# Lubricant Basestock and Additive Effects on Diesel Engine Emissions

Shawn D. Whitacre, National Renewable Energy Laboratory
Hsing-Chuan Tsai and John Orban, Battelle Memorial Institute

## INTRODUCTION

The Advanced Petroleum Based Fuels – Diesel Emission Control (APBF-DEC) activity is a joint government/industry research effort studying the needs of future low-emission diesel engine systems. The previously completed Diesel Emission Control – Sulfur Effects (DECSE) project[1] quantified the impact of diesel fuel sulfur on the performance and short-term durability of diesel emission control devices [diesel oxidation catalysts (DOC), lean-$NO_x$ catalysts, $NO_x$ adsorber catalysts, and diesel particle filters]. Because some of these new technologies have demonstrated a sensitivity to fuel-borne sulfur, considerable research was conducted and regulations limiting the permissible levels of sulfur in diesel fuel were promulgated. However, the sensitivity of the devices is so extreme, and the durability requirements of heavy-duty commercial vehicles are so long, that a reduced fuel sulfur level may not be enough to guarantee the long-term performance of new emission control systems, if other sources of catalyst poisons are found to exist.

Diesel lubricant is known to be consumed during the normal operation of the engine in small but not insignificant quantities. While the quantities may be small, the sulfur content of lubricant oil is typically higher than that of fuel by an order of magnitude or more, elevating the level of concern accordingly. Other constituents of the lubricating oil, such as anti-wear additives, have been found to be a potential problem for gasoline systems and are expected to cause similar concerns for diesel exhaust systems.

To address this concern, a cooperative research project is underway to study lubricant formulation (basestocks and additives) effects on diesel emission control system performance and durability. The research is funded through Department of Energy's Office of FreedomCAR and Vehicle Technologies and leverages participation from the Engine Manufacturers Association (EMA), the Manufacturers of Emissions Control Association (MECA), as well as the American Petroleum Institute (API), National Petrochemical & Refiners Association (NPRA), the American Chemistry Council, and various California regulatory agencies. Four conventionally available lubricant basestocks were tested in combination with commercial and experimental lubricant additive systems. Experimental design ensured that the formulations tested would be the most useful for determining the realistic impact of lubricant oil formulation.

It is anticipated that the results of this study will be critical in defining the needs of future lubricant formulations for both light-duty and heavy-duty diesel engines. EPA's Tier II emission standards for passenger cars and light trucks will be phased in between 2004 and 2009. These fuel neutral standards necessitate the use of emission catalysts in order for diesel engines to comply. The heavy-duty emission standards that will go into effect in 2007 will be the first standards [for both particulate matter (PM) and nitrogen oxides ($NO_x$)] to require catalytic emission control systems. Also, in 2004 EPA will extend the requirement for emission control system (ECS) durability on heavy-duty engines to 435,000 miles, reiterating the need for engine fluids that do not hinder the performance of the emission control system over time.

Should a need for substantial lubricant reformulations be identified, industry would require significant development time to research "catalyst compatible" formulations that are cost-competitive and continue to deliver superior engine protection and long life that engine customers demand. In addition, engine manufacturers recognize that the lubricant reformulations may drive the need for more robust engine hardware that is tolerant of modified oil chemistry, an endeavor requiring significant development time as well.

## ENGINE AND TEST HARDWARE

A 1999 International T444E-HT engine was used in this study. The engine is direct-injected, electronically controlled, turbocharged and aftercooled, with a displacement of 7.3L in a V8 configuration with two valves per cylinder. It is equipped with a Siemens electronic control unit and hydraulically actuated electronic unit injectors. The engine produces 157 kW (210 hp) peak power at 2400 rpm and 680 Nm (500 ft $lb_f$) peak torque at 1500 rpm.

The base engine as provided meets the applicable EPA emission standards for 1999 on-highway certification (4.0 g/bhp hr $NO_x$ and 0.1 g/bhp hr PM). Additional retrofit hardware was installed to allow cooled exhaust gas recirculation (EGR) and closed crankcase ventilation (CCV). It is believed that such systems will be commonplace on engines meeting future regulations (EPA 2004 and 2007).

The EGR system is a high pressure loop configuration which routes exhaust gas from upstream of the turbo through a heat exchanger and into the intake, downstream of the compressor and intercooler. A valve installed on the outlet of the cooler allows modest control of EGR rate. In addition, exhaust backpressure control is used to drive EGR flow.

The CCV system redirects pressurized crankcase vapors to the pre-compressor intake stream. Because these vapors have the potential to condense on the walls of the intercooler and within the compressor, an impactor type CCV filter, provided by Fleetguard-Nelson, is installed. This particular filter is designed to remove nearly 100% of the oil droplets and up to 70% of the aerosol in the engine blowby. Collected oil is drained back into the engine sump.

Test fuel was stored in an underground 10,000-gallon tank. A 7-gallon reservoir tank was located in the test cell and received fuel from the primary tank. Fuel was drawn from the reservoir by the engine's fuel pump and sent through a Max Machinery Model 213 fuel meter where mass flow was determined. A custom-built fuel conditioner adjusted the temperature of the fuel to 100° F ±10° (CFR 86.341-79). A return line from the engine fed back into the reservoir, completing the fuel circuit.

## EMISSION MEASUREMENTS

Emissions were measured during four steady-state test modes from the OICA (13-mode) procedure. Figure 1 is a performance curve measured on the International T444E illustrating the four steady-state test conditions utilized. Each mode was run for 30 minutes to allow enough time for adequate sampling of PM and $SO_2$ emissions. The engine was allowed to stabilize at each mode before sampling was initiated. Before the start of an evaluation, the engine was triple flushed with the test oil to be evaluated. A 2-hour "break-in" was conducted and evaluations commenced. Each day's testing consisted of two evaluations, each consisting of four steady-state modes.

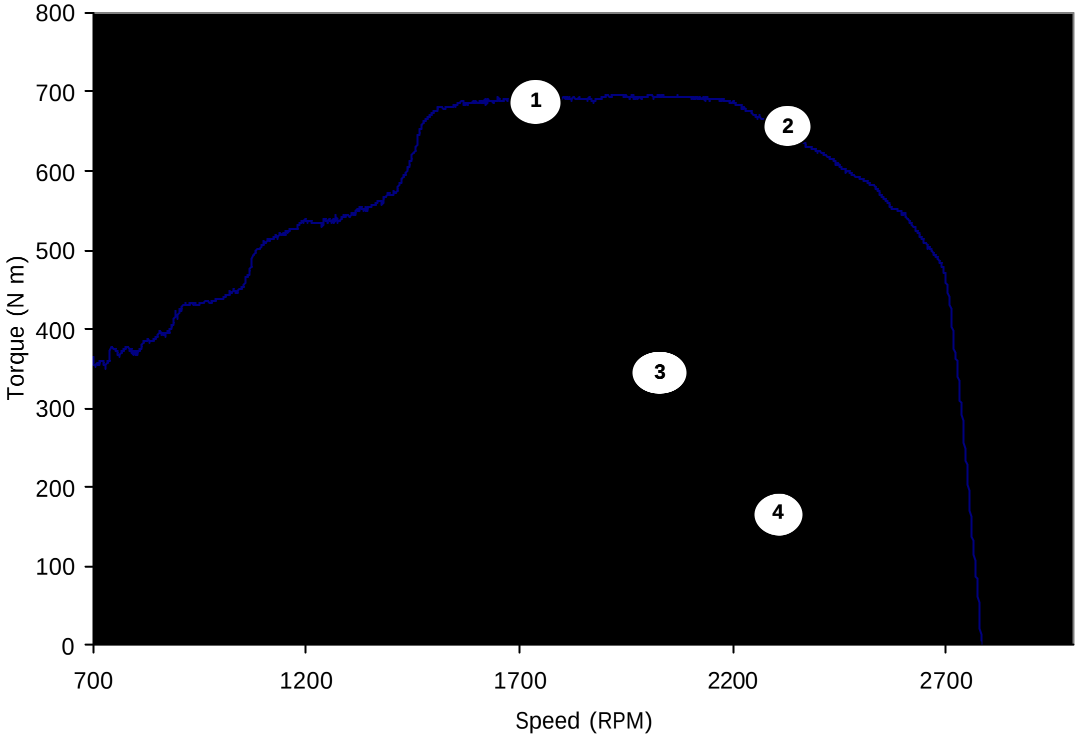


**Figure 1:** International T444E performance curve and steady-state emission test points.

During the 4-mode evaluation testing, exhaust from the engine was ducted into a 15" diameter dilution tunnel. The dilution tunnel flow rate was controlled by a critical flow venturi system (CVS) rated at 2700 standard cubic feet per minute (SCFM). Dilution air entering the tunnel was transported through four, 8 sq. ft. HEPA filters to remove background particulate matter. These filters are manufactured with blower fans attached to lower the pressure drop across them and to reduce the load on the tunnel blower system. The filters form a box attached to the entrance of the dilution tunnel.

Gaseous emissions were sampled in accordance with the Federal Register (CFR 86.1310-90) guidelines for measuring emissions from heavy-duty engines. $NO_x$ was measured via chemiluminescence using a Horiba Model CLA-220 heated $NO_x$ analyzer. Carbon monoxide

(CO) and carbon dioxide ($CO_2$) were measured with Non-Dispersive Infrared (NDIR) analyzers. Hydrocarbons (HC) were measured using a heated Flame Ionization Detector (FID).

Sulfur dioxide ($SO_2$) was measured via a wet chemistry technique modeled after EPA Methods 6, 8, and 16. In this method, dilute exhaust is sampled from the tunnel and is passed through a heated filter (to remove PM) and then through a set of impingers that are immersed in an ice bath. The impingers are filled with a 3% aqueous hydrogen peroxide solution. $SO_2$ in the dilute exhaust reacts with the impinging solution and is converted into a sulfate which can be detected post-analysis using an ion chromatograph. Because sampling during each test mode is integrated instead of measured in real-time, part-per-billion (ppb) sensitivity is possible with this technique.

Three separate PM filters were collected simultaneously during the four-mode steady-state evaluation cycle. Three PM sampling trains were installed: one with standard PM sampling filters (EMFAB TX40HI20WW – 70 mm), a second utilizing a separate sample filter (47 mm TEFLO - low metals background, high efficiency) for metals analysis, and a third, larger sampling train (using Pallflex T60A20 70 mm filters) for collecting sufficient quantities (>5mg) of PM for polycyclic aromatic hydrocarbon (PAH) analysis.

The main PM sampling system begins with a stainless steel sample probe with 0.333” diameter that collects a sample stream from the tunnel. This sample stream is then deposited into a secondary dilution tunnel where it is mixed with room air to reduce the temperature below $125^{o}$F as specified in the CFR. The secondary dilution tunnel consists of an enclosed section of 4” stainless steel pipe approximately 18” in length. The exit of the secondary dilution tunnel leads to the 47 and 70 mm filters for metals and PM measurement respectively. The system is designed to keep filter face velocities below 100 cm/s while providing enough dilution air to keep the filter face temperature below $125^{o}$F. The 47 mm filter alone is insufficient to meet these criteria, and so this system employs a parallel filter construction. A third sampling train (for PAH) operates on a separate secondary dilution tunnel. All PM samples were collected as a composite of the four test modes.

## TEST FLUIDS

The lubricants tested in this project included a variety of additive packages and basestocks. They were selected to span a range of important chemical and physical properties. All test oils used the same olefin co-polymer viscosity index improver, which was provided to each lubricant blender, dissolved in a light fraction of the same Group II base oil.

### *Additive Packages*

The additive companies participating in this project made available a number of commercial and experimental packages for selection. A statistical design was employed to select twelve packages that would adequately span the range of properties of interest, balance the contribution between additive suppliers, and temper any co-linearities that might exist between individual properties. For instance, zinc and phosphorous content are highly correlated due to the fact that they are typically present in the same additive molecule, zinc dithiophosphate (ZDTP). Of the twelve packages selected, six were down selected for testing in all of the available basestocks. The remaining six were only tested in the Group II basestock. In addition, a reference fluid containing a commercial additive package in Group II basestock was used.

Additive packages were given letter designations (A-L). The reference additive was labeled R. Table 1 summarizes the properties of the additive packages selected. It should be noted that these are solely the contributions from the additive package. Anything present in the basestock would be added to these totals in a finished formulation.

### *Basestocks*

Basestocks were selected from each of the four major base oil categories as defined by API. They span the commercially available offerings in terms of sulfur content, saturation, viscosity index, and volatility. Table 2 provides details of the basestocks tested. All twelve additive packages were blended in the Group II stock. Only the first six (A-F) were blended in all four basestocks. Finished lubricant formulations are defined by a letter and a number designating the additive package and the basestock (e.g. A2, C1).

### *Test Fuel*

All tests were conducted with the ultra-low sulfur (4.5-ppm S as measured at ATL) base fuel developed previously for the DECSE projects. An initial shipment of 6,000 gallons of fuel was delivered via tanker truck to the steam-cleaned underground tank in May 2001. This volume proved to be inadequate to meet the needs of the full program and a second delivery of 3,500 gallons was delivered in February, 2002. However, the second fuel batch possessed a lower sulfur content: ~0.5 ppm. When combined with the small volume of residual 4.5 ppm sulfur fuel, the new blend contained ~1.0 ppm sulfur. This fuel was used for all tests after March 10, 2002.

## EXPERIMENTAL DESIGN

The additive packages were selected to span the practical ranges of elemental composition and ash content and to balance contributions from the various suppliers. A principal component analysis was used to select packages that eliminate co-linearities (e.g. zinc vs. phosphorus) that could confound the analysis. The test matrix included a randomized test sequence within oil groups, and duplicate tests to test repeatability both within-day and day-to-day. The reference oil (R2) was tested periodically and the results were used to account for testing trends (like the fuel change). During selected reference oil tests, oil consumption was also measured for use in a mass balance analysis.

**TABLE 1:** Lubricant additive composition

| **Element** | **A** | **B** | **C** | **D** | **E** | **F** | **G** | **H** | **I** | **J** | **K** | **L** | **R** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ash Level (%) | 1.2 | 0 | 1.2 | 1.5 | 1.85 | 0.75 | 1.44 | 1.40 | 0.6 | 1.4 | 0.3 | 0.23 | 1.35 |
| S | 0 | 5 | 4950 | 4500 | 6590 | 2785 | 3246 | 2921 | 4226 | 2224 | 20 | 725 | 4454 |
| Ca | 3484 | 0 | 3950 | 800 | 4770 | 1820 | 3130 | 3130 | 1748 | 4128 | 870 | 415 | 3412 |
| Zn | 0 | 0 | 0 | 1900 | 1560 | 860 | 1319 | 865 | 0 | 0 | 0 | 225 | 1269 |
| N | 0 | 950 | 2000 | 1200 | 970 | 1286 | 1182 | 1137 | 0 | 1560 | 2235 | 1457 | 855 |
| P | 0 | 670 | 600 | 1700 | 1420 | 760 | 1201 | 788 | 0 | 0 | 0 | 587 | 1156 |
| B | 1099 | 0 | 0 | 300 | 150 | 60 | 1235 | 143 | 0 | 0 | 985 | 176 | 0 |
| Cl | 100 | 0 | <100 | 200 | 0 | 126 | 0 | 0 | 100 | 18 | 0 | 60 | 80 |
| Mo | 0 | 0 | 0 | 0 | 170 | 0 | 0 | 284 | 0 | 0 | 0 | 0 | 0 |
| Mg | 0 | 0 | <50 | 1700 | 0 | 0 | 277 | 277 | 0 | 0 | 0 | 0 | 0 |

All values in ppm, unless otherwise specified

**TABLE 2:** Lubricant basestock properties

| **API Group** | **Supplier** | **Refinery** | **Sulfur content (ppm)** | **% Saturates** | **Viscosity grade** |
|---|---|---|---|---|---|
| Group I | Valero | Paulsboro | 4800-5600 | 75 | 15W40 |
| Group II | Excel | Lake Charles | <20 | 99+ | 15W40 |
| Group III | Motiva | Port Arthur | <5 | 99+ | 10W40 |
| Group IV | BP | *Synthetic- PAO** | 0 | - | 5W40 |

*poly-alpha olefin

## TEST RESULTS

This report summarizes the results of 57 lubricant evaluations. An evaluation consists of back-to-back runs of the four mode steady state test sequence previously described. This total includes all repeat runs and periodic testing of the reference oil.

### *Oil consumption*

Because of the potential to influence lubricant derived emissions, the oil consumption rate was closely monitored throughout the project. Alternate reference evaluations included a 38-hour peak power aging sequence between tests. At each of these points, oil consumption was measured gravimetrically. Figure 2 shows the trend of the oil consumption rate over the duration of the project. Oil consumption remained constant (30 g/hr) for a majority of the early part of testing and dropped uniformly (22 g/hr) during the later tests. The 4-mode weighted oil consumption rate for this engine was determined to be 0.18 g/bhp hr.

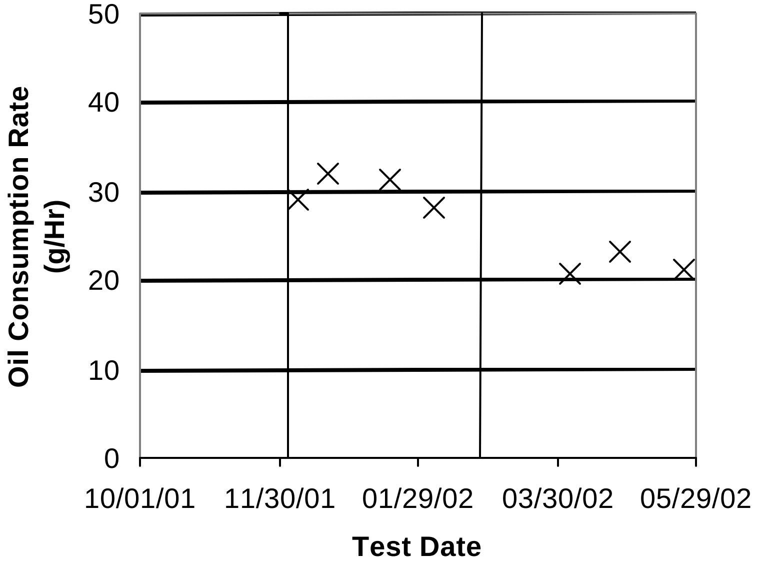


**Figure 2:** T444E oil consumption rate as a function of test date

*Emissions of regulated pollutants*

By and large, the emissions of the regulated gaseous pollutants were not significantly influenced by the lubricant formulation. This section will include a brief summary of those results. Four mode weighted emissions of HC, CO, and $NO_x$ are plotted in Figures 3-5. Lubricant formulation has modest effects on regulated emissions (? 10% for CO and $NO_x$, ? 20% for PM, and ? 30% for HC).

Total PM emissions are plotted in Figure 6 as a function of the lubricant additive package and the basestock. As was the case for the gaseous emissions, the total PM mass was not significantly effected by the additive package or the basestock. While the lack of effect was not surprising for the gaseous emissions, some effect on PM might have been expected. It has been suggested that such an effect may have been apparent under a different (transient) duty cycle than the modal steady-state tests run here.

*$SO_2$ emissions*

Lubricant derived sulfur emissions are under increased scrutiny because of their potential to impact catalyst performance. Specifically, the lubricant's contribution to total $SO_2$ emissions needs to be better understood because of its well documented tendency to significantly hinder $NO_x$ adsorber catalyst performance.[2] Speculating that lubricant derived $SO_2$ emissions could equal or outweigh those derived from ultra-low sulfur fuels (<15-ppm S), California is presently considering regulations to limit sulfur in the lube oils used in catalyst equipped engines.

Figure 7 illustrates the effect of lubricant formulation on emissions of $SO_2$. Because all tests were run with the same ultra-low sulfur fuel, any differences in these emissions were attributable to the lubricant. When reviewing these results, it is important to consider the additive and basestock properties listed in Tables 1 & 2. It is evident that each impacts $SO_2$ emissions, but the magnitude of the effects do not directly correlate with the difference in the test oil's sulfur content. A notable comparison is between oil formulations B2 and E1 which represent the lowest and highest sulfur containing formulations tested. The $SO_2$ emission rate is 3 times higher for the E1 formulation, though its total sulfur content of this oil is roughly 36 times that of the B2 formulation.

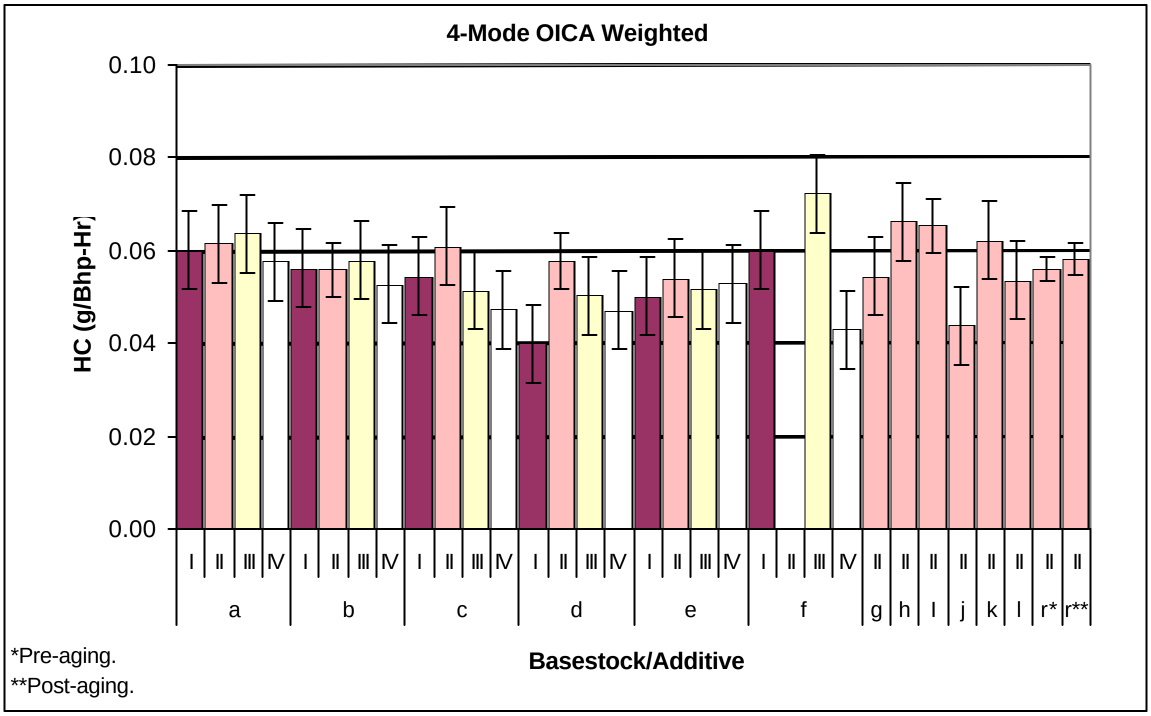


**Figure 3:** Weighted HC emissions as a function of oil formulation

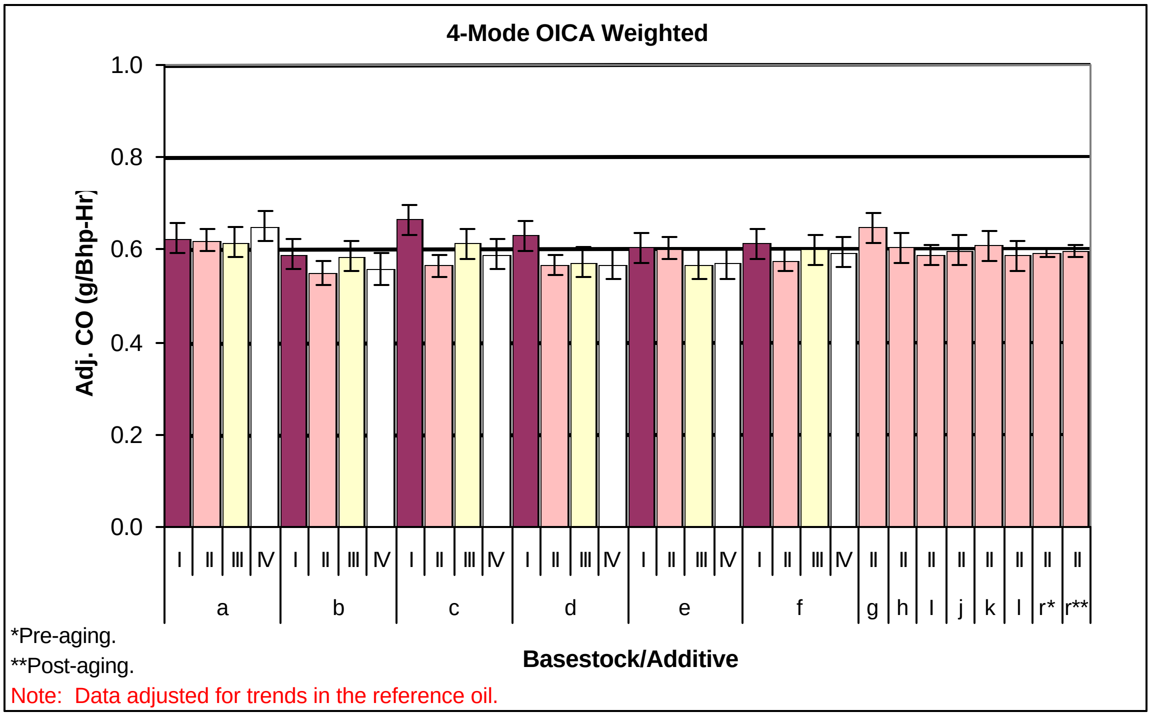


**Figure 4:** Weighted CO emissions as a function of oil formulation

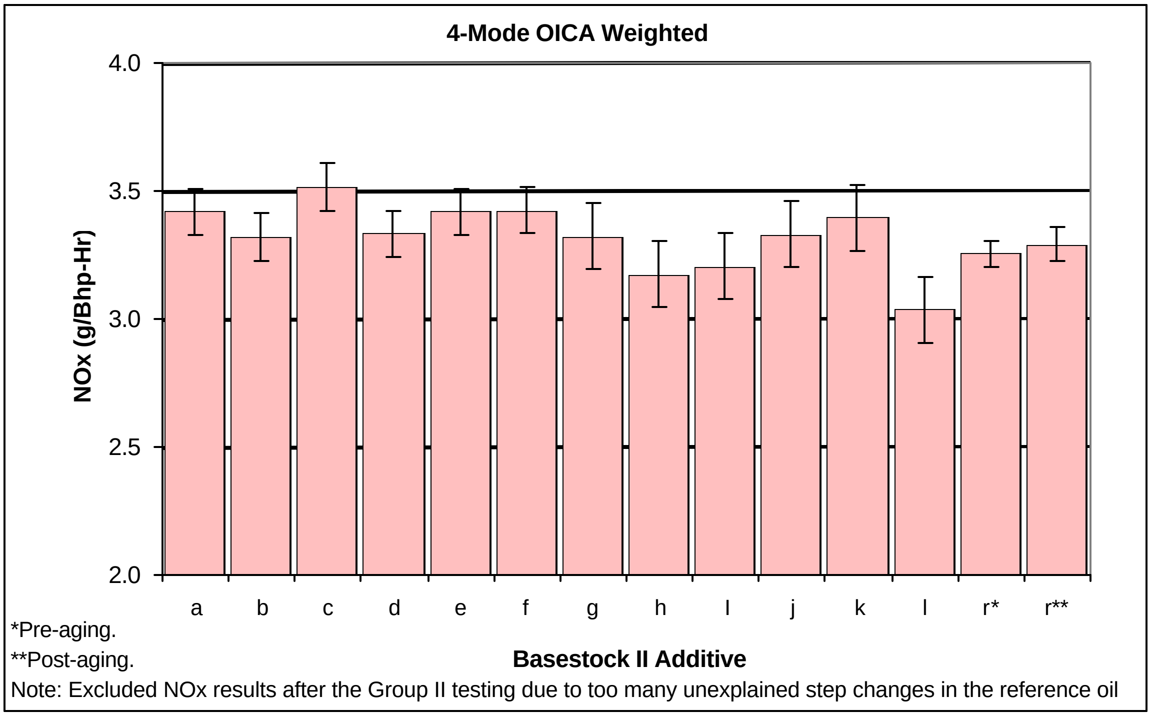


**Figure 5:** Weighted $NO_x$ emissions as a function of oil formulation

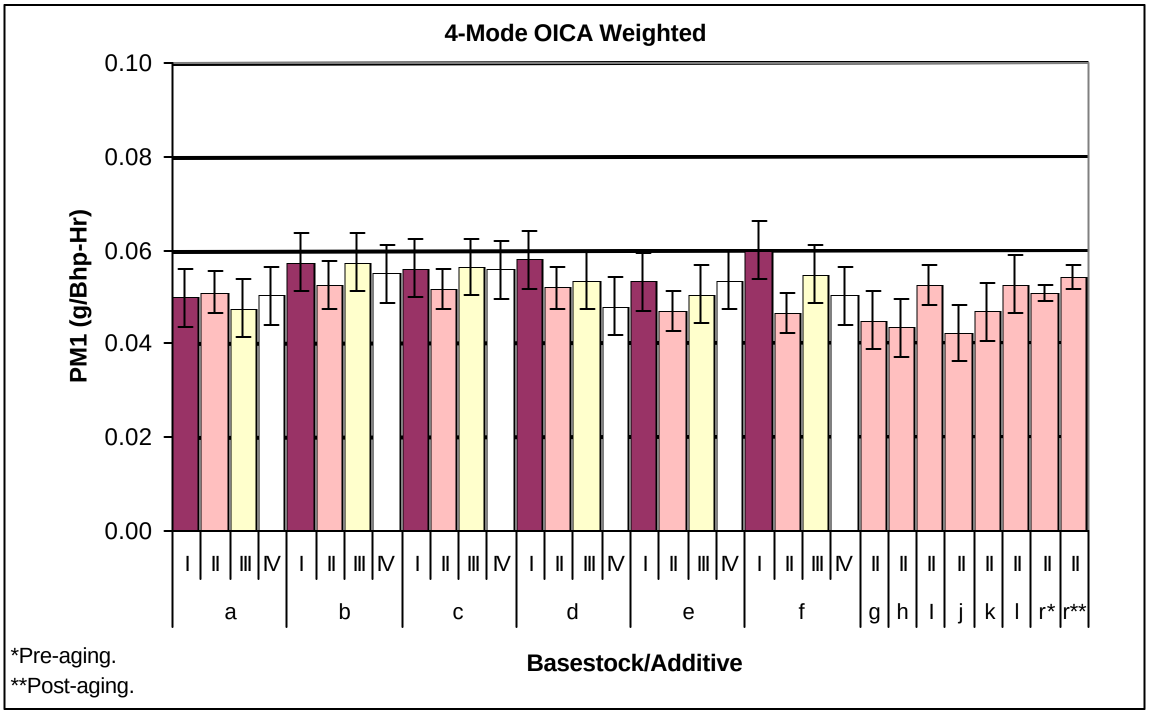
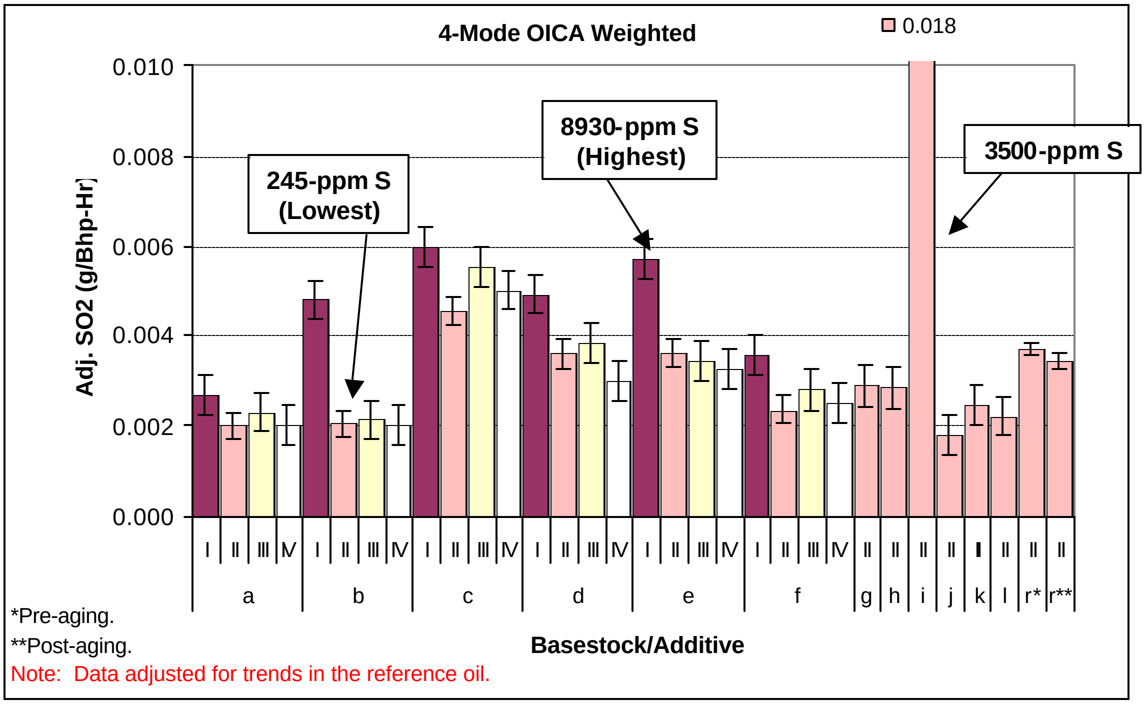


**Figure 6:** Total PM emissions (4-mode composite) as a function of oil formulation



245-ppm S (Lowest)

8930-ppm S (Highest)

3500-ppm S

*Pre-aging.

**Post-aging.

Note: Data adjusted for trends in the reference oil.

**Figure 7:** Weighted $SO_2$ emissions as a function of oil formulation

A basestock effect is also apparent. Group I oils gave the highest total $SO_2$ emissions, though the difference does not account for its much higher sulfur content. The Group I basestock contains 5000-ppm compared to the other basestocks which were under 20-ppm S.

The tests with oil I2 proved interesting because the $SO_2$ emissions were significantly higher than could be explained by its sulfur content (3500-ppm S). While its total sulfur content was lower than many of the oils tested, the $SO_2$ emissions were an order of magnitude higher. Concerned that this was due to experimental or measurement error, I2 was retested and the results confirmed the previous measurements. This suggests that the *source* of the sulfur is perhaps more important than the total level when predicting impact on catalyst performance or emissions.

### *Mass Balance*

The remainder of this analysis involves a detailed mass balance that attempts to match system inputs (fuel and oil consumption) with outputs (emissions). The approach employed here is best illustrated by the block diagram shown in Figure 8.

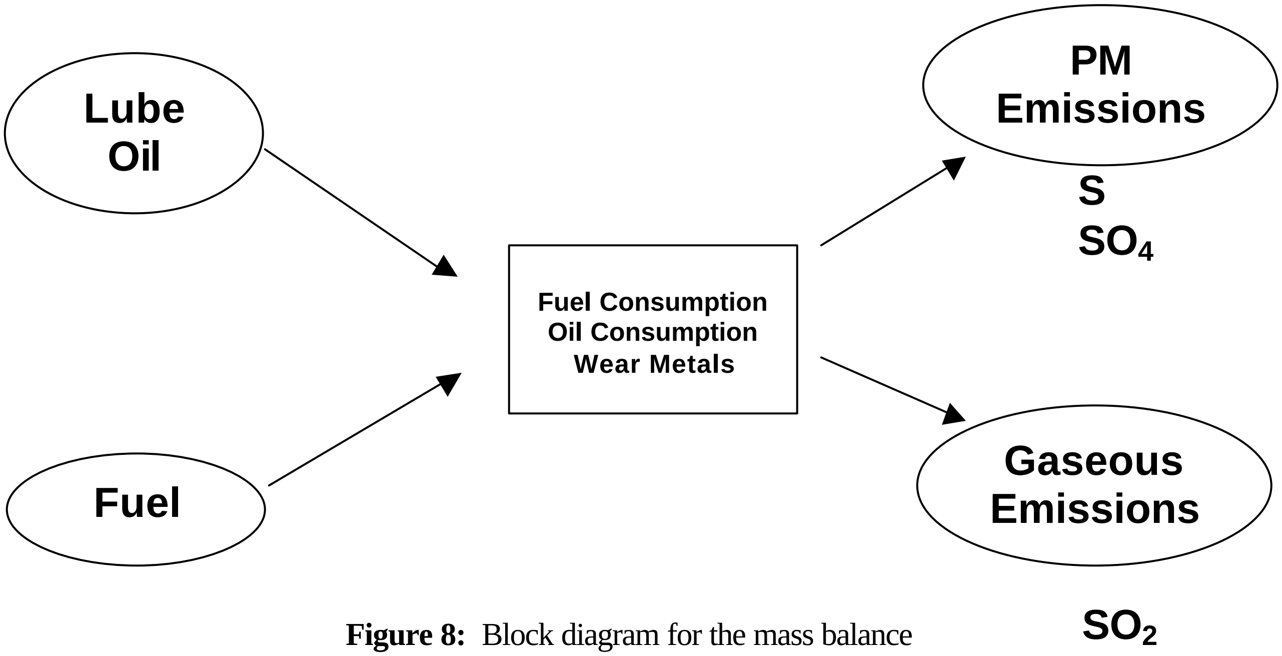


**Figure 8:** Block diagram for the mass balance

In this approach, the properties of the fuel and lubricants and their known consumption rates can be used to predict the mass rate of emissions for any given element. The predicted mass emissions are compared to the measured emissions to determine recovery rates. A key assumption in the process is that the lubricant is uniformly consumed; i.e. that the composition of the consumed lube oil is the same as that in the crankcase. This is likely not the case and therefore this recovery rate serves as an assessment of this assumption.

The oil consumption rate used in these calculations is the 4-mode weighted oil consumption rate (0.18 g/bhp hr) measured over the duration of the project. Lubricant properties are derived from lube oil samples taken from the oil gallery at the time of the actual emission test. All samples were analyzed at Southwest Research Institute. Fuel properties (sulfur content) were measured from the fuel supply line and were routinely checked throughout the project. The metallic content of the fuel was confirmed to be negligible.

Figure 9 compares predicted and measured calcium emissions. Calcium emissions are directly correlated with the level of calcium in the lube oil. This proved true for all formulations tested; however, only 42% of the calcium was recovered. It has been suggested that the remaining calcium could be collecting in the oil filter.

Figure 10 provides a similar analysis of zinc emissions. In general, zinc emissions correlated with the level of zinc in the lube oil. This was not the case, however, for all of

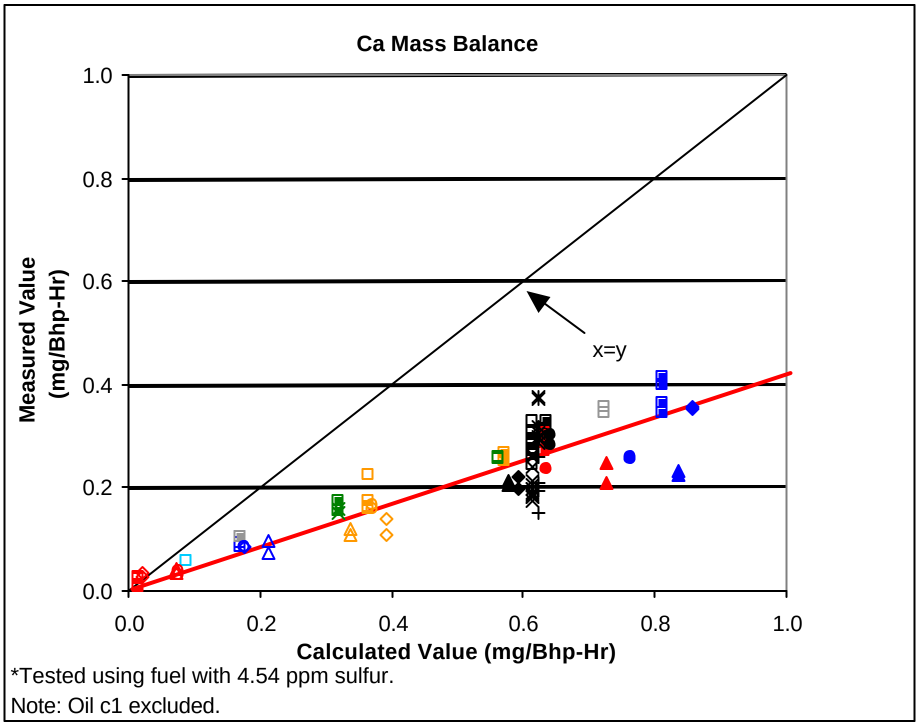


**Figure 9:** Calcium mass balance

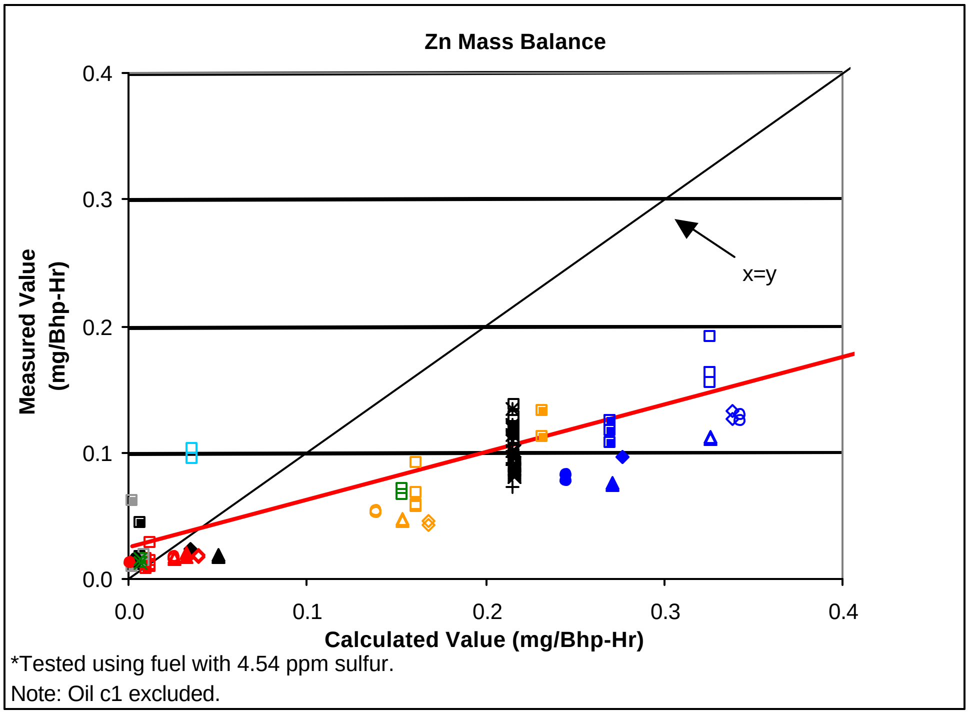
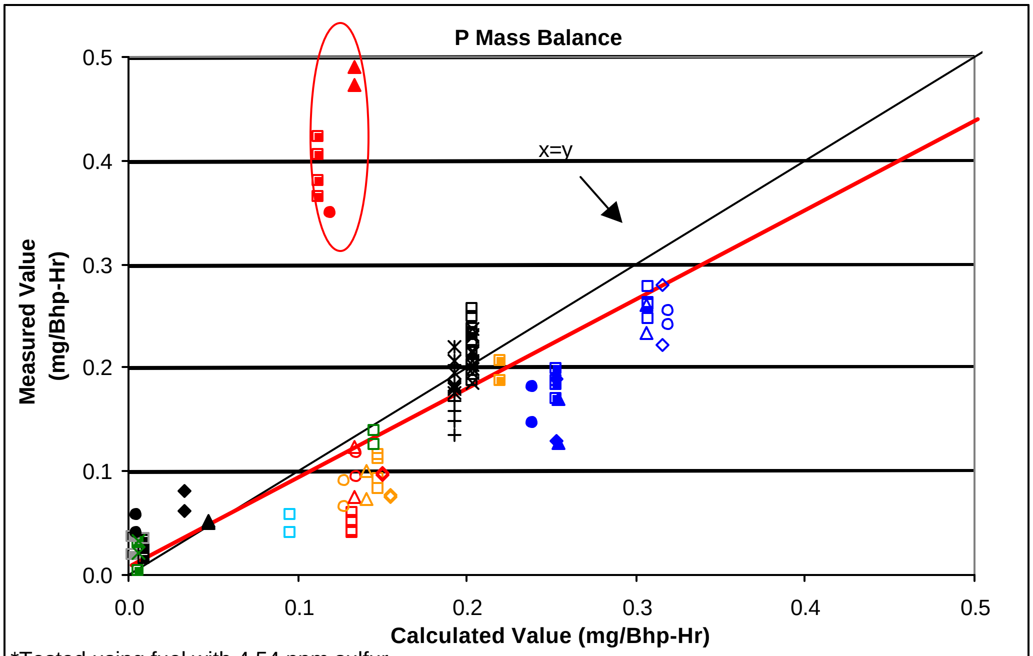


**Figure 10:** Zinc mass balance

the test oils, suggesting a possible formulation dependency. Here, oil L2 yielded zinc emissions that were twice as high as the predicted value, suggesting that the zinc in this package is preferentially consumed. Similar to calcium, the recovery rate for zinc was 38% (neglecting oil L2). Zinc is derived from the anti-wear additives and is therefore surface active. The “missing” zinc is believed to have been lost to a surface.

Phosphorus is a known poison in automotive three-way catalysts. Figure 11 presents the mass balance for phosphorus. Like the other elements, the rate of emissions is directly proportional to the phosphorus level in the oil, although the recovery rate (86%) is much higher. Again, there appears to be a very significant formulation effect. Phosphorus emissions during the oil C2 tests were four times higher than were predicted. This relatively low phosphorus oil (626-ppm P) emitted phosphorus at a rate that would be predicted for a much higher phosphorus concentration in the oil (?2300-ppm P). Should phosphorus be determined to impair diesel catalyst performance, this would suggest that chemical constraints on oils would be unsuitable for preventing high rates of contamination.

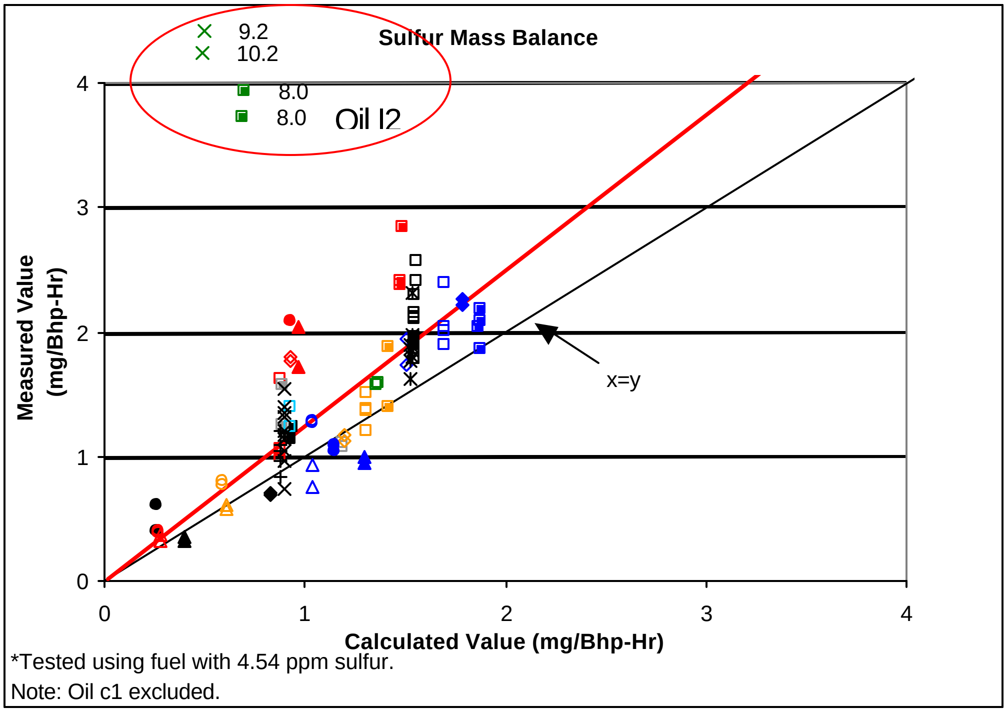


*Tested using fuel with 4.54 ppm sulfur.

Note: Oil c1 excluded.

**Figure 11:** Phosphorus mass balance

The final mass balance involves sulfur. Unlike the previous elements studied, sulfur is present in both the fuel and the lubricant and is emitted in both the gaseous phase (as $SO_2$) and in the PM (elementally and as the sulfate). Therefore, the mass balance must account for these various inputs and outputs. Consistent with previous analyses, Figure 12 shows the relationship between the measured and predicted emission rates.



*Tested using fuel with 4.54 ppm sulfur.

Note: Oil c1 excluded.

**Figure 12:** Sulfur mass balance

With the exception of one oil (Oil I2 as previously discussed), the total sulfur emissions were consistent with the concentration of sulfur in the lubricant, with the fuel contribution considered constant. Oil I2 shows a strong formulation effect and again illustrates the danger of chemical limits. This relatively moderate sulfur (3500-ppm) containing oil emitted sulfur at a rate that would have been predicted for a 10,000-ppm S oil!

As shown, the measured emissions are slightly higher than would have been predicted. Because the fuel sulfur contribution significantly effects this prediction, it is likely that the uncertainty in the measurement of fuel sulfur level contributes to this error.

## CONCLUSIONS

This study has revealed some important insights into the relationship between lubricant oil formulation and exhaust emissions. For instance, sulfur content in the oil is generally related to sulfur emissions in the exhaust, but the type of sulfur compound in the oil can have a significant impact on $SO_2$ emission levels. Indications of a similar dependency were noted for phosphorus. Furthermore, some compounds, such as zinc and calcium, may be found in the exhaust in lower quantities, on average, than predicted by the measured oil consumption while certain experimental additive systems generated higher than expected emissions of sulfur and phosphorus.

Overall, there has been significant insight gained in the relationship between oil formulation and engine out-emissions. The second phase of this project is underway and is investigating techniques for increasing the lubricant-derived exhaust emission components by up to tenfold in order to conduct accelerated testing. The results of the second phase and the detailed analysis of the first phase results will provide the necessary foundation for research involving actual catalytic emission control systems, utilizing accelerated aging techniques as necessary.

## ACKNOWLEDGEMENTS

The authors would like to thank the following individuals who have contributed greatly to this research and this report: Lisa Lanning, Chris Tennant, Michael Traver, Brian Mace, Brian Ridge and Tom McDaniel of ATL; Steve Goguen and John Garbak (DOE); Bill Runkle (Valvoline); John Campbell (BP); Charlie Passut (Ethyl); Cliff Venier (Pennzoil-Quaker State); Mark Cooper, Rick Klein and Wim Van Dam (Chevron Oronite); Cherie Cotter (CARB); Dave Stehouwer (Cummins); Dwayne Tharp (Caterpillar); Ewa Bardasz (Lubrizol); Bob Farina and Jim McGeehan (ChevronTexaco); Frank Bondarowicz (International); Glenn Mazzamaro and Michael Weismiller (Ciba); Greg Shank (Mack); Steve Arrowsmith and Pat Fetterman (Infineum); Ralph Cherrillo (Shell Global Solutions); Steven Jetter (ExxonMobil); and Wendy Clark (NREL).

## REFERENCES

[1] http://www.ott.doe.gov/decse/
[2] Dou, D. and Bailey, O. “Investigation of $NO_x$ Adsorber Catalyst Deactivation” SAE 982594.