State of California
California Environmental Protection Agency

Multi-Media Assessment of Lubrizol's PuriNOx Water/Diesel Emulsion

Date of Release: March 2004

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Summary of Multi-Media Assessment of Lubrizol's PuriNOx Fuel

I. Introduction

The Lubrizol Corporation (Lubrizol) has developed PuriNOx, a water-emulsified diesel fuel, that is designed to reduce emissions such as particulate matter (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.

The Lubrizol Corporation has requested that the Air Resources Board (ARB) verify PuriNOx as a diesel emission control strategy pursuant to Title 13 California Code of Regulations, section 2700, et seq. As a requirement for verification, PuriNOx must undergo a multi-media assessment to determine if the use of PuriNOx results in a significant adverse impact on public health or the environment in comparison to diesel fuel meeting the ARB motor vehicle diesel fuel specifications (CARB diesel).

In accordance with Health and Safety Code section 43830.8, an interagency multi-media working group conducted a multimedia evaluation of PuriNOx. The multi-media evaluation includes the impact on air, water, and soil that may result from the production, use, or disposal of PuriNOx.

A. Multi-media Working Group

An interagency working group was formed to oversee the multi-media assessment. The interagency multi-media working group includes representatives from CAL/EPA, ARB, State Water Resource Control Board (SWRCB), Office of Environmental Health Assessment (OEHHA), and Department of Toxic Substances Control (DTSC). Members of the interagency multi-media working group are listed in Attachment A.

For the Lubrizol evaluation, ARB staff is responsible in coordinating the overall multi-media effort and to evaluate the air quality assessment. SWRCB staff is responsible in evaluating the surface and ground water quality assessments. SWRCB contracted with the Lawrence Livermore National Laboratory as a consultant in reviewing this assessment. OEHHA staff is responsible for evaluating potential human health impacts. DTSC staff is responsible for evaluating the potential for PuriNOx to pose hazardous waste concerns.

As part of the evaluation, Cal/EPA contracted with the University of California to conduct a peer review of the multi-media working group's evaluation. The University of California, Davis and the University of California, Berkeley were selected to conduct the peer review. Given in Attachment G are the University of California peer review comments. CAL/EPA responses, where appropriate, to the peer reviewer comments are included in Attachment H.

B. Environmental Policy Council

Pursuant to the California Health and Safety Code section 43830.8, a multimedia assessment and peer review must be conducted when ARB establishes a specification for a motor vehicle fuel. Before adoption of a new or modified motor vehicle fuel specification, the Environmental Policy Council must determine if the proposed fuel specification poses a significant adverse impact on public health or the environment. In making its determination, the Environmental Policy Council must consider the following:

- Emissions of air pollutants, including ozone-forming compounds, particulate matter, toxic-air contaminants, and greenhouse gases.
- Contamination of surface water, groundwater, and soil.
- Disposal of waste materials, including agricultural residue, forest biomass, and municipal solid waste.

If the Environmental Policy Council determines that the proposed fuel specification poses a significant adverse impact on public health or the environment, or that alternatives exist that would be less adverse, the council shall recommend alternative specifications or other measures that the state board (ARB) or other state agencies may take to reduce any adverse impact on public health or the environment.

II. Summary

The following are summaries of ARB, OEHHA, SWRCB, and DTSC staff evaluations on the impact PuriNOx fuel has on human health and the environment. The evaluations are based on the relative differences between CARB diesel fuel and PuriNOx fuel. Two versions of the fuel were evaluated; PuriNOx generation 1 (Gen1) and PuriNOx generation 2 (Gen2) water emulsified diesel fuels. The evaluations include assessments of the impact of using PuriNOx fuel on air emissions, water, soil, hazardous waste, and human health. The complete evaluations are contained in the attachments.

A. Air Emissions Evaluation

ARB staff completed an air quality evaluation on Lubrizol's PuriNOx water emulsified diesel fuel (Attachment B). The evaluation includes a description of the impact of using Gen1 and Gen2 PuriNOx fuels on criteria pollutants, toxic air contaminants, and ozone precursors. To estimate PuriNOx emission impacts, 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 of one percent that Lubrizol predicts will be used in California in 2010.

1. Criteria Pollutants

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 NOx and PM were reduced by 14 percent and 58 percent, respectively. Reactive organic gases (ROG) emissions increased by 87 percent. When evaluating the emission effects of PuriNOx fuel on an absolute basis, mass emission reductions for NOx is greater than mass emission increases of hydrocarbons. For example, comparing Gen1 to CARB diesel in a 1991 DC series 60 engine shows a mass emissions 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: Particulate Matter (PM)

ARB identified diesel PM as a toxic air contaminant in 1998, and determined that diesel PM accounts for about 70 percent of the toxic risk from all identified toxic air contaminants. Evaluation of available data submitted by Lubrizol show the use of Gen1 reduces total PM emissions on average by 58 percent from on-road conventional diesel fuel. Also, PM emissions from off-road engines were on average reduced by 28 percent, however, these estimates are based on the test of one engine of less than 100 hp.

Gen2 PM emission reductions were reported in the South West Research Institute (SWRI) study by Spreen 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 Gen2, Gen2 PM emission reductions were greater than Gen1 when tested on the same engine, therefore the average 58 percent PM reduction appears to be a conservative estimate for both Gen1 and Gen2 fuels.

3. 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, benzene, toluene, ethyl benzene, xylenes, 1,3-butadiene, and some polycyclic aromatic hydrocarbons (PAHs) have also been reported. Although the increase of these pollutants is of concern, the magnitude of their mass emissions is small compared to the decrease in mass emissions of PM. OEHHA 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.

4. Ozone Precursors

The use of PuriNOx fuel as compared to CARB diesel fuel decreases NOx emissions by about 14 percent but increases ROG emissions by 87 percent. However, PuriNOx emissions of ROG are about 29 percent of the NOx emissions in diesel exhaust. In other words, 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.

5. Estimated 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. 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 PM by 0.22 tons/day. This corresponds to a 1.1 percent reduction of NOx and a 6 percent reduction of the PM from all 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 a 9 percent increase of the ROG from on road heavy-duty diesel engines, or about

0.12 percent increase of the ROG from all sources. For the South Coast Air Basin, the impacts on ozone of PuriNOx are very small (less than a ppb ozone). However this change is in the direction of higher peak ozone. For 1,3-butadiene, benzene, ethyl benzene, and toluene, formaldehyde, and acetaldehyde, increases from 0.0002-0.0003 tons/day may occur.

6. PuriNOx Gen1 and Gen2 Emissions of Greenhouse Warming Gases

No life-cycle analysis has been performed on PuriNOx Gen1 and Gen2 fuels to determine the net effect on emissions of greenhouse gases. 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. 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. Water Evaluation

The staff of the SWRCB evaluated the impacts on surface water and groundwater from the use of PuriNOx (Attachment C). As part of the process, SWRCB staff identified information needs that Lubrizol should address regarding potential impacts on surface and groundwater in California. The information needs included the following:

- Information on the composition, manufacturing and transportation of PuriNOx fuel.
- Possible release scenarios.
- Fate and transport model for releases into surface and groundwater.
- Uncertainty in the current state of knowledge regarding PuriNOx.

In response to the information needs, Lubrizol conducted a surface and groundwater study which included a literature review; modeling of soil, air, water, and sediment by fugacity modeling; and aquatic toxicity, soil column, and biodegradation tests. Based on this study, Lubrizol found that possible impacts associated with the use of PuriNOx do~~es~~ not significantly differ from ultra low sulfur diesel fuel.

As part of the process, Lubrizol contracted with the Lawrence Livermore National Laboratory (LLNL) to conduct a review of the data and data analysis developed by Lubrizol regarding the potential impacts to surface and groundwater (Attachment D). LLNL found that many of the additives used in PuriNOx are also widely used in industry,

in diesel fuel, and lubrication products. LLNL also found that knowledge gaps still exist and there is a need to fill these knowledge gaps in the future. These knowledge gaps include:

- Analytical methods for PuriNOx components of greatest concern
- Biodegradation studies.
- Aquatic toxicity test data.
- Soil column studies of sufficient quality to provide quantitative assessments.
- Study on assessment of actual environmental distributions after a known release of PuriNOx additive or PuriNOx fuel.

In review of the Lubrizol study and the LLNL evaluation, SWRCB staff found that there are no identified issues that would preclude the limited use of PuriNOx while concurrently addressing the knowledge gaps on a timely basis.

C. Public Health Evaluation

OEHHA staff conducted a human health and transport, fate, and toxicity assessment (Attachment E) based on data provided by Lubrizol.

1. Toxic Screening

Using the differences in emission rates of PuriNOx and CARB diesel, a screening risk assessment for carcinogenic substances in diesel exhaust was conducted. An upper bound of lifetime cancer risk attributable to the substitution of PuriNOx fuel for 10 percent of the heavy-duty on-road diesel is less than one in a million excess cancers. One class of toxic air contaminants, nitrosamines, were not reported and the absence of nitrosamine data is of concern to OEHHA.

2. U.S. EPA Tier II Toxicity Testing

Part of Lubrizol submission package was a report of results from animal toxicity data (U.S.EPA Tier II) conducted to comply with U.S. EPA registration (40 CFR Part 79.60, Registration of Fuel Additives). OEHHA staff evaluated the Gen 1U.S.EPA Tier II data and concluded that many of the effects observed with PuriNOx fuel are consistent with known toxicity of diesel combustion emissions. Also, the lack of concurrent positive controls i.e., animals exposed to CARB diesel combustion emissions precluded an assessment of the toxicity of PuriNOx-blended diesel relative to that of unmodified CARB diesel. The study also was not sufficiently sensitive to detect small but possibly significant changes in toxicity of a toxic, complex mixture.

3. Transport, Fate and Health Risk Assessment of Components of PuriNOx Gen1 and Gen2 Additive Packages

OEHHA conducted an assessment of the transport, fate and toxicity of components of PuriNOx Gen1 and Gen2 additive packages. The assessment included an evaluation of the mobility of the additives in soil and groundwater. Partitioning into environmental media, including organisms and aquatic sediment and persistence in environmental media were also evaluated. Finally, the additives were evaluated for toxicity and hazard to humans.

OEHHA concluded that none of the additive components are known to be significantly more toxic than diesel fuel, although toxicity test data on high-molecular weight additives contained in PuriNOx fuel were not available. One concern of the high-molecular-weight additives is that they may accumulate in aquatic sediments and organisms.

D. Hazardous Waste Evaluation

DTSC evaluated the potential impact of PuriNOx fuel and additives on human health and the environment due to hazardous waste and constituent releases to the groundwater and soil (Attachment F).

DTSC staff identified potential release scenarios for the additive package and PuriNOx fuel during transportation, blending and storage processes and concluded that the management of potential spill scenarios of PuriNOx fuel and its additives are similar to that for CARB diesel fuel.

DTSC staff reviewed PuriNOx additives for toxic properties and determined that they will not contribute significantly to the hazardous properties of diesel fuel due to their low concentrations. However, the most significant impact from accidental release will be soil contamination due to the strong adsorption of the additive, therefore making them more difficult to remove if an accidental release should occur.

III. Conclusions

The multi-media working group's conclusions on the impacts of PuriNOx fuel on public health and the environment are summarized below.

A. Conclusions on Air Emissions Impact

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

- PuriNOx significantly reduces PM and NOx emissions in diesel exhaust.
- PuriNOx significantly reduces emissions and health risk from PM in diesel exhaust, a toxic air contaminant identified by the ARB.
- The 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 emission reductions for NOx and PM when compared to Gen1 results. Emissions of toxic air contaminants and aldehydes for Gen2 appear to be similar to Gen1. Since no Gen2 data was available, no conclusion could be made with respect to PAH or nitro-PAH emissions, however staff have no reason to believe that these emissions will differ from the use of Gen2 or 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. 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 gas emissions.

B. Conclusions on Water Impacts

SWRCB staff concurs with LLNL report findings, conclusions and recommendations for further studies. Although there are knowledge gaps in the assessment, SWRCB staff concludes that the risk to the water environment are minimal and acceptable given the limited and controlled use of PuriNOx.

C. Conclusions on Public Health Impact

OEHHA staff concluded that PM and NOx are significantly decreased in PuriNOx emissions as compared to CARB diesel fuel. OEHHA concluded that while certain individual toxic air contaminants are significantly increased in PuriNOx emissions; the benefit from the reduction of PM and NOx appears to outweigh the risk from increases in toxic air contaminants. OEHHA staff expressed the concern that substances present in PuriNOx Gen1 and Gen2 fuels, but not in conventional diesel fuel, might result in nitrosamine formation during combustion. Finally, the high-molecular weight

components of the PuriNOx fuel additive package have the potential to accumulate and persist in environmental media. Insufficient data are available to assess what, if any, risk they pose to the environment or to humans.

D. Conclusions on Hazardous Waste Impact

DTSC staff concluded that since most chemicals in the additive packages have low water solubility and were used in the fuel industry for many years that when compared with regular diesel, PuriNOx most likely will not cause significant impact of groundwater.

However, the application of the PuriNOx fuel may potentially cause some increase in soil contamination due to the strong soil adsorption of the additive chemicals. It may be more difficult to remove these additives from contaminated soil than diesel fuel; therefore, soil cleanup technology needs to be further studied.

IV. Recommendations

The multimedia working group recommends that the Environmental Policy Council:

A. Find that the limited and controlled use of PuriNOx Gen1 and Gen2 formulations as described in the multimedia assessment does not pose a significant adverse impact on public health and the environment as compared to California diesel fuel.

B. Condition the finding in IV-A due to the knowledge gaps identified in the multi-media assessment as follows:

1. Lubrizol shall provide additional information and studies to fill the knowledge gaps identified in the multi-media assessment. The information and requested studies shall be reviewed and approved by the appropriate Board, Department, or Office (BDO) of Cal/ELPA and shall be coordinated through ARB. Before the submission of information and design of the studies requested, Lubrizol shall consult with the appropriate BDOs of Cal/EPA.

2. The following information and studies shall be provided according to the schedule below.

   - Analytical methods for PuriNOx components of greatest concern (completed within 1 year).
   - Results from refined soil column studies (completed within 1 year).
   - Information on product compatibility (completed within 1 year).
   - Results from aquatic toxicity testing (initiate development of a study design immediately and complete within 5 years with annual progress reports).
   - Results from biodegradation studies (completed within 2 years).

3. Prior to any expansion above 35 million gallons per year of the proposed distribution and use of PuriNOx, the following studies shall be conducted.

   - An environmental fate and transport study. Such a study should be either a controlled release to land/groundwater or a known release if one has occurred and is acceptable for analysis. Included in the study is an analysis of remediation measures.
   - Conduct comparative emissions tests for nitrosamines and products that can lead to nitrosamine formation.

4. In the event that the requested information, studies, or any other relevant available information indicate significant risks to the environment, the use of PuriNOx will be reviewed by the Governor's Environmental Policy Council for consideration for appropriate action.

V. Attachments

A. Members of Interagency Multimedia Working Group
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)
C. State Water Resources Control Board's Evaluation of Multimedia Impacts Resulting From The Use Of PuriNOx Fuel In California: Impacts To Water (Public Version)
D. Lawrence Livermore National Laboratory's Review of the Data Supporting Lubrizol's Evaluation of Multimedia Impacts Resulting from the Use of PuriNOx Fuel in California
E. Office of Environmental Health Hazard Assessment's Impact Assessment of PuriNOx^{TM} Generation 1 and Generation 2 Diesel Fuel (Public Version)
F. Department of Toxic Substances Control's Review and Comments to Lubrizol Final Report: Multimedia Evaluation, PuriNOx Fuel (Public Version)
G. University of California Peer Review Comments
H. Staff's Responses to Peer Review Comments