VSP dataset analyzed for this study does not contain sufficient information to pinpoint the certification class of each vehicle. Nevertheless, there is no question that a split based on the 1993 model year is biased toward Tier 0 vehicles on the pre-1993 side and Tier 1/LEV vehicles on the 1993 and newer side. Thus, there is a clear distinction between the relative emissions control design of the two data subsets.[8]

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[6] Note that both Tables Q-2 and Q-3 include "All Data" and "Outliers Removed" statistics. The former includes data for all 39 dataset vehicles. The latter excludes data for vehicles with either CH_4/X or X/CH_4 ratios that vary from the average ratio by more than ±2 standard deviations, where X indicates the independent parameter (i.e., either THC or NMHC). Data identified as outliers are indicated in Figures Q-2 and Q-3 as solid markers.

[7] If $CH_4/THC = x$ and $CH_4/NHMC = y$, then $y = CH_4/(THC-CH_4) = CH_4/(THC-THC(x)) = CH_4/(THC(1-x)) = x/(1-x)$. So if $x \cong 0.10$, then $y = 0.11 \cong 1.1x$.

[8] Despite the seeming clarity of this distinction, t-tests were conducted for the two samples. This testing indicates that the probability of the two samples being from the same population is <0.1 percent for THC, NMHC, and CH_4.

Table Q-4 indicates the results of the data subset analysis. To factor out the influence of mileage accumulation to the maximum extent possible, statistics were calculated on a stratified basis by 50,000 mile increment mileage accumulation bins. Statistics were then compared across the two samples only when five or more datapoints were present in comparable mileage bins. This results in comparisons for two mileage bins, 50,000-100,000 miles and 100,000-150,000 miles. As indicated, the 1993 and newer vehicle organic emissions have generally declined by 50 to 70 percent for THC, NMHC, *and* CH_4 relative to comparable mileage 1992 and older vehicles. To truly confirm the lack of mileage bias, a comparison of the 100,000-150,000 mile data for 1993 and newer vehicles to the 50,000-100,000 mile data for 1992 and older vehicles indicates that the *minimum* reduction in THC, NMHC, *and* CH_4 emission rates is between 30 and 50 percent, with the 50 percent reduction being applicable to methane. Clearly, methane emissions have declined between the two periods, while methane-to-THC and methane-to-NMHC ratios have remained relatively stable as described above. Therefore, it should be possible to estimate both current and future certification emission rates for methane on the basis of the derived relations.

Using the CH_4-to-NMHC regression results and U.S. light duty vehicle certification standards for NMOG, the methane emission rates for current and future vehicles were estimated. Since the regression relations are based on NMHC emissions, as opposed to NMOG emissions, the NMOG standards were converted to NMHC equivalent standards using the allowable certification adjustment factor of 1.04 as specified in the Code of Federal Regulations.[9] A certification compliance margin of 30 percent was also assumed, consistent with assumptions utilized for the CO_2 emissions analysis portion of the study. So in effect, the target NMHC emission rate for a given NMOG standard is equal to:

$$\text{Target NMHC} = \left[\frac{\text{NMOG Standard}}{1.04} \right] \times 0.70$$

For Tier 1 standards, which were expressed in terms of NMHC, the NMOG adjustment was not performed. For Tier 0 standards, which were expressed in terms of THC, the NMOG adjustment was similarly not performed and the NMHC portion of THC was estimated using the Tier 0 NMHC-to-THC standard ratio developed by the U.S. Environmental Protection Agency (EPA) for natural gas vehicles (0.34/0.41).[10] Estimated methane emission rates were then developed on the basis of the previously described regressions as:

$$CH_4 = 0.133 \text{ (Target NMHC)}$$

The resulting emission rates are presented in Table Q-5. As indicated, estimated emission rates range from 0.039 g/mi for a Tier 0 passenger car to 0.010 g/mi for a 2002 "fleet average" NLEV vehicle. Perhaps the best indication of the accuracy of these estimated emissions can be gleaned from a comparison of the estimated Tier 1 passenger car emission rate of 0.029 g/mi to the

[9] 40 CFR §86.1810-01(p) allows NMOG emissions to be estimated as NMHC emissions times 1.04.

[10] Because natural gas vehicles have inherently higher methane emission rates than gasoline vehicles, the EPA established an equivalent stringency Tier 0 standard for natural gas vehicles in terms of NMHC. A standard of 0.31 g/mi NMHC was determined to be equivalent to the 0.41 g/mi Tier 0 THC standard for gasoline vehicles.

Table Q-4. Average Hydrocarbon Emission Rates for Split VSP Database

Organic Species	Odometer (miles)	Pre-1993 Vehicles		1993 and Newer Vehicle		Percent Change (a)
		Average Emission Rate (g/mi)	Number of Observations	Average Emission Rate (g/mi)	Number of Observations	
THC	0-50,000		0	0.115	5	
	50,000-100,000	0.464	6	0.223	10	-52%
	100,000-150,000	0.943	5	0.314	6	-67%
	150,000-200,000	0.823	4	0.335	1	
	200,000-250,000	0.714	1		0	
	250,000-300,000		0		0	
	300,000-350,000	0.461	1		0	
	All Data	**0.704**	**17**	**0.228**	**22**	**-68%**
	50,000-150,000	**0.682**	**11**	**0.257**	**16**	**-62%**
NMHC	0-50,000		0	0.106	5	
	50,000-100,000	0.381	6	0.200	10	-47%
	100,000-150,000	0.830	5	0.271	6	-67%
	150,000-200,000	0.750	4	0.296	1	
	200,000-250,000	0.613	1		0	
	250,000-300,000		0		0	
	300,000-350,000	0.398	1		0	
	All Data	**0.614**	**17**	**0.202**	**22**	**-67%**
	50,000-150,000	**0.585**	**11**	**0.227**	**16**	**-61%**
CH_4	0-50,000		0	0.009	5	
	50,000-100,000	0.089	6	0.024	10	-73%
	100,000-150,000	0.120	5	0.044	6	-63%
	150,000-200,000	0.079	4	0.039	1	
	200,000-250,000	0.110	1		0	
	250,000-300,000		0		0	
	300,000-350,000	0.062	1		0	
	All Data	**0.095**	**17**	**0.027**	**22**	**-72%**
	50,000-150,000	**0.103**	**11**	**0.032**	**16**	**-69%**

Notes: (a) Only stratifications with five or more component datapoints are included.

Table Q-5. Estimated Methane Emission Rates

Certification Level	NMOG Standard (g/mi)	NMHC Target (g/mi)	Predicted CH_4 (g/mi)	CO_2 Equivalent (g/mi)	Change from PC Tier 0	Change from PC Tier 1	Change from 02 NLEV
Tier 2,Bin 1/ZEV	0.000	0.000	0.000	0.000	-100%	-100%	-100%
Tier 2,Bin 2/SULEV	0.010	0.007	0.001	0.021	-98%	-97%	-91%
Tier 2,Bin 3/ULEV I/ULEV II	0.055	0.037	0.005	0.113	-87%	-83%	-50%
Tier 2,Bin 4	0.070	0.047	0.006	0.144	-84%	-78%	-37%
Tier 2,Bin 5/LEV I/LEV II	**0.090**	**0.061**	**0.008**	**0.185**	**-79%**	**-72%**	**-19%**
Tier 2,Bin 6	0.090	0.061	0.008	0.185	-79%	-72%	-19%
Tier 2,Bin 7	0.090	0.061	0.008	0.185	-79%	-72%	-19%
Tier 2,Bin 8	0.125	0.084	0.011	0.257	-71%	-61%	+13%
TLEV	0.156	0.105	0.014	0.320	-64%	-52%	+41%
Passenger Car Tier 1	0.310	0.217	0.029	0.662	-26%	0%	+191%
Passenger Car Tier 0	0.422	0.295	0.039	0.900	0%	+36%	+296%
2002 NLEV Fleet Average	0.111	0.075	0.010	0.227	-75%	-66%	0%
2002 LEV Fleet Average	0.101	0.068	0.009	0.207	-77%	-69%	-9%
2010 LEV Fleet Average	0.050	0.034	0.004	0.103	-89%	-85%	-55%

Notes: (1) For NMOG standards, the equivalent NMHC standard equals the NMOG standard divided by 1.04.
(2) For all fleet average standards, passenger car and LDT1/2 standards are weighted by 55 percent and LDT3/4 standards are weighted by 45 percent on the basis of the 2009 Martec market forecast described in Section II of the study report. Basically, the entire large truck and minivan classes are assumed to be LDT3/4, as is 60 percent of the small truck class.
(3) The target emissions level is 70 percent of the applicable standard.
(4) Predicted CH_4 equals the target NMHC emissions times 0.133.
(5) CO_2 equivalent emissions equal CH_4 emissions times 23 (the GWP of CH_4).

estimated 100,000 mile methane emission rate for 1993 and newer vehicles from the ARB VSP dataset used to develop the CH_4-to-NMHC regression relations.[11] Although the 1993 and newer vehicles in the ARB dataset are likely to reflect a mix of LEV I and Tier 1 vehicles, the fleet average LEV standard for NMOG was dominated by Tier 1 vehicles through the late 1990s. Thus, it is reasonable to expect that the ARB dataset for 1993 and newer vehicles is similarly dominated by Tier 1 vehicles. In fact, a basic regression analysis of these data indicate an expected 100,000 mile methane emission rate of 0.034 g/mi, which compares well with the certification estimated rate for Tier 1 vehicles of 0.029 g/mi. As a result, it seems likely that the estimated methane emission rates presented in Table Q-5 provide a reasonably accurate depiction of current and future emissions.

[11] Since the certification standards used to develop the estimated CH_4 emission rate are 100,000 (or 120,000) mile standards, measured emissions at 100,000 miles are an appropriate comparison metric.

Table Q-5 also indicates that by 2009, methane emissions can be expected to decline by about 19 percent, to 0.008 g/mi (about 0.2 g/mi CO_2 equivalent), from the estimated 2002 fleet average emission rate of 0.010 g/mi. This reduction will come about due to the imposition of the Tier 2 program and the improved combustion and aftertreatment efficiencies it is expected to promote. Since the Tier 2 program is already adopted, the incremental costs that will accrue to capture this methane reduction benefit are already accounted for under the Tier 2 program and thus no additional cost is incurred from a GHG perspective. As is also indicated, it is possible to promote further methane reductions through even further advances in combustion and aftertreatment efficiency. However, since the total expected CO_2 equivalent emission rate in 2009 is less than 0.2 g/mi, the overall GHG reduction potential is quite limited. For example, adding advanced technology required to certify vehicles to the Tier 2, Bin 3 level will reduce emissions by another 40 percent, but this translates into an absolute CO_2 equivalent reduction of less than 0.1 g/mi. Technology capable of meeting Tier 2, Bin 2 levels will increase the added reduction to almost 90 percent, with the absolute reduction increasing to about 0.15 g/mi CO_2 equivalent.

As additional emission reduction potential is clearly occurring "at the margin" due to already low methane emission rates, the cost effectiveness of additional reductions is relatively high. In developing the NLEV program, the EPA estimated the incremental retail cost of a ULEV I vehicle relative to a LEV I vehicle at $30. [8] This estimate properly reflects the technology required to reduce NMOG emissions from Tier 2, Bin 5 levels to Tier 2, Bin 3 levels while holding NO_x control constant, and is generally consistent with similar cost impacts estimated by the ARB. [9] As indicated in Table Q-6, this implies a cost effectiveness of about $2,500 per ton of equivalent CO_2 reduction, *assuming all associated costs are attributed to methane reduction*.

ARB estimates for the incremental retail cost of a SULEV vehicle relative to a ULEV II vehicle provide similar insight into the cost effectiveness of controlling methane to the Tier 2, Bin 2 level. These costs are estimated at about $70 per vehicle after correcting for the increased rhodium loading estimated to be needed for reducing ULEV II NO_x to SULEV levels. [10] This implies a cost effectiveness of about $3,700 per ton of equivalent CO_2 for reducing methane from Tier 2, Bin 5 to Tier 2, Bin 2 levels, or a marginal cost effectiveness of about $4,600 per ton of equivalent CO_2 for reducing methane from Tier 2, Bin 3 levels. Of course, reductions of NMOG also accrue, which could be used to offset a portion of the imposed cost. Since methane reductions accrue in proportion to NMOG reductions, it seems most logical to consider future methane reduction as an integral component of Tier 2 and LEV II program reviews. This would maintain a consistent approach to continued program development, while properly reflecting both the criteria and GHG emission benefits of such programs.

It is also important to note that the methane relationships presented in this study are derived from data for stoichiometric control technology. Existing research indicates that, unlike NMHC conversion, the methane conversion efficiency of typical stoichiometric three-way catalysts falls off fairly rapidly at lean conditions. [11] This is likely due to the reduced exhaust temperatures associated with lean combustion and, as a result, methane emissions for combustion technologies such as lean gasoline direct injection and diesel may need to be investigated further as detailed research data become available. At the same time, it is also likely that the excess air combustion

Table Q-6. Cost and Cost Effectiveness of Methane Reductions

Reduction Strategy	CH_4 Change (g/mi)	CO_2 Equivalent Change (g/mi)	Marginal Cost	Cost Effectiveness ($/ton CO_2)
Tier 2,Bin 5 to Tier 2, Bin 3	0.003	0.072	$ 30	$ 2,526
Tier 2,Bin 5 to Tier 2, Bin 2	0.007	0.164	$ 100	$ 3,683
Tier 2,Bin 3 to Tier 2, Bin 2	0.004	0.092	$ 70	$ 4,584

Notes: (1) Cost effectiveness is based on a lifetime mileage estimate of 150,000 miles.

associated with such technologies will produce lower engine-out methane emissions than is the case with stoichiometric technology, but this should be confirmed during certification testing.

In the absence of specific data on advanced lean burn technology, this study relies on an estimated methane emission rate derived from the EPA's MOBILE6.2 emission factor model for light duty diesel passenger cars and trucks. [15] The EPA model was executed for two evaluation years, 2002 and 2009, and methane emission rates were calculated as the difference between model-estimated THC and NMHC emission rates. The resulting methane emission rate, 0.005 g/mi, was identical for both evaluation years and is, in a general sense, quite consistent with the emission rates presented in Table Q-5 for stoichiometric technology. An emission rate of this magnitude certainly reflects inherently low methane emissions, given that it is equivalent to emissions associated with highly advanced aftertreatment technology (i.e., Tier 2, Bin 3 technology). Moreover, the emission rate also appears to be reasonably consistent with the methane emission rates of larger diesel engines as measured in several emissions test programs. For example, a test program conducted by the Center for Environmental Research and Technology at the University of California-Riverside found the average methane emission rate of fifteen 1982 though 1996 light and medium heavy duty diesel vehicles to be 0.011 g/mi. [16] Therefore, in the absence of more representative test data, a lean burn emission rate of 0.005 g/mi has been assumed for this study.

Q.3 Nitrous Oxide Emissions

As indicated in Section Q.1, N_2O is emitted from light duty vehicles due to the incomplete reduction of engine-out NO_x emissions in current catalytic aftertreatment systems. However, as was the case with methane emissions, it is important to recognize that current vehicles produce and emit substantially less N_2O than their older counterparts. Moreover, even in the absence of additional regulation, it is almost certain that future vehicles will exhibit even lower emission rates. Although there are currently no specific standards that directly limit emissions of N_2O, existing standards for NO_x do effectively result in reduced N_2O emissions through the design and implementation of advanced combustion and catalyst technologies.

Although the existing body of research on N_2O emissions is somewhat limited, available research does provide for a basic theoretical understanding of the N_2O formation process that is consistent with available test data. At low catalyst temperatures, NO_x reduction by carbon monoxide (CO) is believed to proceed according to the following pathway:[12] [3,4]

$$2NO + CO \rightarrow N_2O + CO_2$$
$$N_2O + CO \rightarrow N_2 + CO_2$$

As indicated, N_2O is formed as an intermediate reaction product, which can be emitted due to low temperature inefficiencies in carrying out the subsequent dissociation reaction. The N_2O formation reaction appears to dominate up to about 300ºC. At higher catalyst temperatures, N_2O formation ceases as the NO_x reduction reaction proceeds in accordance with the single step reaction:

$$2NO + CO \rightarrow N_2 + CO_2$$

Thus, N_2O formation is primarily a function of catalyst warmup. This has been confirmed through several research testing programs that clearly show N_2O formation rates peaking during vehicle start-up operations as the aftertreatment catalyst moves through its warm up stage. In effect, measured FTP emissions of N_2O are dominated by emissions during Bag 1 and Bag 3 of the driving cycle. [3,4,12]

Of course, the same dominance of Bag 1 and 3 emissions would occur for an engine-out exhaust species undergoing inefficient conversion due to low catalyst temperatures. However, several test programs have demonstrated that engine-out N_2O emissions are consistent with background N_2O concentrations, so that there is little uncertainty but that N_2O emissions are formed within the aftertreatment catalyst and not within the vehicle engine. [3-6] At the same time, it should be recognized that N_2O can form within the combustion chamber through reactions with intermediate combustion products such as:

$$HN + NO \rightarrow N_2O + H$$
$$HCO + NO \rightarrow N_2O + CO$$

However, such N_2O is also rapidly removed to create OH radicals:

$$N_2O + H \rightarrow N_2 + OH$$

so that engine-out N_2O is very low. [3]

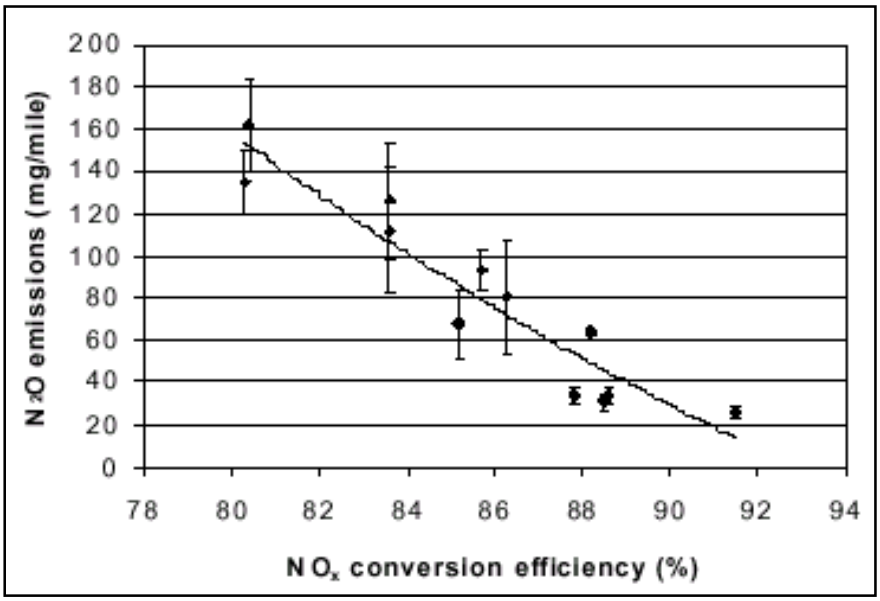
Given the demonstrated formation mechanism, it is widely believed that the control of vehicle N_2O emissions is a function of improved aftertreatment systems. As was the case with organic compounds (see Section Q.2), emissions control of NO_x (and thus NO) has evolved over the years. Both advanced engine technologies and improved catalytic aftertreatment techniques have reduced NO_x emissions to a fraction of that emitted by older vehicles. For example, a 2002

[12] The indicated reactions are simplified depictions of a more complex catalytic reaction process, but they effectively present the important elements of the N_2O formation process.

model year vehicle emits about 80 percent less NO_x than a 1981 era vehicle. By 2009, the reduction will increase to about 95 percent through continuing combustion and aftertreatment improvements. As was the case with methane, these improvements should result in decreases in N_2O emissions commensurate with increases in catalytic aftertreatment efficiency. As will be shown below, typical N_2O emissions are approaching levels associated with non-catalyst vehicles, but it is likely that a reasonable lower limit for N_2O emissions will continue to be greater than would be the case if catalytic aftertreatment systems were eliminated. Of course, associated increases in criteria pollutant emissions (i.e., HC, CO, and NO_x) due to catalyst removal would be several orders of magnitude larger than the net reduction in N_2O.

Expectations for continued N_2O reductions are consistent with existing research. In a review of N_2O emissions research, the EPA generally found that emission factors decline for three-way catalyst equipped vehicles as NO_x control efficiency increases. [13] Similarly, a recent test program conducted under rigorously controlled conditions across a set of controlled usage vehicles found a clear relationship between NO_x aftertreatment efficiency and N_2O emissions, as depicted in Figure Q-4. [4] Nevertheless, to confirm this relationship, the 39 vehicle ARB VSP dataset previously described in Section Q.2 above was utilized to estimate study-specific N_2O emission rates. [7] While 39 vehicles is certainly a limited dataset, it should be recognized that unlike methane, N_2O is generally not measured as part of the standard vehicle certification process in the U.S., so there is not an extensive library of available N_2O data. In fact, the VSP dataset includes approximately the same volume of N_2O emission rate data as all previous test programs combined. Moreover, it provides a snapshot of emissions from actual in-use vehicles.

Figure Q-4. N_2O Emission Rate Versus NO_x Conversion Efficiency [4]



Since the VSP dataset was previously described in Section Q.2, readers are referred to that section for additional background. Figure Q-1 and Table Q-1 of Section Q.2 provide an overview of the vehicle fleet represented in the VSP dataset. For this study, the relationship between measured N_2O and measured NO_x emission rates was investigated. Figure Q-5 and Table Q-7 present the results of this analysis. As expected from the findings of previous researchers, statistically significant relations between N_2O and NO_x emissions were found. As shown in Table Q-7, valid relations exist for all three bags of the FTP after outliers were removed.[13] When all data were considered, valid relationships were found for Bags 2 and 3, but not Bag 1. The lack of a Bag 1 relationship prior to the removal of outliers is the result of a single vehicle with very high NO_x and very low N_2O emissions (a carbureted 1981 Chevrolet Van with 5.1 g/mi NO_x and 0.02 g/mi N_2O). Data for this vehicle are consistent with very low aftertreatment efficiency, as N_2O emissions approach those of non-catalyst vehicles. This same vehicle was also identified as an outlier for both the Bag 3 and composite cycle analyses, but because N_2O emissions decline substantially for all vehicles during Bag 2, it was sufficiently consistent with the other VSP data for the Bag 2 analysis.

As shown in Table Q-7, N_2O generally is emitted at a rate about 2 to 3 percent of the NO_x emission rate, except during the start portions of the FTP cycle (i.e., Bags 1 and 3) when an additional 0.02 to 0.03 g/mi is emitted. Over the full cycle, the N_2O emission rate is equal to about 3 percent of the NO_x emission rate plus 0.015 g/mi:

$$N_2O = 0.0295\ (NO_x) + 0.0150$$

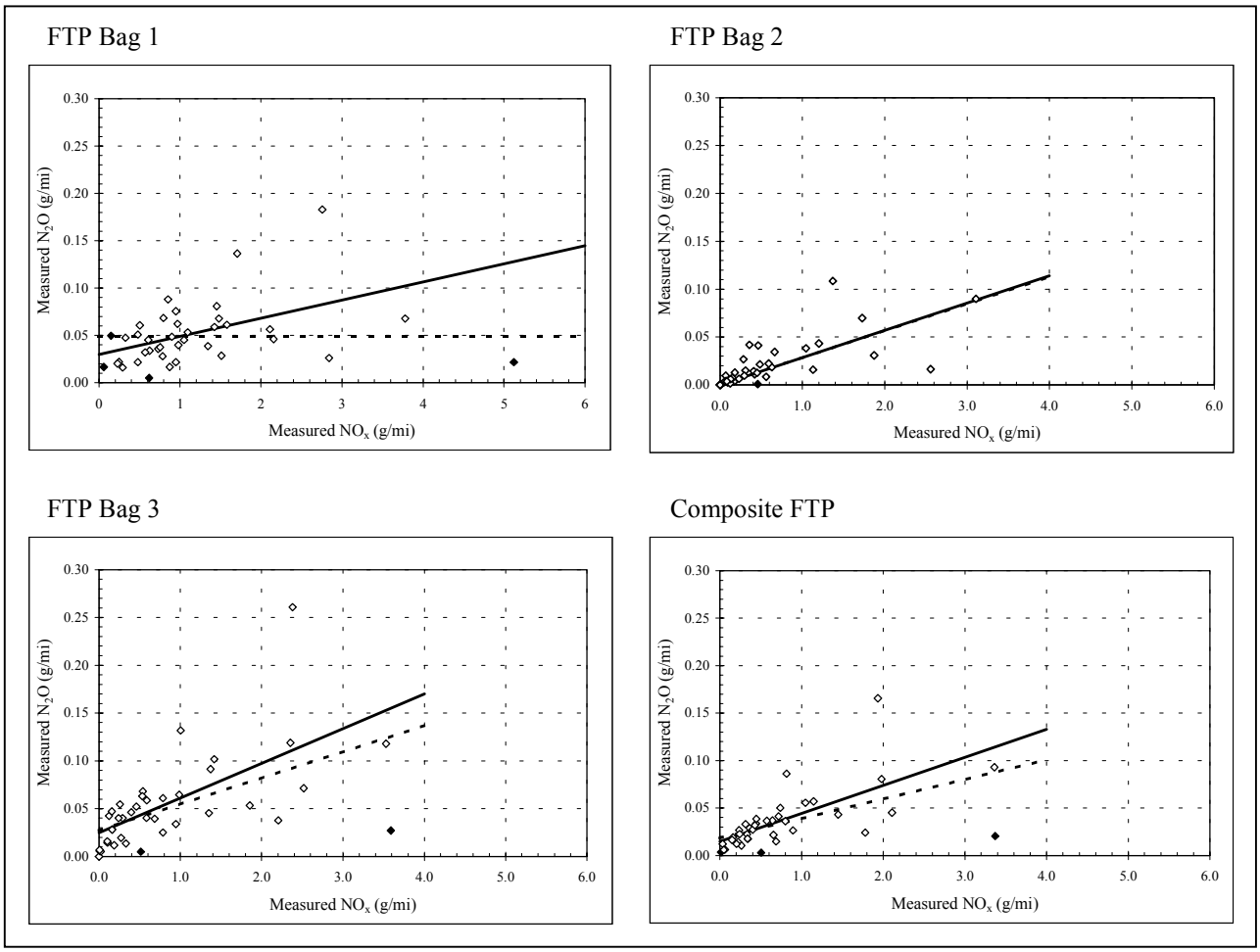
Thus, as NO_x is reduced, N_2O is also reduced proportionally *to a lower limit of 0.015 g/mi*. Such a finding is quite consistent with previous research, where maximum N_2O formation occurs during catalyst warmup, from about 100ºC to 300ºC for new catalysts or 200ºC to 400ºC for aged catalysts.

Figure Q-6 illustrates the sensitivity of N_2O formation to catalyst temperature. Since all catalysts will pass through the maximum N_2O formation temperature band after vehicle startup, there is a period of time during which N_2O emissions increase while NO_x declines (as NO is converted to N_2O). After the catalyst passes this band, both NO_x and N_2O conversion efficiencies increase and additional N_2O emissions are generally proportional to NO_x emissions. Thus, the volume of N_2O generated during initial catalyst warmup represents a practical lower limit for current three-way catalyst technology and N_2O reductions below this level will require significant advances in warmup characteristics.

Interestingly, the shift in the N_2O formation window to higher temperatures with catalyst aging results in a rather uncommon phenomenon relative to other emission species affected by catalyst aftertreatment. For aged catalysts, such as those represented in the ARB VSP dataset analyzed in this study, N_2O emissions during Bag 3 generally equal or exceed those of Bag 1. This is due to

[13] Consistent with the methane analysis described in Section Q.2, outliers are identified as vehicles with either N_2O/NO_x or NO_x/N_2O ratios that vary from the average ratio by more than ±2 standard deviations. Data identified as outliers are indicated in Figure Q-5 as solid markers.

Figure Q-5. N_2O Emission Rate Versus NO_x Emission Rate



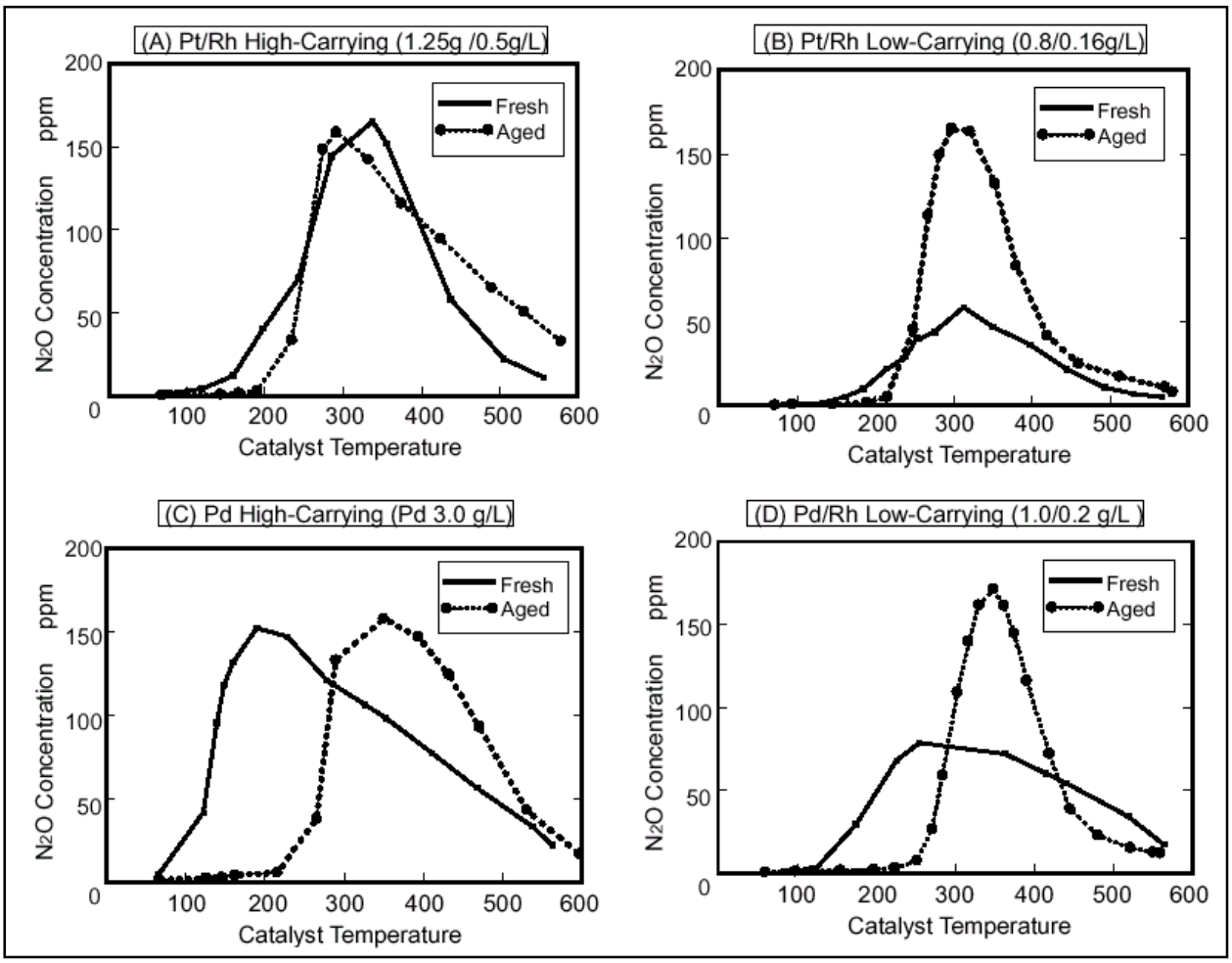
Note: The dotted and solid lines indicate regression-based relations. Dotted lines include all data, solid lines exclude outliers (defined as datapoints that vary from the average N_2O/NO_x or NO_x/N_2O ratio by more than two standard deviations).

Table Q-7. Regression Statistics for N_2O (g/mi) Versus NO_x (g/mi)

Statistic	All Data				Outliers (±2σ) Removed			
	Bag 1	Bag 2	Bag 3	Composite	Bag 1	Bag 2	Bag 3	Composite
Intercept	0.0491	0.0000	0.0272	0.0183	0.0301	0.0000	0.0249	0.0150
Slope	0.0000	0.0283	0.0275	0.0207	0.0191	0.0285	0.0362	0.0295
r^2	0.00	0.46	0.31	0.32	0.21	0.45	0.43	0.48
n (obs)	39	39	39	39	35	37	35	35

Slope and intercept statistics are selected at 95 percent confidence level.

Figure Q-6. N_2O Formation Rate Versus Catalyst Temperature [14]



the fact that the shift upwards in the N_2O formation temperature band can result in a somewhat longer period during Bag 3 (as compared to Bag 1) in which catalyst temperatures are within the band.

As was the case with the methane analysis described in Section Q.2, a secondary statistical analysis was conducted to ensure that the derived N_2O-to-NO_x relations were not simply a function of equivalently emitting vehicles measured at different mileage accumulations during their deterioration cycle. In this secondary analysis, the VSP data were split into two component datasets, one for 1992 and earlier vehicles (17 vehicles) and one for 1993 and newer vehicles (22 vehicles). As described in more detail in Section Q.2, this split was selected on the basis of a general shift in emission standard stringency beginning in 1993 when the first Tier 1 vehicles were required to be sold in California.[14]

[14] T-tests indicate that the probability of the two samples being from the same population is about 0.2 percent for NO_x and about 3 percent for N_2O.

Table Q-8 indicates the results of the data subset analysis. To factor out the influence of mileage accumulation to the maximum extent possible, statistics were calculated on a stratified basis by 50,000 mile increment mileage accumulation bins. Statistics were then compared across the two samples only when five or more datapoints were present in comparable mileage bins. This results in comparisons for two mileage bins, 50,000-100,000 miles and 100,000-150,000 miles. As indicated, the 1993 and newer vehicle emissions have generally declined by 30 to 50 percent for N_2O and 50 to 60 percent for NO_x relative to comparable mileage 1992 and older vehicles. Clearly, N_2O emissions have declined between the two periods, while N_2O-to-NO_x ratios have remained relatively stable as described above. Therefore, it should be possible to estimate both current and future certification emission rates for N_2O on the basis of the derived regression relations.

Using the N_2O-to-NO_x regression results and U.S. light duty vehicle certification standards for NO_x, the N_2O emission rates for current and future vehicles were estimated. As with the methane analysis discussed in Section Q.2, a certification compliance margin of 30 percent was assumed, consistent with assumptions utilized for the CO_2 emissions analysis portion of the study. So in effect, the target NO_x emission rate for a given NO_x standard is equal to:

$$\text{Target } NO_x = NO_x \text{ Standard} \times 0.70$$

Estimated N_2O emission rates were then developed on the basis of the previously described regression as:

$$N_2O = 0.0295\ (NO_x) + 0.0150$$

The resulting emission rates are presented in Table Q-9. As indicated, estimated emission rates range from 0.046 g/mi for a Tier 0 passenger car to 0.021 g/mi for a 2002 "fleet average" NLEV vehicle. Perhaps the best indication of the accuracy of these estimated emissions can be gleaned from a comparison of the estimated Tier 1 passenger car emission rate of 0.027 g/mi to the estimated 100,000 mile N_2O emission rate for 1993 and newer vehicles from the ARB VSP dataset used to develop the N_2O-to-NO_x regression relations.[15] As described in Section Q.2, the 1993 and newer vehicles in the ARB dataset are likely to reflect a mix of LEV I and Tier 1 vehicles, but the fleet average LEV requirements were such that Tier 1 vehicles were sold in substantial quantities through the late 1990s. Thus, it is reasonable to expect that the ARB dataset for 1993 and newer vehicles is similarly dominated by Tier 1 vehicles. In fact, a basic regression analysis of these data indicate an expected 100,000 mile N_2O emission rate of 0.029 g/mi, which compares well with the certification estimated rate of 0.027 g/mi.

The estimated N_2O emission rate for Tier 1 vehicles also compares favorably with emission rates estimated by the EPA. [13] As published, the EPA estimated N_2O emission rates for Tier 1 vehicles of 0.046 g/mi for passenger cars and 0.064 for light duty trucks appear to be much higher than the estimate of 0.027 g/mi from Table Q-9. However, the EPA emission rates are for a 285 ppm sulfur gasoline, while those estimated in this study are for low sulfur California fuel.

[15] Since the certification standards used to develop the estimated N_2O emission rate are 100,000 (or 120,000) mile standards, measured emissions at 100,000 miles are an appropriate comparison metric.

Table Q-8. Average NO_x and N_2O Emission Rates for Split VSP Database

Organic Species	Odometer (miles)	Pre-1993 Vehicles		1993 and Newer Vehicle		Percent Change (a)
		Average Emission Rate (g/mi)	Number of Observations	Average Emission Rate (g/mi)	Number of Observations	
NO_x	0-50,000		0	0.098	5	
	50,000-100,000	0.709	6	0.339	10	-52%
	100,000-150,000	1.901	5	0.747	6	-61%
	150,000-200,000	1.548	4	0.444	1	
	200,000-250,000	0.688	1		0	
	250,000-300,000		0		0	
	300,000-350,000	0.801	1		0	
	All Data	**1.261**	**17**	**0.400**	**22**	**-68%**
	50,000-150,000	**1.251**	**11**	**0.492**	**16**	**-61%**
N_2O	0-50,000		0	0.009	5	
	50,000-100,000	0.035	6	0.025	10	-29%
	100,000-150,000	0.065	5	0.033	6	-50%
	150,000-200,000	0.056	4	0.039	1	
	200,000-250,000	0.015	1		0	
	250,000-300,000		0		0	
	300,000-350,000	0.036	1		0	
	All Data	**0.048**	**17**	**0.024**	**22**	**-49%**
	50,000-150,000	**0.049**	**11**	**0.028**	**16**	**-43%**

Notes: (a) Only stratifications with five or more component datapoints are included.

As described further below, sulfur has been shown to have a significant influence on N_2O emission rates, as might be expected given its detrimental influence on catalyst efficiency. Thus, the EPA emission rates are not directly comparable with those estimated in this study. The EPA did, however, test two Tier 1 vehicles on both the 285 ppm sulfur gasoline and indolene containing 24 ppm sulfur. The results of this comparative testing showed that N_2O emission rates were reduced by 28 and 49 percent on the low sulfur fuel.[16] While this is certainly a limited test sample, it does indicate that the EPA estimated N_2O emission rates, when corrected for fuel sulfur content, are more likely within a range of 0.024 to 0.046 g/mi, which is reasonably consistent with the 0.027 g/mi emission rate estimated in this study. As a result, it seems likely

[16] One Tier 1 vehicle had measured N_2O emission rates of 0.039 g/mi with 24 ppm sulfur and 0.054 g/mi with 285 ppm sulfur, for a net emission rate reduction of 28 percent. The second Tier 1 vehicle had measured N_2O emission rates of 0.115 g/mi with 24 ppm sulfur and 0.227 g/mi with 285 ppm sulfur, for a net emission rate reduction of 49 percent.

Table Q-9. Estimated N_2O Emission Rates

Certification Level	NO_x Standard (g/mi)	NOx Target (g/mi)	Predicted N_2O (g/mi)	CO_2 Equivalent (g/mi)	Change from PC Tier 0	Change from PC Tier 1	Change from 02 NLEV
Tier2,Bin 1/ZEV	0.000	0.000	0.015	4.4	-67%	-45%	-28%
Tier2,Bin 2/SULEV	0.020	0.014	0.015	4.6	-66%	-44%	-26%
Tier2,Bin 3	0.030	0.021	0.016	4.6	-66%	-43%	-25%
Tier2,Bin 4	0.040	0.028	0.016	4.7	-66%	-42%	-24%
Tier2,Bin 5/LEV II/ULEV II	**0.070**	**0.049**	**0.016**	**4.9**	**-64%**	**-40%**	**-21%**
Tier2,Bin 6	0.100	0.070	0.017	5.0	-63%	-38%	-18%
Tier2,Bin 7	0.150	0.105	0.018	5.4	-61%	-34%	-13%
Tier2,Bin 8	0.200	0.140	0.019	5.7	-58%	-30%	-8%
LEV I/ULEV I	0.300	0.210	0.021	6.3	-54%	-23%	+2%
PC Tier 1/TLEV	0.600	0.420	0.027	8.1	-40%	0%	+32%
PC Tier 0	1.500	1.050	0.046	13.6	0%	+68%	+122%
2002 NLEV Fleet Average	0.276	0.193	0.021	6.1	-55%	-24%	0%
2002 LEV Fleet Average	0.262	0.183	0.020	6.0	-56%	-25%	-1%
2010 LEV Fleet Average	0.061	0.043	0.016	4.8	-65%	-41%	-21%

Notes: (1) For all fleet average standards, passenger car and LDT1/2 standards are weighted by 55 percent and LDT3/4 standards are weighted by 45 percent on the basis of the 2009 Martec market forecast described in Section II of the study report. Basically, the entire large truck and minivan classes are assumed to be LDT3/4, as is 60 percent of the small truck class.
(2) The target emissions level is 70 percent of the applicable standard.
(3) Predicted N_2O equals the target NO_x emissions times 0.0295 plus 0.0150.
(4) CO_2 equivalent emissions equal N_2O emissions times 296 (the GWP of N_2O).

that the N_2O emission rates estimated in this study provide for a reasonably accurate depiction of current and future emissions.

Table Q-9 indicates that by 2009, N_2O emissions can be expected to decline by about 21 percent, to 0.016 g/mi (about 4.9 g/mi CO_2 equivalent), from the estimated 2002 fleet average emission rate of 0.021 g/mi. This reduction will come about due to the imposition of the federal Tier 2 program and the improved combustion and aftertreatment efficiencies it is expected to promote. Since the Tier 2 program is already adopted, the incremental costs that will accrue to capture this N_2O reduction benefit are already accounted for under the Tier 2 program and thus no additional cost will accrue from a GHG perspective.

However, as is also indicated, the 2009 N_2O emission rate is approaching the lower emissions limit (estimated in this study as 0.015 g/mi) imposed by the necessity of conventional three-way catalysts to pass through the warmup temperature band during which the bulk of N_2O formation occurs. Faster excursions to catalyst temperatures above about 400ºC could allow even this

lower limit to be "broken," but there is no available data with which to access the likelihood of significant breakthroughs in this area. It is also important to recognize that the EPA estimates that N_2O emissions for non-catalyst vehicles are in the range of 0.017-0.019 g/mi. [13] This is actually a bit higher than the lower limit emission rate estimated in this study and so is not necessarily a precise comparative datapoint, but the clear implication is that emission rates for catalyst equipped vehicles are approaching those for non-catalyst vehicles.

Nevertheless, it is possible to promote modest additional N_2O reductions through further advances in aftertreatment efficiency. For example, adding advanced technology required to certify vehicles to the Tier 2, Bin 2 level will reduce emissions by a additional 6 percent, but that translates into an absolute CO_2 equivalent reduction of less than 0.3 g/mi. As was the case for methane, since additional emission reduction potential is occurring "at the margin" due to already low emission rates, the cost effectiveness of additional reductions is relatively high. ARB estimates for the incremental retail cost of a SULEV vehicle relative to a ULEV II vehicle provide insight into the cost effectiveness of controlling N_2O to the Tier 2, Bin 2 level. These costs are estimated at about $80 per vehicle. [10] As indicated in Table Q-10, this implies a cost effectiveness of about $1,600 per ton of equivalent CO_2 reduction, *assuming all associated costs are attributed to N_2O reduction*. Of course, as described in Section Q.2, reductions of methane also accrue, as do reductions in NO_x and NMOG, which could be used to offset a portion of the imposed cost. As both the N_2O and methane reductions accrue in proportion to NO_x and NMOG reductions, it seems most logical to consider these reductions as integral components of Tier 2 and LEV II program reviews, as opposed to independent GHG considerations. This would maintain a consistent approach to continued program development, while properly reflecting both the criteria and GHG emission benefits of such programs.

Table Q-10. Cost and Cost Effectiveness of N_2O Reductions

Reduction Strategy	N_2O Change (g/mi)	CO_2 Equivalent Change (g/mi)	Marginal Cost	Cost Effectiveness ($/ton CO_2)
Tier 2,Bin 5 to Tier 2, Bin 2	0.001	0.305	$ 80	$ 1,585
Added Reduction due to CH_4		0.164		
Total GHG Reduction	0.001	0.469	$ 80	$ 1,031

Notes: (1) Cost effectiveness is based on a lifetime mileage estimate of 150,000 miles.

As was the case with the methane analysis presented in Section Q.2, it is important to note that the N_2O relationships presented in this study are derived from data for stoichiometric control technology. Existing research indicates that the N_2O formation rate over typical three-way catalysts is quite sensitive to perturbations in air-fuel ratio. At both very rich and very lean conditions, N_2O formation is low due to high active site adsorption rates for non-NO species (CO under rich conditions and oxygen under lean conditions). However, at slightly rich and slightly

lean conditions, significant NO adsorption occurs while additional free sites for subsequent N_2O dissociation are limited. [17] Thus, for stoichiometric technology, N_2O is minimized as air-fuel ratio control is optimized. Since future emission standards will result in the introduction of further advances in mixture control as well as continuing improvements in catalyst light off performance, the expectation of continuing N_2O emission reductions for stoichiometric technology, as suggested by the Table Q-9 emission rates, is reasonable.

Current diesel engines emit relatively low levels of N_2O due to the absence of catalytic reduction technology. However, the introduction of lean burn aftertreatment technology targeting NO_x control, whether for advanced gasoline or diesel engines, could alter current lean burn N_2O emission rates. [18,19] Lean burn aftertreatment technology such as NO_x adsorbers or selective catalytic reduction (SCR) systems must function under mixture regimes well removed from stoichiometry. Under such conditions and depending on the effectiveness of associated control strategies, N_2O formation could be significant. Current research indicates that N_2O concerns may be more pronounced with SCR systems, but due to the ongoing nature of lean burn aftertreatment system development, it is not possible to assign a reliable N_2O emission rate to any lean burn systems at this time. Given the awareness of aftertreatment developers to N_2O emission concerns, it seem reasonable, however, to assume that design goals will be for emission rates equal to or less than those for current stoichiometric systems. Therefore, for purposes of this study, N_2O emission rates for lean burn technologies are assumed to be the same as those for 2009 (i.e. Tier 2, Bin 5) stoichiometric technology. Clearly, the validity of such an assumption should be monitored as such systems enter the marketplace.

N_2O decomposition catalysts have been patented and are in the initial stages of investigation in the industrial sector. However, these systems are essentially untested in the automotive sector and are likely to face significant challenges such as mechanical and thermal durability, as well as potential sensitivity to exhaust contaminants such as sulfur. [20] Given the ability of the aftertreatment industry to produce the highly effective catalyst systems available in the automotive sector today, there is little doubt that with sufficient leadtime, effective N_2O decomposition catalysts could be introduced. However, given continuing N_2O reductions, the cost effectiveness of additional N_2O decomposition solutions is uncertain. Due to the lack of a prototype system on which to base a costing analysis, no specific cost estimates are developed for this study, but such systems could be considered if alternative lean burn solutions are not found.

Finally, existing research has demonstrated the sensitivity of N_2O formation to fuel sulfur content. [3,4,13] Test data show N_2O emission rate increases of up to 300 percent when fuel sulfur is increased from 20 to 300 ppm. However, this is not considered to be a significant issue in this study as existing federal and California rules require the sulfur content of both gasoline and diesel fuel to be less than 30 ppm on average in the timeframe considered. Thus, all N_2O emission rates estimated in this study assume low sulfur fuel availability. Current emission rates for in-use vehicles may be higher than indicated, but those rates should decline as low sulfur fuels assume a dominating market share over the next few years. Moreover, in any established regulatory structure, emission rates would almost certainly be measured over existing certification cycles for which low sulfur fuels are commonly used.

Q.4 Summary

As described in Sections Q.2 and Q.3 above, emission rates for methane and nitrous oxide have been estimated using an emissions testing dataset for in-use vehicles provided by the ARB. Table Q-11 presents a summary of the estimated emission rates. In general, current emissions of both methane and N_2O appear to be quite low relative to emissions of CO_2, estimated at about 0.2 and 6 grams CO_2 equivalent per mile of travel. Moreover, as shown in Figures Q-7 and Q-8, emission rates of both compounds have declined substantially over the last two decades.

A combined CO_2 equivalent emission rate of about 6 g/mi compares to typical tailpipe CO_2 emission rates for current light duty vehicles that range from about 250 g/mi for small cars to 500 g/mi or more for large trucks. Thus, the combined GHG impact of methane and N_2O represents from 1-2 percent of the total CO_2 equivalent emissions from light duty vehicles (ignoring the GHG impacts of emitted water vapor). As presented elsewhere in this study, advanced technology vehicles could achieve reduced CO_2 emission rates in the 2009 to 2015 timeframe of between 150 and 250 g/mi. In this same timeframe, the combined impact of methane and N_2O emissions is estimated to decline to about 5 g/mi, so the combined GHG impact of these species could increase to between 2 and 3 percent of the total GHG impact of light duty vehicles *if* low CO_2 emission technologies are introduced in significant volumes.

Reductions in methane and N_2O emissions beyond those expected to occur by 2009–2015 are possible. However, because the total possible reduction is capped at 5 g/mi CO_2 equivalent, these reductions tend to be relatively expensive from a cost effectiveness standpoint, ranging upwards from about $1,000 per ton of CO_2, as detailed in Sections Q.2 and Q.3 above. These estimates should be considered in the context of a current absence of regulatory controls on either methane or nitrous oxide. In this absence, research into potential reduction technologies and costs, as well as emission rates is somewhat limited. So it is possible that future developments will improve the cost effectiveness of additional reductions. However, barring significant error in the estimated emission rates, the absolute level of reductions possible at any cost is quite limited.

Table Q-11. Estimated Methane and N_2O Emission Rates

Basic Technology Configuration	Methane		Nitrous Oxide	
	2002	2009-2015	2002	2009-2015
Grams per Mile - Expressed as Direct Methane or Nitrous Oxide				
Stoichiometric	0.010	0.008	0.021	0.016
Lean Burn	0.005	0.005	0.016	0.016
Grams per Mile - Expressed as CO_2 Equivalent				
Stoichiometric	0.23	0.18	6.1	4.9
Lean Burn	0.12	0.12	4.9	4.9

Figure Q-7. Methane and N_2O Emission Rates by Certification Class

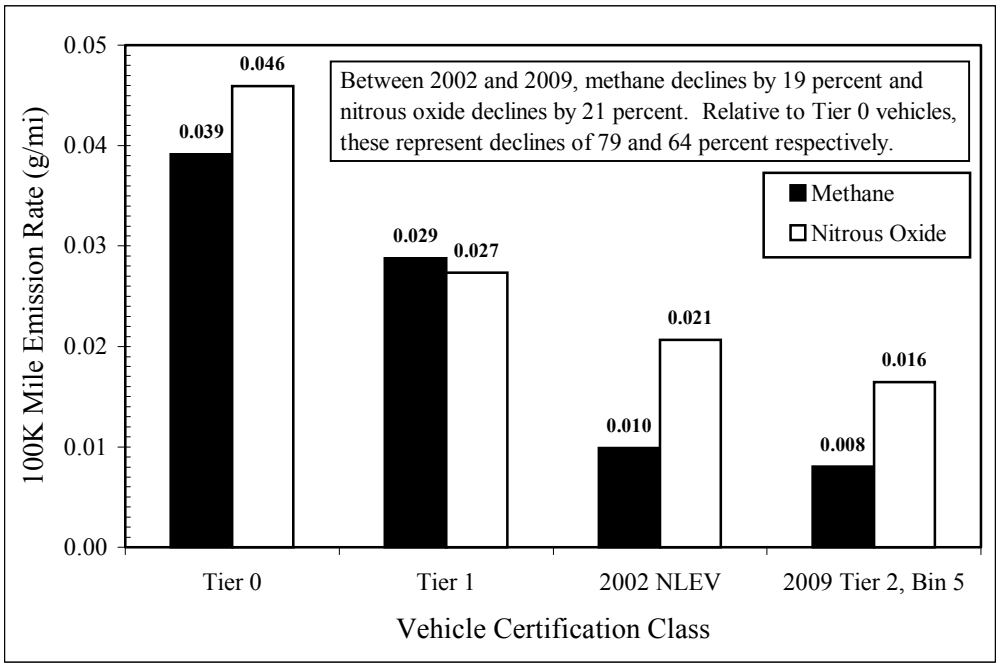
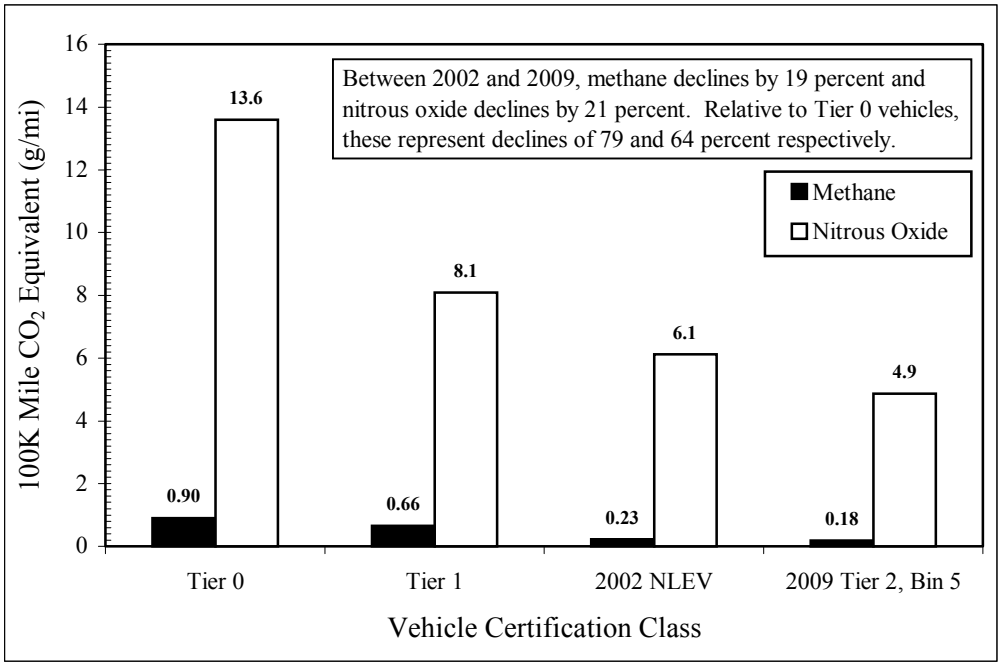


Figure Q-8. CO_2 Equivalent Methane and N_2O Emission Rates by Vehicle Certification Class



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