United States Environmental Protection Agency

Air and Radiation

EPA420-P-02-007
December 2002

---

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

## Draft Technical Report

*Printed on Recycled Paper*

EPA420-P-02-007
December 2002

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

## Draft Technical Report

Assessment and Standards Division
Office of Transportation and Air Quality
U.S. Environmental Protection Agency

*NOTICE*

*This technical report does not necessarily represent final EPA decisions or positions. It is intended to present technical analysis of issues using data that are currently available. The purpose in the release of such reports is to facilitate the exchange of technical information and to inform the public of technical developments which may form the basis for a final EPA decision, position, or regulatory action.*

# Table of Contents

# I. Nature and Purpose of this Technical Report

This Report presents a technical analysis of the effect of Lubrizol's PuriNOx diesel/water emulsion on exhaust emissions from diesel-powered vehicles. It analyzes pre-existing data from various emissions test programs to investigate these effects. The conclusions drawn in this Technical Report represent the current understanding of this specific technical issue, and are subject to re-evaluation at any time.

The purpose of this Technical Report is to provide information to interested parties who may be evaluating the value, effectiveness, and appropriateness of the use of PuriNOx. This Report informs any interested party as to the potential air emission impacts of biodiesel. It is being provided to the public in draft form so that interested parties will have an opportunity to review the methodology, assumptions, and conclusions. The Agency will also be requesting independent peer reviews on this draft Technical Report from experts outside the Agency.

This Technical Report is not a rulemaking, and does not establish any legal rights or obligations for any party. It is not intended to act as a model rule for any State or other party. This Report is by its nature limited to the technical analysis included, and is not designed to address the wide variety of additional factors that could be considered by a State when initiating a fuel control rulemaking. For example, this Report does not consider issues such as air quality need, cost, cost effectiveness, technical feasibility, fuel distribution and supply impacts, regional fleet composition, and other potentially relevant factors.

State or local controls on motor vehicle fuels are limited under the Clean Air Act (CAA) - certain state fuel controls are prohibited under the Clean Air Act, for example where the state control applies to a fuel characteristic or component that EPA has regulated (see CAA Section 211(c)(4)). This prohibition is waived if EPA approves the State fuel control into the State Implementation Plan (SIP). EPA has issued guidance describing the criteria for SIP approval of an otherwise preempted fuel control. See “Guidance on the Use of Opt-in to RFG and Low RVP Requirements in Ozone SIPs,” (August, 1997) at: http://www.epa.gov/otaq/volatility.htm.

The SIP approval process, a notice and comment rulemaking, would also consider a variety of technical and other issues in determining whether to approve the State fuel control and what emissions credits to allow. An EPA Technical Report like this one can be of value in such a rulemaking, but the SIP rulemaking would need to consider a variety of factors specific to the area, such as fleet make-up, refueling patterns, program enforcement and any other relevant factors. Additional evidence on emissions effects that might be available could also be considered. The determination of emissions credits would be made when the SIP rulemaking is concluded, after considering all relevant information. While a Technical Report such as this may be a factor in such a rulemaking, the Technical Report is not intended to be a determination of SIP credits for a State fuel program.

## II. Draft Review Process

This draft technical report describes a methodology for quantifying the effect of PuriNOx on exhaust emissions of regulated pollutants using data that has been collected by Lubrizol. We are making this methodology available to the public in order to take comment before we approve a set of specific emission benefits that can be attributable to PuriNOx. Following EPA's peer review guidelines, we are also submitting this draft technical report to outside experts to obtain independent peer review. After we receive comments from interested parties and our independent peer reviewers, we will make any modifications to the analysis deemed appropriate and release a final technical report.

Comments on this draft technical report will be accepted through January 15, 2002. Comments may be sent to David Korotney at korotney.david@epa.gov, or through regular mail to:

David Korotney
U.S. EPA National Vehicle and Fuel Emissions Laboratory
2000 Traverwood Drive
Ann Arbor, MI 48105

## III. Background

In September of 2001, Lubrizol approached the EPA with a collection of emissions data on its water/diesel emulsion called PuriNOx. Lubrizol sought formal EPA verification of the emission benefits of PuriNOx for use in marketing and for emission credit accounting purposes in SIPs. Lubrizol was already in negotiations with officials at the Texas Natural Resources Conservation Committee concerning use of PuriNOx in the Houston area to meet their significant NOx shortfall. We confirmed that Texas was indeed seriously considering the use of PuriNOx as one element of its overall strategy, and would be looking to the EPA to establish the exact level of NOx benefits that could be claimed in a SIP. Based on this near-term need, we agreed that it would be appropriate to assign a specific set of emission benefits to PuriNOx.

Lubrizol had already obtained an emissions verification from the California Air Resources Board (ARB) in January 2001 under their "Interim Procedure for Verification of Emission Reductions for Alternative Diesel Fuels." This verification, based on new testing conducted by ARB, established the NOx and PM reductions associated with PuriNOx as being 14 and 63 percent, respectively. PuriNOx can now be assigned these reductions in any California credit trading program or grants program as well as their SIP. The emissions data collected by the ARB added to a pre-existing database assembled by Lubrizol and analyzed by Air Improvement Resources (AIR) in April 2001. This database contained eight highway and nonroad engines and nearly 50 separate tests. In analyzing this data, AIR concluded that PuriNOx produced average NOx and PM reductions of 19 and 54 percent, respectively.

The obvious context in which emission benefits of a fuel or fuel additive should be verified is the fuels testing protocol being developed by EPA[1]. This protocol requires a specific amount of emissions data to be collected on engines falling into several categories under certain test conditions, and specifies the analytical framework under which benefits should be quantified. However, at the time that discussions between Lubrizol and the EPA were going on, this protocol did not exist. The EPA determined that it would be appropriate to formally assign a set of benefit estimates to PuriNOx for use in SIPs using existing data based on:

1. The substantial volume of existing emissions data on PuriNOx
2. The interest in the use of PuriNOx in both California and Texas
3. The analyses performed and conclusions drawn by other parties about PuriNOx
4. Emulsions had been studied for several decades and the combustion mechanisms involved in NOx reductions are largely understood

We decided not to require Lubrizol to wait to submit an application under the fuels testing protocol, but the emerging protocol would provide a reference point for what constitutes a sufficient dataset during our analysis of existing PuriNOx data.

The data that Lubrizol collected on PuriNOx included a wide variety of equipment types, test conditions, and contexts. Not all were directly relevant to the estimation of emission benefits for use in SIPs, though they might be useful in a qualitative fashion. For instance, additional data that Lubrizol collected but which was not used to quantify the emission benefits of PuriNOx included:

- Data on versions of PuriNOx containing different amounts of water than the 20% water/80% diesel blend that Lubrizol ultimately decided to register with the EPA.
- Data on engines that had been recalibrated/repowered for the use of PuriNOx. Since the primary conditions under which PuriNOx was to be used would involve engines that had not been specifically recalibrated/repowered for the use of PuriNOx, this data was not directly relevant.
- Data on chassis running on dynamometers. Test cycles for chassis cannot exactly duplicate the Federal Test Procedure (FTP) required for engine certification. In addition, emission inventories are based on engine certification data, not chassis data.
- Data collected via portable monitors on equipment in the field. The representativeness of data from these monitors has not yet been demonstrated.

We also determined that any data collected on steady-state cycles would not be appropriate for determining emission effects of PuriNOx for PM or CO, based on previous investigations of test cycle impacts on fuel/emission effects. However, even with these exclusions, we had a substantial set of emissions data on PuriNOx permitting us to quantify its effects on emissions.

## IV. Historical research on emulsions

Aqueous emulsions have been studied for at least 30 years as an alternative to conventional gasoline and diesel fuels. The cooling effect of the presence of water in an engine has been known to reduce emissions from engines, specifically oxides of nitrogen ($NO_x$) and particulate matter (PM). Until recently, emulsions have not actually been considered as a viable option for use in commercial engines due to various outstanding problems (see Section IV.B). However, manufacturers and researchers are now pursuing emulsions more enthusiastically as alternative fuel options and are optimizing them for maximum emissions reduction potential.

The idea behind fuel-water emulsions arose from the idea of using water as a cooling mechanism for engines. Direct injection of water was an idea that investigators studied prior to emulsions. It was widely known that the cooling effect of water could help to reduce $NO_x$ emissions and the delayed effect that water had on injection could also serve to reduce PM emissions. However, the feasibility of this idea was questioned in light of the wear and tear on the engine due to water coming in contact with engine parts. Fuel-water emulsions were considered a more feasible alternative to direct water injection due to the fact that water could be mixed with the fuel prior to introducing the fuel into the engine. Unlike water injection, there would not have to be a separate supply mechanism in the engine to introduce the water.

### A. Studies of water impacts on combustion

#### 1. Early efforts to reduce combustion temperatures

The idea that temperature is the dominant effect on NOx emissions has been widely known. Thus, efforts to decrease peak combustion temperatures, and subsequently NOx, has been studied by many researchers. Beginning research to achieve reductions in temperature included methods to dilute the fuel-air mixture with an inert or noncombustible substance. This idea was then replaced with the idea of injecting an inert or noncombustible liquid-phase substance into the engine. This substance would have the characteristic of being able to reduce the temperature through charge dilution without adding a significant loss in power. Because of its high heat of vaporization, low vapor pressure, and low boiling point, water was chosen as the ideal cooling substance.

The concept of adding water to engines as a cooling mechanism was first studied in the form of direct injection of water into the engine, where cooling water is injected into the cylinder at a predetermined rate. This approach had been studied as far back as the 1930s in gasoline engines to reduce engine knock and in aircraft engines during World War II. It had been widely known that water can be injected into the manifold to reduce peak temperatures and thus decrease emissions of NOx. This idea had not been fully explored due to the cost of providing auxiliary water tanks and injection systems on vehicles. In addition, direct water injection tended to produce some engine corrosion problems that led researchers to develop the idea of mixing the water with the fuel in an emulsion to help decrease the amount of water coming into contact with engine components and to provide for more thorough mixing of the water and fuel.

### 2. Micro-explosion phenomena

The reason behind the cooling effect of a fuel emulsion is a result of the micro-explosion phenomena. Micro-explosions, also called secondary evaporation, help to accelerate the evaporation of fuel droplets in emulsions and are strong enough to eject fragments of torn droplets several millimeters away from the spray boundary at high speeds, which can help to improve the air-fuel mixing.

Micro-explosions are extremely important in macro emulsions in which the emulsifier-encased water droplets are suspended within the fuel. On emerging from the injector into the combustion chamber, the lighter components quickly evaporate, breaking the fuel/water droplets into multiple smaller droplets. This effect is due to the fact that micro-explosions occur in what is commonly termed as an ‘eddy’, or a turbulent wave front. When one droplet of emulsified fuel explodes, then a pressure wave may induce all of the droplets within the same eddy to explode at once.

Ambient temperature has an important influence on the occurrence and the strength of the explosions. At an optimum temperature, the water droplets go to a superheated state and vaporize and explode at the same time (tearing up the droplet and expanding the spray volume). However, because of the strong intermolecular forces of water, if the temperature is not high enough, the water in the emulsion droplets will evaporate before being heated, resulting in no micro-explosion. Likewise, if the temperature is too high, some of the droplets explode immediately, and some droplets do not reach the superheated state as soon. Both of these situations can result in weaker explosions due to the fact that all of the explosions are not occurring simultaneously.

Droplet size is also of importance in micro-explosions. If the initial droplet size is too small, the available water in the fuel will tend to evaporate before the droplet reaches a superheated state. Thus, either no explosion will occur, or the explosion is too small to be observed.

### 3. Determination of amount of water to be used

Many studies not only looked at the effect of the addition of water to diesel engines, but also the effect based on the percentage of water added. As each study used different types of engines and performed the tests over various cycles, no conclusive ‘optimum’ percentage was found, however all studies did experience significant problems in performance and a decrease in emissions benefits (and in some cases, an emissions increase) when the water content was 50% or greater. It was theorized by scientists that did work on the impact of micro-explosions that emulsions with a larger concentration of water may actually lose more water, as a large concentration of water will significantly lower the surface temperature. The ambient temperature is therefore not high enough to produce many micro-explosions due to the surface tension of the water (which is greater due to the increase in water).

### 4. Modification of engines

Early studies suggested that to achieve emission reduction benefits and to reduce operational problems, significant engine modifications would be necessary before using emulsions. Specifically, adjustment of the injection timing for optimization of the engine performance might be necessary. Many believed that the power loss that resulted from the increased ignition delay negated the PM benefits that emulsions achieved. Further investigation into the use of water emulsions found that optimization of the water concentration, use of surfactants and additives, and high shear mixing were actually needed to achieve emissions benefits to make emulsions a less costly, simple alternative to hardware-based efforts to reduce emissions in existing diesel engines. Current emulsions may be dispensed directly into an engine (without the need for engine modifications) without sacrificing emissions performance.

### 5. Combinations of emulsions and aftertreatment

Many studies did work to look at the effect of using emulsions combined with other emission reduction technologies, such as exhaust gas recirculation (EGR), oxidation catalysts, and particulate traps. Use of emulsions with these technologies does not have a significant negative impact on emissions, and in many cases was found to result in lower emissions when employed simultaneously.

EGR is best when used at low to middle load ranges. When used alone, EGR has shown no significant impact on $NO_x$ emissions and can increase fuel consumption and particulates when employed at high loads. However, improvements in combustion and emissions benefits with the use of emulsified fuels occurs at high load operations. At these conditions, when EGR is used in conjunction with emulsified fuel, $NO_x$ is reduced and the increase in smoke and fuel consumption are suppressed. Compared to conventional fuel, emulsified fuel with EGR results in lower $NO_x$ concentrations regardless of temperature and engine loading.

In a London bus study[2] the exhaust emissions from an engine running with an ultra-low sulfur diesel fuel were compared to those of the engine with an oxidation catalyst, an oxidation catalyst with emulsified fuel, a particulate trap, and a particulate trap with emulsified fuel. It was found that emissions reductions for HC and $NO_x$ are slightly better when only the catalyst is used. However, reductions for all pollutants from the baseline fuel are observed when both the catalyst and emulsified fuel are used. Similarly, for emulsified fuel with a particulate trap, emission reductions were observed for all pollutants except CO.

## B. Problems related to emulsions

### 1. Engine corrosion

Early emulsions researchers did not have a complete understanding of the additives and conditions necessary to keep emulsified fuel from stratifying and there was a tendency for the water and fuel to separate within days of mixing. This led to problems with corrosion of engine parts as the water was able to come into direct contact with the engine. The increased density due to the addition of water also tended to break injector tips in spark ignition engines. Since this problem was associated primarily with the stability of emulsions, it has been addressed largely through advances in maintaining fuel storage stability.

### 2. Stability of fuel

Emulsions are not solutions of water and diesel fuel, but rather are suspensions of (in the case of PuriNOx) water droplets in fuel. Since water is more dense than diesel fuel, water droplets have a tendency to settle if the fuel is not agitated periodically. The process generally begins with agglomeration wherein water droplets collect into groups, followed by coalescence into larger droplets, and finally settling. The result is that the fuel becomes increasingly stratified, with a higher concentration of water in the bottom of a tank than at the top of the tank. This process will occur under any conditions and cannot be eliminated, but it can be slowed using a number of different approaches.

Emulsion stability can be improved by increasing the surfactant concentration, as surfactants resist the droplet tendency to coalesce. Droplet size is also an important component in improving emulsion stability. Smaller droplets settle slower which enhances stability. To achieve this, high shear mixing is needed to break larger droplets into smaller ones. Stability of the emulsion can also be improved by increasing the treat rate of the additive package and the level of anticreamer (which reduce the amount of oil separation and water separation, respectively). By taking samples at the top, middle and bottom of the fuel sample, some researchers found that after two months, there was a negligible amount of settling of the larger droplets.

Finally, fuel storage stability can be maintained by specifying the minimum interval within which the fuel must be agitated. Most emulsion producers include this type of condition on the viability of their products.

### 3. Power loss

The loss in engine power is usually proportional to the concentration of water in the emulsion, though some emulsion products such as PuriNOx claim a less than strictly proportional loss in engine power. Although the engine can be "repowered" to ensure that the same amount of hydrocarbon fuel reaches the combustion chamber as would be the case if no water was present, many applications of emulsions assume no such engine changes. In these cases, the engine is effectively derated, i.e. the peak rated power cannot be reached on the emulsified fuel. Under more typical conditions when the engine is operated below its rated power level, an operator would generally only notice that it required somewhat greater pressure on the accelerator to maintain the same level of vehicle performance.

In some experiments, emission reduction results from using water emulsions were compared with using the emulsion on the same engine that was repowered. The results showed that the further reductions in emissions due to repowering the engine were only 2-10% greater than without repowering[3]. In fact, data from one study[4] shows that there was actually a decrease in emission benefits when an engine was repowered. For this engine, emission benefits for NOx and PM were 1.6 percent and 2.2 percent greater when the fuel was used as fill-and-go (i.e. without repowering the engine).

## C. Emission impacts of emulsions

The addition of water to diesel fuel has been proven to significantly reduce $NO_x$ and PM emissions. These benefits have been observed both with and without modifications to the test engine. It was discovered that the effectiveness in lowering the peak combustion temperature is dependent on the engine timing and decreases as engine timing is advanced. Greater reductions in both PM and $NO_x$ can also be attained with the combined use of emulsions and aftertreatment technologies such as PM traps and oxidation catalysts.

### 1. $NO_x$

$NO_x$ emissions increase exponentially with the rise in combustion temperature. The evaporation of the water in the emulsified fuel helps to lower the peak combustion temperature, which impedes the formation of $NO_x$. Studies have found that, in emulsions of up to 50% water, $NO_x$ emission reductions have an approximate linear relationship with the percentage of water added to the fuel.

Some of the earliest studies found that $NO_x$ emissions increased when the engine was operated with low water content (10-20%) at idle and low engine speeds. However, under normal engine running conditions with emulsions that have been optimized, $NO_x$ emissions decrease.

The cooling effect that water has on combustion temperature may be more beneficial in terms of NOx reductions if the peak combustion chamber temperature is higher. This result stems from the fact that the relationship between combustion temperature and NOx formation is highly nonlinear, so that a fixed reduction in temperature will have a different impact on NOx for engines with different base combustion temperatures.

### 2. PM

It is often difficult for an emission reduction technology to reduce $NO_x$ without causing adverse effects on particulate emissions and fuel consumption. Water emulsions have been shown to eliminate the concern of the $NO_x$-PM tradeoff as benefits have been achieved for both $NO_x$ and particulates simultaneously.

The initial pre-mix burn period of the combustion cycle is fuel rich and leads to the formation of polycyclic aromatic hydrocarbons, or PAHs, precursors to soot/PM. Soot is formed from partially burned fuel products of this combustion. While the majority of the soot is burned with the fuel, this unburned portion becomes an exhaust emission- PM.

The introduction of water alters the quantities of fuel and air during the pre-mix period and acts as a source of oxygen, thus making it a less fuel rich environment and allowing for less soot to be oxidized and left as a pollutant. Reductions in particulate emissions tend to be on the order of two to three times the amount of water added to the fuel.

An early study on water emulsions found that engine timing does not have an effect on the kinetic chemical changes that result from the water, and thus advancing the timing will not have a significant effect on PM reduction unless the timing is severely advanced (at which time the engine may have severe performance problems). However, later studies have found that the ignition delay with the use of emulsified fuels tends to be 2-5 degrees longer than with conventional diesel fuel, which results in enhanced combustion. More complete combustion leads to less products of fuel left in the engine that can form into pollutants.

Previous concerns with water emulsions dealt mainly with the loss in engine power. Many felt that this was the reason behind the reductions in PM, however a study performed on a UK mining drill rig found that the impact on PM is not simply the result of the loss in power[5]. One study[6] looked specifically at the chemical impact that the water had on in-cylinder soot formation. A single cylinder engine derived from a six-cylinder heavy duty diesel engine was used in the study. Using this engine, the in-cylinder temperature was reduced to match the heat release curve of that of a 10% emulsified fuel and results were then compared with those of an engine running on conventional diesel fuel at a decreased temperature. The study reported a greater decrease in soot formation in the pre-mix portion of combustion and throughout the entire combustion cycle. This result indicated that the inclusion of water chemically alters combustion and inhibits soot formation.

### 3. Other pollutants

For the majority of the work that was performed with regard to water emulsions only $NO_x$ and PM were the pollutants of concern. Some more recent studies made efforts to look at other pollutants such as CO and HC. A general trend that was found in many of these studies is that CO and HC tended to increase with the use of emulsified fuels. However, some studies also noted that while HC did increase, the total ozone precursors ($HC+NO_x$) decreased. Also, even significant increases in HC on a percentage basis often did not result in an exceedence of the engine certification standard. The only work that actually showed a decrease in HC emissions was a study of PuriNOx performed on a London bus in conditions when the emulsified fuel was used in conjunction with an oxidation catalyst or a particulate trap.

# V. Analysis of PuriNOx emissions data

PuriNOx is the Lubrizol Corporation's commercially available diesel-water emulsion. The summer version of the fuel which is the focus of our analysis is comprised of approximately 20% water and small amounts of a proprietary additive package that includes the emulsifier as well as other additives that assist in storage stability, cold weather operability, etc. PuriNOx is intended to be primarily a 'fill-and-go' technology, meaning that engine modifications are not required or even encouraged. Thus no data on repowered engines was included in our analysis. As described in Section III, we also excluded data collected on chassis, in-use emission monitors, and alternative versions of PuriNOx having different concentrations of water. Steady-state emissions data for PM and CO was also excluded for both highway and nonroad engines.

This Section summarizes our review of the available engine data on PuriNOx. We first present a summary of the engines tested, the test conditions, and the statistical significance of the results. We then present a more in-depth analysis of the NOx effects, since the effects of emulsions on NOx emissions has been studied extensively in the past. Section VI presents a methodology for applying the estimated emissions effects for PuriNOx to the in-use fleet. Comments are requested on all aspects of our analysis.

## A. Summary of available data on PuriNOx

There were a total of thirteen engines tested on PuriNOx which met our analytical requirements. Some of these engines were tested in multiple conditions, e.g. with and without an oxidation catalyst, with two different lubricant oils, or on two different test cycles. Each of these unique operating conditions was identified as a unique engine in our database. Each engine and the number of PuriNOx observations made is shown in Table V.A-1.

Table V.A-1
Engines tested on PuriNOx

| ID | Engine | Use | Group[β] | Test cycle | PuriNOx observations |
|---|---|---|---|---|---|
| H-a | '96 DDC Series 50 w/ catalyst | Highway | HH | FTP | 3 |
| H-b1 | '99 DDC Series 60, lube oil #1 | Highway | HH | FTP | 3 |
| H-b2 | '99 DDC Series 60, lube oil #2 | Highway | HH | FTP | 3 |
| H-c1 | '91 DDC Series 60, lube oil #1[α] | Highway | HH | FTP | 21 |
| H-c2 | '91 DDC Series 60, lube oil #2 | Highway | HH | FTP | 3 |
| H-d | '00 DDC Series 50 w/ EGR | Highway | EGR | 8 mode | 2 |
| H-e | '94 Caterpillar 3176 | Highway | HH | 8 mode | 1 |
| H-f | '01 Cummins5.9L | Highway | MH | FTP | 1 |
| N-a1 | '99 Perkins 1004.4T on high sulfur | Nonroad | 0 - 100 hp | Euro trans | 3 |
| N-a2 | '99 Perkins 1004.4T on low sulfur | Nonroad | 0 - 100 hp | Euro trans | 3 |
| N-a3 | '99 Perkins 1004.4T on high sulfur | Nonroad | 0 - 100 hp | 8 mode | 3 |
| N-a4 | '99 Perkins 1004.4T on low sulfur | Nonroad | 0 - 100 hp | 8 mode | 3 |
| N-b1 | '95 DDC 6V92 w/ catalyst | Nonroad | 175-300 hp | 8 mode | 1 |
| N-b2 | '95 DDC 6V92 | Nonroad | 175-300 hp | 8 mode | 1 |
| N-c | '00 Caterpillar 3508 | Nonroad | 300+ hp | 8 mode | 1 |
| N-d | '90 Caterpillar 3306 | Nonroad | 175-300 hp | 8 mode | 1 |
| N-e | '96 Caterpillar 3406B | Nonroad | 300+ hp | 8 mode | 1 |
| N-f | '85 Deutz F8L413 | Nonroad | 175-300 hp | 4 mode | 1 |
| N-g | '96 Deutz F6L912 | Nonroad | 100-175 hp | 8 mode | 1 |

[α] For all test programs in this table, the base fuel was used both as a reference fuel and also to produce PuriNOx. For engine H-c1, the base fuel met the California specifications for highway diesel fuel while the fuel used to produce PuriNOx was a commercial California diesel fuel. This disparity is expected to result in a more conservative estimate of emission benefits.

[β] "Group" is a weight class for highway engines and a horsepower group for nonroad engines, consistent with the fuels testing protocol. See Section VI for details. LH = light-heavy, MH - medium-heavy, HH = heavy-heavy, EGR = exhaust gas recirculation

The data collected on engine H-c1 was generated under the auspices of the emissions verification protocol established by the California Air Resources Board. This "Interim Procedure for Verification of Emission Reductions for Alternative Diesel Fuels" required that the fuel used as a baseline should meet CARB's specifications for diesel fuel sold in California, including a 10 vol% cap on aromatics content. The conventional diesel fuel used to make PuriNOx, however, was required to be a commercial diesel fuel. Thus the fuel used to establish a baseline was different than the fuel used to produce PuriNOx. Although for our analysis we only considered data for which the baseline fuel was the same as the fuel used to make PuriNOx, the approach taken by CARB was thought to result in a more conservative estimate of the emission benefits of alternative diesel fuels tested under their protocol. We therefore chose to leave this substantial amount of data in our database.

Lubrizol also collected baseline data on the commercial diesel fuel that was actually used to make PuriNOx. Only two emission measurements were made with this commercial diesel fuel, and this data was not included in the CARB verification nor in our analysis. However, this data does provide a more direct comparison of PuriNOx with conventional diesel fuel. It may, therefore, be appropriate to replace the 21 measurements on the CARB specification fuel with the two measurements on the commercial diesel fuel. Doing so would reduce the amount of data available for our analysis, but may provide a more apples-to-apples comparison of the emission effects of PuriNOx. We welcome comment on this alternative approach.

The emissions measurements on PuriNOx for the engines listed in Table V.A-1 showed a reduction in NOx and PM in every single case, and an increase in HC in almost every single case. CO effects of PuriNOx were less consistent. Figures V.A-1 through V.A-4 show the measured emission impacts of PuriNOx for every engine.

Figure V.A-1
Impact of PuriNOx:  NOx emission reductions with 90% confidence intervals

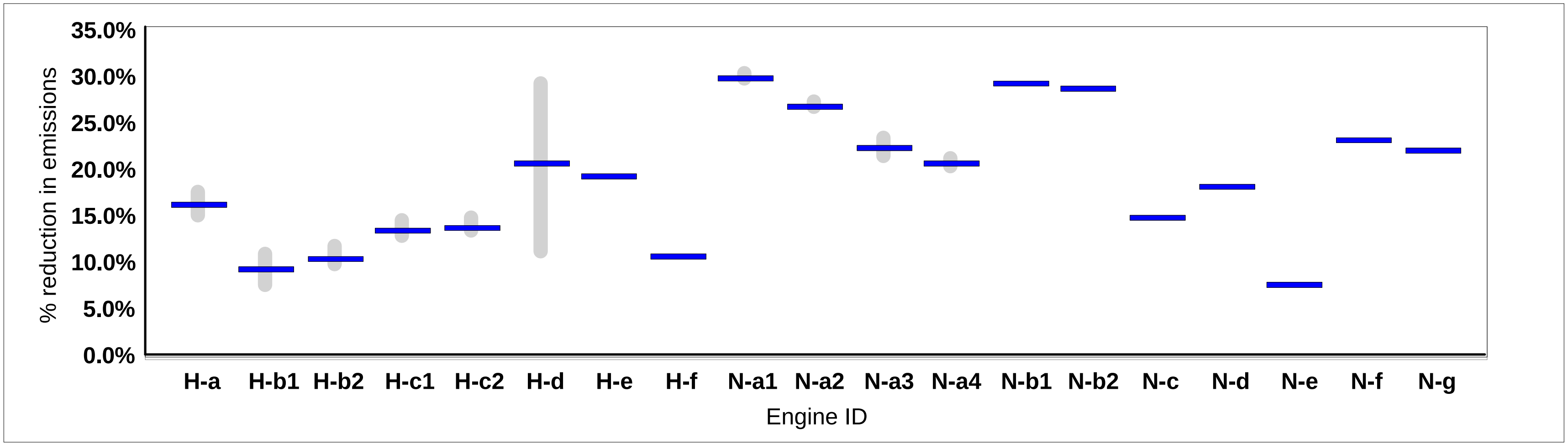


Figure V.A-2
Impact of PuriNOx:  PM emission reductions with 90% confidence intervals

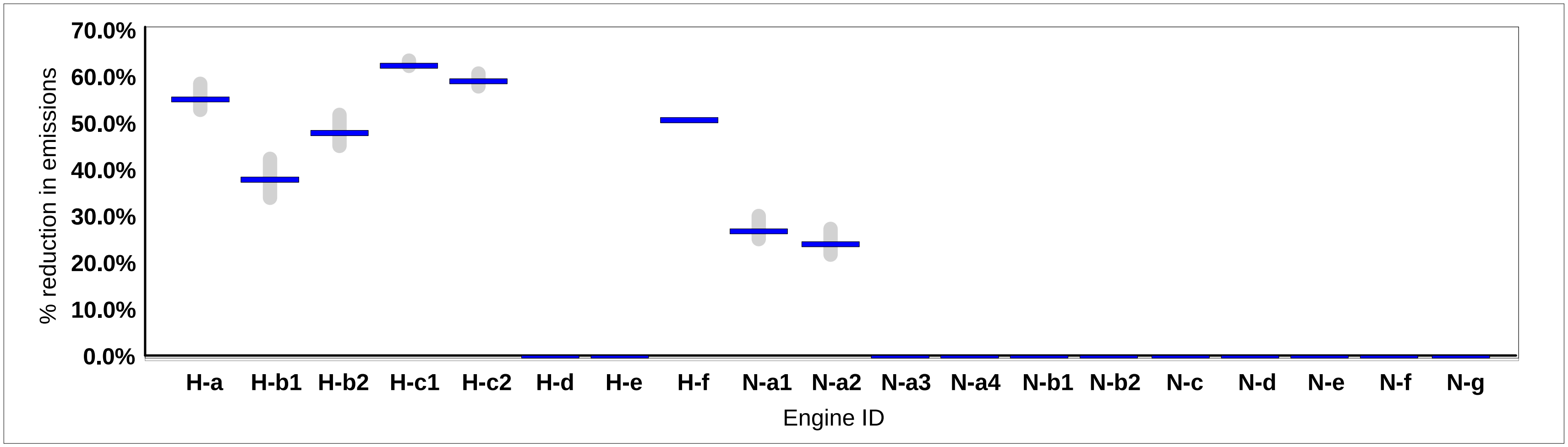


Figure V.A-3
Impact of PuriNOx: HC emission reductions with 90% confidence intervals

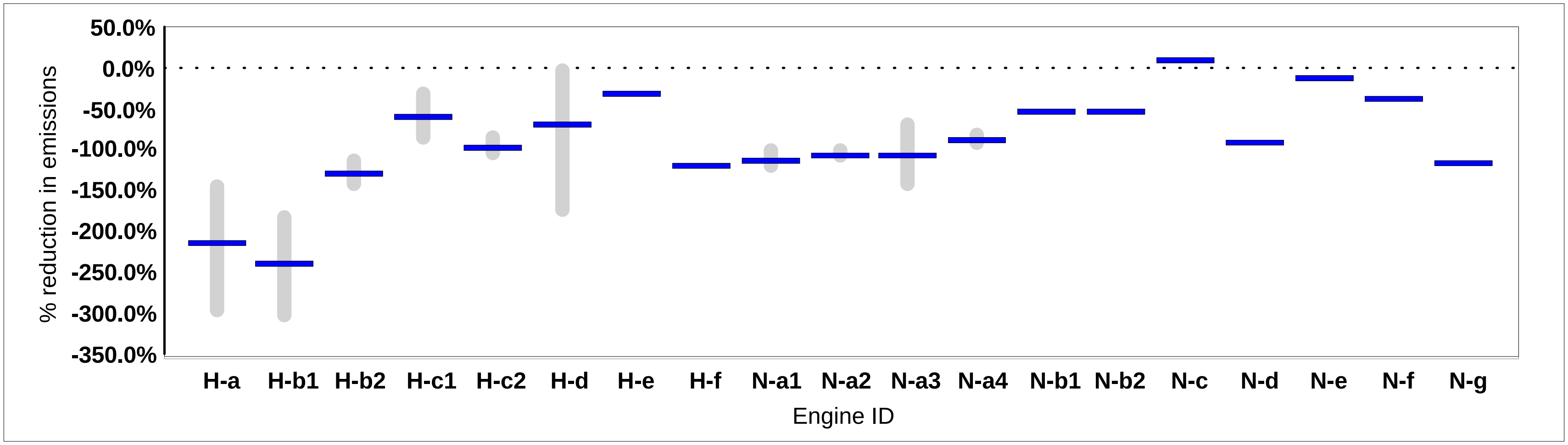
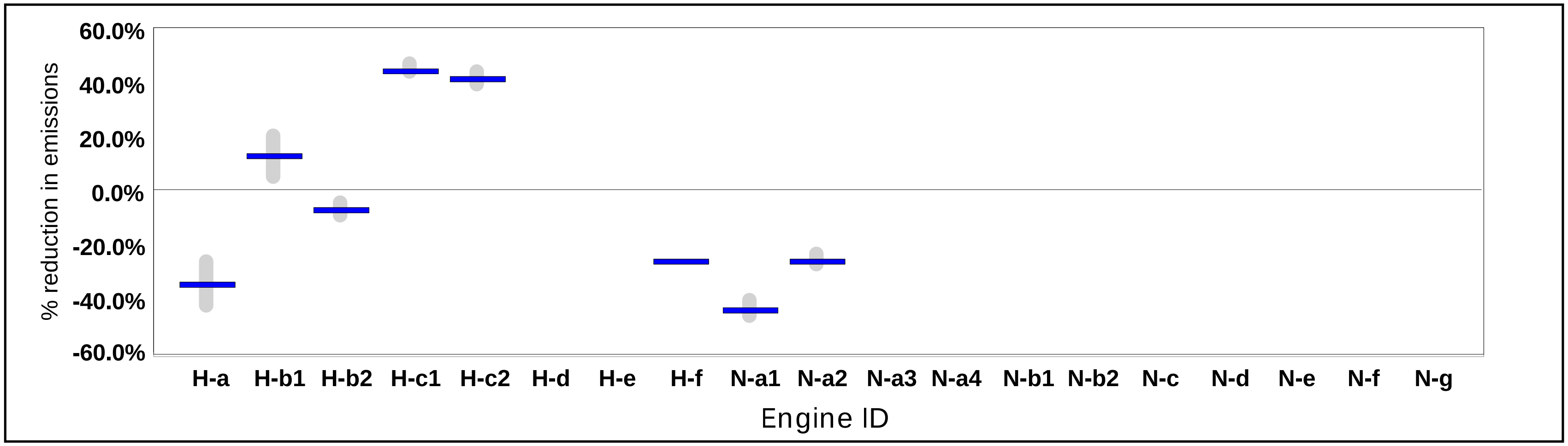


Figure V.A-4
Impact of PuriNOx: CO emission reductions with 90% confidence intervals



We conducted t-tests to determine if emission effects for highway engines could be considered to be different than those for nonroad engines. For NOx, PM, and HC, highway and nonroad were indeed distinguishable. We therefore calculated the average emission effects separately for highway and nonroad for these three pollutants. To do this, we used a least-squares regression of the following form:

$$\ln(\text{emissions}) = a \times \text{PURINOX} + \sum(b_i \times \text{ENG}_i)$$

where

ln(emissions) = Natural log of NOx, PM, HC, or CO in g/bhp-hr
PURINOX = Categorical independent variable; 1 for PuriNOx and 0 for base fuel
$\text{ENG}_i$ = Categorical independent variable; 1 for engine i and 0 for all other engines
$a$ = Regression coefficient representing the effect of PuriNOx
$b_i$ = Regression coefficient representing the effect of engine i

The average percent reduction in emissions can then be calculated for all engines from:

$$\% \text{ reduction in emissions} = [1 - \exp(a)] \times 100\%$$

We used this least-squares approach rather than simply weighting the engine-specific average emission effects by the number of observations because this latter approach would not have permitted us to assess statistical significance. Results are given in Table V.A-2.

Table V.A-2
Average % reduction for all engines

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

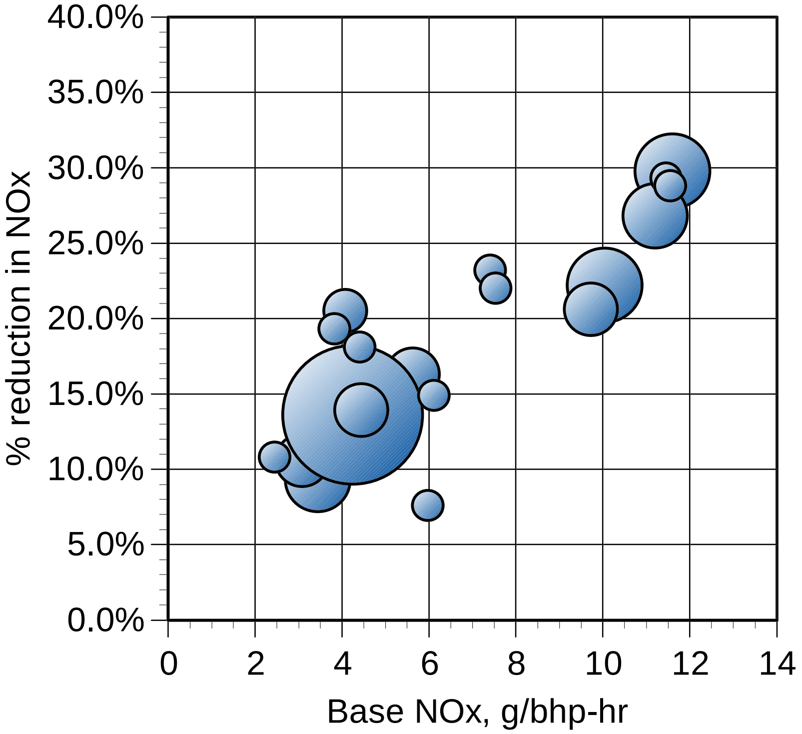
[α] CO calculation was done with highway and nonroad data together. Results are shown to be identical for highway and nonroad.

As can be seen in Table V.A-2, all emission impact estimates are highly significant. Given the variety and number of engines tested, these results suggest that PuriNOx will produce significant reductions in NOx and PM for the in-use fleet.

## B. Analysis of NOx effects

We also investigated an alternative approach to estimating the effect that PuriNOx has on NOx emissions. Based on previous research on emulsions and our understanding of the cooling effect that water has on combustion temperatures, we hypothesized that PuriNOx would have a bigger impact on NOx emissions when combustion temperatures were high and a smaller impact on NOx when combustion temperatures were low. Since combustion temperature is correlated with NOx emissions, we plotted the average % reduction in NOx for each engine with that engine's average base fuel NOx emissions. We included both highway and nonroad data in this analysis. The results are shown in Figure V.B-1. Each "bubble" represents the average effect of PuriNOx on a single engine, and the size of each bubble is proportional to the amount of data collected on that engine.

Figure V.B-1
Bubble plot of engine-by-engine PuriNOx effects on NOx



From this graph it appears that the effects of PuriNOx on NOx emissions are in fact correlated with the base fuel NOx emissions. This correlation provides some explanation for why highway and nonroad NOx effects are so dramatically different (13.7% versus 24.4% as shown in Table V.A-2). Highway engines are subject to more stringent controls than nonroad engines, and as a result have lower NOx emission rates.

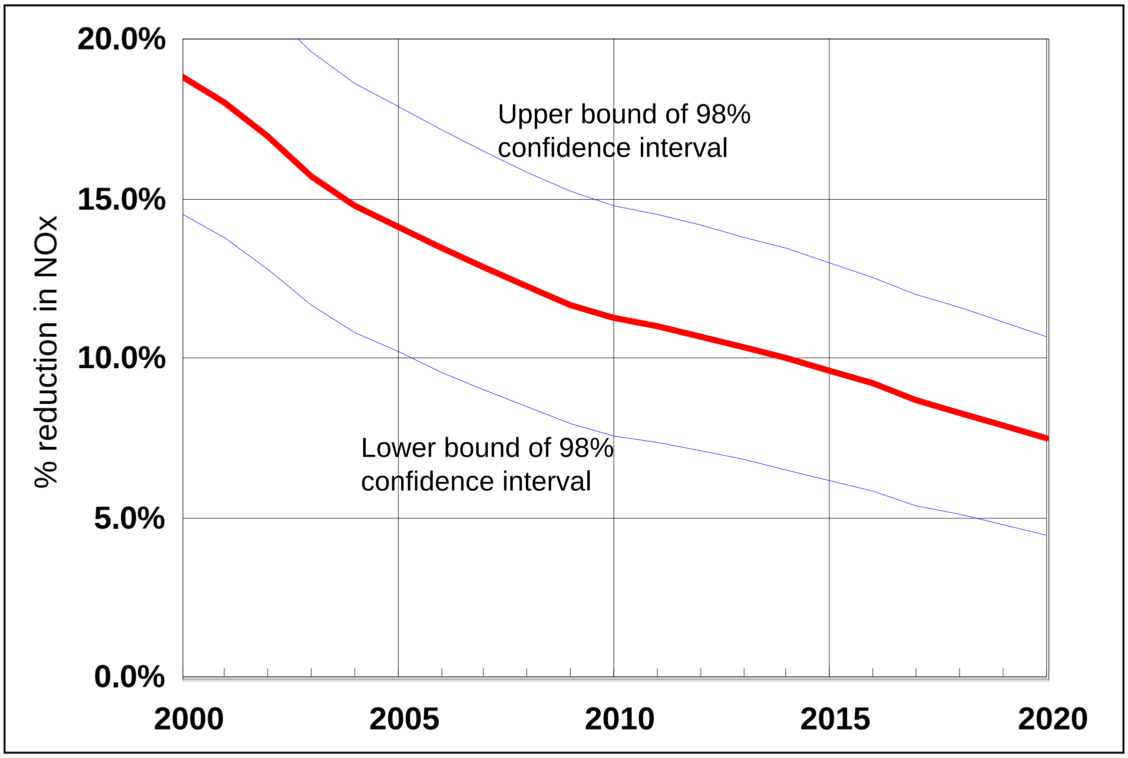
We generated a correlation between percent reduction in NOx due to the use of PuriNOx and base NOx emissions using least-squares regression analysis. This regression produced the following equation:

$$\% \text{ reduction in NOx} = [1 - \exp(-0.01052 - 0.03358 \times \text{base NOx})] \times 100\%$$

where "base NOx" represents the average NOx emissions in g/bhp-hr when the engine is operated on conventional diesel fuel. This equation can be used to represent both highway and nonroad engines, since the regression equation was based on all engines in the database and because it appears to explain most of the differences between highway and nonroad effects of PuriNOx on NOx.

We can use the above correlation to predict the impact that PuriNOx would have on NOx for the in-use fleet. This calculation requires that we predict the impact of PuriNOx on the heavy-duty highway (or nonroad) NOx inventory in each calender year using the model-year specific NOx emissions. Since NOx standards have been decreasing over time, the fleet-wide impact of PuriNOx would as well. This trend is shown in Figures V.B-2 and V.B-3 for highway and nonroad engines, respectively. These graphs also include estimated 98% confidence intervals[a].

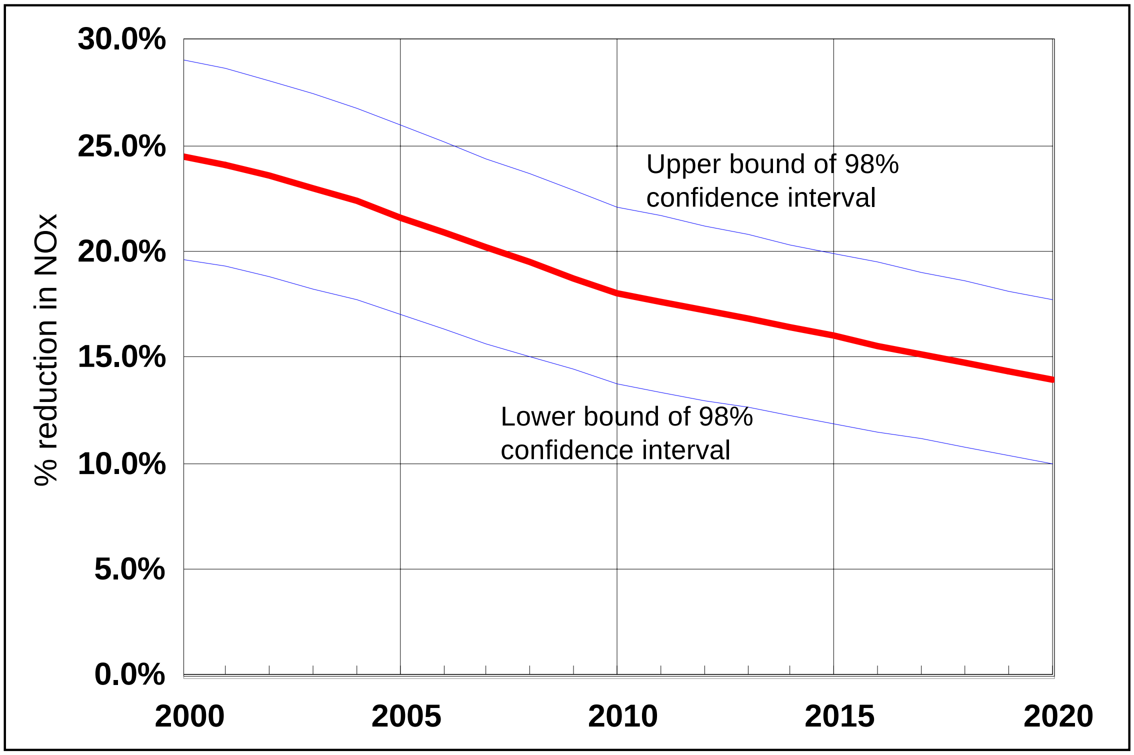
Figure V.B-2
Predicted NOx impact of PuriNOx for in-use heavy-duty highway fleet



---

[a] The upper and lower bounds actually represent prediction intervals rather than confidence intervals. Whereas confidence intervals encompass the true population mean, prediction intervals encompass additional, single measurements. As such, prediction intervals are wider than confidence intervals. The utility of the prediction interval is described in more detail in Section VI.

Figure V.B-3
Predicted NOx impact of PuriNOx for in-use heavy-duty nonroad fleet



For the purpose of accounting for the use of PuriNOx in a SIP, one would need to use NOx benefit estimates representing the calender year in which attainment was being modeled in the SIP. For many SIPs this is 2007. Table V.B-1 compares the predicted 2007 NOx benefits of PuriNOx based on the regression lines shown in Figures V.B-2 and V.B-3 with the average values presented in Table V.A-2.

Table V.B-1
Comparison of % reduction in NOx via two alternative approaches

| | Simple average (Table V.A-2) | Predicted 2007 benefit based on correlation with base NOx |
|---|---|---|
| *Highway engines* | | |
| Average | 13.7 | 12.9 |
| Low end of 98% confidence interval | 12.7 | 9.0 |
| High end of 98% confidence interval | 14.8 | 16.5 |
| *Nonroad engines* | | |
| Average | 24.4 | 20.2 |
| Low end of 98% confidence interval | 22.3 | 15.7 |
| High end of 98% confidence interval | 26.3 | 24.4 |

# VI. Estimating emission impacts of PuriNOx for the in-use fleet

As described in Section III, the fuels testing protocol under which alleged emission benefits of fuels or additives can be verified was not available during the time that EPA was assessing the emission benefits of PuriNOx. We therefore decided not to require Lubrizol to wait to submit an application under the fuels testing protocol.

However, an analytical approach to estimating PuriNOx emission impacts that maintains some level of conceptual similarity to the protocol might be prudent. To this end we have compared the available PuriNOx data to the protocol's requirements for minimum number of engines, minimum number of observations, and engine groupings. In this Section we first present these elements of the fuels testing protocol and show how the existing PuriNOx data compares. We then present a methodology for discounting the estimated emission impacts of PuriNOx for use in SIPs.

## A. Comparison of PuriNOx data to protocol requirements

The fuels testing protocol requires that data be collected on engines falling into several groups. For highway engines, these groups are defined by weight class, with an additional group for engines equipped with exhaust gas recirculation (EGR). For nonroad engines these groups are defined by horsepower. Table V.A-1 identified the engine group assignments for every engine tested on PuriNOx. We have estimated the average emission effects of PuriNOx for each of these groups using the least-squares regression approach described in Section V.A. For NOx, rather than use the simple average effects for each engine group, we have applied the predicted 2007 highway and nonroad effects shown in Table V.B-1 to each engine group, since these benefit estimates represent our best understanding of how PuriNOx affects NOx. The results are shown in Table VI.A-1.

Table VI.A-1
PuriNOx emission impacts by protocol group

| | % reduction due to the use of PuriNOx | | | |
|---|---|---|---|---|
| | NOx | PM | HC | CO |
| *Highway engines* | | | | |
| Light-heavy duty | 12.9 | n/a | n/a | n/a |
| Medium-heavy duty | 12.9 | 51.1 | -116.7 | -25.2 |
| Heavy-heavy-duty | 12.9 | 58.2 | -87.8 | 33.3 |
| EGR-equipped | 12.9 | n/a | -63.6 | n/a |
| *Nonroad engines* | | | | |
| 0 - 100 hp | 20.2 | 26.1 | -99.2 | -34.7 |
| 100 - 175 hp | 20.2 | n/a | -111.1 | n/a |
| 175 - 300 hp | 20.2 | n/a | -53.7 | n/a |
| 300 + hp | 20.2 | n/a | 0.0 | n/a |

Under the requirements of the protocol, emission effects of a given fuel/additive for each engine group such as those in Table VI.A-1 would be applied to the inventory associated with that group in the context of a SIP. However, the protocol also requires a minimum number of engines and minimum number of emission measurements for every group, and the existing PuriNOx data does not meet these requirements in every case. A summary of these protocol requirements and the degree to which the existing PuriNOx data fulfills these requirements is given in Tables VI.A-2 and VI.A-3.

Table VI.A-2
Number of engines tested

| | Protocol requirements | NOx | PM | HC | CO |
|---|---|---|---|---|---|
| *Highway engines* | | | | | |
| Light-heavy | 1 | 0 (0%) | 0 (0%) | 0 (0%) | 0 (0%) |
| Medium-heavy | 2 | 1 (50%) | 1 (50%) | 1 (50%) | 1 (50%) |
| Heavy-heavy | 2 | 4 (100%) | 3 (100%) | 4 (100%) | 3 (100%) |
| EGR | 2 | 1 (50%) | 0 (0%) | 1 (50%) | 0 (0%) |
| *Nonroad engines* | | | | | |
| 0 - 100 hp | 2 | 1 (50%) | 1 (50%) | 1 (50%) | 1 (50%) |
| 100 - 175 hp | 2 | 1 (50%) | 0 (0%) | 1 (50%) | 0 (0%) |
| 175 - 300 hp | 2 | 3 (100%) | 0 (0%) | 3 (100%) | 0 (0%) |
| 300 + hp | 1 | 2 (100%) | 0 (0%) | 2 (100%) | 0 (0%) |

Table VI.A-3
Number of emission measurements[α]

| | Protocol requirements | NOx | PM | HC | CO |
|---|---|---|---|---|---|
| *Highway engines* | | | | | |
| Light-heavy | 12 | 0 (0%) | 0 (0%) | 0 (0%) | 0 (0%) |
| Medium-heavy | 24 | 2 (8%) | 2 (8%) | 2 (8%) | 2 (8%) |
| Heavy-heavy | 24 | 71 (100%) | 69 (100%) | 71 (100%) | 69 (100%) |
| EGR | 24 | 4 (17%) | 0 (0%) | 4 (17%) | 0 (0%) |
| *Nonroad engines* | | | | | |
| 0 - 100 hp | 24 | 39 (100%) | 21 (88%) | 39 (100%) | 21 (88%) |
| 100 - 175 hp | 24 | 2 (8%) | 0 (0%) | 2 (8%) | 0 (0%) |
| 175 - 300 hp | 24 | 8 (33%) | 0 (0%) | 8 (33%) | 0 (0%) |
| 300 + hp | 12 | 4 (33%) | 0 (0%) | 4 (33%) | 0 (0%) |

[α] An emission measurement is here defined as one test of a single fuel on a single engine. Two such tests, one on base fuel and another on PuriNOx, are therefore required to provide a single estimate of % change in emissions

Based on the above comparison between the protocol requirements and the existing PuriNOx data, we can recommend additional testing that Lubrizol could conduct. For instance, there is no data on light-heavy-duty highway engines. There is also very little data on medium-heavy-duty highway, EGR-equipped highway, and nonroad engines falling in the 100 - 175 hp group. Additional data from these four groups would go a long way towards rounding out the existing database. Given the more pronounced lack of data for PM and CO (due to the fact that we disregarded any PM or CO measurements taken on steady-state test cycles), it might be prudent to take more than the minimum number of emission measurements for any additional engines that are tested on PuriNOx.

## B. Discounted emission effects for use in SIPs

Although the existing PuriNOx data would not be sufficient were Lubrizol required to meet all the requirements of the protocol, we believe that it can still be used to estimate emission impacts of PuriNOx for SIP purposes for several reasons:

1. Emulsions have been studied for several decades and the combustion mechanisms involved in NOx reductions are largely understood
2. Every single NOx and PM measurement on PuriNOx showed a benefit
3. Chassis and in-use monitor data that we excluded from our analysis supports the average effects shown in Table V.A-2.

However, when estimating the emission impacts of PuriNOx for SIP purposes, it may be prudent to take into account the fact that the existing PuriNOx data does not meet all the requirements of the protocol as shown in Tables VI.A-2 and VI.A-3. We have developed a methodology for estimating the fleet-wide emission impacts of PuriNOx in a conservative fashion that "discounts" the existing data based on the comparisons shown in Tables VI.A-2 and VI.A-3. Our proposed approach permits the average emission effects presented in Table VI.A-1 to be applied to the in-use fleet only to the degree that the existing PuriNOx data meets the minimum engine and emission measurement requirements of the protocol. Any "missing" engines or emission measurements would then be assigned the low end of the confidence limit as calculated in Section V. For each pollutant and engine group, this approach can be represented mathematically as:

$$\begin{aligned}\text{\% reduction in emissions}\\ \text{for use in SIPs} &= (\text{discount factor})_{ij} \times (\text{ave \% reduction})_{ij}\\ &\quad + (1 - \text{discount factor})_{ij} \times (\text{LCF \% reduction})_{ij}\end{aligned}$$

where

(discount factor)$_{ij}$ = Discount factor for pollutant i and engine group j, derived below
(ave % reduction)$_{ij}$ = Average % reduction in emissions for pollutant i and engine group j from Table VI.A-1
(LCF % reduction)$_{ij}$ = Low end of confidence limit for % reduction for pollutant i and engine group j

We first calculated "discount factors" representing the degree to which the existing PuriNOx data met the requirements of the protocol. To do this, we averaged the % values in Tables VI.A-2 and VI.A-3 for each pollutant and engine group. The results are shown in Table VI.B-1.

Table VI.B-1
Discount factors

| | NOx | PM | HC | CO |
|---|---|---|---|---|
| *Highway engines* | | | | |
| Light-heavy | 0.0 | 0.0 | 0.0 | 0.0 |
| Medium-heavy | 0.3 | 0.3 | 0.3 | 0.3 |
| Heavy-heavy | 1.0 | 1.0 | 1.0 | 1.0 |
| EGR | 0.3 | 0.0 | 0.3 | 0.0 |
| *Nonroad engines* | | | | |
| 0 - 100 hp | 0.8 | 0.7 | 0.8 | 0.7 |
| 100 - 175 hp | 0.3 | 0.0 | 0.3 | 0.0 |
| 175 - 300 hp | 0.7 | 0.0 | 0.7 | 0.0 |
| 300 + hp | 0.7 | 0.0 | 0.7 | 0.0 |

We then identified the low end of the confidence limit for each pollutant. Since some engine groups (e.g. the medium-heavy highway engine) had only a single measurement of the effect of PuriNOx, we were unable to estimate a confidence interval for every pollutant and engine group. Instead, we used the 98% confidence intervals for PM, HC, and CO that had been estimated for highway and nonroad engines, and applied these values to all engine groups. These values were presented in Table V.A-2.

Given the additional analysis we presented in Section V.B on NOx emission effects of PuriNOx, we decided not to use the low end of the confidence interval for NOx as presented in Table V.A-2. Instead, we determined that more realistic lower limits for the in-use NOx benefits of PuriNOx would be based on the curves shown in Figures V.B-2 and V.B-3. These curves include a "prediction interval" which establishes the interval within which a single additional NOx emissions measurement would likely reside. The prediction interval is necessarily broader than a confidence interval, as the confidence interval establishes the interval within which the true population mean is likely to reside. Thus the lower end of the prediction interval provides a very conservative estimate of the NOx benefits of PuriNOx. For our purposes, we chose a calender year of 2007 since it is for this year that many nonattainment areas conduct their inventory analyses in support of efforts to reach attainment. The final set of values representing the low end of the confidence limit for use in calculating the in-use emissions impacts of PuriNOx are shown in Table VI.B-2.

Table VI.B-2
Low end of confidence limits (% reduction in emissions)

| | NOx | PM | HC | CO |
|---|---|---|---|---|
| Highway engines | 9.0 | 55.6 | -120.2 | 13.4 |
| Nonroad engines | 15.7 | 16.8 | -100.1 | 13.4 |

Finally, we combined the discount factors from Table VI.B-1, the average emission effect values from Table VI.A-1, and the low ends of the confidence limits from Table VI.B-2 to estimate the emission impacts of PuriNOx that we believe could appropriately be used in SIPs. The final values are given in Table VI.B-3. Note that for cases in which the lower end of the confidence limit would actually increase the estimated benefits of PuriNOx when combined with the average emission effects, we simply used the average effect for a more conservative estimate.

Table VI.B-3
Final emission impacts of PuriNOx (% reduction)

| | NOx | PM | HC | CO |
|---|---|---|---|---|
| *Highway engines* | | | | |
| Light-heavy | 9.0 | 55.6 | -120.2 | 13.4 |
| Medium-heavy | 10.2 | 51.1 | -119.1 | -25.2 |
| Heavy-heavy | 12.9 | 58.2 | -87.8 | 33.3 |
| EGR | 10.2 | 55.6 | -103.2 | 13.4 |
| *Nonroad engines* | | | | |
| 0 - 100 hp | 19.3 | 23.3 | -99.4 | -34.7 |
| 100 - 175 hp | 17.0 | 16.8 | -80.1 | 13.4 |
| 175 - 300 hp | 18.8 | 16.8 | -72.8 | 13.4 |
| 300 + hp | 20.2 | 16.8 | -30.0 | 13.4 |

In cases wherein the fleet mix is known, the emission impacts for each engine group given in Table VI.B-3 could be applied separately. If the fleet mix is not known, the values for each engine group may need to be weighted together according to some estimate of fleet distribution appropriate to the area where PuriNOx is being used.

Note that the values for CO in Table VI.B-3 do not indicate a consistent increase or decrease. This result is not surprising given that CO responses to PuriNOx from engine to engine as shown in Figure V.A-4 could be either positive or negative. However, the statistically significant overall CO benefit is heavily influenced by engine H-c1. One possible alternative approach to generating an estimate of CO effects of PuriNOx is to assume that the lower end of the confidence limit for CO is zero. Thus we request comment on assigning zero CO benefit for cases in which the existing PuriNOx data falls short of the protocol's requirements.

## References

1. "Generic Verification Protocol for Determination of Emissions Reductions Obtained By Use of Alternative or Reformulated Liquid Fuels, Fuel Additives, Fuel Emulsions, and Lubricants for Highway and Nonroad Use Diesel Engines and Light Duty Gasoline Engines," EPA Cooperative Agreement No. CR826152-01-03

2. Barnes, A., D. Duncan, J Marshall, A. Psaila, J. Chadderton, A. Eastlake, "Evaluation of Ester-Blended Fuels in a City Bus and an Assessment of Performance with Emission Control Devices", SAE Paper No. 2000-01-1915.

3. Ibid.

4. "Comparative Analysis of Vehicle Emission Using PuriNOx Fuel and Diesel Fuels", Air Improvement Resource, Inc., April 4, 2001.

5. Duncan, D.A., D.A. Langer, J.C. Marshall, "Emulsion fuels- improving the environment today", presentation at the SAE Conference, Vienna, Austria, April, 2001.

6. Ibid.