technical note technical note

# Lead Deposit Effects on Unleaded Aviation Fuel Antiknock Performance

August 2012

DOT/FAA/TC-TN12/31

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16. Abstract

To investigate the potential impact of preexistent lead deposits on unleaded fuel antiknock performance of piston aircraft engines, full-scale engines were operated on leaded fuels prior to testing with unleaded fuels. The full-scale engine results showed an increase in unleaded fuel antiknock performance equivalent to 1 to 4 Motor Octane Number (MON) when tested after engine operation with leaded fuel. The MON increase was more pronounced at leaner fuel mixtures, and the effect subsided with continued operation with unleaded fuel. However, it is important to note that this result was based on a short-duration (76-hour) lead exposure test and engine operation with leaded fuel for longer periods may increase the persistence of this effect. Based on these experimental findings, and those cited in this report, it is highly recommended that detonation tests with unleaded fuel be performed with a clean engine that was not previously used for leaded fuel operation. Test engines that must be periodically operated for short durations with leaded fuel should be run for at least 30 to 45 minutes with an unleaded fuel after any Pb fuel operation and prior to detonation tests with unleaded fuels, provided the engine was initially lead-free.

These laboratory tests were performed without engine fuel filters, fuel pockets, or plumbing wells that would allow liquid leaded fuel to be trapped in the fuel system. Use of such traps requires increased operating purge times using unleaded fuels after using Pb-based fuels to eliminate Pb effects on the tests.

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## LIST OF ACRONYMS

| | |
|---|---|
| 100LL | 100 Motor Octane Number low lead |
| DI | Detonation intensity |
| EGT | Exhaust gas temperature |
| FAA | Federal Aviation Administration |
| IUPAC | International Union of Pure and Applied Chemistry |
| MON | Motor Octane Number |
| ORI | octane requirement increase |
| Pb | Lead |
| TO | Takeoff |

# EXECUTIVE SUMMARY

At the request of the Federal Aviation Administration unleaded aviation gasoline program sponsor, tests were conducted to determine the impact on detonation performance of piston aircraft engines operating on leaded fuel prior to testing aromatic unleaded fuels. The results showed the full-scale engine antiknock performance of unleaded fuel experiences the equivalent of a 1 to 4 Motor Octane Number (MON) increase when tested after engine operation with leaded fuel. The MON increase was more pronounced at leaner fuel mixtures, and the effect subsided with continued operation with the unleaded fuel. However, it is important to note that this result was based on a short-duration (76-hour) lead exposure test and engine operation with leaded fuel for longer time periods may increase the persistence of this effect. Based on these research findings, and those cited in this report, it is highly recommended that detonation tests with unleaded fuel be performed with a clean engine that was not previously used for leaded fuel operation. Test engines that must be periodically operated for short durations with leaded fuel should be run for at least 30 to 45 minutes with an unleaded fuel after any lead (Pb) fuel operation and prior to detonation tests with unleaded fuels, provided the engine is initially lead-free.

Further, these tests were performed without engine fuel filters, fuel pockets, or plumbing wells that would allow liquid leaded fuel to be trapped in the fuel system. Use of such traps requires increased operating purge times using unleaded fuels after using Pb-based fuels to eliminate Pb effects on the tests.

# INTRODUCTION

## PURPOSE.

These tests compare the full-scale engine detonation performance of unleaded fuels before and after the engine underwent a 76-hour lead (Pb) exposure phase of operation on leaded fuel.

## BACKGROUND.

Performing unleaded fuel tests in an engine that has operated with Pb-based fuels could affect the unleaded fuel test results. Pb can deposit in liquid fuel form in the fuel delivery system, filters, plumbing that has trapped volume, and intake ports; and combustion of leaded fuel could produce leaded fuel deposits in the engine combustion chamber.

# TEST PREPARATION

## TEST ENGINE.

The test engine was a Lycoming IO-540-K with the specifications displayed in table 1. The test engine had approximately 14.6 hours of leaded fuel operation, with no single leaded fuel operation lasting more than 1.4 hours. The majority of tests on this engine were with unleaded fuels. Further, after any detonation tests with 100LL (100 Motor Octane Number (MON) low lead) aviation gasoline, the engine underwent a 30- to 45-minute purge cycle operation on isooctane (2,2,4-Trimethylpentane in International Union of Pure and Applied Chemistry (IUPAC) nomenclature) fuel for cleansing.

Table 1. Lycoming IO-540-K Engine Specifications

| Engine | Manufacturer | Rated Power | Rated RPM | No. of Cylinders | Compression Ratio | Induction | Magneto Static Ignition Timing |
|---|---|---|---|---|---|---|---|
| IO-540-K | Lycoming | 300 | 2700 | 6 | 8.7:1 | Natural | 20° |

A 100LL fuel was detonation-tested immediately before, and immediately after, the Pb exposure phase as a baseline to account for any barometric effects or engine octane requirement shift during the tests.

## TEST FUELS.

During the engine Pb exposure phase, two local 100LL fuels were used. Table 2 shows the Pb content and specification of those fuels.

Table 2. Specification Properties for Two Locally Purchased 100LL Fuels Used for the Pb Exposure Phase

| Test | Property | 100LL Fuel 1 | 100LL Fuel 2 |
|---|---|---|---|
| D5059A | Lead, mL TEL/gal | 1.46 | 1.87 |
| D2700 | Motor Octane Number | 103.5 | 103.4 |
| D909 | ASTM Supercharge rating, mL TEL/gal | 1.69 | 1.47 |

TEL = Tetraethyl lead (Tetraethylplumbane in IUPAC nomenclature)

To quantify the engine's pre- and post-Pb exposure MON demand, the following reference fuels were used for engine detonation tests:

- Aromatic Fuel (approximately 50% total aromatic)
- 100LL Fuel—102.3 MON from local fixed-base operator. This fuel was used as the baseline to account for daily differences, pre- and posttest, along with engine octane requirement changes throughout the testing. As such, the engine detonation tests were run on the 100LL fuel immediately prior to, and immediately after, the Pb exposure phase.
- Paraffinic Fuel (isooctane primary reference fuel). Data from the tests with isooctane fuel were not very useful because, in many cases, the engine was experiencing detonation at very rich mixtures.

Table 3 shows the properties of the 100LL fuel used in the detonation tests.

Table 3. Select Laboratory Properties for 100LL Fuel

| Test | Value |
|---|---|
| D2700 MON (BRE/30.0 in./300°F) | 102.3 |
| D909 ASTM Supercharge rating | 1.43 |
| Performance number | 132.0 |
| D5059A lead, mL TEL/gal | 1.90 |

BRE = Bracketing equilibrium
TEL = Tetraethyl lead (Tetraethylplumbane in IUPAC nomenclature)

Table 4 shows the properties of the aromatic fuel used in the detonation tests.

Table 4. Composition and Select Laboratory Properties for Aromatic Test Fuel

| Component | Mass (%) |
|---|---|
| Isopentane | 9.2 |
| PRF Isooctane | 39.5 |
| *o*-Xylene | 2.8 |
| *m*-Toluidine | 2.5 |
| *n*-Butane | 2.6 |
| *p*-Xylene + *m*-Xylene | 40.5 |
| Ethylbenzene | 2.6 |
| Lead content | <0.01 g/gal |

| Test | Value |
|---|---|
| MON (ASTM D2700) | 101.1 |
| Distillation 10% (°C) | 70.6 |
| Distillation 40% (°C) | 112.6 |
| Distillation 50% (°C) | 115.9 |
| Distillation 90% (°C) | 140.8 |
| Sum 10% +50 (°C) | 186.6 |
| Final boiling point (°C) | 184.5 |
| Vapor pressure, DVPE (kPa) | 41.02 |

PRF = Primary Reference Fuel
DVPE = Dry vapor pressure equivalent
Isopentane = 2-Methylbutane in IUPAC nomenclature
*n*-Butane = normal butane, butane in IUPAC nomenclature
*m*-Toluidine = meta-toluidine (3 amino-1-methylbenzene in IUPAC nomenclature)
*m*-Xylene = *meta*-Xylene (1,3-Dimethylbenzene)
*o*-Xylene = *ortho*-Xylene (1,2-Dimethylbenzene)
*p*-Xylene = *para*-Xylene (1,4-Dimethylbenzene)

INSTRUMENTATION.

The engine and supporting test equipment were instrumented with standard engine instrumentation, and all sensors were calibrated before and after the tests.

The individual cycle detonation index calculation method used was the Federal Aviation Administration (FAA) William J. Hughes Technical Center (hereafter, referred to as Technical Center) algorithm found in ASTM D6424 with the following levels of detonation intensity (DI) specified:

- Light-knock DI: 10 to 40 bars
- Moderate-knock DI: 40 to 100 bars
- Heavy-knock DI: >100 bars

The DI is determined by the percentage of cycles of a 100-engine cycle moving window that experienced at least light detonation. The data were examined at both a 2% and 6% DI for threshold comparison purposes.

## TEST PROCEDURES

All detonation tests were operated at 475° +5°F maximum CHT (cylinder head temperature), 103° ±3°F induction air temperature, 245° ±7°F oil temperature and at takeoff (TO), 85%, and 75% power settings. For the detonation tests, the fuel mixture was adjusted from rich stop to either heavy detonation or lean of peak EGT (exhaust gas temperature), whichever occurred first.

Prior to the Pb exposure phase, the engine's MON demand was measured by detonation tests on isooctane fuel, followed by the aromatic fuel, then 100LL fuel. Following the 100LL fuel detonation test, the 76-hour Pb exposure phase was performed by engine operations at rich fuel mixture using 100LL fuel. This 76-hour Pb exposure phase included daily engine shutdown intervals and periodic oil sampling.

Following the Pb exposure phase, the engine's MON demand was measured again by detonation tests in reverse sequence so that the 100LL fuel was tested first to provide a compensation for engine drift and environmental conditions. After the 100LL fuel was detonation-tested, the aromatic fuel was detonation-tested, followed by the isooctane fuel.

### ANALYSES.

OBSERVED DATA. Table 5 shows the Pb content in the lubricating oil stabilized during the Pb fuel operation to levels between 3000 to 4000 parts per million.

Table 5. Oil Samples, Pb Content

| Oil Sample Description and Date | ASTM D5185 Pb Content (mg/kg) |
|---|---|
| Pre-Pb, 16 Jun 11 | 110 |
| Intermediate run, 28 Jun 11 | 3000 |
| 50 hours, 12 Jul 11 | 3800 |
| Postdetonation run, 18 Jul 11 | 3400 |

The 100LL fuel was detonation-tested immediately prior to, and immediately after, the Pb exposure phase to baseline any changes to the engine, pre- and posttest. Immediately after the post-Pb exposure phase and 100LL fuel tests, the aromatic fuel was tested. The tests were performed in order from TO power, 85% power, and 75% power, respectively. Following the aromatic fuel test, isooctane fuel was tested.

The following post-Pb exposure phase detonation test sequence shows the timing of the testing for the various fuels and power settings:

- Aromatic fuel at TO power—0-13 minutes after Pb exposure phase and 100LL fuel operation
- Aromatic fuel at 85% power—13-21 minutes after Pb exposure phase and 100LL fuel operation
- Aromatic fuel at 75% power—21-28 minutes after Pb exposure phase and 100LL fuel operation

Figure 1 shows the typical DI repeatability at TO power. This repeatability improved at lower-power settings. This figure also shows that an aromatic fuel of 101.1 MON performed considerably worse than the 102.3-MON 100LL fuel. This difference was much greater than the difference in MON and is typical of what is found when attempting to translate unleaded fuel MON to full-scale engine antiknock performance.

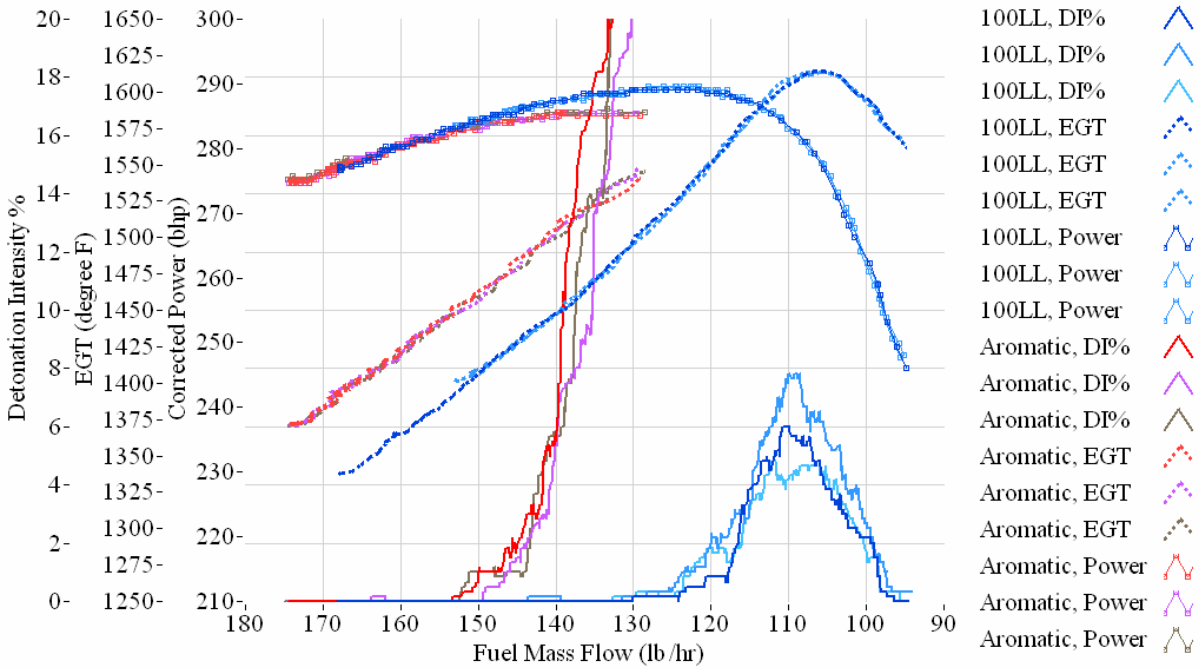


Figure 1. Typical Repeatability of Test Data

Figures 2 and 3 show TO power at pre- and post-Pb exposure phase test results for the aromatic and 100LL fuels. The isooctane fuel test results are not shown because the engine was frequently experiencing detonation at the richest fuel mixtures when operating on this fuel. Further, isooctane fuel consumption did not begin until after 28 minutes of engine operation, which is well after any effect of Pb memory on the aromatic fuel had been detected, thus these test results were not deemed to be useful.

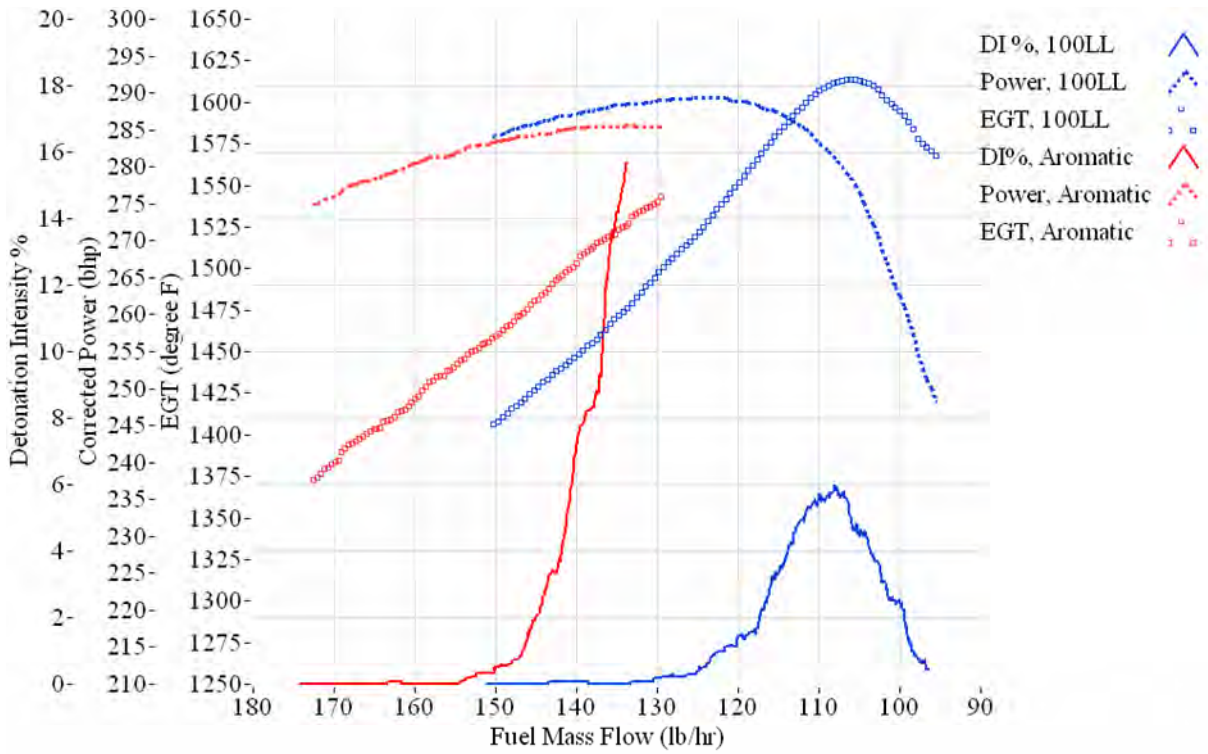


Figure 2. Pre-Pb Exposure Detonation Results at TO Power

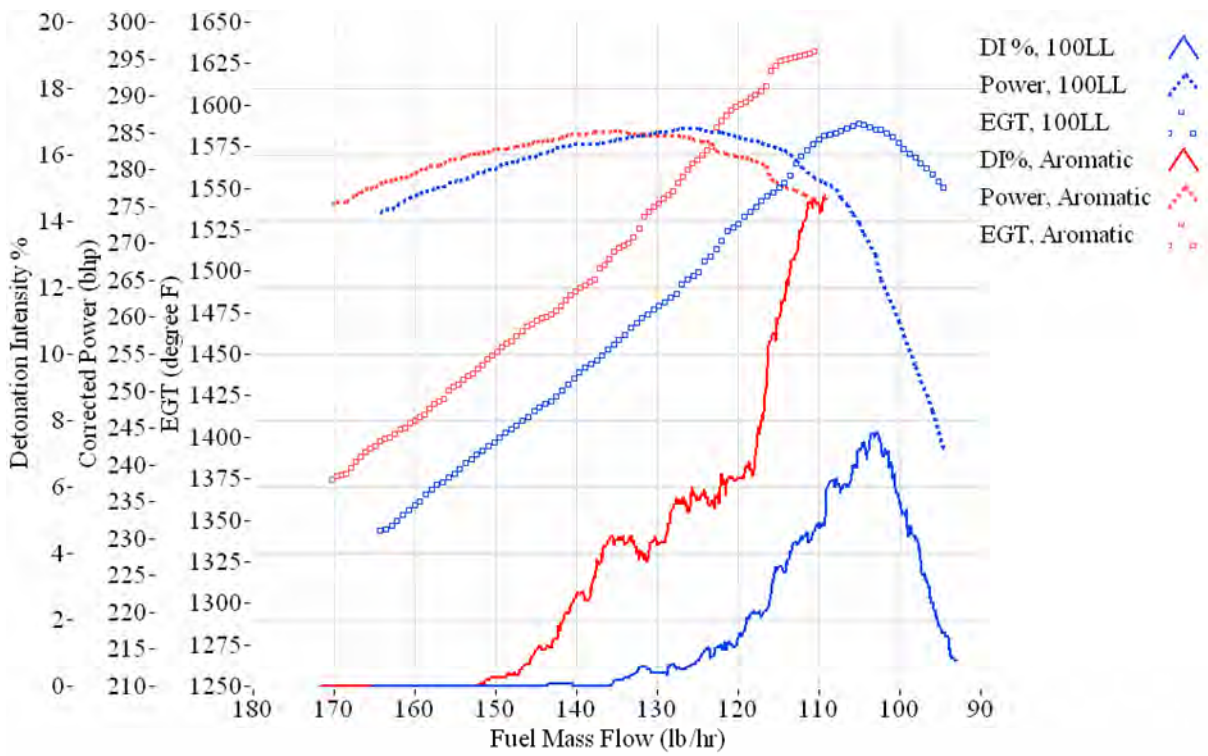


Figure 3. Post-Pb Exposure Detonation Results at TO Power

Figures 2 and 3 compare the performance of the aromatic fuel to the 100LL for both the pre- and post-Pb exposure conditions at TO. The TO power setting was the first setting tested on the aromatic fuel after the Pb exposure. The data clearly suggest that there was an effect, beyond data repeatability, from Pb exposure.

The detonation performance of 100LL will be relatively constant between pre- and post-Pb exposure because the fuel already contains Pb. Therefore, a comparison of the relative detonation performance difference between the aromatic fuel and 100LL for both the pre- and post-Pb exposure tests will isolate the Pb effect from other environmental or engine effects. This difference was shown at both the 2% and 6% DI levels to show how the Pb memory effect changes with continued engine leaning. A comparison of figure 4 to 5 shows the aromatic fuel was more resistant to detonation during the post-Pb exposure run, and this improvement was more pronounced at the higher DI (and leaner fuel mixture strength).

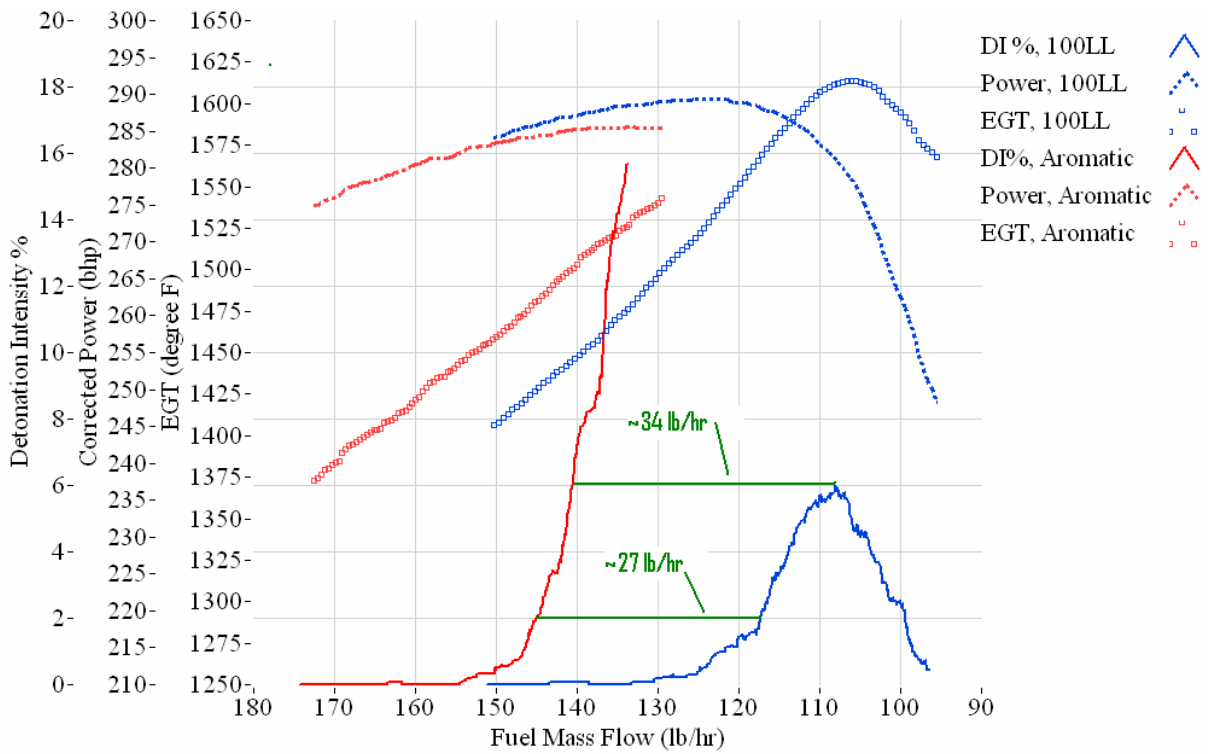


Figure 4. Pre-Pb Exposure Detonation Difference Between the Aromatic and 100LL Fuels

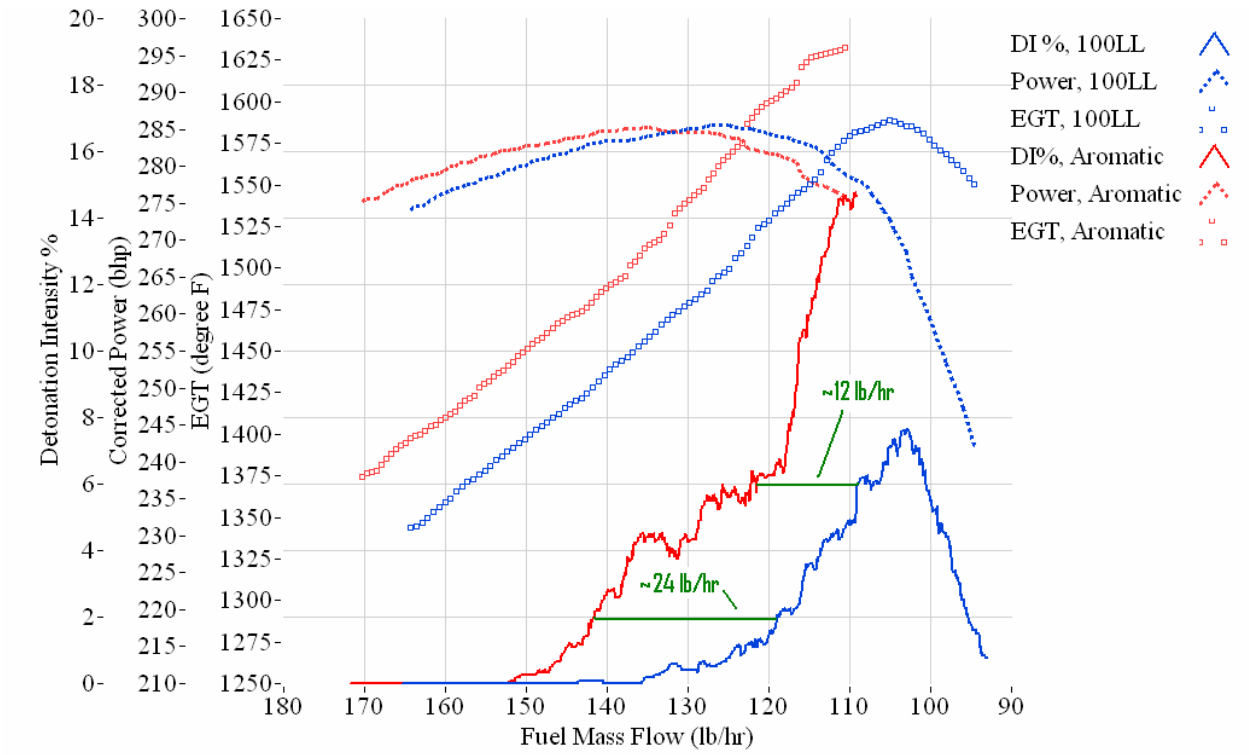


Figure 5. Post-Pb Exposure Detonation Difference Between the Aromatic and 100LL Fuels

The difference in detonation performance between the aromatic fuel and 100LL lessened from 27 to 24 lb/hr after Pb exposure at the 2% intensity level. However, at the leaner condition that produced the 6% intensity level, the difference between the aromatic fuel performance and the 100LL performance lessened even more, from 34 to 12 lb/hr. In other words, while the performance of 100LL remained relatively unchanged, the performance of the aromatic fuel improved by 22 lb/hr. Based on the correlation of Coordinating Research Council engine and MON test data, these differences equate to between 1 and 4 MON.

These differences between pre- and post-Pb exposure tests (shown in figures 4 and 5) decreased with time, as shown in figures 6 through 9 for 85% and 75% power, respectively.

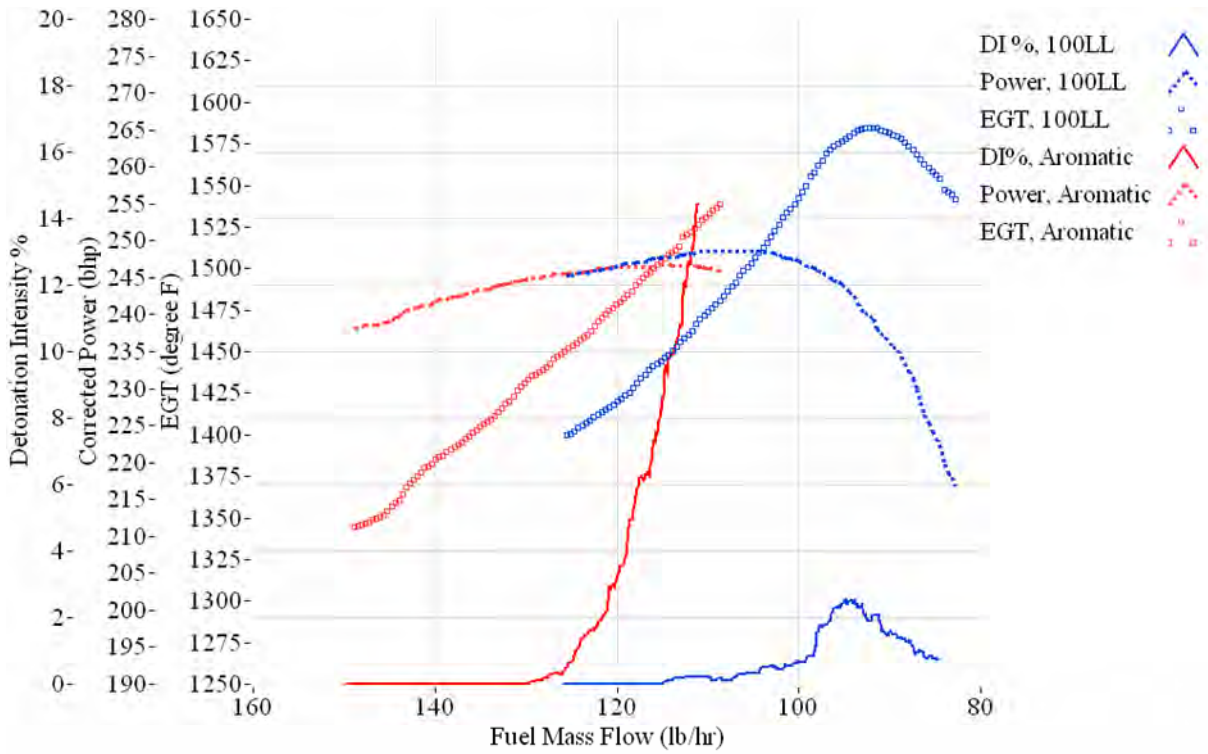


Figure 6. Pre-Pb Exposure at 85% Power

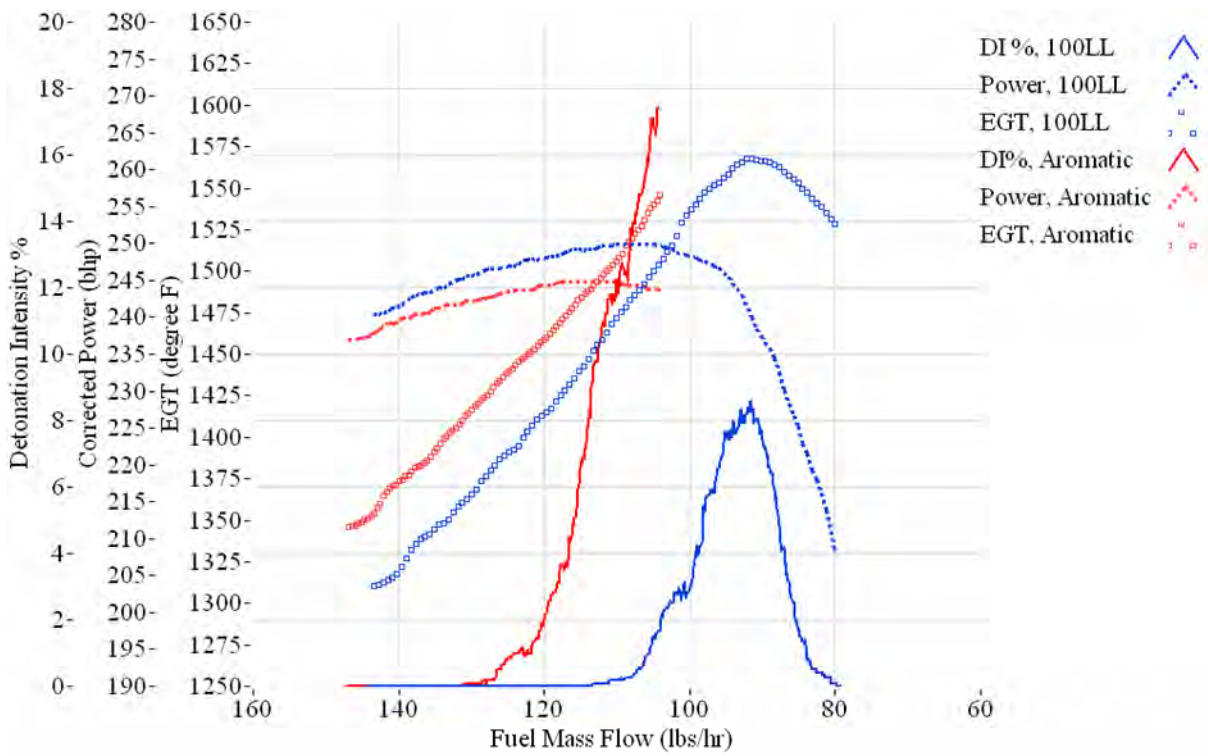


Figure 7. Post-Pb Exposure at 85% Power

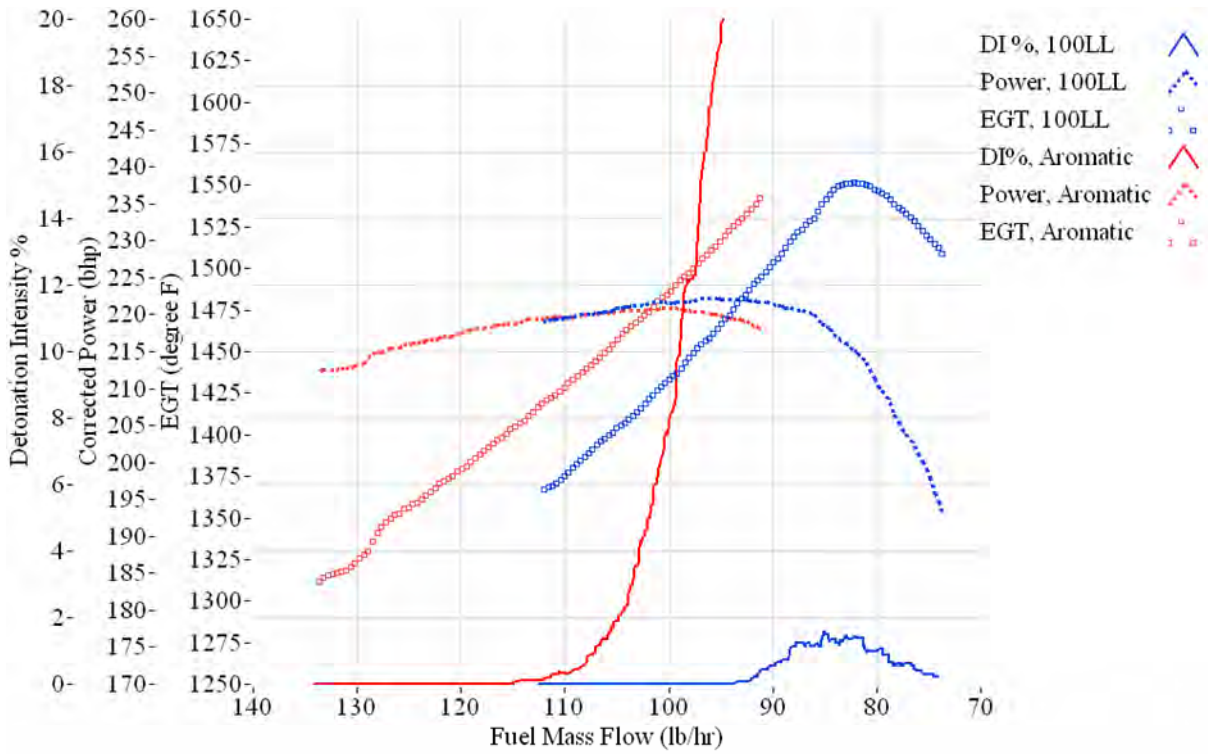


Figure 8. Pre-Pb Exposure at 75% Power

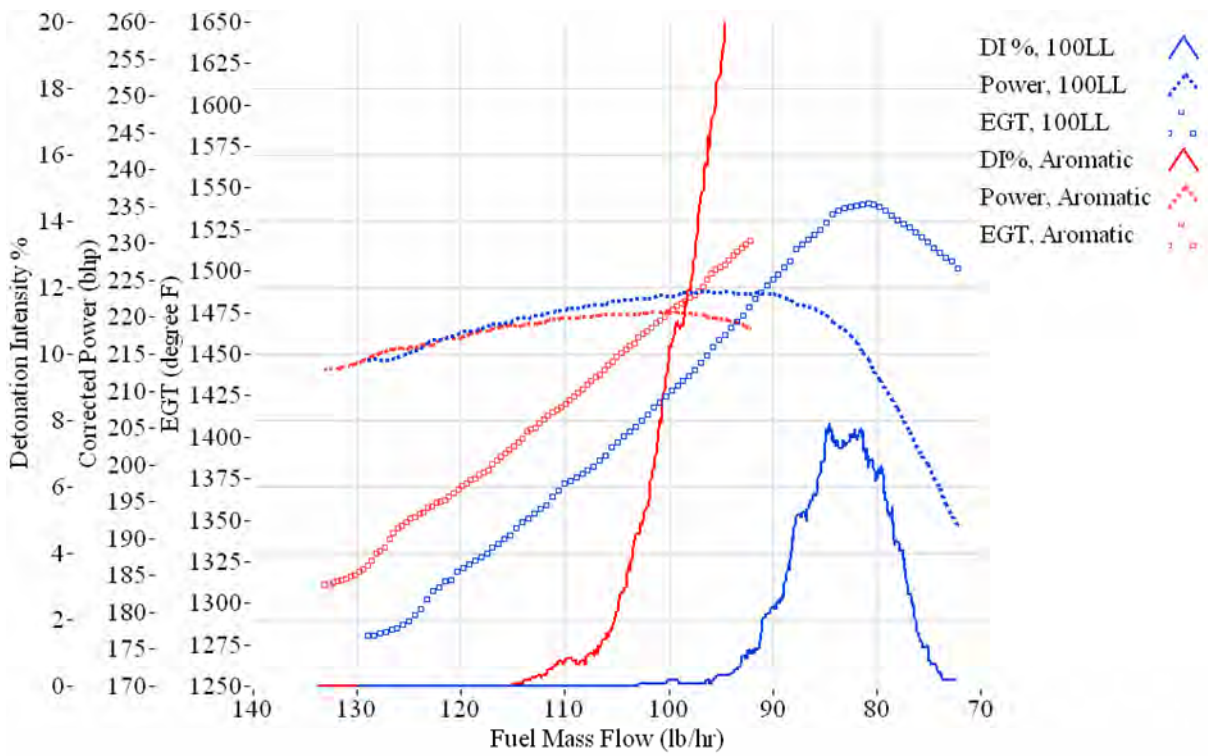


Figure 9. Post-Pb Exposure at 75% Power

At these lower-power conditions, a slight octane requirement increase (ORI) was noted when operating with 100LL fuel. This change was the opposite of the octane requirement decrease noted with the aromatic fuel. The 100LL fuel ORI is theorized to be caused by the accumulation of combustion chamber deposits that affect the heat transfer of the cylinder heads. See reference 1 for a discussion of the effect of combustion chamber deposits on ORI. With the unleaded aromatic fuel, this effect is most likely eclipsed by the Pb memory effect, which produces an improvement in unleaded fuel antiknock performance.

DATA CORRECTED FOR ENVIRONMENTAL OR OTHER EFFECTS. The data were further reviewed by using 100LL fuel test results as the baseline to account for different barometric and engine effects. Figures 10 through 17 show the DI, corrected engine power, and average exhaust gas temperature versus fuel-air mixture equivalence ratio for the 100LL and aromatic fuels. Figures 10 through 12 show 100LL fuel pre- and post-Pb exposure for TO, 85%, and 75% power, respectively. In the figures, equivalence ratios on the left that are greater than one are for fuel mixtures rich of peak EGT, and those that are less than one indicate fuel mixtures lean of peak EGT. Thus, moving from left to right shows mixtures from rich to lean. Differences in the 100LL fuel data indicated engine daily fluctuations and an engine octane requirement shift during the tests. Also, in these figures the DI data were plotted up to its peak value.

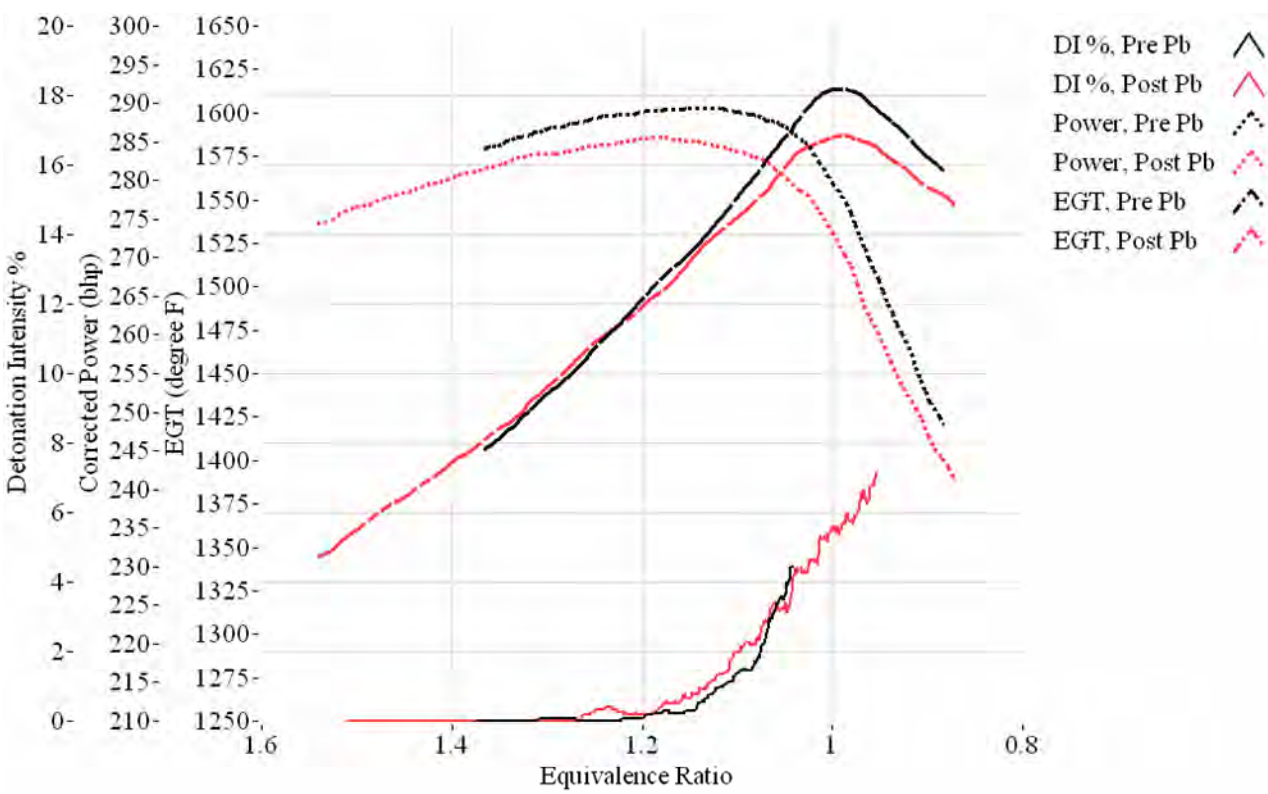


Figure 10. The 100LL Fuel at TO

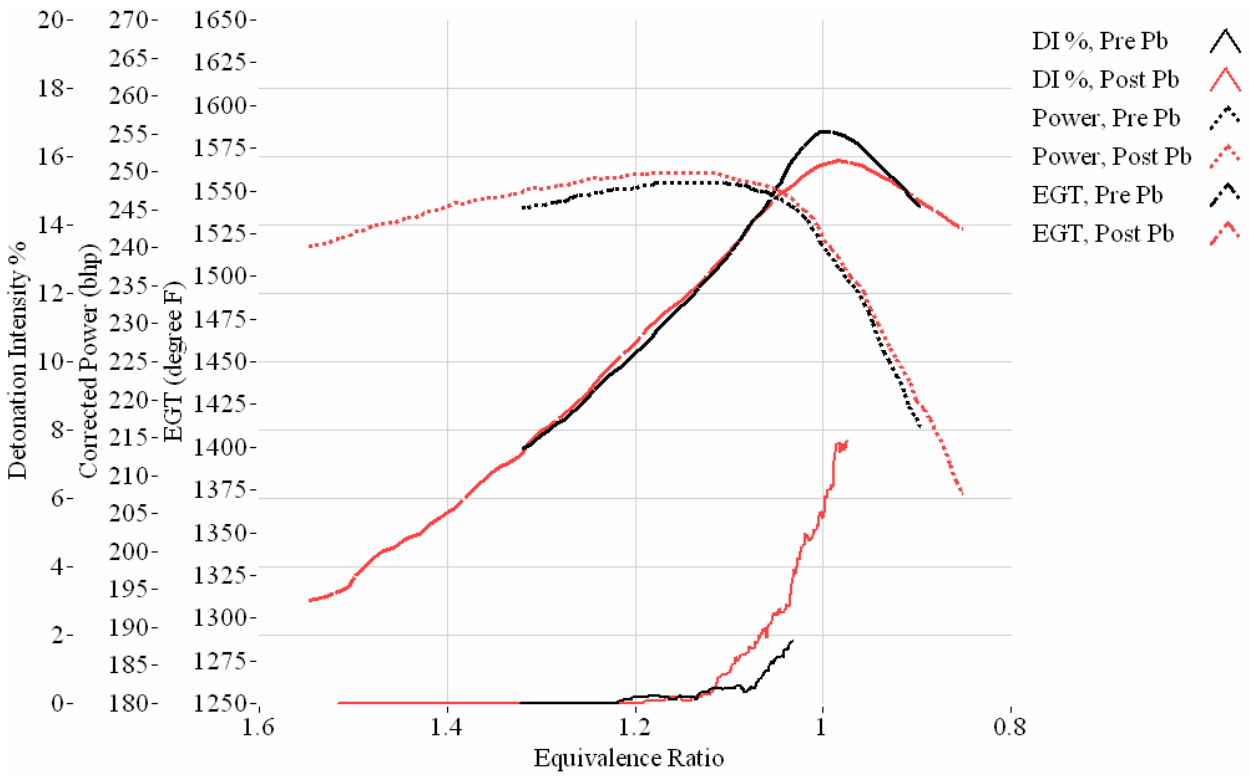


Figure 11. The 100LL Fuel at 85% Power

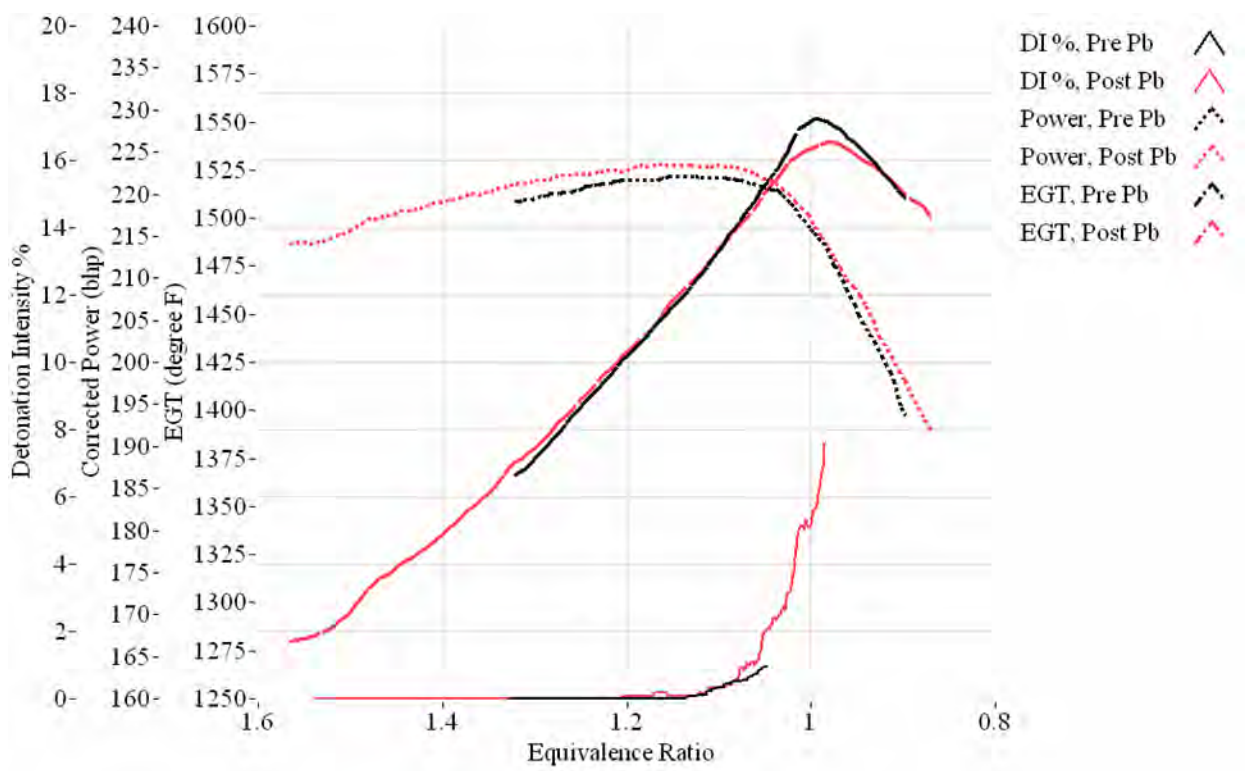


Figure 12. The 100LL Fuel at 75% Power

The detonation response, both pre- and post-Pb exposure, for the aromatic fuel for TO, 85%, and 75% power settings are shown in figures 13, 14, and 15, respectively. The post-Pb exposure data are corrected for the environmental and engine effects that are indicated in the above 100LL fuel data. The data still show there was a significant shift in the aromatic test fuel detonation response between the corrected post- and pre-Pb exposure tests with the corrected post Pb result showing considerably better detonation performance (or conversely lower octane demand from the engine). This result is indicative of Pb deposit effects on the fuel. As expected, the 85% power setting detonation differences between pre- and post-Pb exposure for the aromatic fuel diminished, with the 75% power setting showing even smaller differences. As previously discussed, tests on the aromatic fuel covered the first 28 minutes of engine operation on an unleaded fuel after the Pb exposure. It is theorized that these diminishing detonation effects with time are due to the continuous removal of Pb deposits from the combustion chambers as the tests progressed.

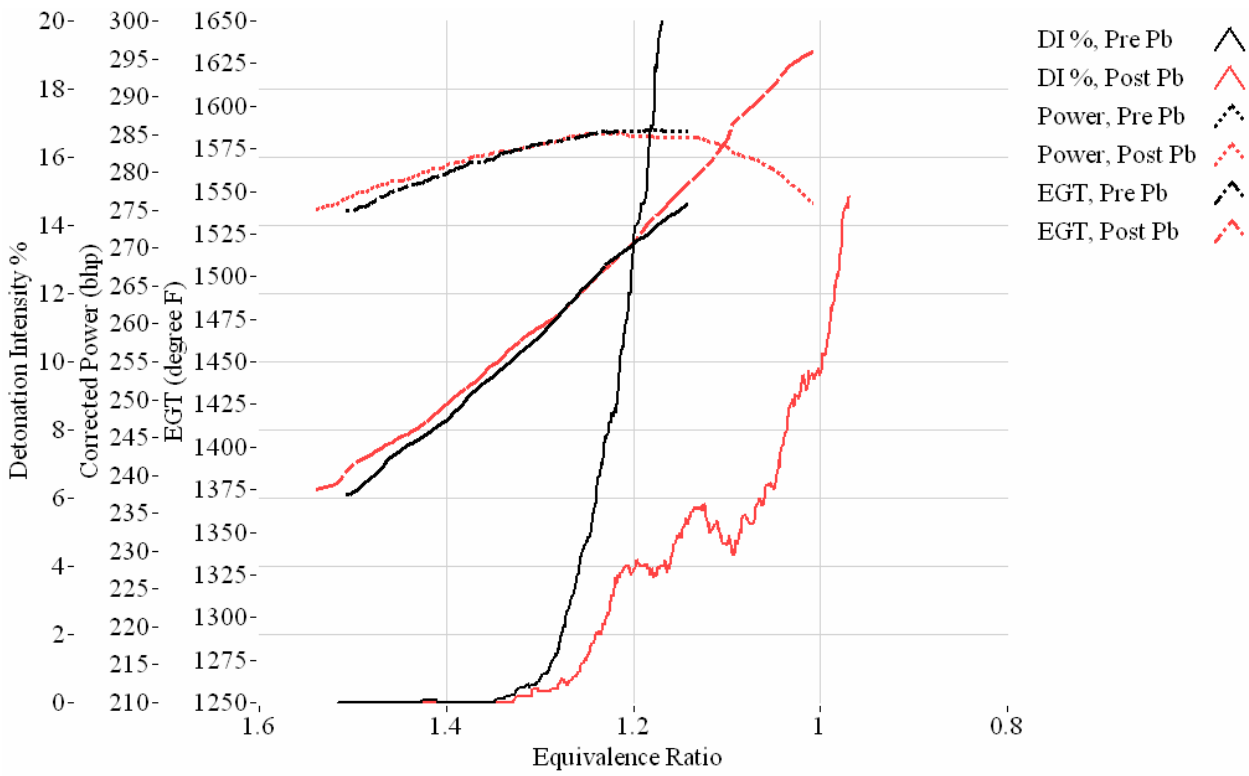


Figure 13. Aromatic Fuel at TO

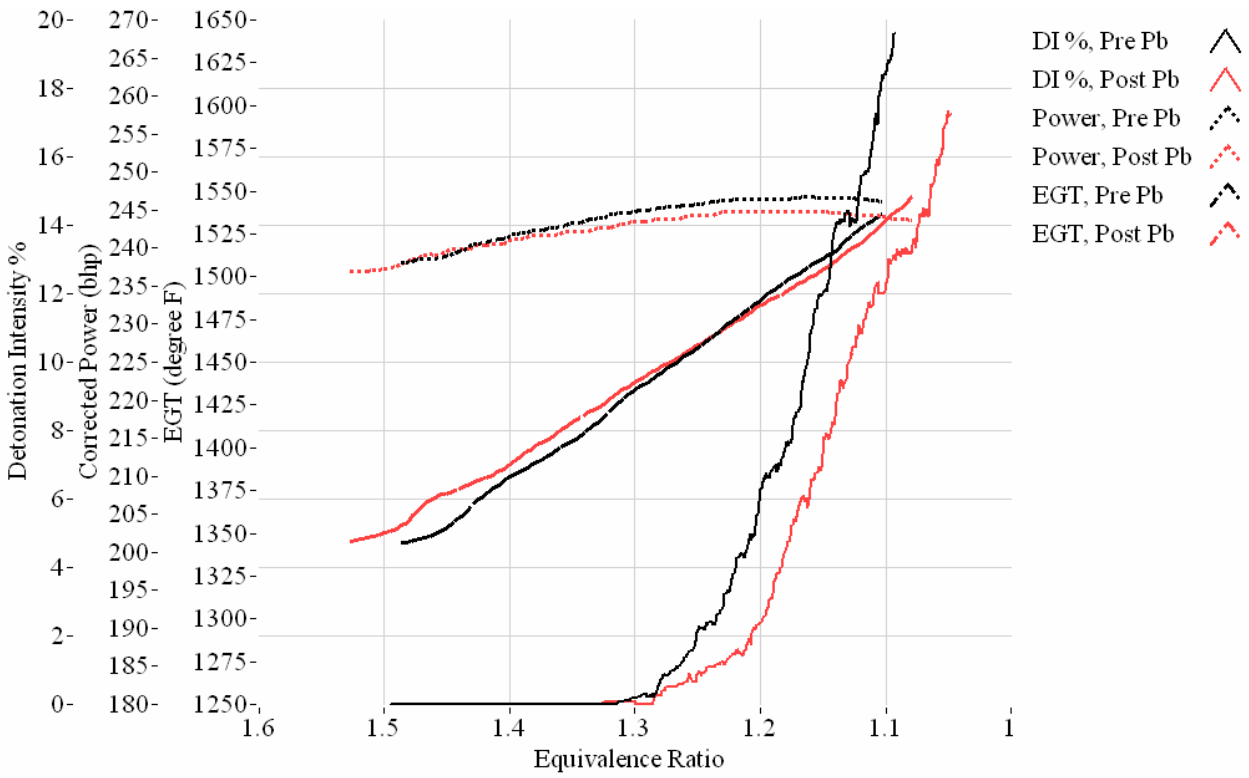


Figure 14. Aromatic Fuel at 85% Power

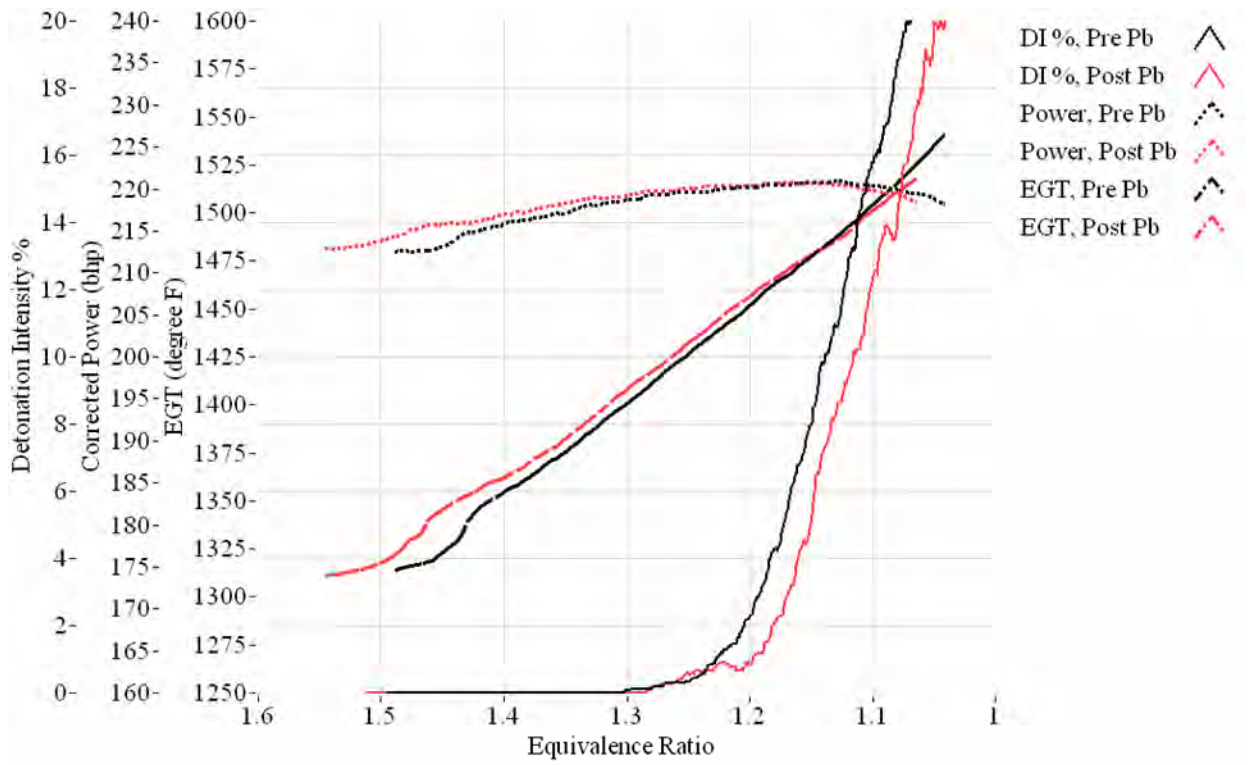


Figure 15. Aromatic Fuel at 75% Power

The aromatic fuel results on a fuel mass flow basis are shown in figures 16 through 18.

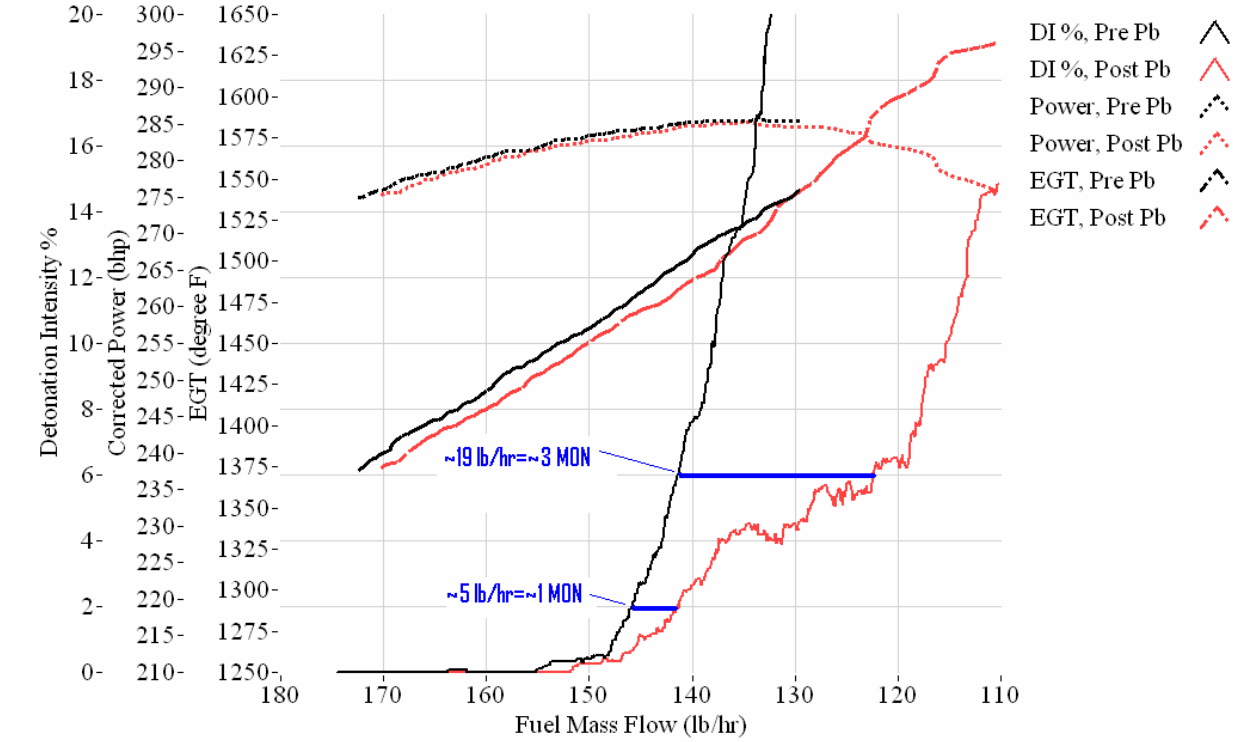


Figure 16. Aromatic Fuel at TO

The TO power setting on the aromatic fuel was the first unleaded fuel test after the Pb exposure and was performed in the first 13 minutes of unleaded fuel operation. At the 6% DI level, the difference in detonation fuel mass flow was approximately 19 lb/hr. Based on past Technical Center research using the same engine with aromatic fuels, this fuel mass flow difference translates into roughly 3 MON. At the 2% DI level, the fuel mass flow difference was equivalent to approximately 1 MON.

Examining the gray and orange slope approximation lines for the detonation onset in figure 17 (which displays the same data as figure 16 but with DI slope lines shown), the performance response to detonation from mixture leaning increased as the fuel mixture was leaned in the post-Pb tests.

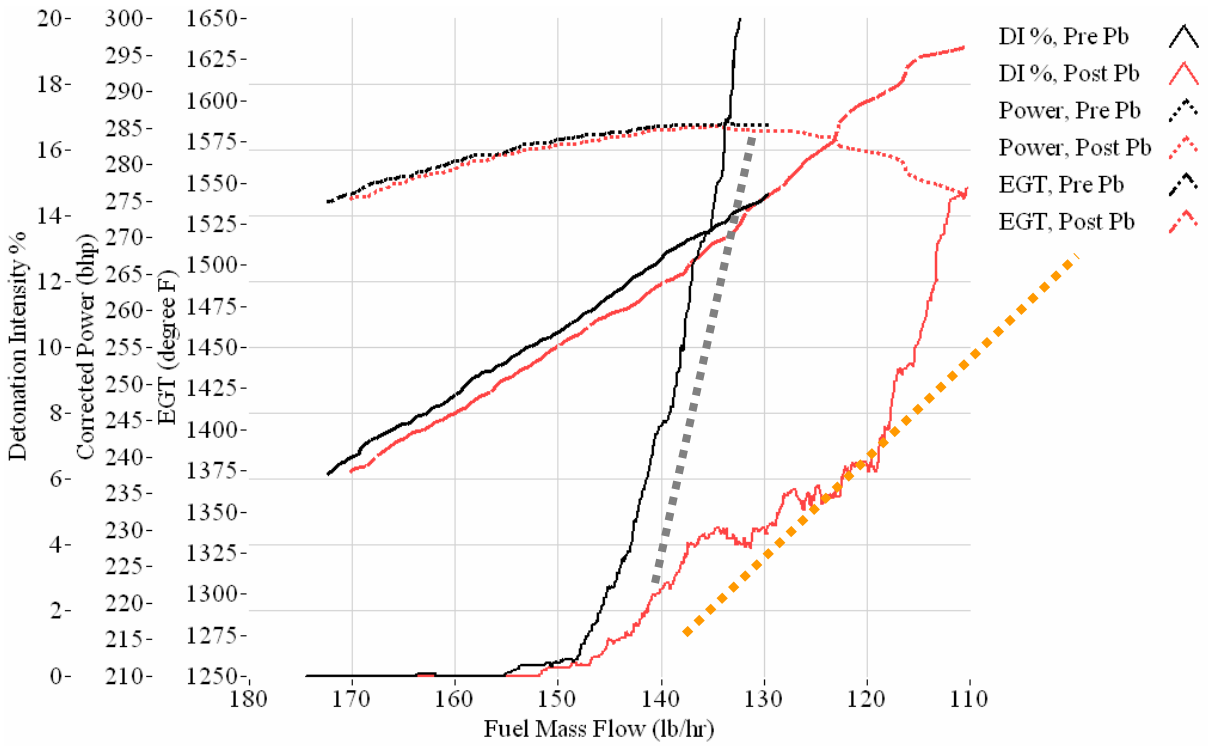


Figure 17. Aromatic Fuel at TO With Detonation Onset Slope Lines

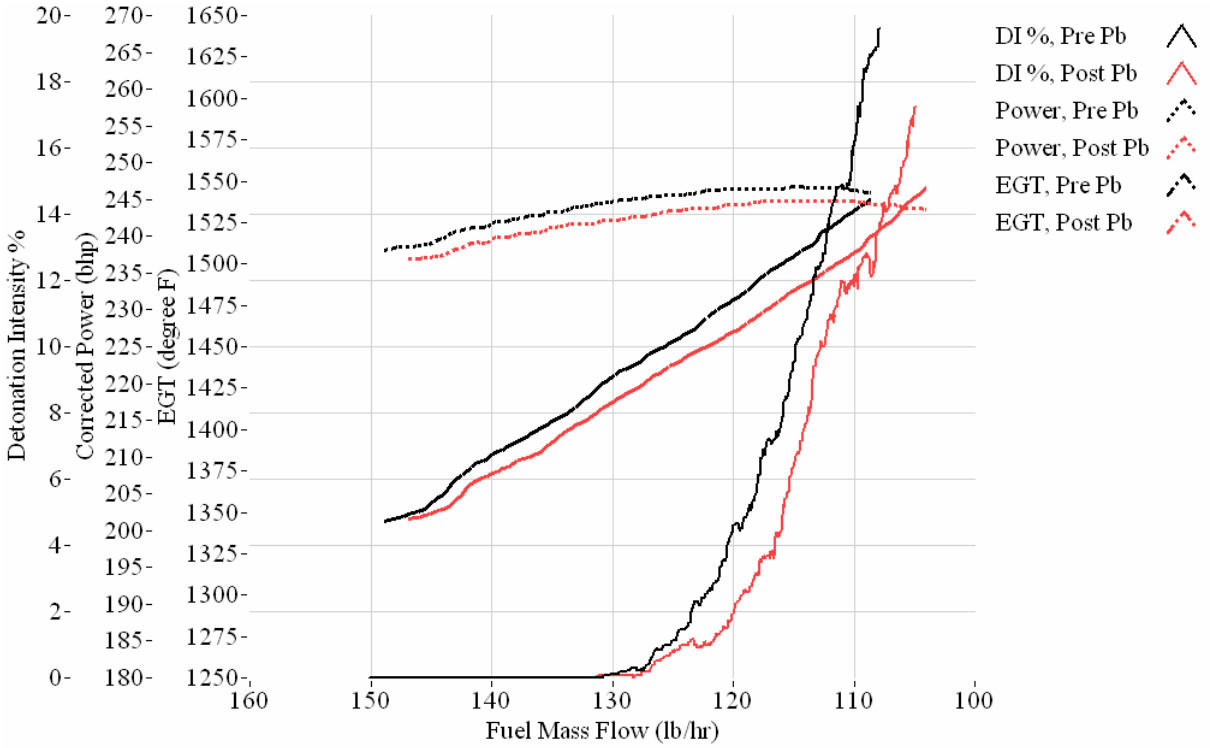


Figure 18. Aromatic Fuel at 85% Power

For 85% and 75% power settings (figures 18 and 19), both the difference in DI and the rate of DI increased, with fuel mixture leaning decreased, after the Pb exposure phase. This was probably due to the gradual removal of deposits from the cylinders by the unleaded fuel.

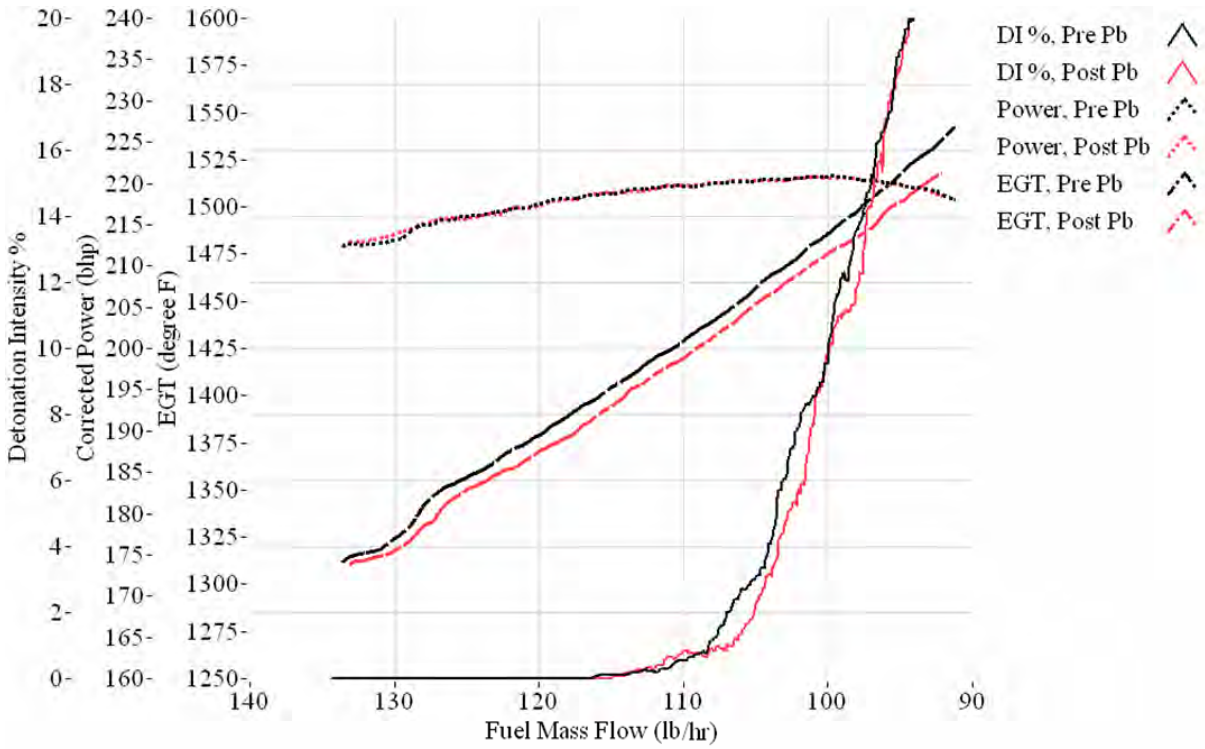


Figure 19. Aromatic Fuel at 75% Power

The Technical Center engine test results are consistent with reference 2, in which it was found that Pb deposits in an engine decay exponentially and are detectable in the exhaust gas for the first 22 minutes of operation on an unleaded fuel. In that research, DeMik and colleagues ran three high-Pb time engines: a Lycoming IO-360 (fuel-injected, 200-hp), an O-235 (115-hp), and an O-290 (135-hp). These engines were operated on an aromatic-based fuel from Swift Enterprises, the exhaust gases from each engine were periodically sampled every 2 minutes, and Pb species were measured. In all three cases, the lead content in the exhaust decayed exponentially over the first 21 to 22 minutes until it was no longer detectable.

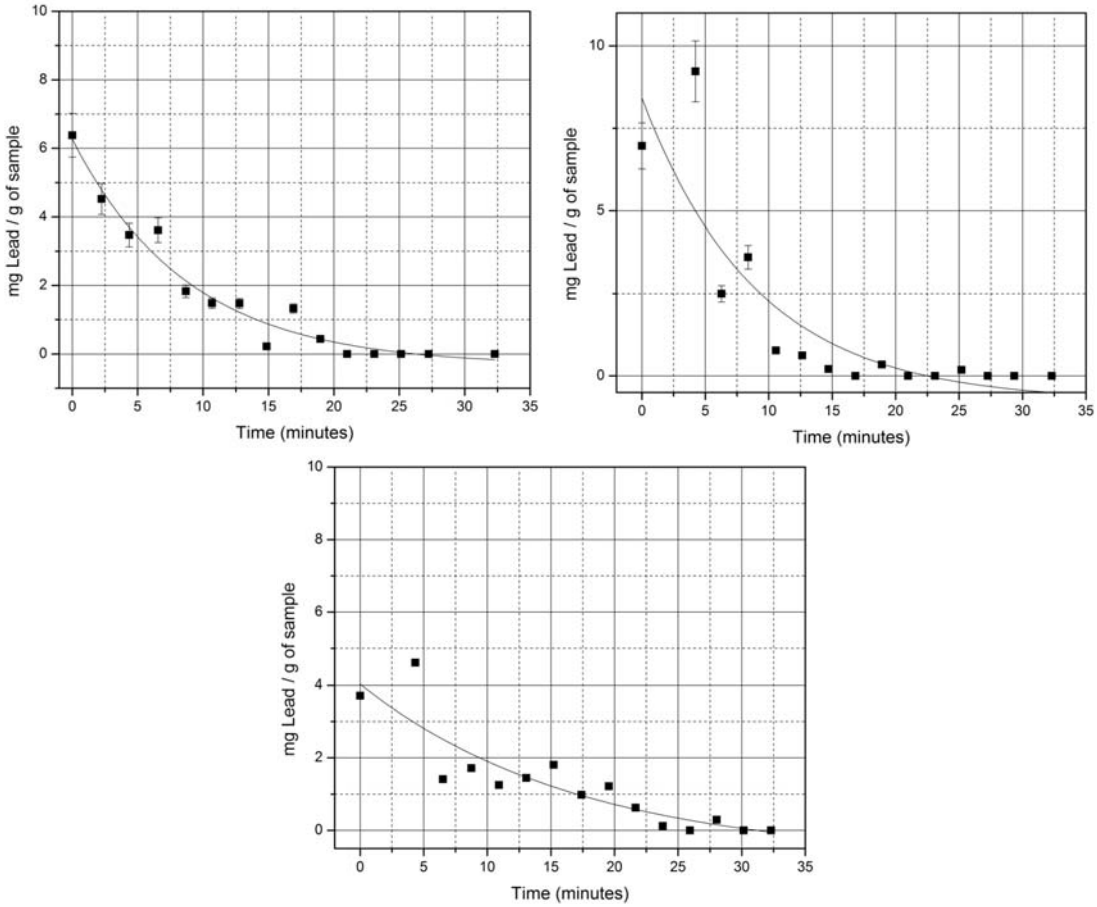


Figure 20. Lycoming O-235, O-290, and IO-360 Engines Lead Memory [2]

In reference 3, Cessna/Air BP states the following effect of engine Pb deposits on detonation performance: "the engine(s) exhibited better knock performance than with the original unleaded fuel, this hysteresis declined to undetectable levels in just 15-20 minutes." This finding and timeline matches that found by DeMik [2].

The Lewis University study [2] correlates well with other aromatic fuel tests conducted at the Technical Center. To confirm this, the Pb content in the exhaust that was measured in the Lewis study was converted to an equivalent Pb concentration in liquid fuel. The data from the three engines tested by Lewis University showed an average of roughly 6 mg Pb/g of exhaust at the beginning of motor operation with the unleaded fuel from Swift Fuels, LLC. Assuming the Swift fuel was 85% mesitylene (1,3,5-trimethylbenzene) and 15% isopentane by volume, a simple stoichiometric calculation was performed to determine the equivalent Pb concentration of incoming fuel that would produce this Pb concentration in the exhaust stream, with the simple assumption of complete combustion of the incoming Swift fuel to $CO_2$ and $H_2O$. This calculation indicated an equivalent incoming fuel Pb concentration of 0.47-grams of Pb per gallon of incoming Swift fuel. Other testing experience with Pb added in this range to high-aromatic fuels revealed similar improvements in the antiknock performance of the fuel. In reality, the Pb memory effect of the engine manifests itself in the form of lead on the walls of the

cylinder, so the localized Pb concentration affecting combustion and localized effective antiknock performance MON near the cylinder wall is higher than indicated.

Reference 4 reports that coating a glass cylinder with lead oxide quenched the presence of potentially detonation-forming oxygenated intermediates during combustion.

## CONCLUSIONS

The antiknock benefit to unleaded fuel when tested in a full-scale engine previously operated with leaded fuel was found to be approximately equivalent to between 1 and 4 Motor Octane Number (MON), depending on the unleaded fuel mixture strength. This lead (Pb) benefit effect increased with leaner fuel mixtures.

As detonation tests with the unleaded aromatic fuel continued over the first 28 minutes of unleaded fuel operation, the difference in unleaded fuel performance between pre- and post-Pb testing became less pronounced. Again, as stated above, this persistence was due to a relatively short-duration (76-hour) Pb exposure.

The 100-MON, low-lead (100LL) fuel was detonation-tested immediately before, and immediately after, the 76-hour Pb exposure phase in the engine as the control.

Based on the research findings cited in this report, it is recommended that detonation tests with unleaded fuel be performed with a clean engine that has not been operated with leaded fuel. Further, detonation tests that compare unleaded and leaded fuel performance should be done with the unleaded fuels first, followed by leaded fuels, with at least a 30- to 45-minute unleaded fuel operation prior to testing unleaded fuels again, provided the engine is initially lead-free.

These tests were performed without engine fuel filters, fuel pockets, or plumbing wells that allow leaded fuel to be trapped in the fuel system. The use of such traps and the effect they would have on Pb entering the liquid fuel phase were not addressed in these tests. Further, the use of such traps would require increased operating purge times using unleaded fuels after using Pb-based fuels to eliminate Pb effects on testing.

## REFERENCES

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3. Gonzalez, C. and Clark, A., “Significance of Leaded Hydrocarbon Fuels Knock Ratings on the Detonation Characteristics of a General Aviation Piston Engine,” Cessna/Air BP report, November 2001.

4. Sharma, K. and Bardwell, J., “The Role of Lead Oxide as an Inhibitor of Combustion,” *Combustion and Flame*, Vol. 9, Issue 1, 1965, pp. 106-108.