Attachment G. University of California Peer Review Comments

BERKELEY LAB

ENVIRONMENTAL ENERGY
TECHNOLOGIES DIVISION

Feb. 13, 2004

Mr. Gary Yee
Manger Industrial Section
Air Resources Board
PO Box 2815
Sacramento, CA 95812

Dear Mr. Yee:

Enclosed is my review of the multimedia assessment of PuriNOx fuel. A copy of this letter will be sent by email to you and the others listed below. I am also returning the documents requested separately. If I have kept some documents that you need, please let me know.

Best regards,

Donald Lucas

Donald Lucas
70-108B
LBNL
Berkeley, CA 94720
510-486-7002

Email Cc. Dean Simeroth, Bob Okamoto, Lesley Crowell

ERNEST ORLANDO LAWRENCE BERKELEY NATIONAL LABORATORY
ONE CYCLOTRON ROAD | BERKELEY, CALIFORNIA 94720 | TEL: 510.486.5001 FAX: 510.486.7290

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

Scientific Peer Review

Donald Lucas

Environmental Energy Technologies Department
Lawrence Berkeley National Laboratory and the University of California, Berkeley
Berkeley, CA 94720
510-486-7002
D_lucas@lbl.gov

Feb.13, 2004

Introduction

This is a review for an interagency multimedia working group that includes CAL/EPA, the Air Resources Board, the State Water Resources Control Board, the Office of Environmental Health Assessment, and the Department of Toxic Substance Control. This review is prepared under Interagency Agreement #98-004 Task Order #41-2 between the University of California and the California Environmental Protection Agency.

This review covers many documents. I have reviewed several documents in detail, including the following:

Lawrence Livermore National Laboratory (LLNL) "Review of the Data Supporting the Lubrizol Evaluation of Multimedia Impacts Resulting from the Use of PuriNOx fuel in California," Sept., 2003. UCRL-LR-55299.

State of California, California Environmental Protection Agency, "Multi-Media Assessment of Lubrizol's PuriNOx Water/Diesel Emulsion, Draft, Dec., 2003.

State of California, California Air Resources Board, "Assessment of Emission of Lubrizol's PuriNOx Water/Diesel Emulsion on Exhaust Emissions from Heavy-Duty Diesel Engines," Draft, Dec., 2003 and a revised version dated January, 2004.

State of California, Office of Environmental Health Hazard Assessment, "Draft Staff Report on Health Impacts of PuriNOx Generation I and Generation II Additive Packages and Diesel Fuels"

Letters from Dean C. Simeroth, dated Dec. 12, 2002, and Jan. 31, 2001.

Letter from Lubrizol dated Sept. 25, 2003.

Confidential Addendum to the Office of Environmental Health Hazard Assessment's "Staff Report on PuriNOx Generation 1 and Generation 2 Additive Packages and Diesel Fuel.

I also examined several other documents, but in less detail, including numerous appendices from Lubrizol.

I attended a meeting on Nov. 18, 2003, where several reviewers were given presentations by different California EPA staff and LLNL personnel. I also attended a meeting on Feb. 5 with state staff, who answered many questions and clarified several issues.

Proposed Revisions

The Lubrizol Corporation has developed PuriNOx, a water-emulsified diesel fuel that is designed to reduce emissions of particulate matter (PM) and nitrogen oxides (NOx). Lubrizol has requested that the Air Resources Board (ARB) verify PuriNOx as a diesel emission control strategy. PuriNOx must undergo a multi-media assessment to determine if its use 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.

Multimedia Working Group Recommendations

The multimedia working group found and recommended that:

A. The limited and controlled use of PuriNOx as described in the multimedia assessment does not pose a significant and adverse impact on public health and the environment.

B. Knowledge gaps exist

1. Lubrizol should conduct the following additional studies:

   Develop analytical methods for PuriNOx components of greatest concern
   Biodegradation studies to fill data gaps
   Aquatic toxicity testing
   Refined soil column studies
   Feasibility study on soil cleanup
   Toxicological test to compare PuriNOx fuel with regular diesel
   Comparative emissions tests for nitrosamines and precursors

2. Prior to any expansion of the proposed distribution and use of PuriNOx, an environmental fate and transport study must be conducted.

3. If any of the recommend studies identify risks to the environment, the use of PuriNOx will be reviewed by the Environmental Policy Council.

I agree with and support the recommendations made by the multimedia working group. The recommendations are supported by the scientific evidence and are reasonable. The recommendations cover a wide range of scientific fields, and I am not an expert in all of these areas. My review is thus weighted towards those areas involving air emissions and combustion.

My major conclusions and comments from reviewing the material presented to me are that there are significant air emissions benefits from using PuriNOx fuels, especially in reduced PM and NOx levels, and probably in greenhouse gas emissions. There are increases in some reactive organic compounds, but the increases and their effects are small compared to the decreases in PM and NOx. The added risk from PuriNOx fuels is primarily from potential releases to the water and/or soil, where there are no potential benefits. The overall impact of PuriNOx fuels thus depends on whether the emissions benefits outweigh the potential harm from a release or spill of the fuel and/or fuel components. Since PuriNOx will be used initially in a controlled and limited fashion, I agree with the first recommendation above.

There are some significant knowledge gaps identified in the material reviewed; recommendations are presented in under section B1. I believe the most important of these is the lack of analytical methods to detect PuriNOx components of greatest concern. The comparative emissions tests for nitrosamines, the toxicology tests, and the aquatic toxicity tests are the next highest ranked needs. The other recommended studies rank lowest.

I strongly agree with and support the recommendation regarding any expansion of the use of PuriNOx (B2). Apparently successful use of a relatively small quantity of a fuel or fuel component should not be grounds for a major expansion in either distribution or quantity of particular components. The widespread use of MTBE as a major component in California gasoline is an example that should not be repeated, where greatly increased use led to problems that were not always evident when smaller concentrations and quantities were allowed.

It is also important the approval for PuriNOx fuels be conditional on the results of the conditional studies, or any new information that may be acquired.

Additional comments

These comments are listed in no particular order.

Environmental Policy Council

In the charge to the Air Resources Board, the Environmental Policy Council must consider the emission of air pollutants, including greenhouse gases. However, there seems to be no or little discussion of this point in the documents provided. In particular, in Section II, A (Air Emissions Evaluation), there is a summary of criteria pollutants, toxic emissions including particulate matter, and ozone precursors, but greenhouse gas emissions are not discussed.

There are some data presented on fuel consumption in the Air Improvement Resource, Inc. final report (April 4, 2001) that can be used to estimate CO_2 emissions. While the total volume of fuel consumed increased, the diesel fuel consumption decreased 9.8%, which leads to a corresponding reduction in CO_2 emissions. I did not find any measurements for other greenhouse gases such as methane and nitrous oxide, but these compounds, if emitted, would most likely be at levels orders of magnitude below those of CO_2.

Air Emissions

Air emissions data from PuriNOx fuels were reviewed by the ARB staff. They examined experimental data from several sources, and estimated emission impacts in the South Coast Air Basin and the Sacramento area.

I agree with the Air Resources Board Assessment statements about the toxic emissions in that they discuss not only the total mass emissions, but also their relative amounts and their cancer risk factors. The Air Improvement Resource, Inc. report (April 4, 2001) lumps all of the toxic emissions together (including PM) and uses mass as the only metric. While the PM mass is lower, the emissions of other air toxics appear to increase. The ARB correctly recognized that not all air toxics are equally potent.

These experimental test results are from a variety of engines, fuels, test equipment, and operating conditions. There is a very limited amount of data with Gen2 fuel. These different conditions are not necessarily a negative, since they show that the PuriNOx fuels generally have a similar effect on emissions. However, they do make quantitative analysis difficult. For example, changes in emissions from a driving test cycle are lumped with steady-state operations. The changes are averaged, with the results presented as percentage differences from results using conventional CARB fuel. The values exhibit large differences, and I am not sure how valid the statistical treatment presented in the 12/03/03 Air Emissions Assessment document is. The value of 58% reduction in PM emissions is a reasonable value to use in this assessment, but I would not be surprised if additional testing or analysis showed that this value has a large uncertainty. I am concerned that few of the tests were performed with Gen2 fuel. I agree that using the average 58% reduction is a conservative estimate.

Ozone precursors are compared using the change in mass emissions for NOx and ROCs. The NOx decreases by 14% while the ROCs increase by 87%. However, the total mass emissions of NOx are higher, so for each ton of increased ROG emissions, the NOx will decrease by 3.4 tons. I caution against using either percentage changes or mass changes to evaluate the ozone forming potential from PuriNOx emissions. I would prefer that the changes by incorporated into a model that predicts ozone levels in the same targeted areas (South Coast and Sacramento), or at least discuss the directional change expected from the PuriNOx emissions. This could be done for each targeted area, or discussed in more general terms, such as NOx or hydrocarbon limited scenarios.

Other toxic species emissions appear to increase using PuriNOx. The comparison of PM emissions to other species such as formaldehyde and acetaldehyde with PM is reasonable, with the cancer unit risk factor and magnitude of the emissions compared. I agree that the ARB and OEHHA assessment that these species from PuriNOx emissions do not significantly increase cancer risks compared to conventional CARB fuel.

The ARB used a market penetration of 25% of the centrally fueled fleet, which is higher than the Lubrizol prediction. It is a reasonable assumption, especially since the emissions should simply scale with use.

I agree with the multimedia working group recommendation that comparative emissions tests be conducted for nitrosamines and products that can lead to nitrosamine formation. The chemical formula and possible reaction pathways for PuriNOx components suggest that nitrosamines could be formed, so requiring the emissions tests is prudent.

In summary, the data presented indicate that air emissions will improve significantly from the use of PuriNOx fuel. However, there is also a significant uncertainty associated with the quantification of the improvements.

Toxicity Testing

OEHHA staff is of the opinion that the U. S. EPA Tier 2 test data on PuriNOx fuel is not adequate for the evaluation of whether the toxicity of the emissions from this fuel are different from emissions from CARB fuel. I agree, mainly because the test data are not of a comparative nature using the same engine and test conditions, differing only in the fuel composition.

Test method for PuriNOx

I am concerned about several statements that indicate that no established laboratory method exists for detecting and quantifying some components of the PuriNOx fuel. In the Livermore review, this is noted and commented upon (ES-5): "Notably, most PuriNOx additive components are not compounds that are routinely analyzed by commercial analytical laboratories and in fact many are not amenable to standardized analytical methods developed by U.S. Environmental Protection Agency and other agencies. …Therefore, in the event of a significant release, analysis or most components would require a custom analysis, typically requiring expensive analytical equipment … that is rarely available in commercial environmental laboratories." Later (ES-8), potential difficulties in the analysis are described, especially for those components of greatest concern (Section III.5.1).

While methods may not be needed for every component, it is not clear how a PuriNOx fuel spill will be differentiated from other diesel fuel spills. Could one or more specific component in PuriNOx be used that is not present in other fuels? More than one compound would be desirable to cover both soluble and non-soluble species. Waiting for a spill to develop these methods is not the ideal course of action. I strongly agree with the multimedia working group recommendation that analytical methods for PuriNOx components of greatest concern need to be developed.

Distribution and Storage (LLNL report, page 6.)

While the potential for a release of the bulk additive is relatively small, transport by rail or tanker truck may not be as well controlled as the PuriNOx fuel itself, since the fuel will be used in centrally fueled facilities. The potential for a rail accident was recently revisited when the U.S. Supreme Court rejected California's attempt to bolster rail standards for a mountain grade in

Siskiyou County near the Sacramento river that was the site of a chemical spill in 1991. While I agree that the greatest chance for spills will be where the fuel is stored and distributed, the possibility of an accident outside these facilities is not zero. It might be useful to ask Lubrizol if they have any documents that consider accidents or release scenarios for their production facilities that are outside of California, where larger amounts of the additives are handled.

LLNL Evaluation

The SWRCB contracted with the Lawrence Livermore National Laboratory as a consultant to review the surface and ground water quality assessments. This appears to be an appropriate way to bring additional expertise to this difficult and complex evaluation. Their review appears thorough, and their recommendations are well supported.

After discussion with members of the multimedia working group, I learned that many of the concerns about the validity of various tests and experiments were because Lubrizol performed tests before consulting with the working group. In the future, more interaction of the company with the working group early in the approval process should reduce the number of knowledge gaps and reduce the need for additional testing.

PM Risks

The documents assume that a reduction in diesel PM mass will lead to a proportional reduction in risk, especially the cancer risk. Some caution should be taken here since changing the fuel composition will certainly not only change the mass of diesel PM, but will probably change the chemical composition of the resulting particles, and it is not clear that all of the possible carcinogenic compounds in the exhaust will be reduced by the same fraction. It was noted in the Staff Report on Health Impacts of PuriNOx Generation 1 and Generation 2 Additive Packages and Diesel Fuels (Dec., 2003) that the particles from PuriNOx combustion contain a larger amount of organic substances per gram of particles than from CARB fuels, and that the toxicity reduction may not be as great as the reduction in PM mass.

While 94% of the mass of diesel particles are contained in particles smaller than 2.5 microns, diesel particles produced by modern engines are better characterized by sizes in the hundreds of nanometers and smaller. There was a limited study on one engine that measured ultrafine particle number and volume concentration, but the results were inconclusive.

Diesel Test Methods

There is a recognized need to standardize emission test methods and analytical test methods for diesel engines. While adoption of standards will require considerable effort and time (and is certainly outside the scope of this study), efforts should continue towards this goal.

Lubrizol Letter Sept. 5, 2003 to various state and LLNL personnel

This statement is directed towards Lubrizol, and not the multimedia working group. In Section 6, there is a claim that since “the components within the PuriNOx additive consist only of carbon, hydrogen, oxygen and nitrogen ---the same elements which compose diesel fuel itself. The absence of heteroatom chemistry provides further support that the formation of unusual combustion products is unlikely.”

Broad statements such as this should be avoided – this implies that combustion of all organic compounds is the same, which is certainly not true.

July 16, 2003 Lubrizol report

In the cover letter of this report, Lubrizol request that .. “Generation 1, Generation 2, and future related additive formulation utilizing chemical compositions fall within the scope of the this multimedia comparative analysis …” Given the differences in the formulation of Gen1 and Gen2 additive packages, and the scarcity of data from Gen2 fuels, I do not think that such a blanket approval should be granted, and that Lubrizol should discuss any changes in the formula(s) with the multimedia working group before being allowed to use another formula. Allowances for small changes in relative component levels could be made, but the introduction of any new chemicals should be reviewed.

Comments on the Multi-Media Assessment Process

As mentioned above, it is necessary to judge whether air emission benefits outweigh potential water and soil contamination. This is a difficult question to answer, especially when the harmful effects of spills cannot be readily quantified. Even if the effects of spills could be quantified, issues such as the relative importance of human health effects compared with environmental degradation make for hard judgments. I am encouraged by the approach of the multimedia working group, in that they examined the issues from different perspectives, and that they are meeting and discussing these issues not only amongst themselves but with others.

Having the reviewers meet with was an excellent idea, and should be encouraged for future reviews. It would help if drafts were available before the meeting, however. For this review, confidentiality and legal issues prevented that from happening.

If time allows, the reviewers could also meet after reviewing the documents, but before they finish their final report. I did attend a meeting with the staff on Feb. 5 where many issues and questions that I had were clarified, but no other reviewers attended. There is a follow-up meeting planned to review the process, and I plan to attend.

Finally, a simple numbering scheme for the documents would be helpful. There are a large number of documents and letters that are difficult to reference since they have identical or similar titles.

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SCHOOL OF PUBLIC HEALTH
DEPARTMENT OF BIOMEDICAL AND
ENVIRONMENTAL HEALTH SCIENCES

EARL WARREN HALL
BERKELEY, CALIFORNIA 94720

TO: Gary M. Yee
Air Resources Board
1001 I Street
P.O. Box 2815
Sacramento, CA 95812

FROM: Professor Thomas E. McKone
School of Public Health
University of California
140 Warren Hall #7360
Berkeley, CA 94720-7360
temckone@lbl.gov

Attached is my peer review of State of California's "Evaluation of Multimedia Impacts Resulting from the PuriNOx Fuel in California". My work was carried out pursuant to Interagency Agreement # 98-004, Task Order # 41-2. As requested I reviewed the evaluation reports organized by the State Environmental Policy Council including separate reports prepared by the Multimedia Working Group, the Air Resources Board, the State Water Resources Control Board, the Office of Environmental Health Hazard Assessment, and Department of Toxic Substances Control, as well as the reports prepared by Lubrizol. There are two copies of my review. This version, which has the name "McKPuriNOxReview15Feb04Public.doc" provides my full review in a version that is acceptable for public release. In a separate document, I provide a version that discusses some of the proprietary information and is not acceptable for public release.

Thomas E. McKone, Ph.D.

cc: Dean C. Simeroth, ARB
Dr. Robert Okamoto, ARB
Lesley Crowell, ARB

Interagency Agreement # 98-004

TASK ORDER #41-2

Scientific Peer Review of the California Multimedia Working Group's Evaluation of Multimedia Impacts Resulting from the Use of PuriNOx™ Fuel in California

Review Comments by T.E. McKone

University of California, Berkeley

INTRODUCTION

As requested, I reviewed the evaluation reports organized by the State Environmental Policy Council including separate reports prepared by the Multimedia Working Group (MWG), the Air Resources Board (ARB), the State Water Resources Control Board (SWRCB), the Office of Environmental Health Hazard Assessment (OEHHA), and Department of Toxic Substances Control (DTSC), as well as the reports prepared by Lubrizol. In preparing this review I focused on how information was used to inform conclusions. I gave particular attention to the how the multimedia evaluation was carried out and whether the approach was truly "multimedia" or a collection of individual assessments that are grouped together under a multimedia banner.

BACKGROUND AND RESOURCES FOR MY REVIEW

As background resources and primary references, the materials provided to me were voluminous but for the most part useful and tractable. In addition to large box of reports and binders (that have take over most of my office), I learned a great deal about the PuriNOx multimedia review by attending a half-day meeting on November 18 at the California Environmental Protection Agency (Cal-EPA) Building in Sacramento at which members of the multimedia working group including ARB, OEHHA, DTSC, and SWRCB scientists made formal presentations describing their findings and recommendations with regard to PuriNOx. I found this meeting particularly useful and informative.

Among the reports that I used for making my findings and recommendations below, are the reports prepared by Lubrizol for submission to the State of California as well as the evaluation reports prepared by the ARB, SWRCB, OEHHA, DTSC, and the Multimedia Working Group. In the sections below, I provide a brief summary of what I believe to be the key issues presented in each of these reports. These issues provided the bases for the conclusions of my peer review. Therefore I try here to draw attention not only to issues that are important factors behind the recommendations of the MWG, but also to highlight issues that may require additional research and evaluation.

The Lubrizol Multimedia Evaluation for PuriNOx

This report consists of a main report and seventeen appendices with appendices to some of the appendices. The thousands of pages of material here were extensive but tractable. For both the Generation 1 (Gen 1) and Generation 2 (Gen 2) versions of PuriNOx, this report provides a summary (with details in the Appendices) of emissions testing and emissions toxicity from diesel engines burning the PuriNOx fuel as well as chemical, environmental, and toxicity characteristics of each of the additive package materials. I found it particularly useful that Lubrizol provided the information necessary for and then carried out a multimedia fate assessment for each of these components. This report also included a summary of human health information needed for a risk assessment; a discussion about the manufacture, transport, and storage of additive package; and environmental release scenarios. The report then details the potential impact of releases to soil and water bodies of either PuriNOX additive or PuriNOx fuel.

The California Air Resources Board Report

The ARB prepared a report in which they evaluated the impacts of the use of PuriNOx in exhaust emissions from heavy-duty diesel engines in California. They considered both Gen 1 and Gen 2 PuriNOx. The baseline for comparison was the emissions from heavy-duty diesel engines burning diesel fuel compliant ARB requirements. In this evaluation, they considered criteria pollutants emissions, air toxic emissions, direct emissions measurements, diesel PM, additives, other toxics, the chemistry of CARB and PuriNOx fuels, and ozone precursors.

The ARB found that for both Gen 1 and Gen 2 PuriNOx formulations, diesel PM emission significantly reduced (an average 58 percent reduction). <u>But these results are based on a limited number of studies (9 studies including CARB verification and U.S. EPA Tier 1 studies).</u>

For toxic air pollutants, they found an increase of toxic volatile organic compounds including 1,3-butadiene, BTEX, formaldehyde, acetaldehyde and increases of some PAHs but no observed increases in nitro-PAHs. But it should be noted that diesel emissions are not a significant source of toxic air pollutants relative to automobiles. <u>Once again these results are based on a limited number of tests (particularly for Gen 2 PuriNOx).</u> A case study of how PuriNOx would impact overall air emissions in the South Coast Air Basin (SCAB) found an insignificant health impact from toxic air pollutants even with a large increase PuriNOx use.

In the conclusions of the report, the ARB staff recommends that the use of PuriNOx as described in the 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 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 reactive organic gases (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.

State Water Resources Control Board

Lawrence Livermore National Laboratory (LLNL) was contracted by Lubrizol to conduct an independent review of the data and data analyses included in Lubrizol's report, and to assess how the report addressed the potential impacts to surface and groundwater that may result from the proposed use of PuriNOx fuel in California. The purpose of the independent review by LLNL was to assist the SWRCB in completing its evaluation of a multimedia assessment study of the use of PuriNOx fuel. The SWRCB presented the LLNL report as its input to the MWG.

The LLNL report determined that the most likely release scenarios for blended PuriNOx fuel during distribution and storage are very similar to those for ultra low sulfur diesel (ULSD). That is, over the long term, release of PuriNOx fuel from leaking USTs (underground storage tanks) poses the most likely release scenario. Therefore it is important to consider for a release of blended PuriNOx fuel from a UST the impact of the additive package on the fate and transport of the diesel hydrocarbons in the fuel or already present in soil as a result of previous releases or routine fueling operations.

Among the key recommendations in the LBNL / SWRCB report are those for an assessment of actual environmental distributions after a known release of PuriNOx additive or PuriNOx fuel; analytical methods for PuriNOx components of greatest concern; biodegradation studies to fill important data gaps; aquatic toxicity studies and soil column studies.

Office of Environmental Health Hazard Assessment (OHHEA)

In reviewing the multimedia report from Lubrizol, OEHHA noted that although PM and NOx emissions are significantly lower for both Gen 1 and Gen 2 PuriNOx relative to ULSD, other hazardous air pollutants are up slightly or significantly in the post-combustion emissions from diesel engines burning Gen 1 or Gen 2 PuriNOx. To evaluate the health significance of these emissions, the OEHHA conducted a screening level risk assessment for carcinogenic emissions from PuriNOx combustion in the South Coast Air Management District. The results of this study are that upper bound of lifetime cancer risk attributable to substitution of Gen 2 PuriNOx for 10% of heavy-duty on-road diesel is less than 10^{-6} lifetime risk. However, the absence of data on nitrosamine levels in PuriNOx diesel combustion emissions is a concern for OEHHA.

OEHHA also provided in their report a review and evaluation of the US EPA toxicity testing. The OEHHA did not differ significantly from the US EPA in interpretation of the toxicity experiment results. OEHHA did observe that the US EPA Tier II study was not sufficiently sensitive to detect small but possibly significant changes in toxicity of a toxic, complex mixture.

Then OEHHA also provided a brief summary of the multimedia transport, fate and toxicity assessment of components of PuriNOx Gen 1 and Gen 2 additive packages. OEHHA was the only Cal-EPA agency to evaluate the results and implications of the Lubrizol multimedia mass balance assessment based on fugacity models. In their evaluation, OEHHA used the multimedia mass balance calculations to evaluate the PurNOx additive chemicals in terms of mobility in air, soil, and groundwater; partitioning into environmental media including organisms and aquatic sediment; persistence in individual environmental media (but not overall environmental persistence); and multimedia toxicity and hazard to humans. Based on its multimedia evaluation, OEHHA determined that there are no PuriNOx components that are known to be significantly more toxic than diesel fuel, but this observation is limited by lack of toxicity test data on high-molecular-weight components. They noted that high-molecular-weight components may accumulate in aquatic sediments and organisms.

Based on its overall evaluation, OEHHA concluded that PM and NOx are significantly decreased in PuriNOx emissions relative to diesel emissions, that certain toxic air contaminants are significantly increased in PuriNOx emissions; and that the benefit from the reduction of PM and NOx appears to outweigh the risk from increases in toxic air contaminants. They noted that only the high-molecular-weight components of PuriNOx fuels have the potential to accumulate and persist in a multimedia environmental, but that data are not adequate to assess what, if any, risks these particular compounds pose to the environment or to humans. The OEHHA supports recommendations for ecological toxicity testing made by the State Water Resources Control Board. OEHHA further recommends that combustion emissions testing of PuriNOx fuel and CARB fuel be required to be completed during the same period required for ecological toxicity testing.

Department of Toxic Substances Control (DTSC)

DTSC staff prepared an evaluation summary of the hazard of PuriNOx fuel on the environment and human health if PuriNOx and its components become a waste or are released to soil. DTSC Based on its overall evaluation on consideration of the individual components in the PuriNOx additive packages in terms of toxicity, solubility, soil adsorption coefficients, and current commercial applications. Based on this evaluation the DTSC technical staff concluded that there are no considerable hazardous characteristics in the PuriNOx additive packages (both Gen 1 and Gen 2) and these components are unlikely to have significant impact on groundwater. The DTSC staff recommended feasibility study on soil cleanup technologies for the PuriNOx components and toxicological tests to compare PuriNOx fuel with regular diesel.

Multimedia Working Group Report

This is a composite report that provides a summary of the findings and conclusions from each of the agency-specific reports listed above and a list overarching recommendations.

MY FINDINGS AND RECOMMENDATIONS

Major Findings and Recommendations

Based on my peer review of all relevant documents and correspondence, I believe there is sufficient information provided to support the recommendation of the multimedia working group that “limited and controlled use of PuriNOx as described in the multimedia assessment does not pose a significant adverse impact on public health and the environment.” But I recommend that this statement be amended to say “… does not pose a significant adverse impact on public health and the environment relative to other clean diesel fuels approved for use in California.” It should be recognized that in absolute terms, all diesel fuels, including PurNOx, can have significant impact on public health and the environment particularly from the non-additive components. What the report finds is that use of the PuriNOx additive package will have no greater impact than any existing diesel fuel and likely will have a lesser impact. The point is that, given that the vehicles of California are going to use diesel fuel and we need to make choices that truly represent no new impacts and hopefully lower impacts.

I believe there is sufficient information and justification to support the conditions stated as Recommendation IV B in the Multimedia Working Group Report and I support the revised version of Condition IV.B.1 with the wording “prior to any expansion beyond a 1 percent diesel market penetration” in place of the words “two years”.

Lubrizol is in the unique position of being the first company to bring a new fuel to market in California under the Senate Bill 989 requirements for multimedia assessment. Lubrizol has made a commendable effort of providing data and models necessary to build a multimedia assessment.

Since this is only the second multimedia assessment on a new fuel component (including the Cal-EPA internal study on Ethanol), I commend the State for its effort to move health and environmental evaluations more to the “multimedia” approach. Nevertheless, I am not fully convinced that the Multimedia Working Group (MWG) carried out a truly “multimedia” evaluation. Although many would consider this a multimedia approach because it address release to all media, it fails to meet the full requirements of a true multimedia approach. It appears to me that the MWG took a multimedia report and dealt with it primarily by dividing it up among several-single medium agencies. Although this process is necessary, it is not sufficient as a general framework for future multimedia assessments. In the case of OEHHA report, there was a limited effort to look at the PuriNOx components in terms of their multimedia behavior. But for the most part, MWG’s recommendations are based on consideration of single-media assessments with a multimedia assessment as somewhat of an afterthought. But for understanding the potential impacts of any chemical substances it is becoming clear from the environmental science literature that overall (multimedia persistence) is the best predictor of both human and environmental exposures. But multimedia persistence can only be derived from a systematic and well-calibrated multimedia fate assessment. It is fortunate that most of the compounds in PuriNOx are either already well studied or are such large molecules that that they are unlikely to partition into media other than soil. Therefore the concern I raise here is not really applicable to the PuriNOx evaluation. But for future multimedia evaluations, I believe the State should make more of a commitment to imposing a more defensible multimedia assessment and in particular give full consideration to multimedia persistence. Actually Lubrizol is to be commended for providing what I think qualifies as truly a “multimedia evaluation,” in Appendix 12 of its report where they report the results of fugacity modeling. But these fate analyses were rather elementary and failed to give full attention to the issue of multimedia persistence. At the end of this section, I have provided a few paragraphs that provide some recommendations on how the State could carry out a more truly “multimedia” evaluation.

The evaluation reports prepared by Lubrizol and the State lacked any systematic effort to consider uncertainty and the impact that inadequate and incomplete information has on the confidence that should be placed on the finding of the MWG. Multimedia fate and exposure models support decisions to tolerate, regulate or monitor existing and new industrial and agricultural chemicals. In this role, fate/exposure models provide prospective analyses of future risk and retrospective analysis of the links between health outcomes and environmental releases. In using models to support regulation and monitoring policies, decision makers struggle with the question of how likely they are to make unwarranted choices and what the associated health, economic, and political consequences of those choices are. To confront these questions, someone must make some level of effort to characterize the reliability of the predictions made for uncertain models and incomplete data. At a minimum, it would be useful to provide a list of assumptions or data gaps that are most significant sources of uncertainty and some assessment of how decreasing uncertainty would improve the confidence in conclusions.

Other Findings and Recommendations

Given the uncertainties associated with the complexities of the additive package chemistry and with site-specific variables, the limited use of PuriNOx provides some protection against unanticipated impacts. But this initial limited use of PuriNOx also provides an important opportunity to gain practical environmental experience. As was noted in the LLNL report, since some releases of transportation fuels are inevitable, it would be beneficial to use a known release of PuriNOx additive or fuel as a learning opportunity. But this concept must be broadened to other opportunities for “field” evaluations. Most of the currently available information on the chemistry and toxicity of many of the PuriNOx components was collected under controlled laboratory conditions. The limited-use period provides an important opportunity to evaluate how these substances behave in the real world. But to take advantage of this opportunity will require a pro-active strategy on the part of Cal-EPA. The Cal-EPA needs to provide evidence that they have a plan and will initiate this plan for monitoring and feedback as PuriNOx enters the market.

The ARB found and other agencies confirmed that for both the Gen 1 and Gen 2 PuriNOx formulations, diesel PM emission are significantly reduced compared to CARB diesel. However, they did not consider how this reduction applies across the size distribution of PM. Is it uniform across the particle size distribution, skewed toward larger particles or skewed toward the fine or ultra-fine particles? The answer to this question has implications for the ultimate health benefits of this PM reduction.

In the Lubrizol report, environmental half-life and single-medium persistence for many of the compounds are very preliminary and uncertain. The Cal-EPA needs to follow up on a program to monitor fate and persistence to confirm or refute the assumptions used in the multimedia assessment. This is important because the assumptions about media-specific half-lives used in the fugacity model are key inputs to the conclusion that the chemicals in PuriNOx will not have adverse impact on human health and the environment.

The Lubrizol report in particular and even some of the Cal-EPA reports, either directly state or imply that the purpose of the multimedia evaluation is to demonstrate that a release of PuriNOx fuel will not have an adverse impact compare to ULSD. But other Cal-EPA reports tend to focus on the impact of using PuriNOx as a fuel. I think it is important that this issue is addressed consistently among the reports. That is, it should be clearly stated that the multimedia evaluation is used to demonstrate that the **use** of PuriNOx and its associated infrastructure will not have an adverse impact on human health and the environment relative to competing technologies.

Recommendations for Addressing My Major Concerns

Appropriate Framework for Conducting Multimedia Evaluations

A truly multimedia assessment provides not only a fate assessment, but also an assessment of overall persistence and other key attributes such as mobility and long-range transport potential. Persistence in particular is an important indicator of exposure potential both for humans and ecosystems. With the exception of the short section in the OEHHA report, the MWG did not use the PuriNOx study to establish a framework for taking a fully multimedia perspective when considering new fuels or other technologies.

Since 1985 an entire discipline of multimedia modeling of contaminants has evolved and many useful techniques and modeling tools have been developed (McKone and MacLeod, 2003). Multimedia fate models are now widely applied for many types of environmental assessments. The emergence of the multimedia paradigm over the last three decades has focused attention on the long-term behavior and effects of chemicals released from modern industrial economies into the environment. Organic-chemical, inorganic-chemical, and radionuclide contamination of soils, the release of volatile and semi-volatile organic compounds to air and to soil, and toxic-chemical runoff to surface water are all multimedia problems.

Multimedia contaminant fate and exposure models have been useful to decision makers because these models provide an appropriate quantitative framework to evaluate our understanding of the complex interactions between chemicals and the environment. Recently, generic models of contaminant fate have been adapted to conduct rapid screening-level assessments of large numbers of chemicals for persistence (P) and potential for long-range transport (LRT). The P and LRT attributes have been identified as cause for global concern, and have been used as a basis for international bans imposed on specific chemical compounds (UNEP, 1997). Webster et al. (1998) describe a generic Level III fugacity model for comparing chemicals in terms of persistence in the entire environment, rather than half-lives in individual media. Bennett et al. (1999) and Pennington (2001) proposed and applied similar models to calculate multimedia persistence. Generic models for assessing long-range transport potential have been developed by Bennett et al. (1998), who introduced the concept of “characteristic travel distance” for multimedia chemicals, and by Beyer et al. (2000). Faced with a proliferation of generic models for assessing P and LRT, Wania and Mackay (2000) conducted a round-robin comparison of the models and found that, although the magnitude of P or LRT “scores” differed among the models, the relative ranking of a standard group of chemicals according to P or LRT was consistent.

How to Better Address Uncertainty

To confront issues of uncertainty and confidence, someone must to quantify the reliability predictions of the predictions made for uncertain models and incomplete data. Here I review some current methods used to assess the performance of risk-assessment models.

The measurements and models used in the PuriNOx multimedia evaluation have inherent capabilities and limitations. The limitations arise because models are simplifications of the real system that they describe and all assessments using the models are based on imperfect knowledge of input parameters. This realization provides insight into how the models and measurements should be applied and for deciding whether and/or how to make the models more detailed or collect more data. Confronting the uncertainties requires a performance evaluation that estimates the degree of uncertainty in the assessment and illustrates the relative value of increasing model complexity, providing a more explicit representation of uncertainties, or assembling more data through field studies and experimental analysis.

<u>Sensitivity and Uncertainty Analyses</u>

Sensitivity and uncertainty analyses are powerful tools for assessing the performance and reliability of models or data sets. As applied to mathematical models, sensitivity analysis is the quantification of changes in model results as a result of changes in individual model parameters. Uncertainty analysis is the determination of the variation or imprecision in the results of a model based on the collective variation of the model inputs. A full discussion of sensitivity and uncertainty analysis is provided in the texts by Morgan and Henrion (1990) and the volume edited by Saltelli et al.(200). The goal of a sensitivity analysis is to rank input parameters, model algorithms or model assumptions on the basis of their contribution to variance in the model output.

<u>Sensitivity of Multimedia Models</u>

Eisenberg et al. (1998), Eisenberg and McKone (1998) and Hertwich et al. (1999, 2000) have studied parameter variability and sensitivity in multimedia exposure models. For fate and persistence assessments based on multimedia models, these studies indicate that output variance arises primarily from chemical-specific input parameters with media-specific half-lives being most important. Landscape characteristics, such as climate, hydrologic conditions, and soil properties, are generally of minor importance.

<u>Considering Sources of Uncertainty</u>

Uncertainty in model predictions arise from a number of sources, including specification of the problem; formulation of the conceptual model, estimation of input values and calculation, interpretation, and documentation of the results. Of these, only uncertainties due to estimation of input values (parameter uncertainty) can be quantified in a straightforward manner based on variance propagation techniques. Mis-specification of the problem and incorrect model formulation give rise to the wrong models. Having the wrong model results in errors that are potentially large, systematic, and often difficult to discover. As a result the uncertainties resulting from these errors are potentially much larger and more difficult to characterize than parameter uncertainties. Efforts have been made to assess mis-specification and formulation errors using tools such as decision trees or based on elicitation of expert opinions (for example, the case study by Ragas et al. (1999).

Model Evaluation and Confidence Building

Multimedia assessments such as those presented in the PuriNOx evaluation belong to a class of evaluations that cannot be truly validated because the environmental systems and human activities described by these models comprise a system with operative processes that cannot be fully described. It is thus impossible to conduct the controlled experiments needed for true validation of multimedia assessments. As has been pointed out by Oreskes et al. (1994), models of this type are common in earth sciences, economics, and engineering as well as in the policy arena. They cannot be fully verified or validated because descriptions of the operative processes are always incomplete. However, this limitation does not mean that multimedia models should be exempt from performance evaluation. On the contrary, the fact that the models are “non-validatable” requires a more thoughtful and systematic process for building confidence among model users. It is possible to build confidence in these models through a series of evaluation exercises, and they can be used to put bounds on the likely range of outcomes. The greater the number and the diversity of confirming observations that can be made, the more probable it is that the conceptualization embodied in the model is not flawed. Confirming observations do not demonstrate the veracity of the model, but they do support the probability that the model is useful and the hypotheses that it represents are not false. For multimedia assessments in particular, credibility is further enhanced by clearly quantifying the effects of variability and uncertainty in input parameters on any resulting conclusions or recommendations predictions. Communicating the uncertainties associated with contaminant fate and exposure assessments enhances their credibility by highlighting model inputs that control the outcome of the assessment for individual chemicals. Estimates of the uncertainty associated with specific model outputs can be used to inform the decision-making process, and direct future refinements of the model or experimental studies to add additional information to the assessment.

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Review of the multimedia assessment of the PuriNOx diesel formulation conducted for the California Air Resorces Board

Tim Ginn, Graham Fogg, Michael Johnson, and Kate Scow,
University of California, Davis.

Introduction

This letter report provides our peer review under Interagency Agreement #98-004 Task Order 41-1 of the evaluation performed by the interagency multimedia working group and contractors of the multimedia impacts assessment for the potential use of the PuriNOx diesel fuel formulation manufactured by the Lubrizol Corporation. The interagency working group includes representatives from California EPA, California Air Resources Board (ARB), the State Water Resource Control Board (SWRCB), the Office of Environmental Health Assessment (OEHHA), and the Department of Toxic Substance Control (DTSC), and their evaluation task is coordinated by the ARB. This peer review is that requested by ARB in the letter from Dean Simeroth to Timothy Ginn of 4 December 2003, with 18 enclosures. These enclosures comprise the documentation reviewed by our team, and the numbered list appears as Appendix 1 to this letter. The numbering appearing in Appendix 1 is used to cite relevant references throughout this letter report; that is, enclosure 1 in Appendix 1 is referred to as "(1)."

The scope of this review covers the Interagency multimedia working group's evaluation of the Lubrizol multimedia assessment that "the multimedia requirement is satisfied and no additional testing is required" (7, page 2); in particular, we comment on the draft recommendations made by the Interagency multimedia working group in (1), and on the request by ARB in a letter from Dean Simeroth to Timothy Ginn on 12 December 2003 that we consider an optional recommendation for Condition 1 appearing in (1, page 10). We also comment on the Lubrizol request that "the Generation 1, Generation 2 and future related additive formulations utilizing similar chemical compositions fall within the scope of this multimedia comparative analysis and that the Environmental Policy Council notify the Air Resources Board that Lubrizol has satisfied the multimedia evaluateion requirement..." (7, page 2). These issues are discussed in turn below.

Within the context of our scope, we prioritized the 18 documents into three tiers; the summary Interagency evaluation documents (1, 4, 17), the supporting Intragency evaluation documents (2, 3, 5, 6), and the original Lubrizol multimedia assessment documents and data (7, 8 (note this is a set of 17 appendices), 9-16, 18). Our review represents our collective areas of focus and expertise in environmental fate, transport, abiotic/biotic mass transfer, and toxicity, and consequently our review focused primarily on documents 1, 3, 4, 6, 7, 8, 9, 13, 14. The remainder of this letter report is comprised of a statement of summary review issues, separate supporting sections treating:

- environmental fate (K. Scow, lead),
- aquatic toxicity (M. Johnson, lead),
- subsurface transport and fate (G. Fogg, lead),

and a final section with summary recommendations on the conclusions of the multimedia assessment.

Summary Review Statement

It is commendable that the state of California is requiring a multimedia assessment of newly introduced fuels. It is also commendable that Lubrizol has embarked on the first such assessment for its proposed PuriNOx diesel fuels. Although Lubrizol's efforts at multimedia assessment are extensive, some gaps in the analysis were identified in the above reports. After careful review and consideration, we find that Beller et al. (2003) provides a comprehensive review of the potential for PuriNOx fuel to impact water resources. Beller et al. (2003) considered the relevant environmental release scenarios, Lubrizol's laboratory and modeling methods, fate and transport of PuriNOx in the vadose zone and groundwater, cleanup of releases, and aquatic toxicity. They also provided substantive recommendations to address key uncertainties. We endorse these recommendations, and emphasize a priority subset in the list that follows.

1. The use of structural analogs does not suffice to characterize aquatic toxicity to aquatic organisms, and in particular, to marine organisms. The recommendation that such testing be performed is reasonable, even with the relatively small market penetration assumed by CARB. Further toxicity testing should include a full suite of marine organisms.

2. Some of the test methods used by Lubrizol while accepted for fate assessment of pesticides and other strongly sorbed chemicals are not applicable to a mixture as complex as PuriNOx; there remains unaccounted complexity (nonadditive and nonlinear interactions) that may make for a lack of predictability in the behavior of the chemical mixtures (including emulsifiers and dispersants) comprising PuriNOx in the environment.

3. Aerobic biodegradation tests do not reflect anaerobic biodegradation potential of relevant mixtures in expected release environments (subsurface or marine), nor tell about the potential build up of persistant metabolites of concern. Also experiments should use product mixtures and not structural analogs which may not be representative of rates for PuriNOx.

4. Beller et al. (2003) raise several important concerns about the assumption that components of PuriNOx are insoluble or likely sorbed in natural porous media (argued in comparison to the highly mobile MTBE). Some PuriNOx components are highly soluble and not strongly sorbed; there are negative environmental impacts of sorbed contaminants as well.

5. Fate and transport characteristics of PuriNOx components could have been better examined in laboratory column experiments, that should more reflect California subsurface materials. Beller et al. (2003) correctly point out that the soil column experiments conducted by Lubrizol (2003) are inconclusive owing to the small size of the columns, lack of hydraulic characterization, lack of analysis of BTEX compounds, and use of small quantities of fuel.

6. Comparative understanding of the transport of the PuriNOx fuel with respect to ULSD in the vadose zone, and of the overall mass transfer to the aqueous phase, requires at least mixture surface tensions and ultimately larger scale experiments where the in situ product

geometry obtains its natural shape (e.g., perhaps as a lens on the water table, or as residual pore occlusions).

7. Ultimately, the subsurface fate and transport behavior of PuriNOx components and associated petroleum hydrocarbons will become sufficiently understood only when some preexisting or future releases of these compounds can be monitored in controlled field studies. Thus, we believe the field studies recommended by Beller et al. (2003) and the SWRCB are essential.

8. The potential causes of leakages of either PuriNOx-blended fuels include tank material, joint fitting, and/or piping material incompatibility with, or permeability to, PuriNOx-blended fuels. Evidently no data has been collected to assess compatibility or permeability issues, except for some testing (no data) involving additive package with carbon steel materials (7, section 8.1.3). Claims in (7, sections 8.2.3 and 9.5) that leaks and spills are not expected to be greater than those for ULSD/diesel fuel are therefore contingent on assuming that PuriNOx blending does not change compatibilty or permeability of blends with storage and distribution materials overall.

These issues are those of high priority in risk evaluation for PuriNOx package and PuriNOx fuel mixtures use in the state. The detailed review comments from which these issues are extracted follow.

Environmental Fate (K. Scow, lead).

Lubrizol submitted multimedia evaluation report to CARB for use of PuriNOx diesel fuel technology in CA. LLNL was contracted by Lubrizol to conduct independent review of data and data analysis in Lubrizol report and assess how the report addresses potential impacts to surface and groundwater that may result from proposed use. An expert panel (LLNL) did an independent assessment that was submitted to Lubrizol and SWRCB. We are reviewing this assessment for completeness and content.

The major question under consideration by the expert panel was: what is relative risk of PuriNOx to CA water resources and beneficial uses compared to ultra-low sulfur diesel? *This is a comparison rather than an independent assessment.* We believe that, for the most part, LLNL did an objective and thorough job of reviewing the Lubrizol material. Below we summarize some of the major issues raised by the expert panel and add additional comments or clarifications:

1. PuriNOx consists of a complex mixture of chemicals with a broad range of molecular weights and solubilities. Additives to PuriNOx include surface-active compounds (emulsifiers and dispersants). Many of the accepted test methods for environmental fate assessment (and used by Lubrizol) were originally developed for pesticides and other strongly sorbed chemicals and simply are not applicable, without modification, to a material as complex as PuriNOx. Also, Lubrizol often makes blanket conclusions about the overall impact of PuriNOx only considering some of the components of the fuel (and not considering other fuel components that may have widely differing activity in the environment).
2. There is an implicit assumption by Lubrizol that the fact that components of PuriNOx are insoluble or sorbed means they will not present a major environmental problem (argued in comparison to the highly mobile MTBE). This assumption is clearly incorrect; there are negative environmental impacts of sorbed contaminants as well.
3. There is no consideration of the potential complexity (nonadditive and nonlinear interactions) and thus lack of predictability in the behavior of the chemical mixtures comprising PuriNOx, e.g.,
   - Impacts on biodegradation when more than one compound is being metabolized
   - Effect of co-solvents or emulsifiers on bioavailability, cellular membranes
4. There is an misleading implicit assumption in the Lubrizol report that measurement of aerobic biodegradation potential in Sturm tests (with wastewater inoculum, measuring only carbon dioxide) can reflect or account for:
   - Anaerobic biodegradation potential
   - Behavior in mixtures
   - Potential build up of persistent metabolites
   - Biodegradation potential in subsurface environments and marine surface waters
5. The expected release scenarios include potential leaks of components, additive, or fuel mixtures to the vadose zone, with or without prior fuel releases, where the fate and transport depends on the multiphase transport and interfacial geometries in situ. Comparative understanding of the behavior of the PuriNOx fuel with respect to ULSD in the vadose zone requires data on mixture surface tensions, as pointed out in (4). Ultimately larger scale experiments (or monitored field spills) where the product

geometry obtains its natural shape in situ are required for a robust understanding of the subsurface behavior.

6. It is not certain that PuriNOx product or PuriNOx-blended fuels will be compatible with materials to be used in their storage, particularly non-metallic materials involved in surface and underground storage and distribution. Potential interaction of PuriNOx fuels with planned storage materials including thermoplastics associated with flexible piping, and thermoset resin or composite laminate materials associated with rigid pipes and other UST components should be examined using standard methods. Standards for gasolene fuels (Underwriters Laboratory 971 and 1316) are currently under revision with input from California state agencies and it would seem wise to establish communication between the PuriNOx multimedia assessment and the establishment/revision of UST material compatibility/permeability testing.

Specific comments, by section.

p. 2: Conformance of Lubrizol's Data Package to SWRCB Evaluation Criteria

Lubrizol is the first company subject to SB 989 multimedia assessment of their new fuel product. The product, PuriNOx, has additive packages called Gen 1 and 2 and these are complex chemical mixtures with compounds from <50 to >3000 MW with huge range in solubility. These additives have surface-active compounds (emulsifiers and dispersants) that can alter how the diesel components of Lubrizol will behave in environment.

The existing guidelines for multi-media assessment seem to be oriented towards single chemical products or simpler mixtures and are not designed to anticipate non-additive interactions among components of a mixture in the environment. These interactions may include: i) enhancement or suppression of the biodegradation of specific components, as well as of other fuel-associated compounds already present; ii) emulsification and possible transport of relatively insoluble components or compounds already present; iii) synergistic toxic effects.

This review has been conducted to address the existing Lubrizol products (Gen 1 and Gen2) but also to help develop a protocol for assessing new Lubrizol (and possibly other companies') products in future. It is recognized that not all data needed for assessment is available. However it must be emphasized that existing testing methods may not be sufficient for this assessment and quite different approaches (yet to be identified) will have to be developed for multimedia environmental assessment of mixtures of compounds with widely differing chemical properties.

p. 2: Environmental Release Scenarios

As mentioned above, PuriNOx differs from other fuels in its inclusion of emulsifiers and dispersants, added to permit blending of otherwise immiscible components. Chemicals with these properties are sometimes purposely added to contaminated sites with highly insoluble chemicals to increase the availability (and potentially the mobility) of these contaminants. PuriNOx is likely to be released into areas where there have already been releases of diesel and other fuel products. Therefore the possibility of these indirect effects of PuriNOx must be considered within the environmental release scenarios.

In general the expected release scenarios include potential leaks of components, additive, or fuel mixtures to the vadose zone, where the fate and transport depends on the multiphase mixture mechanics, characterized by the density, viscosity, and surface tension of the spill with the air, water, solid, and possibly other fuel products present from prior spills. The surface tensions have been examined with PuriNOx components but evidently not with PuriNOx fuel mixtures. Comparative understanding of the behavior of the PuriNOx fuel with respect to ULSD in the vadose zone, including both multiphase transport and mass transfer through aqueous-fuel and air-fuel interfaces requires at least mixture surface tensions and ultimately larger scale experiments where the in situ product geometry obtains its natural shape (e.g., perhaps as a lens on the water table, or as residual pore occlusions).

Another issue is the potential for unpredictable behavior of chemicals at the interface between fresh and marine waters. Conditions at interfaces fluctuate widely and chemicals subjected to these conditions may behave in unexpected ways (e.g. precipitate out of solution).

p. 4: Consideration About the Comparison of PuriNOx components to MTBE.

There is danger in Lubrizol's assumption that because components of PuriNOx are dissimilar to MTBE that it is unlikely PuriNOx will have a large environmental impact. The expert panel raises several important points related to this issue, including the fact that there are some PuriNOx components that are highly soluble and not strongly sorbed, and thus may behave like MTBE.

p. 5: Capabilities for Routine Analytical Measurement of PuriNOx Components

The expert panel clearly identifies the serious issue that it is not possible to routinely analyze many components of PuriNOx using common and commercially available chemical analytical methods. This is clearly a major gap and hampers the ability to assess the fuel's environmental fate and impacts.

p. 5: Use of Structural Analogs to Characterize Aquatic Toxicity and Biodegradation

Structural analogs are used to estimate the environmental properties of some of the components of PuriNOx. The expert panel points out an example, though, of how structurally very similar chemicals have widely varying biodegradation properties. The same type of situation can occur with respect to the toxicity of compounds of similar structures. Thus in some cases structural analogs may be warranted, in others not. Caution is recommended by the panel; however, it is not clear what caution should be taken.

p. 5: Lack of Anaerobic Biodegradability Data for Many PuriNOx Components

This is a major weakness of the Lubrizol report that is clearly recognized by the expert panel. The Sturm test used to assess biodegradation potential is not appropriate, and even misleading, for this application. I doubt the relevance of this type of test for even evaluating aerobic biodegradation potential in porous media such as the subsurface. In addition, the environments most likely to be subject to PuriNOx releases are usually anaerobic due to oxygen consumption via biodegradation of previous fuel leaks. The potential for anaerobic transformation and/or mineralization of PuriNOx components, and including the mixed formulations, coupled with metabolite identification, must be determined before the fuel can be used in the environment. In addition, more appropriate indicator molecules (e.g. actual constituents of PuriNOx and already existing contaminants at release sites likely to be impacted by PuriNOx releases) must be included in the analyses. The anaerobic conditions tested must cover the potential array of different redox conditions likely to be encountered in the subsurface.

The biodegradation data presented in the Lubrizol report is not very convincing. There is no evident replication and standard deviations to determine whether differences are statistically valid. Also, not enough detail is presented about the conditions of the assay.

p. 5: Potential for Metabolites that Could Degrade Water Quality

The statement by the expert panel about metabolites is ambiguous. Is the panel concluding that potential metabolites of PuriNOx components are unlikely to be a problem? Such a conclusion should be supported by data, at least for structurally similar compounds.

p. 6: Cleanup of Releases

This section of the Lubrizol document is very superficial. The expert panel addresses some possible clean-up scenarios but makes no explicit recommendations for how cleanup of releases should be assessed (e.g. in field study). It seems likely that the most frequent situation will be released to the subsurface and this type of cleanup scenario must be addressed.

p. 7: The expert panel develops the recommendations to address what they consider the key uncertainties in the Lubrizol report:

1. Assessment of Actual Environmental Distributions After a Known Release of PuriNOx Additive or PuriNOx Fuel
2. Development of Analytical Methods for PuriNOx Components of Greatest Concern
3. Biodegradation Studies to Fill Important Data Gaps
4. Aquatic Toxicity Testing
5. Soil Column Studies

I agree with the panel's assessment of what are the major uncertainties needing additional data or study.

Aquatic Toxicity (M. Johnson, lead)

This review covers the multimedia assessment of the PuriNOx diesel formulation conducted for the California Air Resources Board. The focus of my review is the aquatic toxicity component of the CARB evaluation. Several documents were provided in support of the review, however, not all of these documents contained relevant material.

Assumptions used to evaluate the CARB review:

- Release of PuriNOx as a complete fuel package to surface water is unlikely due to the potential release scenarios:
- Release of additive package during transport
- Release of additive package during above or below ground storage
- Release of PuriNOX fuel during blending
- Release of PuriNOX fuel from storage
- Release of PuriNOX fuel during distribution and transport

As a result of these scenarios, the CARB review was reviewed for the evaluation of potential toxicity to aquatic organisms for both the additive package and PuriNOx fuel. It is also assumed that although releases to surface waters are not probable, they are possible. Based on the release scenarios provided, it appears that releases have a higher probability of occurring to coastal marine and estuarine environments that are particularly productive and susceptible to damage from unintended spills.

Conclusions of the CARB Review (Beller et al. 2003):

1. Toxicity testing of PuriNOx additives as a mixture would have been preferable to toxicity testing on individual components.
2. No evaluation of sediment toxicity. Sediment toxicity should be a component of toxicity testing.
3. Acute toxicity tests of components were the only tests performed (i.e., no chronic testing) and further testing should be performed using chronic test protocols.
4. Current analysis as presented by Lubrizol is not sufficient to eliminate the potential for endocrine disrupting effects.
5. Limited solubility of PuriNOx does not equate to lack of toxicity and use of higher solubility structural analogs for estimating toxicity is not valid.

Comments on the CARB review:

1. The review is correct in that evaluation of toxicity of individual PuriNOx components is not sufficient to determine toxicity of PuriNOx. There is no evaluation of PuriNOx fuel, sediment toxicity or chronic toxicity of either PuriNOx additives as a mixture or PuriNOx fuel. As such, there is currently no evaluation of the toxicity of PuriNOx relative to ULSD.
2. As a result of the process of toxicity testing outlined in #1 above, no information are provided by Lubrizol on the toxicity of PuriNOx relative to the toxicity of ULSD. Despite this, conclusions are made that PuriNOx does not pose any greater threat than ULSD (e.g., Multimedia Assessment of Lubrizol's PuriNOx Water/Diesel Emulsion, Cal EPA, Dec 2003). Despite the fact that this may be correct, it is not clear that there are sufficient data to support such a conclusion.
3. Lack of information on the potential endocrine disrupting capabilities should not at this stage be considered problematic. Other chronic effects such as immunotoxicity or neurotoxicity are also lacking. Tests specifically for these effects could be required if preliminary chronic testing indicates potential toxicity.

Conclusions:

Given the lack of testing of the PuriNOx fuel as a mixture and the use of structural analogs to evaluate toxicity of some components, there are currently no data that can be used to evaluate the toxicity of PuriNOx relative to ULSD. It should be noted that any recommendation allowing PuriNOx distribution and use is done with inadequate knowledge of toxicity to aquatic organisms, and in particular, marine organisms. The recommendation that such testing be performed is reasonable, even with the relatively small market penetration assumed by CARB. Further toxicity testing should include a full suite of marine organisms, as a likely release scenario is to marine waters through port operations. Current aquatic toxicity testing data reflects a fresh water suite of organisms (with a few exceptions).

Subsurface Fate and Transport (G. Fogg, lead)

My analysis focuses on fate and transport of potential contaminants from PuriNOx in the subsurface, with particular emphasis on hydrogeologic considerations. In general, I concur with the thorough analysis of (4, Beller et al., 2003). Below I reemphasize what I consider to be their key points and expand on these slightly.

In particular, I agree with (4) that the most likely release scenario is leakage from an underground fuel tank. Accordingly, the assessment of PuriNOx ultimately needs to include reliable field and laboratory monitoring data on fate and transport of the fuel components in the subsurface. A major obstacle to collection of such data is the lack of widely available analytical methods and instrumentation to measure aqueous concentrations of some of the PuriNOx components. This is rather troubling, especially since many of the components have been in use for 20+ years, and monitoring data from preexisting leaks into the subsurface would have provided invaluable hindsight today.

I agree with (4) that many of the uncertainties regarding fate and transport characteristics of PuriNOx components could have been reduced through laboratory column experiments. In (4) it is correctly pointed out that the soil column experiments conducted by Lubrizol (2003, reference 7) are inconclusive owing to the small size of the columns, lack of hydraulic characterization, lack of analysis of BTEX compounds, and use of small quantities of fuel. Furthermore, let me add that the materials that Lubrizol used in the columns (sand loam, loam, clay, silt loam; are not sufficiently representative of the coarse-grained portions of typical California alluvial aquifer systems. These aquifer systems typically contain some clean (relatively free of silts and clays) sands and gravels that often form the ‘fast paths’ for contaminant transport. Such sands and gravels are likely to be higher in permeability and have lower affinity (sorption capability) for dissolved solutes than the coarsest material tested by Lubrizol–the so-called ‘sandy loam.’ The soil column experiments should include at least one more column consisting of sandy sediments (<5% silt and clay) that are typical of California aquifer conditions.

The column experiments reported involve addition of roughly 0.1 pore volumes of product to the column porous media (assuming 0.35 porosity). That would correspond to the top 0.3 cm of the column which consists in all experiments of a sand buffer of 0.5 cm thickness (regardless of the soil type tested). It is possible that the relatively slow flow rates observed in the sandy loam have to do with pore blocking of the product phase in those samples as opposed to samples containing finer grained material, in which product may have lower entry pressures and may have undergone deeper penetration and redistribution. In any case it is possible that a significant amount of the product was retained not in the sample soils but in the sand buffer, and the geometry of the product distribution, and thus how it affected the flow rate and thus contact of effluent with product, in the columns is unknown.

While dissolved contaminants typically migrate most rapidly in connected sand/gravel channels and, for hard-rock aquifer settings, in fractures, cleanup of contaminants tends to be exacerbated when they remain in contact with non-aquifer materials (e.g., silts, clays, unfractured semi-porous rock) long enough for the solutes to migrate into these materials by advection and/or molecular diffusion. This phenomenon can prolong the contaminant sources for many years owing to slow bleed-out of solutes from such non-aquifer materials. Although I believe intensive study of this phenomenon is beyond the scope of the multimedia assessment of PuriNOx, some general consideration should be given to whether the surfactant properties of some of the PuriNOx components would likely influence the rate of migration of PuriNOx components and petroleum hydrocarbons (BTEX and naphthalene) into and out of non-aquifer materials.

The assertion by Lubrizol that PuriNOx will not be a problem of the same magnitude as MTBE because it is much less soluble is certainly not a comforting argument. Clearly, there exist many, problematic environmental contaminants that are much lower in solubility than MTBE. On the other hand, the proposed limited and controlled use of PuriNOx during a trial period contrasts sharply with the abrupt, widespread increase of MTBE use in California during the mid-1990's. This more gradual approach should provide ample opportunity to better define the environmental consequences of PuriNOx use, thereby averting a repeat of the MTBE scenario.

Considering the proposed phased introduction of PuriNOx and the related uncertainties, the course of action recommended by the SWRCB (Martinson memorandum) appears to be prudent. That is, during the "proposed, limited and controlled use of PuriNOx in California," studies would proceed concurrently to address problems concerning analytical methods for monitoring PuriNOx components in the environment, biodegradation potential, aquatic toxicity, and fate and transport potential evaluated through *laboratory* (soil column) studies. The SWRCB Martinson memorandum suggests that these studies be completed within two years, but that additional, *field* studies be ongoing and subject to a later deadline for completion. I gather that the purpose of the 'two-year' studies would be to identify any obviously "unacceptable risks to the environment" that would preclude continued use of PuriNOx in California, even at the proposed, initially low levels. The purpose of the longer-term field studies would be to ascertain whether "any significant expansion of the proposed distribution and use of PuriNOx" should occur. This two-part study approach would seem to provide PurniNOx with the flexibility to continue with its near-term plans, while allowing for adequate environmental protection.

Ultimately, the subsurface fate and transport behavior of PuriNOx components and associated petroleum hydrocarbons will become sufficiently understood when some preexisting or future releases of these compounds can be monitored in controlled field studies. Thus, I believe the field studies recommended by (4) and the SWRCB are essential. The SWRCB Martinson memo does not mention a time frame for the field studies, but I anticipate that approximately 5 years is a reasonable time frame for meaningful results to begin coming out of such a program. Depending on site conditions and rates of transport and reaction, more than 5 years of monitoring may be needed to arrive at conclusive results.

Summary Recommendations

We partly endorse the Recommendations in the draft summary of the multimedia assessment "Multimedia Assessment of Lubrizol's PuriNOx Water/Diesel Emulsion," revised as per the letter from Dean Simeroth to Timothy Ginn of 12 December 2003 (Appendix 2). Specifically, we differ from the recommendations of that letter in that we suggest that the following items in section IV.B.1 are not optional but are required to be done contemporaneously with marketing of PuriNOx:

- The development of analytical methods for PurNOx components of greatest concern,
- Conduct refined soil column studies,
- Conduct aquatic toxicity testing.

In addition, the multimedia assessement at this stage of planned market share of PuriNOx should include contemporaneously,
- Basic compatibility and permeability testing with UST materials to be involved in storage and distribution.

Appendix 1: List of documents under UC Davis review.

Timothy Ginn, Ph.D.
December 4, 2003
Page 3

LIST OF ENCLOSURES

1. California Environmental Protection Agency's Multi-Media Assessment of Lubrizol's PuriNOx Water/Diesel Emulsion
2. Draft 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 and Confidential Versions)
3. Draft State Water Resources Control Board's Evaluation of Multimedia Impacts Resulting From The Use Of PuriNOx Fuel In California: Impacts To Water (Public Version)
4. 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
5. Draft Office of Environmental Health Hazard Assessment's Impact Assessment of PuriNOx™ Generation 1 and Generation 2 Diesel Fuel (~~Public and~~ Confidential Versions)
6. Draft Department of Toxic Substance Control's Review and Comments to Lubrizol Final Report: Multimedia Evaluation, PuriNOx Fuel (Public and Confidential Versions)
7. Lubrizol's Multimedia Evaluation of PuriNOx Fuel Final Report Dr. Stephen Di Biase letter dated July 16, 2003, Registered Copy #31 - #34
8. Lubrizol's Appendices 1-17
9. Lubrizol's Interoffice memorandum from John Mulley dated July 25, 2003 Subject: Interfacial Tension Data for PuriNOX Surfactants
10. Lubrizol letter dated July 31, 2003—Follow up to July 16, 2003 meeting
11. Lubrizol's letter dated September 5, 2003—Summary of August 28 meeting with Lawrence Livermore National Laboratory and Lubrizol
12. Material Data Safety Sheet—
13. American Petroleum Institute Paper: Predicting the Effect of Hydrocarbon and Hydrocarbon-Impacted Soil on Groundwater September 2001
14. Lubrizol's memo dated September 12, 2003—Supplemental Information Supporting The Lubrizol Corporation Comments on Lawrence Livermore National Laboratory Draft Final Report Entitled "Review of the Data Supporting Lubrizol's Evaluation of Multimedia Impacts Resulting from the Use of PuriNOx Fuel In California"
15. Concawe Paper Lubricating Oil Basestocks—June 1997
16. Lubrizol's letter dated September 25, 2003—Supplemental information submitted to Lawrence Livermore National Laboratory on September 12, 2003
17. Air Resources Board Letter to Lubrizol dated January 31, 2001
18. Air Improvement Resource Final Report: Comparative analysis of Vehicle Emissions Using PuriNOx Fuel and Diesel Fuels
19. Lubrizol's Tier II Testing of PuriNOx (Summer Fuel Blend) Exhaust Emissions Final Report Appendices A-H, I-N, O-R, and S-U **(Please note: this enclosure was only sent to UC Berkeley and Dr. Hanspeter Witschi for their air and human health assessment analysis.)**

Appendix 2: Recommendations in D. Simeroth letter 12 December 2004.

ENCLOSURE

IV. Recommendations

The multimedia working group recommends that the Environmental Policy Council:

A. Find that the limited and controlled use of PuriNOx as described in the multimedia assessment does not pose a significant adverse impact on public health and the environment.

B. Due to the knowledge gaps identified in the multimedia assessment, the finding under IV.A. is conditioned on the following:

1. Lubrizol conduct additional studies to fill the knowledge gaps identified in the multimedia assessment to be completed prior to any expansion beyond a 1 percent diesel market penetration, ~~within two years~~. These studies shall include:

   - Development of analytical methods for PuriNOx components of greatest concern.
   - Biodegradation studies to fill data gaps.
   - Conduct aquatic toxicity testing.
   - Conduct refined soil column studies.
   - Conduct a feasibility study on soil cleanup.
   - Conduct toxicological tests to compare PuriNOx fuel with regular diesel. For example, the fish bioassay test described in California Code of Regulations, Title 22, Section 66261.24(a)(6) can be used for the tests.
   - Conduct comparative emissions tests for nitrosamines and products that can lead to nitrosamine formation.

2. Prior to any expansion of the proposed distribution and use of PuriNOx, an environmental fate and transport study must be conducted. 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.

3. In the event that the requested studies described above identify risks to the environment, the use of PuriNOx will be reviewed by the Governor's Environmental Policy Council for consideration for appropriate action.

CalEPA

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

1. The over-all CalEPA Report

The report, entitled "Multi-Media Assessment of Lubrizol's PuriNOx Water/Diesel Emissions" and identified as the first on the list of enclosures sent out on December 4, 2003 by Dean C. Simeroth (ARB, Chief, Criteria pollutants Branch) has been prepared by staff members from ARB, SWRCB, OEHHA and DTSC. Essentially, the report summarizes the Air Emissions Evaluation, the SWRCB water evaluation, the OEHHA evaluation rearguing human health effects and the DTSC evaluation. The report then provides over-all conclusions and recommendations. It will be referred to in the following as the CalEPA Report.

The general conclusion of the report (page 10) states that "the limited controlled use of PuriNOx, as described in the multimedia assessment, does not pose a significant adverse impact on public health and the environment".In general, I could agree with this over-all assessment. I also could agree with the modified recommendation IV.B.Condition 1 as formulated in the letter sent out by D.C. Simeroth on December 22, 2003 that "Lubrizol conduct additional studies to fill the knowledge gaps identified in the multimedia assessment to be completed prior to any expansion beyond a 1% diesel market penetration".

In the following, I will focus on the report prepared by OEHHA staff, dealing with potential human health impacts. Its major conclusions have been incorporated into the CalEPA report.

2. OEHHA Report

The report prepared by OEHHA staff is entitled "Draft Staff Report on Health Impacts of PuriNOxTM Generation I and Generation II Additive packages and Diesel Fuels". A shortcoming of the report is the absence of page numbers. I inserted numbers by hand in the hope that an identical copy will be available for whoever reads these comments.

The over-all OEHHA conclusions indicate that the benefit from reducing PM and NOx seems to outweigh the risk from increases in (other) toxic air contaminants (CalEPA report, page 4). On page 14, second paragraph of the OEHHA report itself it is stated (lines 6-8) "Use of these reformulated fuels may reduce pulmonary morbidity and mortality due pulmonary disease". Also (lines 11-12) "there does not appear to be a significant risk of cancer from any of the increases in emissions". In the body of the report, tables and calculations are provided that support these statements. Therefore I can concur with these over-all conclusions. OEHHA staff has done a commendable over-all job in collecting the relevant data, putting them into the wider framework on what is known about toxic air contaminants and then in conducting a proper risk benefit analysis.

There are, however, several statements or conclusions in the OEHHA report where I have some questions, would be of a different opinion or am not convinced by OEHHA's reasoning as presented in their report. They can be addressed as follows.

a) The need for additional data on nitrosamines

On page 14, lines 13-15, OEHHA states "OEHHA is concerned with the absence of data on nitrosamines produced by combustion and on possible adverse impacts on the environment on releases that contain components in the additive packages". This concern is incorporated into the CalEPA report on page 6, lines 6/7.

A justification for this concern is not really provided, except the statement on the bottom of page 12 of the OEHHA report: "Consideration of products that may be formed from components during combustion reveals a possible formation of carcinogenic nitrosamines". Would this imply that nitrosamines are a major concern in Diesel exhaust emissions in general or only if Diesel with PG1 or PG2 additives is used? This question os of some importance, because nitrosamines are not generally be thought to be a major concern in conventional diesel exhaust emissions. I checked this point with two investigators that have personally conducted diesel exhaust emission toxicity studies and asked about the potential role of nitrosamines. I got the following reply:

a) Laboratory 1, From a comparative study between Diesel exhaust emission (DEE) toxicity and tobacco smoke toxicity):"*.......we measured –nitrosamines in DEE in our study. However, everything was below our detection limits"* (in the same study, nitrosamines were readily detected in a tobacco smoke atmosphere).

b) Laboratory No. 2: *"We did indeed look for nitrosamines in our study of diesel emissions conducted recently within our program. We found traces, but the levels were well below the reliable lower limit of detection. There are nitrosamines in diesel emissions, and probably other combustion emissions, but in the case of properly-functioning contemporary diesels (the only case where we looked), they are very tiny traces. We included nitrosamines in our survey because we anticipated working with tobacco smoke (as well as several other source emissions), and are performing the complete speciation battery on all exposures whether or not we expect all compounds to the present".*

And: *"I don't know if we are the only group that has actually looked for nitrosamines in diesel emissions, but I know of no other reference. Of course, there is no shortage of other carcinogens in diesel emissions".*

In view of these comments from 2 experts in diesel toxicology, OEHHA might be asked to provide, if possible, a more specific rational for the acquisition of nitrosamine data. So far, in looking at the available Diesel literature and given the opinions cited above, it does not seem very likely that such data would substantially modify the hazard assessment for PuriNOx..

b) The call for "positive controls".

On page 10, line 5 from bottom, the statement is made: "However, 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". This concern then also found its way into the CalEPA report on page 6, second paragraph. I would like to offer the following comments to this statement.

The term "positive controls" is not used in its proper meaning, as commonly done by investigators in toxicity studies. Positive controls are an experimental group that allows to detect whether an ***a priori*** expected and well-defined endpoint caused by a toxic agent (organ weight change, genotoxicity data, pathological phenomenon, biological response) can be produced under one's own laboratory conditions (e.g. with the animals and/or the analytical methodologies that are used). For example, if one wanted to examine whether diesel causes an increase in micronuclei, one would add a positive control group injected with a known mutagen, such as mitomycin C. If one wanted to see whether a particular rat strain develops pulmonary fibrosis following inhalation of Diesel exhaust, then positive controls would be animals of the same strain treated with bleomycin or with silica. The correct use of positive controls is nicely documented in the EPA Tier 2 Study Report, prepared by the Lovelace Inhalation Research Institute, page 41, where the known neurotoxin trimethyltin (TMT-10) was used to validate the procedures designed to discover glial fibrillary acid protein (GFAP). Positive controls deliver an absolute answer with regard to one particular endpoint - if, for example positive controls in this experiment had failed to detect GFAP, then it could not be concluded that Diesel did not induce this lesion. However, since GFAP was substantially increased in the positive controls but slightly decreased in the Diesel exposed animals, it can correctly be concluded that Diesel exposure did not result in gliosis-related neurotoxicity.

To parallel the PuriNOX studies with CARB diesel would thus not be a positive control, but a concurrent control that allows - as is rightly stated - to compare toxicity of PuriNOx relative to unmodified CARB diesel. Perhaps such concurrent controls could or should have been included in the Tier II data acquisition studies. But there are also several legitimate reasons why they were not. Cost is one factor, animal welfare considerations are another one (not to use animals unnecessarily by duplicating already existing information). Current practice in animal welfare usually frowns upon doing studies again that already have been done. Before thus questioning the currently available PuriNOx studies, some library work could have been done. Going back for more than 30 years, there is a huge literature on acute and chronic toxicity of Diesel available in the literature and studies (with newer fuels and newer engines) continue to be published. For practically all experimental studies, excellent exposure data are available (chamber concentrations of Diesel exhaust constituents, biomarkers of exposure and of effects). A thorough analysis of the existing literature would probably allow to come at some very sound conclusions on the comparative toxicity of PuriNOx and CARB diesel. If after such an analysis concerns still persist and can be documented, specific recommendations then could be made for targeted experiments. For example, was there a disquieting finding with CARB Diesel that the PuriNOx studies failed to detect? On the other hand, if no toxicity data on CARB Diesel are available, why then can it be used and what are the truly disquieting findings in the PuriNOx studies?

A similar comment can be made regarding the statement made in the CalEPA report on page 6, end of second paragraph:"the study was not sufficiently sensitive to detect small but possibly significant changes in toxicity of a toxic complex mixture". This is akin to say "more research is needed" without really giving good reasons or asking specific questions. If, given the rather large amount of toxicity information already available, OEHHA still feels that the toxicity data are inadequate, they should be able to say why, before additional resources (and animals!) are committed.

c) Additional comments to OEHHA review

I have no additional specific comments with regard to Part 1 (page 1), "Summary and evaluation of diesel engine combustion test data" or Part 3 (page 12), "Environmental partitioning, transport, fate and toxicity of additive components". However, I would come to some different conclusions than did the OEHHA evaluation of Part 2 (page 10), " Summary and evaluation of Tier II submitted to U.S. EPA".

The report raises some technical concerns with the study conducted at the Lovelace Respiratory Research Institute (LRRI) in Albuquerque, NM.. They are - and can be addressed - as follows.

- page 10, last paragraph: *"Whole body exposure deposits particles on the animals' fur. During grooming, the animals ingest these particles. As a result, exposure undoubtedly occurred via two routes, inhalation and ingestion"*.

This statement is essentially correct. It is unavoidable that all exposures to respirable particles are double exposures. Inhaled particles are first deposited in the nasal passages, upper airways and the deep lung, the exact localization depending on particle size, aerodynamic properties, solubility etc. The particles then will, through physiological clearance mechanisms, be transported up the mucociliary escalator, in free form or engulfed by macrophages, and then will be swallowed (some, of course, may cross into the bloodstream while still in the lung). If the alternative technique to whole body exposure, i.e. nose only exposure had been used, "double exposure" still would have occurred, except, of course, at a lesser dose (minus the particles removed from the fur by grooming).

Exposure to and inhalation of particles is thus invariably followed by systemic exposure. The whole body exposure technique used by LRRI could be challenged if there was any evidence that ingested Diesel particles produce systemic toxicity. In this case reducing the ingested dose through nose-only exposure might have given information. However, whether systemic toxicity (what is anticipated?) is a serious toxic effect for Diesel particulates, or whether there is any reason to believe so, I would not know offhand, but I do not recollect such concerns. The literature could tell. In my opinion, LRRI chose the appropriate experimental protocol.

- page 11, lines 4 - 8: *"The concentrations of several gas pollutants, particularly* SO_2 *and* 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 exposure could produce more severe toxic effects than those that would result from constant stable exposure".

The LRRI report does not provide any evidence that episodes of higher than desired exposures would have produced persistent signs of toxicity. Animal weight gain, mortality data, the results of clinical chemistry or histopathology findings fail to give any indication that such episodes would have left permanent marks.. If episodic exposures produced transient or fully reversible changes that have not been report to manifest itself acutely (clinical observations) and have not found to persist (histopathology), how can one conclude that such excursions could have produced more severe toxic effects?

However, there is a much more serious consideration that allows to dismiss outright OEHHA's concern about the "wide variation" in exposure concentrations. In its final report, the LRRI does indeed provide some evidence for possibly large excursions in chamber concentrations. For example, chamber concentrations (LRRI final report, page 52, table 6) given as mean ∀ SD the following numbers for $SO_{2:}$ Low dose: 4.0 ∀ 6. 0 ppb; Mid. dose 8.0 ∀ 15.0 ppb. These are indeed substantial standard deviations that could be indicative of wide fluctuations. The high dose values, given as 15.0 ∀ 4.0 ppb look reasonable.

However, a look at the original exposure data (provided in tabular form in appendix H to the LRRI report) show that these large standard deviations are due to ONE extremely high measurement in the low group (on 1/23/02) and TWO extremely high measurements in the mid group (on 1/22 and 2/5/02). If these values are eliminated for calculating the average, then the average exposure concentrations for SO_2 become 3 ∀ 1 ppb for the low and 5 ∀ 2 ppb for the medium group. In other words, unduly high chamber concentrations were only noted on 1, resp. 2 days out of 80 exposure days. It is questionable whether these "rare" events (1.25% to 2.5% of total study time) would have compromised the results in a serious way.

Moreover, the highest reported "excursion" for SO_2 (measured on 1/22/2002 in the Mid group; Appendix H p. 287)) is reported as having been 0.1 ppm and on 2/5/02 was 0.097 ppm. According to David Bates in his book (second edition, 2002) "A Citizens Guide to Air Pollution", non asthmatic subjects may breathe up to 8 ppm of SO2 without any bronchoconstrictive response and asthmatics are not affected by 0.25 ppm. Given these facts it is difficult to see how two one-day excursions in an animal study to 0.1 ppm could have compromised the experiment. The inference lacks credibility that the two reported excursions of SO_2 to 0.1 ppm might have caused more substantial toxic effects than a throughout stable exposure might have.

Analysis of the raw data for NO_2 shows also variations. However, whenever NO_2 was higher than anticipated (and an explanation for these events is tentatively provided in the report), there was a concomitant decrease in NO levels. (e.g., weeks from 11/19/01 to 12/20/01). The NO_x

data, the average from the NO and NO_2 , show considerably smaller SD's than the values for NO_2 and NO. So exposure to nitrogen oxides was fairly constant. A well known toxicity for NO_2 is bronchiolitis obliterans. If the transient higher levels of NO_2 would have had any lasting effect in this experiment, then one could anticipate to find histopathological lesions in the small airways of the animals. No such findings were reported. In summary, I could not concur with OEHHA's conclusion that the allegedly widely varying exposure concentrations to SO and NO_2 did seriously compromise the experiment.

- page 11, lines 11-12: *"The tier II report provides no indication that the fuel was agitated during the course of the toxicity studies"*

Apparently, the manufacturer recommends periodic stirring of the fuel mixture. On page 16, the LRRI report states that fuel was pumped daily for use from 550 gallons stainless steel transportation totes into 55-gallon drums. Before it can be concluded with certainty that the fuels were not agitated during the experiment, LRRI should be asked whether pumping the fuel daily into smaller containers could have produced adequate mixing,.

- page 11, lines 27 to 30: "*Reductions on body weight gain...were judged unrelated to treatment, although it appears that more rigorous statistical analysis...would indicate that the reductions were indeed statistically significant".*

I assume OEHHA had access to the original data that accompanied the report. If reduced body weight gain was a serious concern to OEHHA, the original data should have been re-analyzed by agency staff.

- page 11, third paragraph: OEHHA questions to what extent it was justified, by LRRI, to label some significant changes in clinical chemistry and hematology as being inconsistent and therefore unrelated to Diesel emissions and exposure. Basically, this is a valid point. Whenever a large number of data are generated, with automated procedures, but possibly without duplicate or triplicate analysis (not of the same samples, but from different animals and/or on different days of exposure), then it is more than likely that some data sets, upon statistical analysis, will yield type I or type II errors. The study director then has the task to judge whether these changes are "biologically relevant" or "treatment related". He develops an informed judgment, based on his experience from previous and similar studies and/or in consultation with knowledgeable colleagues. This has been done by LRRI and the changes in chemistry and hematology were considered to be not treatment related.

OEHHA' concerns about this interpretation are legitimate. However, a more complete reasoning should be given why OEHHA tends not to agree with the interpretation given by LRRI. For example, similar changes (in hematology, blood chemistry) were apparently reported in earlier, similarly conducted studies. What was the then interpretation and how extensive were the changes compared to the present results? How would OEHHA interpret these findings - and how were they interpreted and evaluated by OEHHA in the process of declaring Diesel a toxic air contaminant? LRRI has a long tradition of studying Diesel toxicology and the interpretation of the current data probably relies very heavily on experience gained before. Questions about LRRI's approach should thus be more specific and the reasons for asking them should be fully documented.