Attachment E. Office of Environmental Health Hazard Assessment's Impact Assessment of PuriNOx™ Generation 1 and Generation 2 Diesel Fuel (Public Version)

Office of Environmental Health Hazard Assessment

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MEMORANDUM

TO: Catherine Witherspoon
Executive Officer
California Air Resources Board

FROM: George V. Alexeeff, Ph.D., D.A.B.T.
Deputy Director for Scientific Affairs

DATE: January 21, 2004

SUBJECT: IMPACT ASSESSMENT OF PURINOX™ GENERATION 1 AND GENERATION 2 DIESEL FUEL

The Office of Environmental Health Hazard Assessment (OEHHA) evaluates potential human health impacts that may result from adoption of a fuel specification regulation that approves or requires use of a reformulated motor vehicle fuel in California. OEHHA scientists have reviewed information submitted to the Air Resources Board (ARB) by Lubrizol Corporation in support of an application for approval of PuriNOx™ Generation 1 (PG1) and PuriNOx™ Generation 2 (PG2) diesel fuels.

The attached document, "Staff Report on Health Impacts of PuriNOx™ Generation 1 and Generation 2 Additive Packages and Diesel Fuels," summarizes the review and assessment of potential health impacts that may result from use of PG1 and PG2 additive packages and fuels. In their assessment, OEHHA scientists have considered both increases and decreases in risks to human health that may result from substitution of these alternative fuels for a portion of the market share of diesel fuel meeting ARB specifications.

Following review of information submitted to ARB, OEHHA concludes that use of PG1 or PG2 diesel as an alternative to current California diesel can result in a reduction in diesel fuel combustion emissions of particulate matter (PM), carbon monoxide (CO) and oxides of nitrogen (NO_x). Such use can also result in increased emissions of aldehydes, benzene and other organic toxic air contaminants. Upper-bound estimates of increased lifetime cancer risk attributable to volatile organic chemicals from PuriNOx™ combustion emissions are 3×10^{-7} to 5×10^{-7}, while upper-bound estimates of the magnitude of risk reduction attributable to decreased PM concentrations in PuriNOx™ combustion emissions are 1×10^{-5} to 3×10^{-5}. OEHHA is concerned with environmental toxicity that may result from accidental releases of PG1 or PG2 additive packages and supports the State Water Quality Control Board's request for additional testing for environmental impacts.

If you have any questions about the health impact assessment of PuriNOx™ blended diesel fuels, please contact Dr. Page Painter, Chief, Integrated Exposure Assessment Unit at, (916) 327-1094 or email at ppainter@oehha.ca.gov.

Attachment

cc: Page Painter, Ph.D., Chief
Integrated Exposure Assessment Unit

Staff Report on Health Impacts of PuriNOx™ Generation 1 and Generation 2 Additive Packages and Diesel Fuels

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Integrated Risk Assessment Section and
Air Toxics and Epidemiology Section
Office of Environmental Health Hazard Assessment
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1. Introduction

The Office of Environmental Health Hazard Assessment (OEHHA) evaluates potential human health impacts that may result from adoption of a fuel specification regulation that approves or requires use of a reformulated motor vehicle fuel in California. OEHHA scientists have reviewed information submitted to the Air Resources Board (ARB) by Lubrizol Corporation in support of an application for approval of PuriNOx^{TM} Generation 1 (PG1) and PuriNOx^{TM} Generation 2 (PG2) diesel fuels.

PG1 and PG2 diesel fuels are produced by blending PG1 additive package or PG2 additive package with water and diesel fuel, denoted CARB diesel, that meets California ARB diesel fuel specifications. The chemical identity of components of these additive packages is confidential proprietary information. However, OEHHA scientists evaluating health impacts of PG1 and PG2 diesel fuels have full knowledge of the chemical structure of each component in these additive packages as a result of a confidentiality agreement between Lubrizol Corporation and OEHHA.

Information reviewed by OEHHA scientists includes all data on diesel engine combustion tests submitted by Lubrizol Corporation to ARB. It also includes data submitted to the United States Environmental Protection Agency (US EPA) from chemical analysis of emissions from diesel engines burning CARB fuel or PG1 fuel. OEHHA scientists also reviewed data from biological toxicity tests of combustion emissions from a PG1-fueled engine. The analytical data were submitted to meet US EPA's Tier I data requirements and the biological test data were submitted to meet Tier II requirements for the approval of motor vehicle fuel additives. OEHHA scientists have also reviewed confidential reports, prepared by Lubrizol Corporation, that specify the chemical structure of additive package components as well as their physical and chemical properties. OEHHA scientists have also reviewed literature on toxicity of these components.

2. Summary and evaluation of diesel engine combustion test data

a. Analysis of PG1 diesel fuel combustion emissions

OEHHA scientists have reviewed analytical data on post-combustion emissions from PG1 fuel in the report, "Testing of PuriNOx^{TM} Fuel Using the CARB Interim Procedure for Certification of Emission Reductions for Alternative Diesel Fuels," prepared by Southwest Research Institute for Lubrizol Corporation, December 2000 (December 2000 report). The diesel fuel used to blend the PG1 diesel fuel for these combustion tests was not the diesel fuel used as the reference (control). However, both of these fuels met CARB specifications. Table 1, Table 2 and Table 3 list emissions data from this report. Emission rates are quantified using units of mass per horsepower-hour (hp-hr) calculated as the average rate from seven hot-start runs. Table 1 lists emission rates for total hydrocarbons (THC), carbon monoxide (CO), carbon dioxide (CO_2), oxides of nitrogen (NO_x), particulate matter (PM), particulate sulfate (SO_4) and particulate soluble organic fraction (SOF). Table 2 lists data on volatile organic compound (VOC)

emissions. Table 3 lists data on polycyclic aromatic hydrocarbon (PAH) emissions along with the total benzo(a)pyrene (BAP) potency equivalence factor (PEF) weighted PAH concentration. The PEF, developed for carcinogenic PAHs, is an estimate of the ratio of the carcinogenic potency of the PAH divided by the carcinogenic potency of BAP.

Table 1. Average Levels of NO_x, PM, SOF, SO_4, THC, CO and CO_2 in Combustion Emissions from CARB Diesel Fuel or PG1 Diesel Fuel (7 Runs) from Data Submitted to ARB[1]

Air Contaminant	Emissions Rate Using CARB Diesel (g/hp-hr)	Emission Rate Using PG1 Diesel (g/hp-hr)	Relative Change[2] (%)
NO_x	4.21	3.62	-14
PM	0.191	0.071	-62
SOF	0.047	0.056	+19
SO_4	0.0010	0.0006	-40
THC	0.110	0.166	+51
CO	2.38	1.28	-46
CO_2	534.54	531.52	-0.6

[1] Data from Table 4 in the December 2000 Southwest Research Institute report, "Testing of PuriNOx™ Fuel Using the CARB Interim Procedure for Certification of Emission Reductions for Alternative Diesel Fuels"

[2] Calculated as 100×(PG1 emission rate – CARB emission rate)/(CARB emission rate)

As shown in Table 1, emission rates of NO_x, PM, SO_4 and CO from engines burning PG1 diesel fuel were decreased by 14, 62, 40 and 46 percent, respectively, compared to emissions from engines tested under the same operating conditions burning CARB reference diesel fuel. Emission rates of THC and SOF were increased by 51 and 19 percent, respectively.

Tables D-1 and D-2 in the December 2000 report list emission rates of 227 VOCs containing 12 or fewer carbon atoms (C_1-C_{12} VOCs). For 68 of these quantified compounds, emission rates are higher when PG1 diesel is used. Eleven VOCs with increased emission rates are identified toxic air contaminants (TACs) by the ARB. The emission rates of benzene, toluene, ethyl benzene, 1,3-butadiene, *m*- and *p*-xylene, *o*-xylene, hexane, propionaldehyde, acetaldehyde, formaldehyde and acrolein are increased by 20, 49, 45, 33, 471, 360, 475, 82, 61, 37 and 73 percent, respectively (Table 2), and the sum of the emission rates of quantified C_1-C_{12} VOCs was increased by 50 percent.

Table 2. Average Levels of VOCs Listed as Toxic Air Contaminants and Total Amount of Quantified VOCs in Combustion Emissions from CARB Diesel Fuel or PG1 Diesel Fuel (7 Runs) from Data Submitted to ARB[1]

Air Contaminant	Emissions using CARB Diesel Fuel (mg/hp-hr)	Emissions using PG1 Diesel Fuel (mg/hp-hr)	Relative Change[2] (%)
Benzene	0.64	.77	+20
Toluene	0.7	1.04	+49
Ethylbenzene	0.29	0.42	+45
1,3-Butadiene	0.98	1.32	+33
m- and *p*-Xylene	0.21	1.2	+471
o-Xylene	0.10	0.46	+360
Hexane	0.04	0.23	+475
Propionaldehyde	1.1	2.0	+82
Formaldehyde	15.92	25.06	+57
Acetaldehyde	4.87	7.84	+61
Acrolein	1.5	2.6	+73
Total quantified VOCs	62.1	93.3	+50

[1] Data from Table 6, Table D-1 and Table D-2 in the December 2000 Southwest Research Institute report, "Testing of PuriNOx™ Fuel Using the CARB Interim Procedure for Certification of Emission Reductions for Alternative Diesel Fuels"

[2] Calculated as 100×(PG1 emission rate – CARB emission rate)/(CARB emission rate)

The data on emissions rates of PAHs from the December 2000 report are listed in Table 3. In combustion emissions of PG1 diesel fuel, emission rates of some quantified PAHs are lower and the emission rates of others are higher than the corresponding emission rates from CARB diesel. For carcinogenic PAHs in combustion emissions of PG1 diesel, the emission rate of BAP and the emission rate of BAP PEF-weighted PAHs are nearly equal to the rates determined when CARB diesel is used. The emission rate of BAP PEF-weighted PAHs is calculated by multiplying each emission rate by the corresponding PEF and summing these products. In cases where the PEF is not available, it is set to 0.

While PM emissions on a mass basis are reduced in emissions from diesel engines fueled by PG1 diesel, the particles from PG1-fueled engines contain a larger amount of organic substances per gram of particles than do particles from CARB diesel-fueled engines. Among the compounds absorbed to particles are the PAHs, which have a higher concentration per gram of particles in exhaust from PG1-fueled engines than in exhaust from CARB diesel-fueled engines. Consequently, while the toxicity of particles produced per horsepower-hour from engines fueled with PG1 diesel appears to be reduced, the reduction may not be as great as the reduction in PM mass.

Table 3. Average Levels of PAHs in Combustion Emissions from CARB Diesel Fuel or PG1 Diesel Fuel (7 Runs) from Data Submitted to CARB[1]

Air Contaminant	California BAP PEF[2]	Emission Rate Using CARB Diesel Fuel (mg/hp-hr)	Emission Rate Using PG1 Diesel Fuel (mg/hp-hr)	Relative Change[3] (%)
Naphthalene	n.a.	0.64241	0.27519	-57
2-Methylnaphthalene	n.a.	0.1565	0.14532	-7
Acenaphthylene	n.a.	0.02063	0.0792	284
Acenaphthene	n.a.	0.00503	0.00124	-75
Fluorine	n.a.	0.02769	0.02228	-20
Phenanthrene	n.a.	0.04384	0.03543	-19
Anthracene	n.a.	0.00397	0.00409	+3
Fluoranthene	n.a.	0.00961	0.00745	-22
Pyrene	n.a.	0.01949	0.01565	-20
Benz(a)anthracene	0.1	0.00026	0.00034	+31
Chrysene	0.01	0.00054	0.00059	+9
Benzo(b)fluoranthene	0.1	0.00026	0.00029	+12
Benzo(k)fluoranthene	0.1	0.00024	0.00025	+4
Benzo(e)pyrene	n.a.	0.00044	0.00042	-5
Benzo(a)pyrene	1.0	0.00044	0.00045	+2
Perylene	n.a.	0.00017	0.00008	-53
Indeno(1,2,3-cd)pyrene	0.1	0.00022	0.00016	-27
Dibenz(a,h)anthracene	1.1	0.00014	0.00005	-64
Benzo(ghi)perylene	n.a.	0.00031	0.00031	0
total speciated PAHs		0.932	0.589	-37
Total BAP PEF-weighted PAH		0.000697	0.000615	-12

[1] Data from Table 7 in the December 2000 Southwest Research Institute report, "Testing of PuriNOx™ Fuel Using the CARB Interim Procedure for Certification of Emission Reductions for Alternative Diesel Fuels"

[2] An absence of a published State of California PEF for a specific PAH is denoted n.a.

[3] Calculated as 100×(PG1 emission rate – CARB emission rate)/(CARB emission rate)

OEHHA scientists also reviewed combustion emissions test data submitted to US EPA in the final report, "Fuel Registration Testing for the Lubrizol Corporation." This report, dated June 2000, was prepared by Southwest Research Institute to meet US EPA's Tier I data requirements for vehicle fuel additive registration. The test protocol included both cold engine runs and hot engine runs. The PG1 fuel used in Tier I tests was blended using the same CARB fuel used as the CARB reference fuel.

Table 4. Average Levels[1] of NO_x, PM and CO in Combustion Emissions from CARB Diesel Fuel or PG1 Diesel Fuel from Data Submitted to US EPA[2]

Air Contaminant	Emissions Rate Using CARB Diesel (g/hp-hr)	Emission Rate Using PG1 Diesel (g/hp-hr)	Relative Change[3] (%)
NO_x	3.4	3.1	-9
PM	0.09	0.06	-33
CO	0.9	0.8	-11

[1] Calculated as a weighted average of three cold engine starts and three hot engine starts
[2] Data from Table 6 in the June 2000 Southwest Research Institute report, "Fuel Registration Testing for the Lubrizol Corporation"
[3] Calculated as 100×(PG1 emission rate – CARB emission rate)/(CARB emission rate)

As shown in Table 4, emission rates of NO_x, PM and CO from engines burning PG1 diesel fuel were decreased by 9, 33 and 11 percent, respectively, compared to emissions from engines tested under the same operating conditions burning CARB reference diesel fuel. Emission rates of VOC TACs were increased in PG1 diesel combustion emissions (Table 5).

Table 5. Average Levels of VOCs Listed as Toxic Air Contaminants and Total Amount of Quantified VOCs in Combustion Emissions from CARB Diesel Fuel or PG1 Diesel Fuel from Data Submitted to US EPA[1]

Air Contaminant	Emissions using CARB Diesel Fuel (mg/hp-hr)	Emissions using PG1 Diesel Fuel (mg/hp-hr)	Relative Change[2] (%)
Benzene	0.3	0.4	**+33**
Toluene	0.5	0.8	+60
Ethylbenzene	1	n.d.[3]	
m- and p-Xylene	0.5	0.6	+20
1,3-Butadiene	0.45	0.8	+78
Acetaldehyde	2.7	5.8	+115
Formaldehyde	7.5	15.8	+111
Propionaldehyde	1	2.4	+140
Acrolein	0.9	2.1	+133
Total quantified VOCs	31.2	60.9	+95

[1] Data from Table 6 in the June 2000 Southwest Research Institute report, "Fuel Registration Testing for the Lubrizol Corporation"
[2] Calculated as 100×(PG1 emission rate – CARB emission rate)/(CARB emission rate)
[3] Emissions below the limit of detection are denoted n.d.

In combustion emissions from PG1 diesel fuel, emission rates of quantified nitro PAHs are lower than the corresponding emission rates from CARB diesel (Table 6). For

carcinogenic PAHs in combustion emissions from PG1 diesel, the emission rate of BAP and the emission rate of BAP PEF-weighted PAHs are lower than the rates determined when CARB diesel is used.

Table 6. Average Levels of Certain PAH and Nitro Aromatic Compounds in Combustion Emissions from CARB Diesel Fuel or PG1 Diesel Fuel from Data Submitted to US EPA[1]

Ir Contaminant	California BAP PEF	Emission Rate Using CARB Diesel Fuel (mg/hp-hr)	Emission Rate Using PG1 Diesel Fuel (mg/hp-hr)	Relative Change[2] (%)
1-Nitropyrene	n.a.[3]	0.0000860	.000043	-50
2-Nitropyrene	n.a.	0.000015	0.0000021	-86
7-Nitrobenz(a)anthracene	n.a.	0.00000071	0.00000045	-37
6-Nitrochrysene	n.a.	0.00000064	0.00000013	-80
Benz(a)anthracene	0.1	0.000700	0.000420	-40
Chrysene	0.01	0.000960	0.000610	-36
Benzo(b)fluoranthene	0.1	0.000620	0.000650	5
Benzo(k)fluoranthene	0.1	0.000330	0.000290	-12
Benzo(a)pyrene	1.0	0.000400	0.000280	-30
Indeno(1,2,3-cd)pyrene	0.1	0.000097	0.000360	271
Dibenz(a,h)anthracene	1.1	0.0000044	0.0000082	86
Total BAP PEF-weighted PAHs		0.000589	0.000467	-21

[1] Data from Table 8 in the June 2000 Southwest Research Institute report, "Fuel Registration Testing for the Lubrizol Corporation"

[2] Calculated as 100×(PG1 emission rate – CARB emission rate)/(CARB emission rate)

[3] An absence of a published State of California PEF for a specific PAH is denoted n.a.

b. Analysis of PG2 diesel fuel combustion emissions

OEHHA scientists have reviewed analytical data on post-combustion emissions from PG2 diesel fuel in the report, "Emissions Performance Testing of Generation II PuriNOx^{TM} Diesel Fuel," prepared by Southwest Research Institute for Lubrizol Corporation, November 2001 (November 2001 report). This report contains data on emission rates of NO_x, PM, THC, CO and C_1-C_{12} VOCs from CARB reference fuel and PG2 fuel blended with the same CARB fuel that was used as reference fuel. No data on PAH emissions are in the report.

As shown in Table 7, both NO_x and PM from engines burning PG2 were reduced by 11 and 48 percent, respectively, compared to CARB diesel emissions from engines tested under the same operating conditions. THC emissions from PG2 diesel fuel were increased by 128 percent.

Table 7. Average Levels of NO_x, PM, THC and CO_2 in Combustion Emissions from CARB Diesel Fuel or PG2 Diesel Fuel (4 Runs)[1]

Air Contaminant	Emission Rate Using CARB Diesel (g/hp-hr)	Emission Rate Using PG2 Diesel (g/hp-hr)	Relative Change[2] (%)
NO_x	3.049	2.723	-11
PM	0.090	0.047	-48
THC	0.053	0.121	+128
CO	0.803	0.854	+6

[1] Data from Table 2 in the November 2001 Southwest Research Institute report, "Emissions Performance Testing of Generation II PuriNOx^{TM} Diesel Fuel"

[2] Calculated as 100×(PG1 emission rate – CARB emission rate)/(CARB emission rate)

Table 3 in the November 2001 report lists emission rates of 225 VOCs containing 12 or fewer carbon atoms. For 42 of these quantified compounds, emission rates are higher when PG2 diesel is used. Nine VOCs with increased emission rates are identified toxic air contaminants (TACs) by the ARB. As shown in Table 8, the emission rates of benzene, ethyl benzene, *m*- and *p*-xylene, propionaldehyde, formaldehyde, acetaldehyde and acrolein were increased by 50, 100, 73, 58, 64, 55 and 200 percent, respectively, and the sum of the emission rates of quantified C_1-C_{12} VOCs was increased by 167 percent.

The total mass of identified and quantified emissions was 0.045 g/hp-hr for CARB diesel fuel and was 0.075 g/hp-hr for PG2 diesel fuel. Therefore, the amount of unidentified hydrocarbon emissions is calculated from the THC emissions in Table 7 to be 0.008 g/hp-hr for CARB diesel fuel and 0.046 g/hp-hr for PG2 diesel fuel. This increase in emission of organic chemicals of unknown identity is slightly greater than the decrease in particulate emissions found in PG2 diesel fuel.

Table 8. Average Levels of VOCs Listed as Toxic Air Contaminants and Total Amount of Quantified VOCs in Combustion Emissions from CARB Diesel Fuel or PG2 Diesel Fuel (4 Runs)[1]

Air Contaminant	Emission Rate Using CARB Diesel (mg/hp-hr)	Emission Rate Using PG2 Diesel (mg/hp-hr)	Relative Change[2] (%)
Benzene	0.8	1.2	+50
Toluene	0.4	0.3	-25
Ethylbenzene	0.3	0.6	+100
1,3-Butadiene	n.d.[3]	0.7	
m- and *p*-Xylene	1.1	1.9	+73
o-Xylene	0.8	0.5	-38
Hexane	n.d.	0.1	
Propionaldehyde	1.9	3.0	+58
Formaldehyde	8.5	13.9	+64
Acetaldehyde	3.1	4.8	+55
Acrolein	0.1	0.3	+200
Total quantified VOCs	45.0	75.0	+167

[1] Data from Table 3 in the November 2001 Southwest Research Institute report, "Emissions Performance Testing of Generation II PuriNOx^{TM} Diesel Fuel"

[2] Calculated as 100×(PG1 emission rate – CARB emission rate)/(CARB emission rate)

[3] Emissions below the limit of detection are denoted n.d.

c. Screening risk assessment for carcinogenic substances in diesel exaust

The amount of the carcinogenic TACs, acetaldehyde, benzene, 1,3-butadiene and formaldehyde, produced by an engine burning PuriNOx^{TM} fuel is greater than the amount of these substances produced by the same engine burning CARB fuel. To assess potential impacts on human health from a substitution of PuriNOx^{TM} fuel for a portion of CARB fuel, OEHHA scientists assumed that, for a carcinogenic substance in air, the cancer risk attributable to the substance is equal to the carcinogenic potency multiplied by the average ambient air concentration of the substance. With this assumption, an upper-bound estimate of the increase or decrease in cancer risk resulting from a substitution of PuriNOx^{TM} fuel for a portion of CARB fuel is produced by the expression

$$Risk = [C_{ambient}] \times [(A_P - A_C)/A_C] \times [E_d/Et] \times P \times F_m$$

where

$C_{ambient}$ is the average ambient outdoor air level of the carcinogenic substance,

A_P and A_C are the amounts of the substance produced per horsepower-hour by engines burning PuriNOx^{TM} fuel and CARB fuel, respectively,

E_d is the estimate of the total releases per day of the substance from heavy-duty on-road diesel vehicles and E_t is the estimate of releases into the atmosphere per day from all anthropogenic sources,

F_m is the maximum market share of PuriNOx^{TM} fuel (chosen to be 0.1 in accordance with ARB's estimate),

P is the upper-bound estimate of carcinogenic potency in units $(\mu g/m^3)^{-1}$.

For a bounding estimate on risk, data were selected from the region of California with the highest ambient levels and the largest estimates of releases of these substances. This region is the South Coast Air Quality Management District (SCAQMD). Data from the Burbank monitoring station, which had the highest average concentrations, were used.

Table 9. Upper-bound estimates of lifetime cancer risks attributable to PuriNOx^{TM} diesel fuel combustion calculated from emission changes in Table 2 assuming that 10 percent of on-road heavy-duty diesel vehicles use PG1 fuel (calculated from ARB data for 2002)

Chemical	Average Ambient Air Concentration ($\mu g/m^3$)	Cancer Unit Risk Factor $(\mu g/m^3)^{-1}$	Upper-Bound Lifetime Risk Increase Attributable to Substance in PG1 Diesel Emissions
Acetaldehyde	3.6	2.7×10^{-6}	9.3×10^{-8}
Formaldehyde	6.7	6.0×10^{-6}	1.5×10^{-7}
Benzene	3.2	2.9×10^{-5}	3.3×10^{-8}
1,3-Butadiene	0.62	1.7×10^{-4}	2.5×10^{-8}

Tables 9 and 10 list upper-bound screening estimates of lifetime cancer risk that might result from substituting PG1 fuel for 10 percent of diesel used in heavy-duty on-road vehicles. The estimates in Table 9 were calculated from data submitted to ARB and estimates in Table 10 were calculated from data submitted to US EPA. Table 11 lists upper-bound screening estimates of lifetime cancer risk that might result from substituting PG2 fuel for 10 percent of diesel used in heavy-duty on-road vehicles. All estimates are below the widely used screening level of 10^{-6}. The upper-bound risk attributable to 1,3-butadiene from PG2 diesel was not calculated because 1,3-butadiene levels were below the limit of detection in combustion emissions of CARB fuel in the testing of PG2 fuel.

The estimates of *Et* used for risk calculations do not include biological sources or formation by atmospheric chemical reaction. For acetaldehyde and formaldehyde, these processes are major components of the total amount added to the atmosphere per day. Inclusion of biological and atmospheric production to the estimate of E_t for these aldehydes would greatly reduce the corresponding upper-bound risk estimates.

Table 10. Upper-bound estimates of lifetime cancer risks attributable to PuriNOx™ diesel fuel combustion calculated from emission changes in Table 5 assuming that 10 percent of on-road heavy-duty diesel vehicles use PG1 fuel (calculated from ARB data for 2002)

Chemical	Average Ambient Air Concentration ($\mu g/m^3$)	Cancer Unit Risk Factor $(\mu g/m^3)^{-1}$	Upper-Bound Lifetime Risk Increase Attributable to Substance in PG1 Diesel Emissions
Acetaldehyde	3.6	2.7×10^{-6}	1.8×10^{-7}
Formaldehyde	6.7	6.0×10^{-6}	4.9×10^{-7}
Benzene	3.2	2.9×10^{-5}	5.6×10^{-8}
1,3-Butadiene	0.62	1.7×10^{-4}	6.0×10^{-8}

Table 11. Upper-bound estimates of lifetime cancer risk increases attributable to PuriNOx™ diesel fuel combustion calculated from emission changes in Table 8 assuming that 10 percent of on-road heavy-duty diesel vehicles use PG2 fuel (calculated from ARB data for 2002)

Chemical	Average Ambient Air Concentration ($\mu g/m^3$)	Cancer Unit Risk Factor $(\mu g/m^3)^{-1}$	Upper-Bound Lifetime Risk Increase Attributable to Substance in PG2 Diesel Emissions
Acetaldehyde	3.6	2.7×10^{-6}	8.7×10^{-8}
Formaldehyde	6.7	6.0×10^{-6}	2.8×10^{-7}
Benzene	3.2	2.9×10^{-5}	3.3×10^{-8}

When the same upper-bound screening analysis is applied to diesel particulate emissions using the average ambient PM10 concentration (60.2 $\mu g/m^3$) from 2002 SCAQMD monitoring stations for $C_{ambient}$, the upper bound on risk reduction resulting from use of PuriNOx™ fuel in 10 percent of heavy-duty on-road vehicles is 2.0×10^{-5}

calculated from the PM reduction for PG1 fuel in Table 1 and 1.1×10^{-5} calculated from the PM reduction in Table 4. The upper-bound estimate is 1.7×10^{-5} from PM emissions data for PG2 fuel in Table 8. Some of the PM reduction in Table 1 may result from the lower sulfur content of PG1 Fuel (compared to the CARB fuel) used for the combustion tests performed for ARB.

OEHHA scientists believe that caution should be used when comparing this estimate with estimates of increased risk in Table 9 and Table 10 because there are uncertainties in the risk estimates. One of the uncertainties is the extent to which substances other than PM**,** *e.g.* nitrosamines, contributed to cancer risk in the epidemiology studies used for estimation of the PM unit risk factor. Applying this risk-bounding methodology to decreases in BAP and BAP PEF-weighted PAH emissions yields estimates of decreases in lifetime cancer risk that are less than 10^{-9} from a ten percent market share for PG1 or PG2 diesel fuel.

d. Screening assessment of chronic toxic effects other than cancer

Table 12. Chronic RELs, and Average Ambient Air Concentrations Levels of TACs Listed in Tables 2, 5 and 8

Air Contaminant	Chronic REL[1,2] (μg/m^3)	Ambient Air Concentration[3,4] (μg/m^3)	Relative Change[5] (%)
Benzene	60	3.22	+20 to +50
Toluene	300	12.0	-25 to +60
Ethyl benzene	2,000	1.62	+45 to +100
1,3-Butadiene	20	0.62	+35 to +78
m- and *p*-Xylene	700	8.02	+20 to +471
o-Xylene	700	2.60	-38 to +360
Hexane	n.a.	n.m.	+475
Propionaldehyde	n.a.	n.m.	+58 to +140
Formaldehyde	3	6.71	+57 to +111
Acetaldehyde	9	3.60	+55 to +115
Acrolein	0.06	n.m.	+55 to +200

[1] The notation n.a. indicates that a chronic REL has not been published for the TAC.
[2] RELs currently published on the OEHHA website (www.oehha.ca.gov)
[3] The notation n.m. indicates that the TAC is not routinely monitored by ARB.
[4] Ambient levels are averages for 2002 from the Burbank monitoring station.
[5] Increases are the minimum and maximum values from Tables 2, 5 and 8.

To screen for non-cancer adverse impacts that might result from increases in TACs following substitution of PG1 or PG2 diesel for 10 percent of the fuel used by on-road diesel vehicles, average ambient air concentrations were compared to chronic

reference exposure levels (RELs) listed in Table 12. For benzene, toluene, ethyl benzene, 1,3-butadiene, *m*- and *p*-xylene, and *o*-xylene, the REL is more than one order of magnitude greater than average annual concentrations. For these air contaminants, it is clear that use of PuriNOx^{TM} fuels will not increase ambient levels to concentrations close to or above the corresponding RELs. This conclusion can not be made for acetaldehyde and formaldehyde. Information is inadequate for evaluation potential chronic impacts due to changes in levels of hexane, propionaldehyde or acrolein.

To assess potential impacts of increases in levels of acetaldehyde and formaldehyde, the source contribution methodology used for upper-bound cancer risk estimates was used. To estimate ambient average levels following substitution of a PuriNOx^{TM} fuel for 10 percent of the fuel used by heavy-duty on-road diesel vehicles, the coefficient of the carcinogenic potency factorin the above equation for cancer risk is added to $C_{ambient}$. The percent increase is estimated by dividing this coefficient,

$$[C_{ambient}] \times [(A_P-A_C)/A_C] \times [E_d/Et] \times F_m,$$

by $C_{ambient}$. This increase is estimated to be 1.9 percent for acetaldehyde and 1.2 percent for formaldehyde using the maximum increases in Table 12. Increases of similar percentages may occur for acrolein and propionaldehyde. The increases in ambient levels of the four aldehydes listed in Table 12 may result in a small increase in adverse effects on mucous membranes of the respiratory system which is the primary target tissue for these chemicals in ambient air.

3. Summary and evaluation of Tier II data submitted to US EPA

Emissions from combustion of ultra low sulfur diesel (ULSD) blended with the PG1 additive mixture were evaluated in a 90-day subchronic toxicity study in male and female rats. Reproductive and developmental toxicity, neurotoxicity, and genotoxicity were also evaluated. Results of these studies were presented in "Final Report, Tier II Testing of PuriNOx (Summer Fuel Blend) Exhaust Emissions" prepared by Lovelace Inhalation Research Institute (2002). These tests were undertaken to comply with the requirements of 40 CFR Part 79, Registration of Fuel Additives, specifically 79.60-79.68, which describes the conditions and conduct of toxicity testing for motor vehicle fuel additives.

In the general subchronic toxicity and recovery studies, groups of ten males and ten females were exposed to low, medium or high concentrations of emissions for 6 hours per day, 5 days per week. Concurrent evaluation of ULSD combustion emissions was not undertaken, ostensibly because the toxicity of diesel emissions in rats has been thoroughly evaluated in several long-term bioassays. [Data have been summarized by U.S. EPA (2002).] However, the lack of concurrent positive control groups in this study (i.e., animals exposed to ULSD combustion emissions) precluded an assessment of the toxicity of PuriNOx-blended diesel *relative* to that of unmodified diesel.

There were several technical concerns with the conduct of this study. Whole body inhalation allows deposition of particulates on the animals' fur. During grooming, the animals ingest these particles. As a result, exposure undoubtedly occurred via two routes, inhalation and ingestion. Particulate concentrations (100, 200 and 400 g/m^3) were used as the measure of exposure concentration and were stable throughout the duration of the study. However, the concentrations of several gas phase pollutants, particularly sulfur dioxide (SO_2) and nitrogen dioxide (NO_2), appeared to vary widely, and the data suggests that animals were occasionally exposed to concentrations that were much higher than the average concentration. Episodic, high level exposures could produce more severe toxic effects than those that would result from constant, stable exposures. In addition, the relative humidity of the test atmospheres was inversely related to particulate concentration. Average relative humidity at the highest test concentration (14.3%) was less than half that of the control atmosphere (29.9%). Potentially, low relative humidity at the higher test concentrations may have exacerbated the toxic effects of PG1 diesel fuel emissions. The instability of the PuriNOx additive mixture blended with diesel fuel may have lead to variable concentrations of gas-phase pollutants. Although the manufacturer of PuriNOx recommends that the fuel be agitated at least weekly to prevent separation, the Tier II report provides no indication that the fuel was ever agitated during the course of the toxicity study.

For the purpose of identifying toxic effects of a complex mixture of toxic chemicals, it is reasonable to expect that a bioassay of this scale would be relatively insensitive. Because of biological variability, studies that incorporate relatively small group sizes are likely to produce inconsistent results that lack statistical significance. Therefore, when interpreting the results of small studies, it is essential to refer to published, relevant scientific literature.

It appears that these considerations were not taken into account in the PuriNOx Tier II report. Statistically significant reductions in serum protein and electrolyte levels were judged to be "inconsistent" and therefore unrelated to emissions exposure even though these effects were also observed in previously published studies of the toxicity of diesel exhaust. Similarly, statistically significant increases in several hematological parameters (hemoglobin, hematocrit, red blood cells and monocytes) in middle and high dose female rats were also judged to be unrelated to emissions exposure even though the same changes were reported in earlier, similarly conducted studies of diesel exhaust. In addition, several statistically significant dose-related changes in organ weights were not noted in the text of the report. Reductions in body weight gain in high dose males and females were judged unrelated to treatment, although it appears that more rigorous statistical analysis of the data (i.e., regression analysis) would indicate that the reductions were indeed statistically significant.

Emissions from the combustion of PuriNOx-diesel blend were separated into particulate and semi-volatile fractions, and tested for their ability to induce mutations in bacterial cells in the Ames *Salmonella* reverse mutation assay. Both fractions were clearly positive in several of the bacterial tester strains, and these results were attributed to the mutagenic products of diesel fuel combustion. However, the data required to

support this conclusion were not provided because emissions from unmodified diesel fuel were not tested. Therefore, the effect of PuriNOx on formation of mutagenic combustion by-products could not be determined. Tests in a bacterial strain that is deficient in the enzyme nitroreductase showed a reduction in mutagenic potency, indicating that nitro aromatic compounds were produced by combustion of the PuriNOx-diesel blend. Mutagenic nitro aromatic compounds are also produced by combustion of unmodified diesel fuel. Nevertheless, unmodified diesel was not tested as a positive control, and it was not possible to determine whether PuriNOx increases or decreases the formation of mutagenic nitro aromatic combustion by-products.

4. Environmental partitioning, transport, fate and toxicity of additive components

PG1 additive package contains two high-molecular-weight (HMW), *i. e.*, greater than 1,000 Daltons, components. It also contains a component of intermediate molecular weight (IMW), *i. e.*, between 250 and 1,000 Daltons, and it contains two low molecular weight (LMW) components, *i. e.*, less than 250 Daltons. OEHHA staff have identified HMW breakdown products of the two HMW components and two LMW breakdown products of the same two components. One of the LMW components is inorganic, and all other components and breakdown products are organic compounds.

The HMW and IMW components of PG1 will form monolayers on water surfaces and will produce emulsions of oil in water and of water in oil. Fugacity considerations are not adequate for assessing mobility of these components in aquatic media because these films are not part of the water phase. These components will be mobile in surface water and may increase mobility of hydrophobic substances in surface water.

The solubility in water of one of the LMW components and both of the LMW breakdown products is greater than 10 g/l. These substances have the potential to leach from vadose-zone soil into groundwater relatively rapidly and to be highly mobile in groundwater. The water solubility of the other LMW component is between 10 and 100 mg/l. It has the potential to leach to groundwater and to migrate with groundwater at an intermediate rate. The HMW components, the HMW breakdown products and the IMW component are highly lipophilic and will bind tightly to organic particles in soil. These substances have very limited potential for leaching into groundwater and migration with groundwater.

The HMW components of PG1 have the potential to be partially oxidized by microorganisms in aquatic environments. However, they contain a HMW moiety that may be highly resistant to degradation. This moiety may accumulate in aquatic organisms and in sediments in aquatic environments. The LMW organic component and breakdown products do not appear to be highly persistent substances in aquatic environments.

The components of PG1 additive package have not been tested for carcinogenicity or reproductive toxicity. However, there are no known carcinogens or developmental

toxicants that are closely related to these components or their breakdown products. None of the components or breakdown products is highly toxic. One of the components may produce hypersensitivity and allergic reactions in some individuals.

The IMW component of PG1 additive package is acutely toxic to the freshwater fish *Onchorhynchus mykiss* and to the freshwater invertebrate *Daphnia magna*. In a standard bioassay using *Onchorhynchus mykiss,* the concentration estimated to kill 50 percent of the fish after 96 hours (96-hour LC50) was estimated to be 1.4 milligrams per liter. In a standard bioassay using *Daphnia magna*, the concentration estimated to immobilize 50 percent of the invertebrates after 48 hours was 4.3 milligrams per liter. No information on toxicity of this substance to humans or other mammals is available.

Consideration of products that may be formed from components during combustion reveals a possible formation of carcinogenic nitrosamines.

PG2 additive package contains one HMW component, one IMW component and four LMW components. For the HMW component, OEHHA scientists have identified HMW breakdown products and one LMW breakdown product. One of the LMW components is inorganic, and all other components and breakdown products are organic compounds.

The solubility in water of three of the LMW components and the LMW breakdown product is greater than 10 g/l. These substances have the potential to leach from vadose-zone soil into groundwater relatively rapidly and to be highly mobile in groundwater. The solubility in water of the other LMW component is between 10 and 100 mg/l. It has the potential to leach to groundwater and to migrate with groundwater at an intermediate rate. The HMW component, the HMW breakdown product and the IMW component are highly lipophilic and will bind tightly to organic particles in soil. These substances have very limited potential for leaching into groundwater and migration with groundwater.

The HMW and IMW components of PG2 will form monolayers on water surfaces and will produce emulsions of oil in water and of water in oil. Fugacity considerations are not adequate for assessing mobility of these components in aquatic media because these films are not part of the water phase. These components will be mobile in surface water and may increase mobility of hydrophobic substances in surface water.

The HMW component of PG2 has the potential to be partially oxidized by microorganisms in aquatic environments. However, this component contains a HMW moiety that may be highly resistant to degradation. This moiety may accumulate in aquatic organisms and in sediments in aquatic environments. The IMW component is of low toxicity and is broken down by microorganisms in soil and water. The LMW organic component and breakdown products do not appear to be highly persistent substances in aquatic environments.

Most of the components of PG2 additive package have not been tested for carcinogenicity or reproductive toxicity. However, there are no known carcinogens or developmental toxicants that are closely related to these components or their breakdown products. Laboratory animal carcinogenicity and reproductive toxicity tests of two of the components have not demonstrated tumor increases or adverse effects on reproduction or development. None of the components or breakdown products is highly toxic.

Consideration of products that may be formed from components during combustion reveals a possible formation of carcinogenic nitrosamines.

5. Overall evaluation and recommendations

Diesel engines burning PG1 or PG2 diesel fuel produce significantly less emissions of particles, carbon monoxide and oxides of nitrogen than do engines burning diesel fuel meeting current ARB specifications. Emissions of SO_4 from PG1 and PG2 diesel were similar to emissions from combustion of the CARB diesel fuels used to blend the corresponding PuriNOx^{TM} fuels. The reduction in SO_4 emissions in combustion tests of PG1 diesel submitted to ARB is interpreted by OEHHA scientists to be due to a difference in sulfur content between the CARB reference fuel and the diesel fuel used to blend the PG1 diesel fuel for these tests. OEHHA scientists conclude that use of these reformulated fuels may reduce morbidity and mortality due to pulmonary diseases, including lung cancer in adults and allergic asthma in children, caused by substances in diesel exhaust. Information on human health impacts of diesel exhaust can be found in the June, 1998 Staff Report of the ARB and OEHHA, "Proposed Identification of Diesel Exhaust as a Toxic Air Contaminant."

Diesel engines burning PG1 or PG2 fuel emit larger amounts of certain aldehydes and unsaturated hydrocarbons than do engines burning standard diesel fuel. Because the absolute amount of these substances in diesel exhaust is small, there does not appear to be a significant increase in the risk of cancer from any of the increases in emissions. Increased emissions of aldehydes may, however, result in a small increase in irritation of mucous membranes of the respiratory system.

OEHHA is concerned with the absence of data on nitrosamines produced by combustion and on possible adverse impacts on the environment from releases that contain components in the additive packages. Therefore, OEHHA recommends combustion emissions testing for nitrosamines using a protocol selected by ARB. OEHHA also recommends that the ecological toxicity tests specified by the state Water Resources Control Board be completed and submitted to Cal/EPA before PG1 and PG2 are approved for general use as motor vehicle fuels in California.