Attachment B. Air Resources Board's Multi-Media Assessment: Air Emissions--Assessment of Emissions of Lubrizol's PuriNOx Water/Diesel Emulsion on Exhaust Emissions from Heavy-Duty Diesel Engines (Public Version)

State of California
California Air Resources Board

Assessment of Emissions of Lubrizol's PuriNOx Water/Diesel Emulsion on Exhaust Emissions from Heavy-Duty Diesel Engines

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Assessment of Emissions of Lubrizol's PuriNOx Water/Diesel Emulsion on Exhaust Emissions from Heavy-Duty Diesel Engines

I. Summary, Conclusions, and Recommendations

A. Summary

The Air Resources Board (ARB/Board) staff have completed an air quality assessment on Lubrizol's PuriNOx water emulsified diesel fuel. Two versions of the fuel were evaluated, PuriNOx generation 1 (Gen1) and PuriNOx generation 2 (Gen2) water emulsified diesel fuels. Staff's evaluation assesses the effect PuriNOx fuel has on emissions from heavy-duty diesel engines based on a relative comparison between diesel fuel complying with the ARB requirements (CARB diesel) and PuriNOx fuel. The evaluation includes an assessment of the impact of using PuriNOx fuel on criteria pollutants and toxic air contaminants and ozone precursors. To estimate PuriNOx emission impacts for the years, 2002 and 2010, staff used a conservative assessment that 25 percent of the centrally fueled fleet (9 percent of all on-road diesel fueled vehicles) would use PuriNOx. This assumption is significantly greater than the fuel use rate than what Lubrizol predicts will be used in California in 2010.

1. Criteria Pollutants

Emission studies that were performed for the United States Environmental Protection Agency (U.S. EPA), the ARB, and a consultant study by Air Improvement Resource (AIR) were submitted for evaluation. Emissions data were obtained from a wide range of conditions including engine type and model year, on and off road applications, and with and without aftertreatment emission controls. On average, emissions of oxides of nitrogen (NOx) and particulate matter (PM) were reduced by 14 percent and 58 percent, respectively. Hydrocarbon emissions increased by 87 percent. When evaluating the emission effects of PuriNOx fuel on an absolute basis, mass emission reductions for NOx are greater than mass emission increases of hydrocarbons. For example, comparing Gen1 to CARB diesel in a 1991 DC series 60 engine should have a mass reduction for NOx of 0.6 grams per brakehorse power hour (g/bhp-hr) and only a 0.06 g/bhp-hr increase for hydrocarbons.

2. Toxic Emissions

Staff's evaluation of toxic emissions is based mainly on two studies: the U.S. EPA Tier 1 and the CARB verification for Gen1 (SWRI report (**1**)). In addition to these studies, data from eight other studies were also used for evaluating diesel PM emissions.

a) Particulate Matter Toxic Emissions

The ARB identified diesel PM as a toxic air contaminant in 1998, and determined that diesel PM has been determined to account for about 70 percent of the toxic risk from all identified toxic air contaminants. The evaluation of the effect that PuriNOx Gen1 has on PM emissions from diesel engines is based on a number of studies, including the U.S. EPA's draft technical report. The U.S. EPA draft technical report (**2**) evaluated PM from the use of Gen1 using available emissions data and found that the use of PuriNOx fuel significantly reduces PM emissions on average by 58 percent from on-road conventional diesel fuel. The U.S. EPA draft technical report also indicated that PM emissions from off-road engines were on average reduced by 28 percent, although the result is based on the test of one engine of less than 100 hp. A study that was not included in the U.S. EPA draft technical report was the study conducted for the U.S. EPA Tier 1 Health Effects program. The EPA Tier 1 study using a 1999 DDC series 60 engine concluded PM was reduced by 33 percent.

Another study was conducted for the ARB Diesel Emission Control Strategy Verification Procedure. For the verification procedure a 1991 DDC series 60 was used and PM emissions were determined to be reduced by 63 percent from the use of PuriNOx.

Gen2 PM emission reductions were reported in the South West Research Institute (SWRI) study by Spreen (**3**) where a 1999 DDC series 60 engine showed a PM reduction of 47 percent. For the same engine, Gen1 showed a PM reduction of 33 percent.

Although there is a limited data set for Gen 2, Gen2 PM emission reductions were greater than Gen1 when tested on the same engine, therefore the average 58 PM reduction appears to be a conservative estimate for both Gen1 and Gen 2 fuels.

b) Other Toxic Emissions

As discussed above, the use of PuriNOx reduces diesel PM emissions and represents a significant reduction (average 58 percent) of the PM mass from diesel exhaust. However, increases in emissions of some toxic species such as formaldehyde, acetaldehyde, BTEX, 1,3-butadiene, and some polycyclic aromatic hydrocarbons (PAHs) have also been reported. Although the increase of these toxics are of concern, the magnitude of their mass emissions is small compared to the decrease in mass emissions of PM. After PM, formaldehyde and acetaldehyde are the toxics with the next highest emission rates but their cancer unit risk factors are approximately two orders of magnitude lower than diesel PM. There have been reported increases in 1,3-butadiene and some PAHs that have cancer unit risk factors of similar magnitude as diesel PM, but their mass emission rates were two to six orders of magnitude lower than PM mass emission rates. The Office of Environmental Health Hazard Assessment staff have evaluated the effect of these toxic emission increases and concluded that the absolute amount of these toxics in diesel exhaust is small and does not appear to be a significant cancer risk compared to diesel PM emissions.

3. Ozone Precursors

The use of PuriNOx fuel as compared to CARB diesel fuel decreases NOx emissions by about 14 percent but increases reactive organic gas (ROG) emissions by 87 percent. However, PuriNOx emissions of ROG are about 29 percent of the NOx emissions in diesel exhaust, that is, for each ton ROG increased, NOx will be reduced by 3.4 tons. Currently, the California State Implementation Plan (SIP) consists of a number of planned control strategies that target ROG and NOx emissions. In implementing the SIP, these strategies are balanced to result in an overall reduction in ozone levels. That is if PuriNOx is to be used as a ozone control strategy, any increases in ROG will be addressed.

4. Emission Impacts for the South Coast Air Basin

The California emissions inventory and the EMFAC model were used to estimate the impact that PuriNOx could have on emissions in the South Coast Air Basin where PuriNOx is currently used in limited applications. Emissions estimates were made for NOx, PM, reactive organic gases ROG, 1,3-butadiene, formaldehyde, acetaldehyde, benzene, ethyl benzene, and naphthalene. Emissions estimates were calculated for 2002 and 2010. Emission estimates were based on the conservative case where staff assumed that 25 percent of the centrally fueled vehicles would use PuriNOx. This is a factor of nine higher than what is projected by Lubrizol in 2012.

For the South Coast Air Basin in 2010, the use of PuriNOx in 25 percent of the centrally fueled vehicles would reduce NOx from on-road heavy-duty diesel vehicles by 2.4 tons/day and PM10 by 0.22 tons/day. This corresponds to a 1.1 percent reduction of NOx and a 6 percent reduction of the PM from on-road heavy-duty diesel engines or about 0.3 percent and 0.07 percent, respectively, from all sources. ROG would increase by 0.7 tons/day, which is 9 percent of the ROG from on road heavy-duty diesel engines or about 0.12 percent of the ROG from all sources. For 1,3-butadiene, benzene, ethyl benzene, and toluene, formaldehyde, and acetaldehyde, increases from 0.0002-0.0003 tons/day may occur. For formaldehyde, the toxic with the highest emission rate next to diesel PM10 emissions would increase by 0.1 ton/day in 2010 but has a risk of about two orders of magnitude lower than PM.

5. PuriNOx Gen1 and Gen2 Emissions of Greenhouse Warming Species

No life-cycle analysis has been performed on PuriNOx Gen1 and Gen2 fuels to determine the net effect on emissions of greenhouse species. However, based on a limited data set, PuriNOx and CARB diesel emissions of carbon dioxide are comparable and within the experimental error. These data also show levels of methane are very low in diesel exhaust and is a minor source as compared to other anthropogenic sources. A comparison of nitrous oxide was not done since it was not measured in any of the studies. In terms of black carbon, another greenhouse warming species, there may be some beneficial effects from the use of PuriNOx. Data indicates that the black carbon content in PM emissions from PuriNOx can be significantly lower in comparison to conventional diesel fuel. However, the overall impact on greenhouse gas emissions from this observation cannot be quantified. Also, there is some evidence that the use of PuriNOx results in a small increase in combustion efficiency which may result in a small reduction in greenhouse gases.

B. Conclusions

In comparison to CARB diesel fuel, staff concludes the following about the use of PuriNOx diesel fuel:

- PuriNOx significantly reduces PM and NOx emissions.

- PuriNOx significantly reduces emissions and risk from PM in diesel exhaust, a toxic air contaminant identified by the ARB.

- Of the specific toxic compounds with increased emission rates, their absolute level in diesel exhaust is small and does not appear to be a significant cancer risk.

- Within the limitations of the dataset, the Gen2 additive chemistry does appear to have similar reductions for NOx and PM when compared with the Tier 1 Gen1 results. Emissions reductions of toxic air contaminates and aldehydes for Gen2 ~~do~~ appear to be similar to those reported for Gen1. Since no data was available, no conclusion could be made on PAH or nitro-PAH emissions, however staff have no reason to believe that their emissions from the use of Gen2 will differ from Gen1.

- Although no greenhouse gas life cycle analysis of PuriNOx has been conducted, PuriNOx should be similar to lifecycle emissions of conventional diesel fuel. Also, there is some evidence that the use of PuriNOx results in a small increase in combustion efficiency which may result in a small reduction in greenhouse gases.

C. Recommendations

Based on staff's air quality assessment, staff recommends that the Environmental Policy Council find that the use of PuriNOx, as described in Lubrizol's multimedia assessment, does not pose a significant adverse impact on public health or the environment from potential air quality impacts, relative to conventional California diesel fuel. Although there are some negative impacts associated with the use of PuriNOx, such as the increase of some specific toxics and an increase in ROG, the net benefits of the significant decrease in toxic PM and a reduction in NOx make this a viable control strategy in improving air quality in California.

II. Introduction

The Lubrizol Corporation (Lubrizol) has developed PuriNOx, a water-emulsified diesel fuel, that is designed to reduce emissions such as PM and oxides of nitrogen (NOx) from diesel fueled engines. Lubrizol is marketing the fuel to centrally fueled heavy-duty diesel fleets throughout the United States including California. Lubrizol has applied for a verification of PuriNOx as a diesel emission control strategy under the California Air Resources Board (ARB) diesel retrofit in-use program Title 13 California Code of Regulations sections 2700-2710. As a requirement for verification, PuriNOx must undergo a multi-media assessment to determine if the use of PuriNOx in heavy-duty diesel engines results in any significant increases in multi media impacts compared to diesel fuel meeting California ARB requirements (CARB diesel).

A multi-media working group including representatives from the CAL/EPA, the State Water Resource Control Board (SWRCB), the Office of Environmental Health Assessment (OEHHA), the Department of Toxic Substance Control (DTSC) and the ARB was formed to oversee the multi-media assessment. The ARB staff is responsible in coordinating the overall assessment and to evaluate and review the air quality part of the multi-media assessment.

State law requires that findings from the multi-media working group along with an independent peer review of the findings from the University of California be presented to the Environmental Policy Council. The Environmental Policy Council is to determine based on the multimedia evaluation whether the use of PuriNOx has a significant adverse impact on public health or the environment in comparison to CARB diesel fuel.

This is a summary of the ARB's staff assessment of the effect PuriNOx fuel has on the emissions from heavy-duty diesel engines. The evaluation is to determine the relative differences between CARB diesel fuel and PuriNOx fuel. The evaluation includes an assessment of the impact of using PuriNOx fuel on criteria pollutants and toxic air contaminants compared to CARB diesel.

III. Description and Potential Use of PuriNOx Fuel

A. Description

PuriNOx is a water emulsified diesel fuel composed of water, an additive package, and CARB diesel fuel. Lubrizol has applied for verification of two formulations of PuriNOx fuel, generation 1 (Gen1) and generation 2 (Gen2). Gen1 and Gen2 have a diesel fuel content of approximately 80 percent and a water content of approximately 20 percent, but mainly differ in the additive composition and content in the fuel.

B. Production and Use of PuriNOx fuel in California

In 2002, two million gallons of PuriNOx fuel was used in California (4**)**. Currently there is the capacity to produce 15-35 million gallons of PuriNOx fuel, annually in California **(**5**).** Based on California diesel sales, over 2.7 billion gallons of on-road diesel fuel was sold in California in 2002. The amount of PuriNOx used represents less than 0.1 percent of diesel fuel used in California and the current PuriNOx production capacity is less than one percent of diesel fuel sold in California.

Lubrizol is currently marketing PuriNOx fuel only to centrally fueled heavy-duty vehicles. The fuel is restricted to centrally fueled fleets since its use can only be controlled and monitored in captive fleets. Also, storing PuriNOx requires separate storage tanks that are usually available only to centrally fueled fleets.

IV. Exhaust Emissions

To verify the benefits of PuriNOx fuel, Lubrizol conducted engine out emission studies for internal research and development, for CARB verification (**6**), and for the U.S. EPA Tier I and Tier 2 health effects testing (**1, 7**). A summary of test parameters are given below.

- Test cycles: Transient and Steady State modes
- Dynamometer: Engine and chassis
- Reference Fuels: CARB diesel, Ultra-low sulfur diesel fuel, EPA 211 test fuel
- Candidate Fuels: Gen1 and Gen2 fuels
- Types of engines: on-road and off road, European and U.S. engines
- Aftertreatment tested: oxidative catalyst
- Emissions characterized: criteria and toxic air pollutants. The CARB verification and the U.S. EPA Tier 1 and Tier 2 health studies include data on toxic emissions.

These studies and others have demonstrated that water emulsified diesel fuels can reduce emissions of PM and oxides of nitrogen (**2**). The use of a cooling agent such as water lowers combustion temperature, therefore, decreasing emissions of NOx. The emulsified water also promotes an increase in turbulent mixing due to the expansion and vaporization of the water within the fuel droplets. This increase in fuel/air mixing reduces the occurrence of fuel rich zones where soot is formed, thus reducing PM emissions.

A. Gen1 Criteria Pollutant Emission Estimates

Most of data submitted for review was for the Gen1 fuel. The following is a review of the Gen1 criteria emission estimates. The emissions impacts of PuriNOx were reported by Air Improvement Resource (AIR) (**8**) and the U.S. EPA draft technical report (2002) **(2).** Included in the U.S. EPA draft technical report is data from a number of studies including a study conducted for CARB verification **(6).** The U.S. EPA noted that the CARB study contained a substantial amount of data due to the number of emission tests that were needed for verification. Another substantial body of emission data was conducted for the U.S. EPA Tier 1 health affects tests.

1. <u>AIR's Study</u>

The AIR study was completed under a contract to Lubrizol in 2001. Lubrizol provided emissions data on 12 engines of which 4 engines were not used for the assessment. One engine equipped with EGR was excluded because emission data was provided too late to be incorporated into the report. The other three engines were excluded because they either were tested on a chassis dynamometer or were tested using repowered calibrations. A summary of the engines and test conditions are given in Table 1.

Table 1. Summary of Engines used for AIR evaluation of emission impacts.

Engine	Application	Model Year	Aftertreat-ment	Test Cycle	Fuel
Caterpillar 3306	off-road	1990	none	8 mode	CARB[1]
Caterpillar 3508	off-road	2000	none	8 mode	diesel
Caterpillar 3406B	off-road	1996	none	4 mode	diesel
DDC Series 50	on-road	1995	catalyst	FTP transient	CARB
DDC 6V92	off-road	1995	with and without catalyst	8 mode	off-highway
Perkins 1004.4T	off-road	1999	none	European transient/8 mode	high/low sulfur
DDC Series 60	on-road	1999	none	FTP transient	CARB
DDC Series 60	on-road	1991	none	FTP transient	CARB

[1]CARB California diesel fuel (400 ppm Sulfur)

For the eight engines studied, the AIR report concluded that PuriNOx reduced emissions for NOx and PM by 19 and 54 percent, respectively, and hydrocarbons (HC) and carbon monoxide (CO) emissions increased by 74 and 18 percent, respectively.

2. The U.S. EPA Draft Technical Report on PuriNOx

In a subsequent study, the U.S. EPA conducted a technical analysis of the effect of Lubrizol's PuriNOx water emulsified diesel on exhaust emissions from diesel engines. The report analyzed pre-existing data from various test programs to investigate these effects. Of the engine test data available, the U.S. EPA concluded that thirteen engine tests met the analytical requirements of their study. Listed are the reasons why other engine tests were excluded from the study.

- Repowered engines data.
- Data collected from chassis dynamometers, in-use monitors, and alternative versions of PuriNOx having different water concentrations.
- Steady-state emissions data for PM and CO were excluded for both highway and nonroad engines.

Table 2 provides information on the 13 engines used for the study.

Table 2. Summary of Engine types and test cycle used for the emissions studies.

Engine	Use	Group	Test Cycle
96 DDC Series 50 w/catalyst	Highway	HH	FTP
99 DDC Series 60, lube oil #1	Highway	HH	FTP
99 DDC Series 60, lube oil #2	Highway	HH	FTP
91 DDC Series 60, lube oil #1	Highway	HH	FTP
91 DDC Series 60, lube oil #2	Highway	HH	FTP
00 DDC Series 50 w/EGR	Highway	EGR	8 mode
94 Caterpillar 3176	Highway	HH	8 mode
01 Cummins 5.9L	Highway	MH	FTP
99 Perkins 1004.4T high sulfur	Nonroad	0-100hp	Euro trans
99 Perkins 1004.4T low sulfur	Nonroad	0-100 hp	Euro trans
99 Perkins 1004.4T high sulfur	Nonroad	0-100hp	8 mode
99 Perkins 1004.4T low sulfur	Nonroad	0-100hp	8 mode
95 DDC 6V92	Nonroad	175-300hp	8 mode
00 Caterpillar 3508	Nonroad	175-300hp	8 mode
90 Caterpillar 3306	Nonroad	300+hp	8 mode
96 Caterpillar 3406	Nonroad	175-300hp	8 mode
85 Caterpillar 3406B	Nonroad	300+hp	8 mode
85 Deutz F8L413	Nonroad	175-300hp	8 mode
96 Deutz F6L912	Nonroad	100-175hp	8 mode

Some of these engines were tested in multiple conditions, e.g. with and without an oxidation catalyst, with two different lubricant oils, or on two different test cycles.

The U.S. EPA report used a least squares approach to evaluate the emission data and concluded that PuriNOx produces significant reductions in NOx and PM for the in-use-fleet. The report also noted that there are significant differences in emissions from highway and nonroad engines. The emission reductions, confidence levels, and probabilities are from the U.S. EPA report and are summarized in Table 3.

Table 3. Average percentage reduction for all engines[1].

	NOx	PM	HC[2]	CO[3]
Highway engine				
Average % reduction	13.7	58.0	-87.2	22.0
Probability that average is different than zero	0.9999	0.9999	0.9999	0.9999
98% confidence interval				
Lower bound of % reduction	12.7	55.6	-120.2	13.4
Upper bound of % reduction	14.8	60.2	-59.2	29.7
Nonroad Engines				
Average % reduction	24.4	27.7	-79.0	22.0
Probability that average is different than zero	0.9999	0.9999	0.9999	0.9999
98% confidence interval				
Lower bound of % reduction	22.3	16.8	-100.1	13.4
Upper bound of % reduction	26.3	37.1	-60.1	29.7

[1]Table from U.S.EPA draft technical report
[2]HC = total hydrocarbon emissions. Reactive organic gas ROG emission increases are assumed to be equal to HC emission increases.
[3]CO calculation was done with highway and nonroad data together. Results are shown to be identical for highway and nonroad.

The U.S. EPA study investigated the relationship between the base NOx emission of the engine and the emission reduction obtained from using PuriNOx fuel. A conclusion of the study was that engines that emit lower NOx emissions using baseline diesel results in lower reduction gains when using PuriNOx fuel based on the following relationship.

% Reduction in NOx using PuriNOx fuel = [1-exp(0.01052-0.03358xbase NOx)]x100%

Since NOx standards are decreasing over time, the U.S. EPA report concludes that the fleet wide impact of PuriNOx would also decrease.

3. <u>The U.S. EPA Tier 1 Report</u>

As part of the U.S. EPA's registration requirement for new fuels, PuriNOx was required to undergo Tier I testing. The purpose of Tier I testing is to determine if the use of PuriNOx fuel can result in the emission of new chemical species that are not emitted from diesel engines when fueled with standard diesel fuel. These study results were not available when the U.S. EPA technical report was published. The study contains a considerable body of emissions data from 42 hot and cold starts for CARB fuel and 21 hot and cold start from Gen1 fuel. A summary of the test conditions and information are listed below:

- Test Engine: Detroit Series 60 model year 1999
- Engine dynamometer/FTP transient test cycle
- Test Fuels: CARB diesel, and Gen1 fuel
- Test sequence for Gen1 fuel and CARB diesel fuel:
  - Three replicates of CARB diesel baseline with each replicate consisting of one cold and six hot start transient FTP cycles.
  - Three replicates of PuriNOx Fuel with each replicate consisting of one cold and six hot start transient FTP cycles.
  - Three replicates of CARB diesel baseline repeat with each replicate consisting of one cold and six hot start transient FTP cycles.
- Toxics and criteria pollutants

Table 4 compares the emissions from the Detroit (DDC) series 60 fueled on Gen1 and CARB fuel.

Table 4. Summary of Tier 1 criteria pollutant emission rates and emission reduction results.

Fuel	NOx (g/bhp-hr)	PM (g/bhp-hr)	HC (g/bhp-hr)	CO (g/bhp-hr)
CARB Baseline	3.4	0.09	0.0	0.9
PuriNOx Gen1	3.1	0.06	0.1	0.8
CARB Baseline Repeat	3.4	0.09	0.0	0.9
	NOx (%)	PM (%)	HC (%)	CO (%)
PuriNOx Emission Reduction	8.8	33.3	NC[1]	11.1

[1]NC = Not calculated because emissions for CARB baseline and CARB baseline repeat were below the detection limit.

4. <u>CARB Verification</u>

Lubrizol contracted Southwest Research Institute (SwRI) to conduct comparative emissions tests to determine the emissions reduction of Gen1 fuel as compared to CARB reformulated diesel fuel.

The test conditions are summarized below:

- Test Engine: Detroit Series 60 model year 1991
- Engine dynamometer/FTP transient test cycle
- Test Fuels: CARB diesel, and Gen1 PuriNOx fuel
- Test sequence for Gen1 PuriNOx and CARB diesel fuel: twenty-one replicates of each fuel
- Toxics and criteria pollutants

The results of the verification comparative emissions tests are listed in Table 5.

Table 5. A summary of CARB emission test results for criteria pollutants from a 1999 DDC 60 fueled with CARB and PuriNOx diesel fuel.

Fuel	NOx (g/bhp-hr)	PM (g/bhp-hr)	HC (g/bhp-hr)	CO (g/bhp-hr)
CARB Baseline	4.21	0.191	0.110	2.38
PuriNOx Gen1	3.62	0.071	0.166	1.28
Emission Reduction	NOx (%)	PM (%)	HC (%)	CO (%)
PuriNOx	14.0	62.8	-50.9	46.2

B. PuriNOx Gen2 Criteria Pollutant Emissions Estimates

Lubrizol conducted a test comparing the emissions from a DDC series 60 engine fueled with PuriNOx Gen2 and CARB diesel fuel (**9**)**.** The test comprised of three hot start FTP heavy-duty diesel engine transient test cycles for each fuel tested. Emission data were collected for criteria pollutants and volatile organic compounds including aldehydes, ketones, alcohols and ethers. No alcohols or ethers were detected. The PuriNOx Gen2 formulation used for this test differs from the current formulation submitted for verification. The emissions from the DDC 60 engine fueled with Gen2 and CARB diesel and the emissions reduction of Gen2 fuel as compared to CARB diesel are given in Table 6.

Table 6. A summary of Gen2 emission results as compared to CARB fuel.

	CARB	Gen2, PuriNOx	Gen2 Difference
	gm/hp-hr	gm/hp-hr	percent
NOx	3.049	2.72	-10.8
PM	.090	.047	-47.8
THC	.053	.121	+128.3
CO	.803	.854	+6.4

ND=not detected

Since Gen1 was not part of this test, a direct comparison between the Gen1 and Gen2 fuels cannot be made. The emissions rates for criteria pollutants are within the historical range reported. The most comparable data is from the U.S. EPA Tier 1 tests were the test conditions are most similar and are compared in Table 7.

Table 7. Comparison of emission data from the U.S. EPA Tier 1 study and the Gen2 emission study

	PuriNOx Gen2 Percent Difference	PuriNOx Gen1 Percent Difference
NOx	-10.8	-8.8
PM	-47.8	-33.3
THC	128.3	NC
CO	6.4	-11.1

The emissions database is considerably smaller for Gen2. The Gen2 emission results are based on one on-road engine whereas Gen1 emissions results are based on a dataset of at least 13 engines consisting of off and on-road engines. Within the limitations of the dataset, the Gen2 additive chemistry does appear to have similar reductions for NOx, PM, THC, total aldehydes, and hydrocarbons when compared with the Tier 1 Gen1 results.

V. Toxic Emissions

Toxic emissions from diesel engines can result from the unburnt fuel, products resulting from the combustion of the fuel and lubrication oil, engine wear, and even from components in ambient air used as combustion air. Emissions from diesel engines form an extremely complex matrix consisting of gaseous and particulate species making chemical analysis a major challenge. Just the unburnt fuel portion of the exhaust is a complex mixture. For example, Blomberg and Schoemakers (**10**) estimate that there are well over a million species in the middle distillate oil fractions alone. Recently Schauer et al (**11**) accounted for 17 percent by mass of the species in a CARB reformulated diesel. Norbeck et al (**12**) fractionated diesel exhaust and tested each fraction using the Kado modified Ames test and concluded that most of the known toxics, such as PAH and nitro-PAHs, were not in the most mutagenic fractions suggesting that there are many unidentified mutagenic and toxic compounds in diesel exhaust.

Lubrication oil has been suggested as a major source of PM in diesel exhaust (**9**) and hence may have toxic species associated with it. Engine wear can contribute to the emissions of chromium, copper and other metallic species. Atmospheric chlorine consumed into the engine as combustion air may serve as a dioxin precursor during diesel combustion.

Aside from the fact that many of the toxic species may be unidentified, the sheer number of species makes an assessment of the total toxics by chemical speciation impractical and the analysis of many species would require advanced measurement technologies and analytical instrumentation. Where advanced chemical instrumentation is available, they are only found in advanced research laboratories and validated chemical methods do not exist. At best a comparison of toxicity can be conducted on a list of selected toxics that are known to be in diesel exhaust and on the potential formation of toxics based on the combustion chemistry of species unique to PuriNOx fuel.

A. Toxic PM Emissions

In 1998 CARB identified PM from diesel-fueled engines as a toxic air contaminant. On a statewide basis, the average potential cancer risk associated with these emissions is over 500 potential cases per million. In the South Coast Air Basin, the potential risk associated with diesel PM emissions is estimated to be 1,000 per million people. Compared to other air toxics CARB has identified and controlled, diesel PM emissions are estimated to be responsible for about 70 percent of the total ambient air toxics risk.

In response to the risk that diesel PM presents, the ARB approved a diesel risk reduction plan in 2000. The plan is based on reducing diesel PM emissions, a toxic air contaminant and a surrogate for the overall toxicity of diesel exhaust. The diesel risk reduction plan contains a number of planned stationary and mobile source control strategies to reduce diesel PM emissions.

Data of PM toxic emissions from PuriNOx Gen1 came from a number of studies, including the U.S. EPA Tier 1 report and the CARB verification. As previously reported the U.S. EPA evaluated toxic PM from the then available emissions data (does not include the U.S. EPA Tier 1 data) and concluded that the use of PuriNOx Gen1 fuel significantly reduces PM emissions by 58 percent from on-road diesel with a lower 98 percent confidence interval of 55.6 and an upper 98 percent confidence interval of 60.2 percent. The U.S. EPA Tier 1 showed PuriNOx reduced PM emissions by

33 percent when using a 1999 DDC series 60 engine. The ARB verification using a 1991 DDC series 60 engines showed PuriNOx reduced PM emissions by 62.8 percent.

The U.S. EPA draft technical report also found PM emissions from off-road engines were on average reduced by 27.7 percent, although the result is based on the test of one engine of less than 100 hp.

Gen2 PM emission reductions were from the SWRI study by Spreen (**3**). A 1999 DDC series 60 engine showed a PM reduction of 47 percent. Although the results are based on a small data set, indications are that the DDC series 60 emission reductions for Gen2 appear to be similar to Gen1.

All the studies consistently show that PuriNOx significantly reduces of emission of PM when compared to CARB diesel.

B. Other PuriNOx Gen1 Toxic Emissions

Data of toxic emissions from PuriNOx Gen1 come mainly from two studies: The U.S. EPA Tier 1 report and the CARB verification. Two assessments were made, the first is the comparative emissions of known toxics such as PAHs, aldehydes, and aromatics and the second is the impact on toxic emissions of components that are unique to PuriNOx fuel (e.g. additives chemistry).

For Tier 1 registration, the U.S. EPA has taken the approach of comparing emissions from a reference diesel fuel (CARB) and compares those emissions to the candidate fuel Gen1. Two hundred compounds including VOC, aldehydes, alcohols, ethers, PAHs and nitro-PAHs were compared in the exhaust of the CARB and Gen1 fuel. The study reported that in general, compounds measured in the exhaust with the CARB fuel were also present in the exhaust of Gen1 fuel.

Toxic speciation was also a requirement for CARB verification. CARB verification requires emission measurements for 1,3-butadiene, benzene, toluene, ethyl benzene, xylenes, formaldehyde, acetaldehyde, and PAHs. Analysis of emissions of other volatile organics, although not required for verification, was included in the verification study.

Presented in Table 8 is a summary of the U.S. EPA Tier 1 and CARB verification of emission rates and emission reductions for volatile organics including aldehydes and key toxics. Generally percent increases in emission rates of these species were higher for the Tier 1 study but mass emission rates were lower. The reason is that the 1999 DDC series 60 engine used for Tier 1 study on average generated lower emissions than the 1991 DDC series 60 engine used for CARB verification. Both studies showed a marked increase in carbonyl emissions, which is important since they can result in increases in toxic emissions and as photochemical precursors increases ozone formation. When comparing the Tier 1 results with the CARB verification results, one should also keep in mind that the Tier 1 emissions are based on both cold and hot start while the CARB verification is based only on hot start data.

Table 8. Summary of Tier 1 emission rates for volatile organics and key toxics.

	Tier I CARB (mg/hp-hr)	Tier I Gen1 (mg/hp-hr)	EPA Tier I percent Difference relative to CARB	Verif CARB (mg/hp-hr)	Verif Gen1 (mg/hp-hr)	Verif percent Difference relative to CARB
formaldehyde	7.6	16.2	+ 113	16.0	25.1	+56
acetaldehyde	2.8	6.1	+118	4.9	7.8	+60
acrolein	0.90	2.20	+144	1.5	2.6	+72
acetone	0.55	1.40	+155	1.1	3.5	+224
propionaldehyde	1.0	2.40	+140	1.1	2.0	+79
crotonaldehyde	0.95	2.60	+174	0.84	1.5	+80
isobutyraldehyde	0.25	0.40	+60	0.43	0.68	+59
methyl ethyl ketone	0.25	0.40	+60	0.43	0.68	+59
benzaldehyde	0.10	0.40	+300	0.31	0.60	+91
isovaleraldehyde	0.30	0.60	+100	0.10	0.17	+67
valeraldehyde	0.10	0.30	+200	0.19	0.30	+62
o-tolualdeyde	0.10	0.30	+200	0.17	0.22	+26
m/p-tolualdehyde	0.90	2.30	+156	0.71	1.2	+63
hexanaldehyde	0.10	0.30	+200	0.23	0.43	+90
dimethylbenzaldehyde	0.10	0.40	+300	0.10	0.18	+83
1,3-butadiene	0.45	0.80	+78	1.0	1.3	+35
benzene	0.35	0.50	+ 43	0.66	0.77	+17
toluene	0.50	0.80	+60	0.69	1.04	+50
xylenes	0.50	0.60	+20	0.33	1.5	+366
ethyl benzene	0.10	ND	NC	0.29	0.40	+37

ND = Below detection limit

NC = Percent reduction not calculated because the PuriNOx emission rate for ethyl benzene was below the detection limit.

Given in Table 9 is a summary of Tier 1 PAHs and nitro-PAHs. Generally for this study, the emissions of nitro-PAHs appear to be lower for the PuriNOx fuel. There are indications that some PAH emission rates are higher for the PuriNOx fuel especially for the higher molecular weight PAHs such as indeno[1,2,3-cd] pyrene and dibenz(a,h)anthracene.

Table 9. Summary of Tier 1 emission rates of PAHs and nitro-PAHs reported as a sum of each species in the vapor phase and PM.

	EPA Tier 1 CARB Ave Emission rate (ug/hp-hr)	EPA Tier 1 PuriNOx (Gen1) Emission rate (ug/hp-hr)	Percent Difference Relative to CARB Ave
2-Nitrofluorene	0.0044	0.0021	-52
1-Nitropyrene	0.091	0.043	-53
7-Nitrobenz(a)anthracene	0.0024	0.00045	-81
6-Nitrochrysene	0.00075	0.00013	+83
6-Nitrobenz(a)pyrene	0.00049	trace	NC
Benzo(a)anthracene	0.51	0.42	-18
Chrysene	0.80	0.61	-24
Benzo(b)fluoranthene	0.40	0.65	+63
Benzo(k)fluoranthene	0.15	0.29	+93
Benzo(a)pyrene	0.285	0.28	-2
Indeno[1,2,3-cd]pyrene	0.0365	0.36	+886
Dibenz(a,h)anthracene	0.0024	0.0082	+249

Presented in Table 10 is a summary of CARB verification emission rates and emission reductions for individual PAHs. Generally, emission rates of PAHs for the PuriNOx fuel are comparable to CARB fuel. This may be in contrast to the Tier 1 study where certain PAHs emission rates were considerable higher with the use of PuriNOx fuel. One explanation is that differences in test conditions such as engine type may play an important role in determining emissions of PAHs.

Table 10. Summary of CARB Verification study emission rates for individual PAHs species reported as the sum of their amounts in the vapor phase and PM

	Verification CARB Emission rate (ug/hp-hr)	Verification PuriNOx (Gen1) Emission rate (ug/hp-hr)	Percent Difference Relative to CARB
naphthalene	487	275	-43
2-methylnaphthalene	38	145	+281
acenaphthylene	20	18	-9
acenaphthene	2	1	-32
fluorene	23	22	-5
phenanthrene	36	35	-1
anthracene	4	4	12
fluoranthene	9	7	-12
pyrene	18	16	-13
benzo[a]anthracene	0.25	0.34	+36
chrysene	0.50	0.59	+18
benzo[b]fluoranthene	0.25	0.29	+16
benzo[k]fluoranthene	0.24	0.25	+4
benzo[e]pyrene	0.43	0.42	-2
benzo[a]pyrene	0.44	0.45	+2
perylene	0.17	0.08	-53
indeno[1,2,3-cd]pyrene	0.21	0.16	-24
dibenz[ah]anthracene	0.13	0.050	-62
benzo[ghi]perylene	0.30	0.31	+3

C. PuriNOx Gen2 Toxic Emissions

As previously discussed Lubrizol conducted a test comparing the emissions from a DDC series 60 engine fueled with PuriNOx Gen2 and CARB diesel fuel (**9**). Emission data were collected for toxic pollutants and volatile organic compounds including aldehydes, ketones, alcohols and ethers. No alcohols or ethers were detected. Also, as previously discussed, the PuriNOx Gen2 formulation used for this test differs from the current formulation submitted for verification in that additive A was not part of the formulation. The toxic emissions from the DDC 60 engine fueled with Gen2 and CARB and the emissions reduction of Gen2 fuel as compared to CARB fuel are given in Table 11.

Table 11. A summary of Gen2 emission results as compared to CARB fuel.

	CARB	Gen2, PuriNOx	Gen2 Difference
	mg/hp-hr	mg/hp-hr	percent
formaldehyde	8.5	13.9	+64
acetaldehyde	3.1	4.8	+55
acrolein	0.1	0.3	+200
acetone	0.9	1.2	+33
propionaldehyde	1.9	3	+58
crotonaldehyde	1.2	1.9	+58
isobutyraldehyde	0.2	0.3	+50
methyl ethyl ketone	0.2	0.3	+50
benzaldehyde	ND	ND	NC
isovaleraldehyde	trace	trace	NC
valeraldehyde	0.1	0.2	+100
o-tolualdeyde	trace	trace	NC
m/p-tolualdehyde	ND	ND	NC
hexanaldehyde	ND	ND	NC
dimethylbenzaldehyde	ND	ND	NC
Total carbonyls	**16.2**	**25.9**	**+60**
Total speciated hydrocarbons	**45**	**75**	**+67**
1,3-butadiene	ND	0.7	NC
benzene	0.8	1.2	+50
toluene	0.40	0.30	-25
xylenes	1.5	2.4	+60
ethyl benzene	0.3	0.6	+100

ND=not detected
trace=less than 0.05 mg/hp-hr
NC=% reduction not calculated

Gen1 was not part of this test, therefore a direction comparison between the Gen1 and Gen2 fuels cannot be made. The most comparable data is from the U.S. EPA Tier 1 tests and are compared in Table 12.

Table 12. Comparison of toxic emission data from the U.S. EPA Tier 1 study and the Gen2 emission study.

	Tier 1 Gen1, Difference	Tier 1 Gen2 Difference
	percent	percent
formaldehyde	+113	+64
acetaldehyde	+118	+55
acrolein	+144	+200
acetone	+155	+33
propionaldehyde	+140	+58
crotonaldehyde	+174	+58
isobutyraldehyde	+60	+50
methyl ethyl ketone	+60	+50
benzaldehyde	+300	NC
isovaleraldehyde	+100	NC
valeraldehyde	+200	+100
o-tolualdeyde	+200	NC
m/p-tolualdehyde	+156	NC
hexanaldehyde	+200	NC
dimethylbenzaldehyde	+300	NC
1,3-butadiene	+78	NC
benzene	+ 43	+50
toluene	+60	-25
xylenes	+20	+60
ethyl benzene	NC	+100

NC = % reduction not calculated

Within the limitations of the Gen2 test, Gen2 emissions of volatile organic toxics are at similar or lower levels when compared to Gen1 emissions.

The emissions database is considerably smaller for Gen2. The Gen2 emission results are based on one on-road engine whereas Gen1 emissions results are based on a dataset of at least 13 engines consisting of off and on-road engines. Within the limitations of the dataset, the Gen2 additive chemistry appears to have similar reductions for NOx, PM, and has similar emissions of total aldehydes, and toxic volatile organic compounds when compared with the Tier 1 Gen1 results.

VI. Effect of PuriNOx Gen1 and Gen2 Additives on Other Toxic Emissions

A review of the PuriNOx additives was conducted to determine the potential impact these additives have on toxic air contaminants. In general, additive components in diesel fuel can contribute to increased emissions of toxic contaminants in two ways, depending on the completeness of combustion: 1) incomplete combustion may result in a portion of the additive components being emitted directly as toxic compounds and 2) upon combustion these additives form toxic air contaminants. These two paths may be present whether the additive compounds are primary components or impurities.

A. Treat rates and applications of additives

Analytical techniques are currently not available for the measurement of many of the additive species or their combustion products in diesel exhaust. However, a qualitative assessment of the potential emission impacts can be obtained by comparing their use and treatrates in commercial products that are combusted in diesel engines. This mainly includes diesel fuels and lubricants.

A comparison of the additives used for both the PuriNOx Gen1 and Gen2 formulations were made with similar types of compounds in diesel fuel and engine lubricants**.** All the PuriNOx formulations' additive concentrations are significantly higher than those used in diesel fuels and in some cases, the additives in PuriNOx are not typically found in diesel fuel. For the purpose of confidentiality, the following discussion refers to PuriNOx additives by a generic letter.

B. PuriNOx Group A Additives

Group A additives are not used in other diesel fuels although additives of the same chemical class are used in very high volumes in engine oil and fuel dispersant additives. Additives related to group A additives are in engine oils at the two to five percent levels. Related additives are used less widely in diesel fuels than in lubricants, however are widely used in gasoline. The additives used in gasoline and of the same chemical class may have some significant chemical structural differences from the PuriNOx group A additives

Currently emission test methods are not available for group A additives and characterizing these additives may be difficult since they consist of many molecular species with a range of molecular weights. Their high molecular weight makes their analysis difficult. Developing test methods may require a major research effort. The destruction efficiency of these compounds in diesel combustion is unknown and would in part depend on the operating conditions of the engine. Because of their high molecular weight (850-2500 daltons) emissions of uncombusted group A additives would probably be in the particulate fraction of the exhaust. Related group A additives are used in high levels in lubrication oil but it is difficult to estimate what percentage of these related group A additives in the lubricant are emitted in diesel exhaust. The amount of group A additives in PuriNOx is much higher than similar additives used in CARB diesel fuel. Conversely, the amount of related group A additives in lubricants is substantially greater than that in PuriNOx. However, as previously noted, it is difficult to estimate emission rates for this source of group A additives without experimental data due to the nature of lubricant combustion.

Based on the chemical structure of some group A additives, there is the possibility that they can react with NOx to form nitrosamines. No emissions tests were conducted for nitrosamines to determine levels in the diesel exhaust. Although there is a possibility of increased emissions of nitrosamine, a quantitative estimate would require conducting additional emissions tests.

C. Group B Additives

Group B additives are also used in diesel fuels but at a considerably lower treat rates than in PuriNOx fuel, therefore emissions of these additives and their combustion products are expected to be higher in PuriNOx fuel than in CARB fuel.

D. Group C Additives

Group C additives are not typically added to diesel fuel. An increase in emissions of these compounds could be expected as well as their products of combustion such as carbonyl compounds.

Based on the chemical structure and level of a group C additive that is used in PuriNOx fuels, concerns has been raised that this additive may increase the formation of nitro-PAHs. The U.S. EPA's Tier 1 study compared the emissions of select nitro-PAHs from a DDC 60 engine using Gen1 and CARB fuel. The study reported emissions of these nitro-PAHs were lower when using Gen1 fuel in comparison to CARB fuel. However, the Tier 1 study did not address other nitro-PAHs and di-nitro PAHs that have been reported in diesel exhaust or that can be potentially found in diesel exhaust (**13**). The analysis of all the nitro-PAHs that can be potentially found in diesel exhaust would be beyond the capability of current chemical analytical techniques.

A second approach to assessing the total amount of nitro-PAHs is to use Salmonella bacteria mutagenic assays such as TA98NR that are specific to nitro-PAHs. The U.S. EPA Tier 2 study conducted mutagenic assay testing using TA98NR tester strains. Both the particulates and semivolatile emissions from a DDC 60 engine fueled with Gen1 were measured. The study did not directly compare the PuriNOx with a CARB reference fuel but concluded that mutagenicity results were as expected and representative of petroleum diesel exhaust and other alternative diesel fuel blends. The study did not do comparable testing on the engine using a reference diesel fuel.

Although the data are not comprehensive, i.e. only one engine tested and only a select few nitro-PAHs were chemically analyzed; the results do not show an increase in nitro-PAHs emissions. The nitro-PAHs results may be explained by the reduction in NOx emissions, a nitrating agent for PAHs.

E. Dioxins

Emissions of dioxins have been reported from diesel fueled heavy-duty diesel engines. The amount of chlorine and metal catalyst such as copper found in the fuel have been reported to affect emissions of dioxins. (**14**, **15**) Since the base fuel used for PuriNOx fuel is a CARB fuel, the amount of dioxins due to the base fuel are not expected to change, however chlorine impurities in the water could increase emissions of dioxins. To address this issue the water used for making PuriNOx fueled was investigated. The process for making PuriNOx fuel requires an additive package to emulsify the water and diesel fuel. Water for the blending units comes from a local source. For example, the blending unit for Ramos Oil is located near Dixon, California and the water used for the blending unit comes from the local water system. The water is purified by deionization or reverse osmosis and a conductivity criteria is used to ensure water used for blending is of suitable purity. Conductivity is also an indicator of ionic species such as chlorides. Table 13 shows the range of conductivity for water used for making PuriNOx fuel. The data is from a PuriNOx fuel blending unit located in Cleveland Ohio.

Table 13. Lubrizol Blending Unit Located in Cleveland, Ohio

Water Conductivity of the Ion Exchanger Outlet Water Before the Resin is Replaced

Resin Tank	Date	Conductivity mS/cm	Gallons	Percent
1	1/26-2/14	0.5-10	7776.4	67.6
1	2/14-3/21	10-100	3724.8	32.4
2	3/21-4/15	0.5-10	6772.1	54.9
2	4/15-4/25	10-100	5566.3	45.1

Inlet water conductivity = 350-450 uS/cm

Presented in the Table 14 is an analysis of the chlorine and chloride levels in deionized water taken from a blending unit located in Dixon California.

Table 14. Ramos Blend Unit Water Sample Analysis

Sample	Sulfate EPA 375.4CLC (mg/L)	Chlorine[2] (total residual) EPA 330.5 (mg/L)	Fluoride (mg/L)	Total Solids (mg/L)	Total Sulfides (mg/L)	Chloride 4500CLC (mg/L)
Ramos Blend Unit Water Sample 11/15/02	BDL[1] (<10)	0.02	BDL[1] (<0.1)	BDL[1] (<20)	BDL[1] (<5)	BDL[1] (<2)

[1]BDL = Below Detection Limit
[2]Conductivity of water for sulfate, chlorine and chloride sample was 0.65 us/cm.
[3]Conductivity of water for fluoride, total solids, total sulfide sample was not recorded.

Water quality of inlet water to the blending unit at the Ramos facility located in Dixon.

Date Sampled	Conductivity
2/23/01	600 mircosiemans/cm
8/7/01	680 microsiemans/cm

Within the limitations of the analytical methods, total chloride in the water sample (less than 2 ppm) was at a concentration typically found in diesel fuel (less than 1 ppm). The conductivity of the water sample tested had a low conductivity of 0.65 uS/cm and was at the lower range of conductivity of water from the ion-exchanger. It would be expected that the concentration of ionic species in water from the ion-exchange resin would be higher when the conductivity is at the upper end of the conductivity range of 100 uS/cm. Since it is difficult to estimate the upper range of chlorine and since the role of chlorine in the formation of dioxins is not well understood, the potential increase in chlorine from the water cannot be quantified.

F. Ultra Fine PM

Ultrafine PM. Warner (**16**) conducted a study comparing emissions of ultrafine PM from a Cummins 1988 L10-300 heavy duty diesel engine fueled with PuriNOx and a 375 ppm sulfur diesel fuel. The engine was run on an engine dynamometer and the idle, mode 9 and mode 11 of the U.S. EPA 13 mode steady state were tested for ultra-fine PM. The study found the particle number and volume concentration for the accumulation range (particles greater than 50 nm to 790 nm) was reduced when using PuriNOx fuel. For the nuclei mode (particles 50 nm and less) there was an increase in particle number and volume concentration for mode 9 and 11 and a decrease for the idle. These results are specific to these experimental conditions and the data should not be extrapolated to other test conditions. These results may not be representative of a "real world" comparision since experimental test conditions can significantly affect test results.

G. Limitations of Other Toxic Emission Studies

When assessing the toxic emissions studies, the limitations of the studies need to be taken into consideration. The following is a summary of the limitations of these studies.

- Emissions are from one class of heavy-duty on-road engines, no toxic emission data from off road engines.
- Emission profiles based on FTP heavy-duty transient test procedure which is an average condition not necessarily representative of all engine operating conditions
- Difficult to experimentally assess emission impacts of additives since emission test methods and analytical methods are not available.
- Less data is available for Gen2 fuel, making conclusion less robust than for Gen1 fuel.
- Significant reduction in PM.
- Indications that under certain conditions ultra-fine PM number and volume concentration is reduced and under other conditions they can increase, however "real world" comparisons between fuels cannot be made due to limitations of current test methodologies.

VII. Emission Inventory Estimates for 2002 and 2010

The California emissions inventory and the EMFAC model were used to estimate the impact that PuriNOx would have on the emission inventories of South Coast Air Basin and the Sacramento Valley Air Basin where PuriNOx is currently used in limited applications. Emissions estimates were made for NOx, PM, reactive organic gases ROG, 1,3-butadiene, formaldehyde, acetaldehyde, benzene, ethyl benzene, and naphthalene. Emissions estimates were calculated for 2002 and 2010. Based on Lubrizol's estimate of producing 40 million gallons of PuriNOx fuel in 2012, less than 1 percent of the vehicles would be fueled on PuriNOx. The AIR report assumed 25 percent of the centrally fueled vehicles or approximately nine percent of the vehicles would be fueled on PuriNOx. Based on the limited applications of the fuel and Lubrizol's estimate of 1 percent market penetration in 2012, the estimate in the AIR report represents a conservative upper limit to the number of fleets. This is further supported since PuriNOx is not applicable to all vehicles in the market. For example, due to the lower energy content of the fuel, PuriNOx may not be compatible with vehicles that work under high load. Also, the limited fuel stability may not be compatible with vehicles that sit idle for long periods of time such as seasonal agricultural equipment or vehicles with low daily mileage traveled.

For the purposes of this study, the 25 percent scenario was also used as the conservative case.

A. Summary of Assumptions and Inputs for Emission Inventory Estimates

A summary of assumptions and inputs are given below.

- EMFAC 2002 ver 2.2 (April 2002 release) used to obtain on-road emissions, vehicle miles (VMTs), and number of vehicles. Emission estimates were based on the annual average.
- 2002 emissions inventory was used to obtain total emissions of NOx, PM10, ROG, formaldehyde, acetaldehyde, benzene, 1,3-butatdiene, and naphthalene
- Used EPA emission reductions for PuriNOx fuel including different factors for highway
- Used EPA predictive equation for NOx reduction for 2010
- Assumed 25 percent of on-road (approximately equivalent to highway) centrally fueled fleets will use PuriNOx-conservative estimate
- Obtained estimates of centrally fueled fleets for AIRs-data reduced from 1997 Census Bureau results
- Conduct separate estimates for highway and nonroad
- Categories of vehicles include light heavy-duty trucks (LHDV), medium heavy-duty trucks (MHDV), heavy heavy-duty trucks (HHDV), heavy-duty urban buses, and school buses. The percentage of trucks centrally fueled were obtained from AIRs.
- All urban buses and school buses were assumed to be centrally fueled.
- Relative emission factors for toxics were obtained from averaging Tier 1 and CARB verification results.
- ROG emission factor assumed ROG from PuriNOx and CARB are of equivalent reactivity.

Presented in Table 15 are the percent reductions of emissions used to determine the emission rates. The emission factors are based on the average of the Tier 1 and CARB verification emission rates.

Table 15. Emission percent reduction based on the average of the Tier 1 and CARB verification studies.

	2002 Emission percent reduction	2010 Emission percent reduction
NOx	13.7	11.3
ROG	-87.2	-87.2
PM	58	58
1,3-butadiene	-56	-56
benzene	-30	-30
ethyl benzene	-37[1]	-37
naphthalene	43	43
formaldehyde	-85	-85
acetaldehyde	-89	-89

[1]Based on CARB verification data only. Ethyl benzene was below the detection limit for the CARB fuel in the Tier 1 study and an emission reduction could not be calculated.

B. Emissions Impact in the South Coast Air Basin

Table 16 shows the on-road emissions for select criteria and toxic emissions for the South Coast Air Basin. The table shows the emission associated with CARB diesel and the emission impact of PuriNOx. For reference, all sources including stationary and mobile sources are included.

Table 16. A comparison of on-road emissions for the South Coast Air Basin

	2002 All Sources[1] (tons/dy)	2002 Diesel[2] (tons/dy)	2002 PuriNOx benefit (tons/dy)	2010 All Sources (tons/dy)	2010 Diesel (tons/dy)	2010 PuriNOx benefit (tons/dy)
NOx	1068	289.3	4.03	733	203	2.4
ROG	809	9.41	-1.0	574	7.7	-0.70
PM10	291	5.2	0.31	299	3.69	0.22
1,3-butadiene	2.78	0.020	-0.0013	1.9	0.016	-0.0010
benzene	11.74	0.21	-0.0071	7.21	0.17	-0.0058
ethyl benzene	5.41	0.03	-0.0014	3.21	0.027	-0.0011
naphthalene	0.56	0.096	0.0005	0.45	0.008	0.0004
Formaldehyde	14.68	1.6	-0.146	10.44	1.3	-0.12
Acetaldehyde	4.85	0.790	-0.077	3.58	.64	-0.98

[1]Sources include all stationary and mobile sources.
[2]CARB and PuriNOx are the on road emission estimates that include LHD trucks, MHD trucks, HHD trucks, School buses and HHDV urban buses.

Generally, overall emission impacts from the use of PuriNOx fuel on a ton/day basis is lower in 2010 than in 2002. This is due to the lower emission rate from heavy-duty diesel engines on the road in 2010 as compared to 2002. For example, PM10 emissions from heavy-duty diesel engines is 3.69 tons/day in 2010 versus 5.2 tons/day in 2002. In addition, PuriNOx NOx emission benefits is expected to decrease from 13.7 percent in 2002 to 11.3 percent in 2010. This is based on the increase number of later model engines emitting less NOx which the U.S. EPA found decreased PuriNOx benefits as previously discussed.

C. Impact of ROG and NOx in the South Coast Air Basin

NOx and ROG are important species in the formation of ozone. For the South Coast basin, the use of PuriNOx in 25 percent of the centrally fueled on-road fleet would reduce NOx by 4 tons/day in 2002 and 2.4 tons/day in 2010. ROG would increase by one ton/day in 2002 and 0.7 tons/day in 2010. Estimates from off-road diesel are more difficult to determine due to estimating the penetration of PuriNOx into off-road market, determining which off-road categories are conducive to PuriNOx use and lack off road emissions test data. The emissions inventory indicates that emissions of NOx and ROG from off-road are roughly the same as for on-road engines and if the same percentage of the engines use PuriNOx, then the off road emission rates attributable to PuriNOx would be comparable to the on road fleet. Thus, for on and off road applications, the use of PuriNOx would decrease NOx by 8 tons in 2002 and 4.8 ton in 2010. ROG from both on road and off road would increase by two tons/day in 2002 and 1.4 tons/day in 2010.

Aldehyde emission data from the EPA Tier 1 and CARB verification studies suggests that diesel engines fueled with PuriNOx emit more ROG than when fueled with CARB diesel. When averaging the aldehyde emissions from both studies the aldehyde emissions increase by 145 percent, therefore, there is an increase in reactivity of the ROG emissions.

For the South Coast Air Basin and using the conservative estimate, the use of PuriNOx would result in a 4.8 tons/day NOx decrease and a 1.4 ton/day increase in ROG. These emissions are less than one percent of the total NOx and ROG emitted from all sources in the South Coast. In the case of the South Coast, where the air basin is hydrocarbon limited, any change in the NOx/hydrocarbon ratio can affect changes in the peak ambient ozone levels. A qualitative assessment of potential impacts of PuriNOx was conducted and the impacts are very small (less than a ppb) but in the direction of higher basin wide peak ozone. Additionally, any increase in ROG due to the use of PuriNOx will need to be accounted for in the ozone non-attainment areas such as the South Coast. Currently, the California State Implementation Plan (SIP) consists of several planned control strategies that target ROG and NOx emissions. In implementing the SIP, these strategies are balanced and result in an overall reduction in ozone levels.

Therefore, if PuriNOx is to be used as a ozone control strategy, any increases in ROG will be addressed.

D. Impact on Toxic Air Contaminants in the South Coast Air Basin

Emission rates for a select number of toxic air contaminants including PM10, 1,3-butadiene, benzene, ethyl benzene, naphthalene, formaldehyde, and acetaldehyde were evaluated for the South Coast Air basin. Emission reductions for PM10 and naphthalene were observed while emission increases were observed for 1,3-butadiene, benzene, ethyl benzene, formaldehyde and acetaldehyde. The 58 percent decrease in PM from the PuriNOx fueled fleet accounts for a .22 ton/day or a 6 percent decrease in PM10 for the year 2010 for the entire South Coast fleet. The greatest increases were for aldehydes with acetaldehyde showing a 89 percent increase in the vehicles fueled with PuriNOx. This corresponds to a 0.063 ton/day or 10 percent increase in acetaldehyde emissions over the entire South Coast heavy-duty diesel fleet.

E. Emission Impact in the Sacramento Valley Air Basin

Table 17 shows the on-road emissions for select criteria and toxic emissions for the Sacramento Valley Air Basin.

Table 17. A comparison of on-road emissions for the Sacramento Valley Air Basin

	2002 All Sources[1] (tons/dy)	2002 Diesel[2] (tons/dy)	2002 PuriNOx benefit (tons/dy)	2010 All Sources (tons/dy)	2010 Diesel (tons/dy)	2010 PuriNOx benefit (tons/dy)
NOx	277.4	65.0	0.86	200.3	41.5	0.47
ROG	217.5	2.6	-0.22	177.8	2.0	-0.16
PM10	225.8	1.4	0.08	237.5	0.92	0.05
1,3-butadiene	0.77	0.0057	-0.0003	0.55	0.0042	-0.0002
benzene	3.1	0.060	-0.0018	2.06	0.045	-0.0014
ethyl benzene	1.44	0.0092	-0.0003	0.97	0.0069	-0.0003
naphthalene	0.32	0.0027	0.0001	0.3	0.0020	0.0001
Formaldehyde	5.0	0.44	-0.038	3.95	0.33	-0.028
Acetaldehyde	2.26	0.22	-0.020~~3~~	1.89	0.16	-0.015

[1]Sources includes all stationary and mobile sources.
[2]CARB and PuriNOx are the on road emission estimates that include LHD trucks, MHD trucks, HHD trucks, School buses and HHDV urban buses.

F. Sacramento Valley Air Basin: NOx and ROG

For the Sacramento Valley Air Basin the use of PuriNOx in 25 percent of the centrally fueled on-road fleet would reduce NOx by 0.86 tons/day in 2002 and 0.47 tons/day in 2010. The ROG would increase by 0.22 ton/day in 2002 and 0.16 tons/day in 2010. Again assuming that off road emissions are the same as on-road NOx and ROG, then the conservative estimate would be a .44 tons/day NOx reduction and a .32 tons/day ROG increase for 2010. Also, the ROG emissions are likely higher due to the higher aldehyde emission rate with the use of PuriNOx fuel.

The conservative estimate for NOx decrease and and ROG increase is less than one percent of the total NOx and ROG emitted from all sources in the Sacramento Valley. The Sacramento Valley is not hydrocarbon limited and a decrease in NOx or HC emissions would likely result in a decrease in peak ambient concentration of ozone. Based on our analysis, where PuriNOx use decreases NOx and increases hydrocarbon emissions, the impact on peak ambient ozone changes are negligible. Peak ambient ozone levels would stay unchanged or slightly increase in downtown Sacramento and would stay unchanged or slightly decrease downwind of Sacramento. However, as stated in the section VI-C, ROG emissions are ozone precursors, therefore, any increase in ROG due to the use of PuriNOx will need to be accounted for in the ozone attainment plan.

G. Toxic Air Contaminants

For the Sacramento Valley air basin, emission reductions were observed for PM10 and naphthalene while emission increases were observed for 1,3-butadiene, benzene, ethyl benzene, formaldehyde and acetaldehyde. The 58 percent decrease in PM from the PuriNOx fueled fleet accounts for a .05 ton/day or a 5.6 percent decrease in PM10 for the year 2010. The greatest increases were for aldehydes with acetaldehyde showing a 89 percent increase in the vehicles fueled with PuriNOx. This corresponds to a 0.015 ton/day or 9.0 percent increase in acetaldehyde emissions over the baseline.

VIII. PuriNOx Gen1 and Gen2 Emissions of Greenhouse Warming Species

No life-cycle analysis has been performed on PuriNOx Gen1 and Gen2 fuels to determine the net effect on emissions of greenhouse species. However, based on a limited data set, PuriNOx and CARB diesel emissions of carbon dioxide are comparable and within the experimental error as indicated in Table 18 (Fanick (1) and Spreen (3)).

Table 18. Summary of emission test resuslts for carbon dioxide from DDC 60 engines fueled with CARB and Gen1 and Gen2 diesel fuels.

ARB		EPA-Tier 1		Spreen	
CARB	**Gen1**	**CARB**	**Gen1**	**CARB**	**Gen1**
g-hphr ave±stdv	g-hphr ave±stdv	g-hphr ave±stdv	g-hphr ave±stdv	g-hphr ave±stdv	g-hphr ave±stdv
538±16	532±4.6	611±10	622±7.0	577±33	585±2

Most of the methane measurements in these studies were below the detection limit and a direct comparison could not be made suffice to say that the levels of methane are very low in diesel exhaust and is a minor source as compared to other anthropogenic sources. A comparison of nitrous oxide was not done since it was not measured in any of the studies. In terms of black carbon, another greenhouse warming species, there may be some beneficial effects from the use of PuriNOx. Data indicates that the black carbon content in PM emissions from PuriNOx can be significantly lower in comparison to conventional diesel fuel. However, the impact on greenhouse gas species cannot be quantified. Also, there is some evidence that the use of PuriNOx results in a small increase in combustion efficiency which may result in a small reduction in greenhouse gases.

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