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Effects of MMT® Fuel Additive on Emission System Components: Comparison of Clear- and MMT®-fueled Escort Vehicles from the Alliance Study

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ABSTRACT

Emission studies were carried out on clear-fueled and MMT®-fueled 100,000-mile Escort vehicles from the Alliance study [SAE 2002-01-2894]. Alliance testing had revealed substantially higher emissions from the MMT-fueled vehicle, and the present study involved swapping the engine cylinder heads, spark plugs, oxygen sensors, and catalysts between the two vehicles to identify the specific components responsible for the emissions increase. Within 90% confidence limits, all of the emissions differences between the MMT- and Clear-vehicles could be accounted for by the selected components. NMHC emission increases were primarily attributed to the effects of the MMT cylinder head and spark plugs on both engine-out and tailpipe emissions. CO emission increases were largely traced to the MMT cylinder head and its effect on tailpipe emissions. NOx emission increases were linked to the MMT catalyst. In addition to heavy deposits on the valves and spark plugs from the MMT vehicle, substantial deposits were also observed on the catalyst, with approximately 20% of the channels totally blocked.

INTRODUCTION

Methylcyclopentadienyl Manganese Tricarbonyl (MMT®) is a fuel additive supplied by Ethyl Corporation as an octane enhancer. Its use at various levels has resulted in numerous studies citing vehicle problems, including catalyst plugging and fouling [1-10], spark plug and engine deposits [2,3,6,11-14], and effects on the oxygen sensor and On-Board Diagnostic (OBD) catalyst monitor system [3,15,16]. Such problems have led to numerous reports of increased exhaust emissions resulting from the use of MMT [3,4,9,17-19], although publications from Ethyl Corporation [6,7,20,21] have noted either little emissions impact of MMT or, in some cases, slight emissions benefits.

To resolve the conflicting data regarding the emissions impact of MMT, the Alliance of Automobile Manufacturers conducted a test program of Low Emission Vehicles (LEVs) over extended mileage (75,000 to 100,000 miles). The Alliance program utilized two vehicle pairs of each model, one vehicle of each pair accumulating mileage on a clear base fuel and the other on the same base fuel with the addition of MMT at a concentration of 8.3 mg Mn/L (0.031 or 1/32 g Mn/US gal). The results of the Alliance study are reported in SAE 2002-01-2894 [18]. The study concluded: "At the end of the program (100,000 miles), NMOG, CO, NOx and CO_2 emissions for the fleet were all statistically higher for MMT-fueled vehicles compared to Clear-fueled vehicles."

The Alliance study did not delve into the causes of the increased emissions associated with MMT fuel, but stated that: "Post-mortem analysis of the converters is planned by the individual automobile manufacturers to determine the cause of degradation in conversion performance with MMT fuel." The present study offers the first step by Ford Motor Company in that direction. One set of Escorts from the Alliance program (Clear-fueled vehicle and MMT-fueled vehicle) was subjected to 60 additional FTP emission evaluations involving various combinations of parts swapping between the two vehicles. The resulting data break down the overall emissions impact of MMT into contributions due to individual engine and emission components.

EXPERIMENTAL

VEHICLES

Two 1998 production California-certified LEV Ford Escorts were acquired from the Alliance study [18]. The vehicles are equipped with a 2.0L-2V 4-cylinder engine with split-port induction and standard platinum-tipped spark plugs. The aftertreatment system consists of a single close-coupled catalyst brick of 1.66 L volume, 62 cells/cm^2 (400 cells/in^2) cell density, 0.165 mm (0.0065 in) wall thickness, and Pd-only catalyst formulation. The front face of the catalyst brick is located 174 mm from the exhaust manifold flange. Two HEGO (Heated Exhaust Gas Oxygen) sensors, positioned in the middle of the gas stream, are located before and after the catalyst. In addition to serving as a Catalyst Monitoring

Sensor (CMS), the rear HEGO sensor also functions as a secondary air-fuel control device.

Each vehicle had accumulated 100,000 miles on a test track utilizing the EPA-proposed Standard Mileage Accumulation (SMA) cycle [18,22]. One vehicle (Alliance Tag: CE16) accumulated mileage on regular grade Chevron unleaded fuel and will be referred to as the "Clear-fueled vehicle" or "Clear-vehicle." The other vehicle (Alliance Tag: AE16) accumulated mileage on the same base fuel with added MMT (0.031 or 1/32g Mn/US gal) and will be referred to as the "MMT-fueled vehicle" ("MMT-vehicle").

The as-received vehicles were inspected and driven on the test track to assess operating performance. For both vehicles the following maintenance was conducted prior to emission testing: 1) replacement of front and rear brakes, 2) change of oil and oil filter, and 3) change of air filter. Feedgas (i.e. engine-out) and tailpipe sample probes were installed and leak-checked before emission testing.

COMPONENT EXCHANGE PROCEDURE

Engine and emission system hardware were systematically exchanged between the MMT- and Clear-fueled vehicles, both individually and in various groupings, to better understand the emission impact of these components. Table 1 describes the engine/emission component exchange and subsequent test sequence. As an example, the first table entry is the MMT-fueled vehicle with MMT engine/emission components except for the spark plugs, which are from the Clear-fueled vehicle. For the engine head exchange, the entire cylinder head, including valve train, fuel injectors, and EGR valve, was swapped between the two vehicles. After each configuration was assembled, the emission system was leak-checked prior to the emission tests.

EMISSION TESTING

Emission testing was conducted at the Ford Vehicle Emission Research Laboratory (VERL) in Dearborn, MI, using California Phase 2 fuel (without MMT). All of the tests were conducted in the same emission cell on a single-roll electric chassis dynamometer. The two vehicles were tested back-to-back in the same vehicle configuration. As an example, the MMT-fueled vehicle with the Clear-vehicle catalyst was tested on the same shift as the Clear-fueled vehicle with the MMT-vehicle catalyst.

For each vehicle configuration, the test sequence included one standard prep cycle (EPA74; FTP Bag 1 + Bag 2) followed by at least three consecutive FTP tests, measuring engine-out modal, tailpipe modal and tailpipe bag emissions of THC, NMHC, CO and NOx. Modal samples were collected using a smooth-approach orifice (SAO) device. The cumulative modal data were within 10% of the bag data, and were used to qualitatively monitor trends during the course of each FTP test. A constant soak time of 24 hours was used between emission tests. The baseline configuration was tested at the beginning, middle, and end of the program to ensure the absence of long-term drift in the emission measurements. Thus, the emissions for the baseline configuration are an average of nine tests. No emission tests were voided and all data points were used in the evaluation.

Appendix 1 compares results of emission tests conducted with the AE-16 (MMT-fueled) and CE-16 (Clear-fueled) vehicles in their original configuration, both in the Alliance study (General Motors Test Laboratories, Van Nuys, CA) and in the Ford VERL Laboratories. The Ford data also contain standard deviation and both 90 and 95% confidence intervals. Note that the emission differences between the Clear- and MMT-fueled vehicles are significant at the 95% confidence level. For determining the component effects, however, we use the 90% interval as a reasonable criterion for engineering judgment. The data between labs are consistent, with VERL giving slightly higher feedgas/tailpipe emissions for THC, NMHC, and CO, and lower feedgas/tailpipe emissions for NOx. Emission differences between the two vehicles are, for the most part, greater in the case of VERL testing than Alliance testing.

RESULTS

Results are presented below, first on the basis of complete swapping effects and second on the basis of individual and group swapping effects. For simplicity, both vehicles - when equipped with All-MMT components or All-Clear components - are referred to as the All-MMT and All-Clear configurations, respectively. Similarly, components from the two vehicles are identified by their source vehicle; the head from the MMT-vehicle, for example, is labeled simply as the MMT head. Summaries of all emission tests are contained in Appendix 2 along with standard deviations and 90% confidence limits.

COMPLETE SWAPPING

NMHC - Fig. 1 shows the NMHC feedgas emissions of the MMT-vehicle (left of the vertical dashed line) and Clear-fueled vehicle (right of the vertical dashed line), both as-received and after complete parts swapping (error bars represent the 90% confidence interval). Averaging the data for the two All-Clear component configurations, and likewise for the two All-MMT component configurations, results in a 38% increase in NMHC feedgas emissions from an average of 2.50±0.06 g/mi for the All-Clear component configurations to an average of 3.45±0.07 g/mi for the All-MMT component configurations. Increases occur in all three bags of the FTP cycle. Corresponding plots of the tailpipe NMHC emissions are presented in Fig. 2. The average emissions increase 118% from 0.055±0.001 g/mi for the All-Clear component configurations to 0.120±0.012 g/mi for the All-MMT component configurations. As with feedgas emissions, tailpipe emission differences between the All-Clear and All-MMT configurations occur in all three bags of the FTP cycle. However, the biggest effect, on a non-weighted mass basis, is in Bag 1, as detailed in the second-by-second cumulative tailpipe emission plots of Fig. 3. The All-Clear and All-MMT configurations diverge sharply throughout Hill 1 and during the acceleration to 55 mph in Hill 2. Note that cumulative NMHC emissions increase steadily throughout Bags 2 and 3 for the All-MMT configurations, whereas only slight growth is observed for the All-Clear configurations.

CO - CO feedgas emissions increase in the All-MMT configurations compared to the All-Clear configurations (Fig. 4), but only by about 10% versus the 38% observed for NMHC. CO tailpipe emissions (Fig. 5) increase by 130% (from 0.63±0.04 g/mi for the averaged All-Clear configurations to 1.45±0.10 g/mi for the averaged All-MMT configurations). The second-by-second plots for tailpipe CO (Fig. 6) are similar to those of Fig. 3 for NMHC, although the gap between the All-MMT and All-Clear emissions develops later for CO (Bag 1/Hill 2) compared to NMHC (Bag 1/Hill 1). Similar to NMHC, cumulative CO emissions increase much more throughout Bags 2 and 3 for the All-MMT configurations compared to the All-Clear configurations.

NOx - Figs 7 (feedgas) and 8 (tailpipe) show results of complete swapping experiments on NOx emissions. Unlike NMHC and CO, feedgas NOx emissions for the 4 configurations are identical within the confidence limits of the data (1.07±0.04 g/mi for the averaged All-Clear configurations versus 1.04±0.07 g/mi for the averaged All-MMT configurations. Tailpipe NOx emissions, however, increase by 143% from the averaged All-Clear cases to the averaged All-MMT cases. The bag-by-bag breakdown of the tailpipe NOx data in Fig. 8 shows a larger relative contribution of Bag 3 in the case of NOx emissions compared to NMHC and CO emissions. This is evident in the second-by-second NOx emission data of Fig. 9, which shows a large separation between All-MMT and All-Clear emissions during the acceleration to 55 mph in Bag 3/Hill 2 (~1600 seconds into the test). That acceleration and its Bag 1 counterpart (~200 seconds into the test) account for most of the emission differences between the All-MMT and All-Clear component configurations.

INDIVIDUAL AND SUB-GROUP SWAPPING

NMHC - Fig. 10 summarizes component effects on NMHC feedgas emissions for the Clear-vehicle. For single component swapping (left of the vertical dashed line), only substitution of the head from the MMT vehicle produces a statistically significant emissions increase. For the grouped components (to the right of the dashed vertical line), only a small emissions increase occurs with the spark-plug/sensor/catalyst combination, but an increase to the All-MMT level occurs with the head/spark-plug combination. Taken together, these data clearly show that the MMT head accounts for most of the increase in NMHC feedgas emissions. The same general trend occurs in the reverse direction (i.e., substituting components from the Clear-vehicle into the MMT-vehicle). As shown in Fig. 11, only the Clear-vehicle head and spark plugs produce significant emission decreases, and only the configurations involving a head switch decrease emissions to All-Clear levels.

The dominating effect of the MMT head on NMHC feedgas emissions carries through to tailpipe emissions, as shown in Fig. 12 for MMT parts swapping into the Clear-fueled vehicle. The effects of sensor, spark plugs, and catalyst, although individually not strong, combine to account for about half the tailpipe NMHC emissions increase in converting the Clear-fueled vehicle to one with all MMT components. The MMT head roughly accounts for the other half. The same observations are generally true of replacing parts on the MMT-fueled vehicle with those from the Clear-fueled vehicle (Fig. 13). The combination of Clear-vehicle spark plugs, sensor, and catalyst drops emissions part of the way to the All-Clear level, but the Clear-vehicle head is needed to reach the All-Clear level. Interestingly, the head swap alone decreases emissions to levels characteristic of the complete component swap.

CO - Figs. 14 and 15 show the effect of the component swaps on CO feedgas emissions. For the Clear-vehicle (Fig. 14), none of the individual MMT-vehicle components increase emissions except for the MMT head, and only the MMT head/spark-plug combination increases CO feedgas emissions to the level of the All-MMT vehicle. Similar effects are observed for the MMT-vehicle (Fig. 15). Only component swaps involving the Clear-vehicle head bring CO feedgas emissions down to levels characteristic of the All-Clear vehicle.

Given the relatively small effect of MMT on feedgas CO emissions, and the dominance of the MMT head in producing those effects, one would expect that a downstream component (either the sensor or the catalyst) would explain the large differences in CO tailpipe emissions noted previously in the complete swapping experiments (Fig. 5). Surprisingly this is not the case. Fig. 16 indicates that substituting the MMT catalyst, sensor, or spark plugs into the Clear-vehicle causes only a small increase in emissions. Substituting the MMT head has the greatest impact, and the combination of the MMT head and spark plugs brings the Clear-vehicle to CO tailpipe emissions characteristic of the MMT-vehicle. The same trend is evident in substituting Clear-vehicle components into the MMT-vehicle (Fig. 17). Replacing the catalyst or sensor has no significant effect on CO tailpipe emissions. Only swaps involving the Clear-vehicle head decrease CO tailpipe emissions to levels of the All-Clear vehicle.

The CO tailpipe results also point out the importance of interactions between components. For example, in Fig. 16, the MMT spark plugs have little impact by themselves, but when combined with the MMT head increase emissions to the All-MMT level. Similarly, in Fig. 17, the Clear catalyst and Clear sensor by themselves do not decrease emissions from the All-MMT level, but, when combined with the Clear spark plugs, bring emissions down nearly to the All-Clear level.

NOx – In keeping with the overall feedgas emission trends for NOx shown in Fig. 7, individual or group component swaps do not reveal a consistent trend across both vehicles, as shown in Figs. 18 and 19. The NOx tailpipe emissions, however, are strongly dominated by the catalyst (Figs. 20 and Fig. 21). None of the other component swaps, either singly or in combination, produces a significant effect on tailpipe NOx emissions.

COMPONENT ANALYSES

HEGO sensors - Fig. 22 shows photographs of the front and rear HEGO sensors from the Clear- and MMT-vehicles. Both the front and rear sensors from the MMT-vehicle contain reddish deposits characteristic of manganese oxide on the outer surface. No off-vehicle analyses were conducted on any of the sensors; nor were their operating characteristics measured in tests other than the parts swapping experiments described above.

Spark plugs - Fig. 23 shows representative Clear- and MMT-vehicle spark plugs. Note the high level of deposits on the center electrode and insulator tip of the MMT-vehicle spark plug compared to the Clear-vehicle counterpart. Spark plug performance characteristics were not measured. However, no OBD codes related to misfire of any type were registered during the course of the emission testing. Nevertheless, engine stumbling was noted with the MMT-vehicle spark plugs when installed on either vehicle. A detailed investigation of transmission performance characteristics confirmed that the observed stumbling was not related to the transmission.

Catalysts - Fig. 24 shows photographs of a region at the front face of the catalyst from the MMT-vehicle (Fig. 24a) and the Clear-vehicle (Fig. 24b) as delivered to Ford. The photos were obtained with a digital camera. The MMT catalyst photo shows plugging of some channels in the region close to the converter wall. Similar photographs near the center of the brick showed evidence of deposit build-up in the channels, but not to the point of plugging. The fraction of completely blocked channels is estimated at 20% from visual examination. No deposits were observed on the catalyst from the Clear-fueled vehicle, as evident in Fig.24b.

Engine head - Fig. 25 shows side-by-side photographs of engine intake and exhaust valves from the Clear- and MMT-vehicle heads. Deposits are visible on both the intake and exhaust valves from the MMT-fueled vehicle as well as over the entire bowl area of the head. An enlarged view of the exhaust valves is shown in Fig. 26. A cylinder leak-down procedure was conducted to quantify the exhaust valve leakage. Higher leakage was observed with the MMT-vehicle head compared to the Clear-vehicle head, measured on both vehicles.

DISCUSSION

NMHC AND CO

Feedgas - The effects of MMT-fuel on both NMHC and CO feedgas emissions are strongly influenced by the cylinder head. Reddish-brown deposits, characteristic of manganese oxides, in the combustion chamber can increase feedgas HC emissions by trapping fuel components and releasing them during the exhaust stroke [11]. In addition, deposits on the valve seats can cause valve leakage, as confirmed by the higher leak-down rates on the cylinder head from the MMT vehicle. In this respect, the Escort vehicle fueled with MMT is similar to the Honda Civics operated on MMT fuel in the Alliance Study. Both the MMT-fueled Civics and Escorts showed significant increases in feedgas HC above 50,000 miles compared to their Clear-fueled sister vehicles [18]. As in our study, one of the pairs of Honda Civics was analyzed for valve leakage and the MMT vehicle was found to have substantial exhaust-valve leakage [18]. Deposits can also accumulate below the cylinder head on the upper cylinder wall and piston crown. However, component swaps involving only the cylinder head (and spark plugs) were sufficient to account for all of the feedgas HC increase between the MMT- and Clear-fueled vehicles. So, we find no evidence that combustion chamber deposits beyond those on the head made a significant contribution to the observed increase in NMHC feedgas emissions on the MMT-fueled vehicle. The fuel injectors and EGR valve were also swapped as part of the head assembly. Additional parts-swapping experiments showed only small effects due to those components, however, and will be reported in a future paper.

CO feedgas emission effects parallel those of NMHC in pointing to the cylinder heads as the main source of differences between the Clear- and MMT-vehicles. The relative effect is much smaller in the case of CO compared to NMHC (10% for CO vs 38% for NMHC), as expected given that CO is a product of incomplete combustion and not directly affected by exhaust-valve leakage or cylinder deposits. Generally, increases in CO feedgas emissions (in feedback-controlled gasoline vehicles) can be traced to rich shifts in A/F ratio. The present study is no exception. Fig. 27 compares FTP, Bag 2 rear-sensor voltage-time traces, averaged over all of the tests with the MMT-vehicle head, compared to corresponding averages obtained with the Clear-vehicle head. The higher mean voltages observed with the MMT head indicate a richer mean A/F ratio presented to the catalyst, consistent with the observed increase in CO feedgas emissions.

The cause of the rich A/F shift induced by the MMT head is not fully understood. Combustion chamber and valve deposits affect the transient response of the feedback control system by acting like a sponge for HC (i.e. storing HC at throttle tip-in and releasing stored HC at throttle tip-out). Analysis of the type shown in Fig. 27, when applied to the primary (i.e. front) oxygen sensors on a second-by-second basis, did not show significant differences in mean A/F between runs made with the MMT and Clear heads. Hence, the high-frequency HC composition perturbations induced by the deposits could not be corrected within the time response of the feedback control system.

Tailpipe - Head effects strongly influence both NMHC and CO tailpipe emissions, but in different ways. For NMHC, two head-related effects, both of roughly equal magnitude, dominate tailpipe emissions. The first is simply an increase in tailpipe emissions due to the higher feedgas emissions associated with deposits and valve leakage. The second is the rich A/F shift noted above. Table 2 contains Bag 2 FTP NMHC efficiencies from all runs made with the MMT head compared to those with the Clear head. In averaging over all combinations with the MMT head, the mean rear sensor voltage is 0.813 (indicating a rich bias) and the mean NMHC efficiency is 98.9%; the corresponding numbers for the Clear-vehicle head are 0.746 (less rich) and 99.6%. Larger differences in efficiency occur in Bag 1. So, in the case of NMHC, the MMT head challenges the catalyst with higher feedgas emissions and richer conditions (i.e., slightly less oxygen relative to the amount of HC presented) than in the case of the Clear head.

CO tailpipe emissions, as with NMHC, are strongly affected by the MMT head. In contrast to NMHC, however, the increase in feedgas CO level is slight and presents little challenge to the catalyst. On the other hand, CO catalytic conversion is much more sensitive than NMHC to rich A/F ratio shifts. This is shown in Table 2, where average Bag 2 CO conversion efficiency is about 87% for component combinations with the MMT head vs 97% for the corresponding combinations with the Clear head.

Finally, it is interesting to note the similarities in component effects for tailpipe NMHC (Figs. 12 and 13) and CO (Figs. 16 and 17). As discussed previously, the head (and to some extent spark-plugs) largely controls the level of tailpipe emissions. For both CO and NMHC tailpipe emissions (Figs. 13 and 17), the Clear head is sufficient to bring the MMT-vehicle emissions down to the All-Clear vehicle level. This implies that head effects (i.e. A/F ratio shift and feedgas emissions increase) are the controlling factor (i.e., equivalent performance can be obtained with either MMT or Clear sensors, spark-plugs, and catalyst). Going the other way (Figs. 12 and 16), the MMT head is not sufficient to bring the Clear-vehicle emissions up to the MMT-vehicle level. Here, the head effects are not completely controlling; the better performance of the other Clear-vehicle components relative to their MMT-vehicle counterparts compensates, to some extent, for the richer A/F ratio and higher feedgas levels induced by the MMT head.

NO_X

Feedgas - In principle, manganese-based cylinder deposits can lead to higher combustion temperatures (due to the insulating effect of deposits) or higher effective cylinder pressures (due to lost combustion chamber volume). However, the absence of significant differences in feedgas NOx emissions between the MMT- and Clear-vehicles suggests either little contribution from those effects or contributions from offsetting factors (e.g., the higher leak-down rates observed with the MMT head could imply lower peak cylinder pressures, thus offsetting possible insulating and cylinder volume reduction effects of the MMT head). Other factors, such as the slight differences observed in mean A/F ratio and possible differences in EGR rates between the two systems (owing to deposits on the MMT catalyst), could also represent compensating effects.

Tailpipe - NOx tailpipe emissions are strongly dominated by the catalyst. The MMT-vehicle catalyst, and no other MMT components, either singly or in combination, significantly affects NOx tailpipe emissions. At first glance this is surprising, given the discussion above of the rich A/F shift induced by the MMT head. Traditionally, rich A/F shifts adversely affect CO and HC conversion and increase NOx conversion. LEV emission systems, however, require much tighter A/F control than earlier vehicles, and often incorporate a slight rich bias in the calibration to ensure compliance with the more stringent NOx standards characteristic of LEV regulations. Such is the case with the Escort vehicles of this study, as noted earlier. Most catalysts show a broad maximum in NOx conversion with A/F rich of the stoichiometric point [23], so the A/F conditions of this study should be nearly optimal for NOx control regardless of the specific component configurations.

The catalyst deposits are the most likely cause of the lower NOx conversion over the MMT poisoned catalyst. By plugging about 20% of the catalyst channels and partially blocking the remainder, the deposits effectively create a higher space velocity (i.e. shorter residence time) through the catalyst. A dynamometer study of space velocity effects on the same Pd-only catalyst formulation as deployed on the Escort vehicles [24] showed a strong decrease in CO/NOx crossover efficiency as the space velocity was increased from 80,0000 h^{-1} to 240,000 h^{-1} at a constant exhaust temperature of 450ºC. Much of the difference in NOx tailpipe emissions between the MMT- and Clear-vehicles occurs during the hard acceleration to 55 mph in the second hill of Bags 1 and 3. These are the highest space velocity conditions of the FTP cycle; and the lower conversions obtained with the poisoned catalyst suggest that contact time is limiting the conversion.

Manganese oxides undergo redox chemistry [16], so the deposits on the catalyst might adversely affect NOx conversion by consuming reductants (i.e., CO and H_2) that are needed to reduce NOx. More detailed understanding of the effect of MMT on NOx emissions will need to await catalyst characterization analyses, which are the subject of an on-going study.

SUMMARY

Parts swapping experiments on a pair of 100,000 mile 1998 Escort vehicles from the Alliance MMT study revealed the following observations as to the cause of substantially higher exhaust emissions on the MMT-fueled vehicle compared to its Clear-fueled counterpart:

- All emissions differences between vehicles could be accounted for by the components investigated (cylinder head, spark plugs, oxygen sensors, and catalyst). Complete swapping of components between the Clear- and MMT-fueled vehicles produced the same emissions characteristic of the original configurations on the partner vehicle (within a 90% confidence interval). No evidence was found for intrinsic differences between the two vehicles contributing to the large emission differences induced by mileage accumulation on clear versus MMT fuel.
- NMHC feedgas emissions of the Clear-vehicle increased by 38%, and CO emissions by 10%, with MMT-vehicle components. No significant effect of MMT-fuel was observed on NOx feedgas emissions.
- Complete exchange of Clear-vehicle components with MMT-vehicle counterparts increased tailpipe emissions of NMHC by 118%, CO by 130%, and NOx by 143%.
- Heavy cylinder head deposits were observed on the spark plugs, valves and other combustion chamber surfaces in the case of the MMT-vehicle.
- The tailpipe emissions impact of MMT on NMHC and CO primarily involved the cylinder head (and to some extent the spark-plugs).
- For NMHC, the increased tailpipe emissions associated with MMT components were caused by a combination of higher feedgas emissions and a rich A/F shift (roughly a 30% relative contribution due to feedgas and 70% due to A/F). For CO, the corresponding contributions were roughly 10% and 90%.
- NOx tailpipe emissions were dominated by the effect of MMT-fuel on catalyst performance.
- Reddish-brown deposits on the catalyst from the MMT vehicle (consistent with manganese oxides) resulted in full plugging of about 20% of the channels and heavy deposits at the front face of the remaining channels. The higher effective space velocity of the MMT catalyst may account for its lower NOx conversion efficiency.

Taken together, these observations show that the effects of MMT fuel additive are spread across a number of engine and emission components. Moreover, NMHC, CO, and NOx all respond in complex and different ways to MMT-derived deposits. Work is continuing in our laboratory to further understand the underlying reasons for the deleterious effect of MMT on vehicle exhaust emissions.

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CONTACT

R. W. McCabe: Tel. +1-313-337-8042; fax: +1-313-594-2963; e-mail: rmccabe@ford.com

Table 1. Vehicle Configurations for Emission Testing

Configuration	Vehicle	Spark Plugs	Oxygen Sensors	Catalyst	Engine Head (1)
Individual Components					
1	MMT	**Clear**	MMT	MMT	MMT
2	MMT	MMT	**Clear**	MMT	MMT
3	MMT	MMT	MMT	**Clear**	MMT
4	MMT	MMT	MMT	MMT	**Clear**
Grouped Components					
5	MMT	MMT	MMT	MMT	MMT
6	MMT	**Clear**	**Clear**	**Clear**	MMT
7	MMT	**Clear**	MMT	MMT	**Clear**
8	MMT	**Clear**	**Clear**	**Clear**	**Clear**
Individual Components					
1	Clear	**MMT**	Clear	Clear	Clear
2	Clear	Clear	**MMT**	Clear	Clear
3	Clear	Clear	Clear	**MMT**	Clear
4	Clear	Clear	Clear	Clear	**MMT**
Grouped Components					
1	Clear	Clear	Clear	Clear	Clear
2	Clear	**MMT**	**MMT**	**MMT**	Clear
3	Clear	**MMT**	Clear	Clear	**MMT**
4	Clear	**MMT**	**MMT**	**MMT**	**MMT**

(1) Engine Head includes cylinder head, valve train, fuel injectors and EGR valve.

Table 2. Average rear sensor voltage and NMHC, CO and NOx efficiency over Bag 2 of the FTP cycle

Combos with MMT Head					**Combos with Clear Head**				
		Bag 2 Average Efficiency (Bag Data)					**Bag 2 Average Efficiency (Bag Data)**		
	Rear Hego	**NMHC Eff (%)**	**CO Eff (%)**	**NOx Eff (%)**		**Rear Hego**	**NMHC Eff (%)**	**CO Eff (%)**	**NOx Eff (%)**
MMT Veh_MHd_Spk_Sen_Cat	0.809	98.4%	86.6%	92.5%	MMT Veh_CHd	0.726	99.6%	97.2%	94.9%
MMT Veh_Ccat	0.841	99.2%	82.7%	97.8%	MMT Veh_CHd_Spk	0.675	99.7%	97.7%	92.9%
MMT Veh_Csen	0.823	97.9%	84.5%	93.4%	MMT Veh_CHd_Spk_Sen_Cat	0.778	99.8%	96.0%	98.9%
MMT Veh_CSpk	0.803	98.7%	91.3%	95.1%	Clear Veh_CHd_Spk_Sen_Cat	0.731	99.8%	97.8%	98.5%
MMT Veh_CSpk_Sen_Cat	0.812	99.8%	94.7%	99.2%	Clear Veh_Mcat	0.737	99.6%	98.3%	95.8%
Clear Veh_MHd	0.810	99.7%	91.0%	99.1%	Clear Veh_Msen	0.774	99.8%	97.5%	98.1%
Clear Veh_MHd_Spk	0.814	99.1%	81.1%	97.3%	Clear Veh_MSpk	0.777	99.7%	97.4%	98.6%
Clear Veh_MHd_Spk_Sen_Cat	0.792	98.2%	84.8%	92.9%	Clear Veh_MSpk_Sen_Cat	0.771	99.0%	93.7%	95.6%
Average - MMT Head	**0.813**	**98.9%**	**87.1%**	**95.9%**	**Ave - Clear Head**	**0.746**	**99.6%**	**96.9%**	**96.7%**
Standard Deviation	***0.014***	***0.7%***	***4.8%***	***2.8%***	***Standard Deviation***	***0.036***	***0.3%***	***1.5%***	***2.2%***

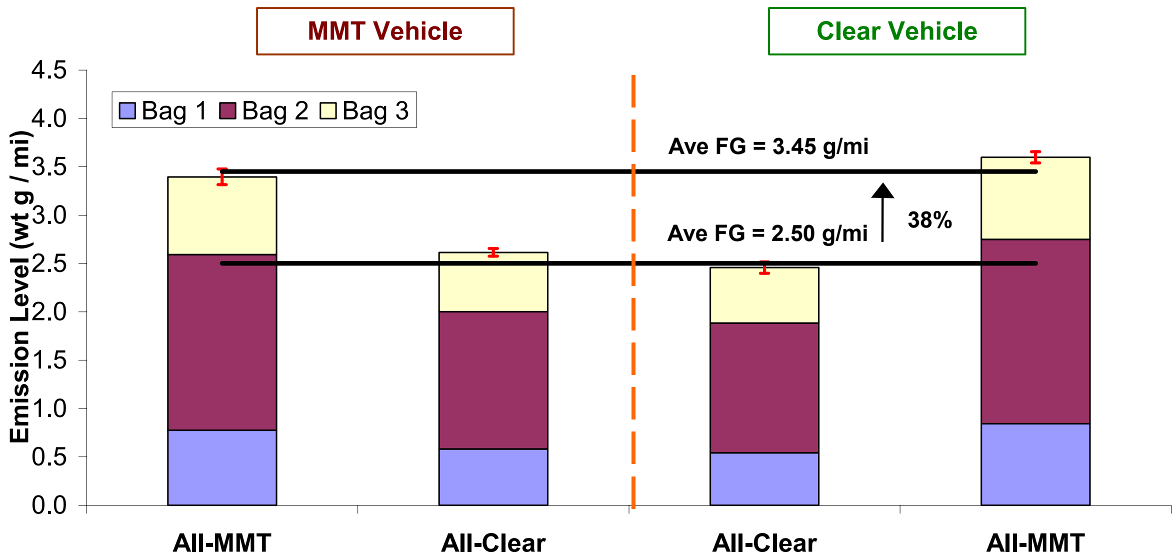


Figure 1. NMHC feedgas emissions of the MMT- and Clear-vehicle, as received and after complete parts swap.

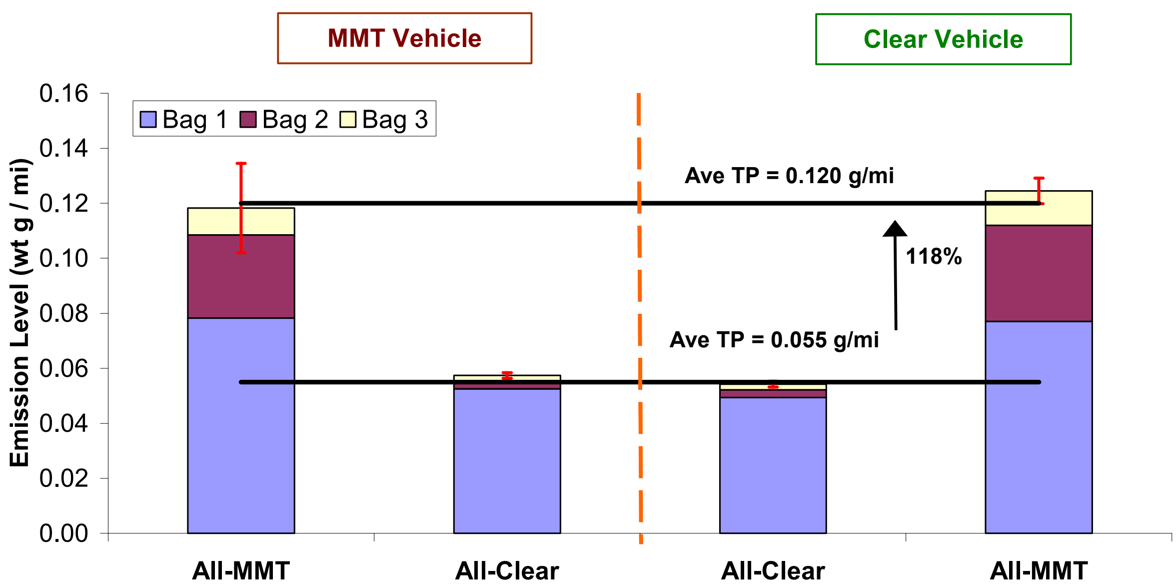


Figure 2. NMHC tailpipe emissions of the MMT- and Clear-vehicle, as received and after complete parts swap.

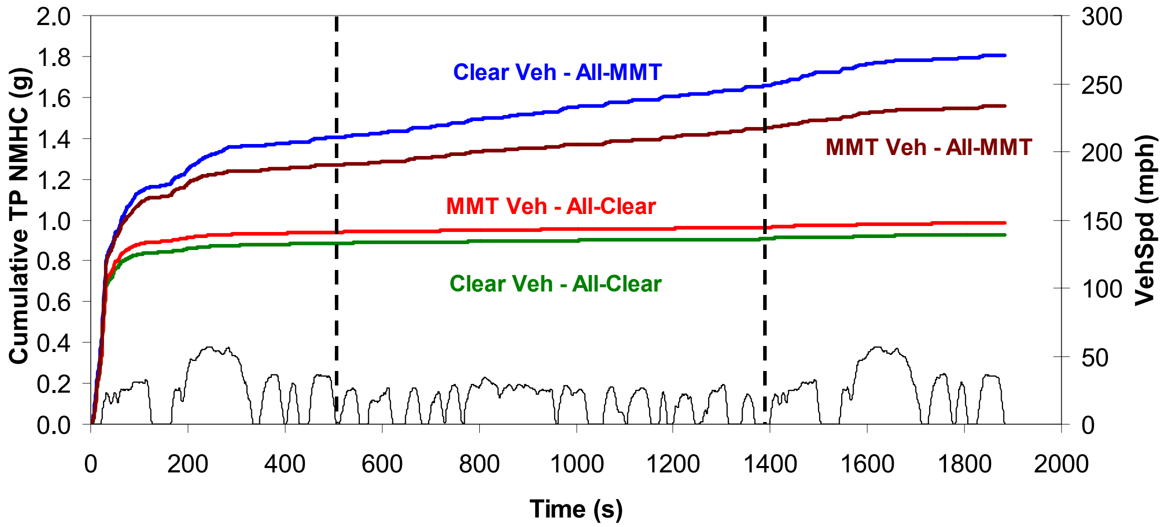


Figure 3. Cumulative NMHC tailpipe emissions of the MMT- and Clear-vehicle, as received and after complete parts swap. The dashed lines separate Bags 1, 2 and 3 of the FTP cycle.

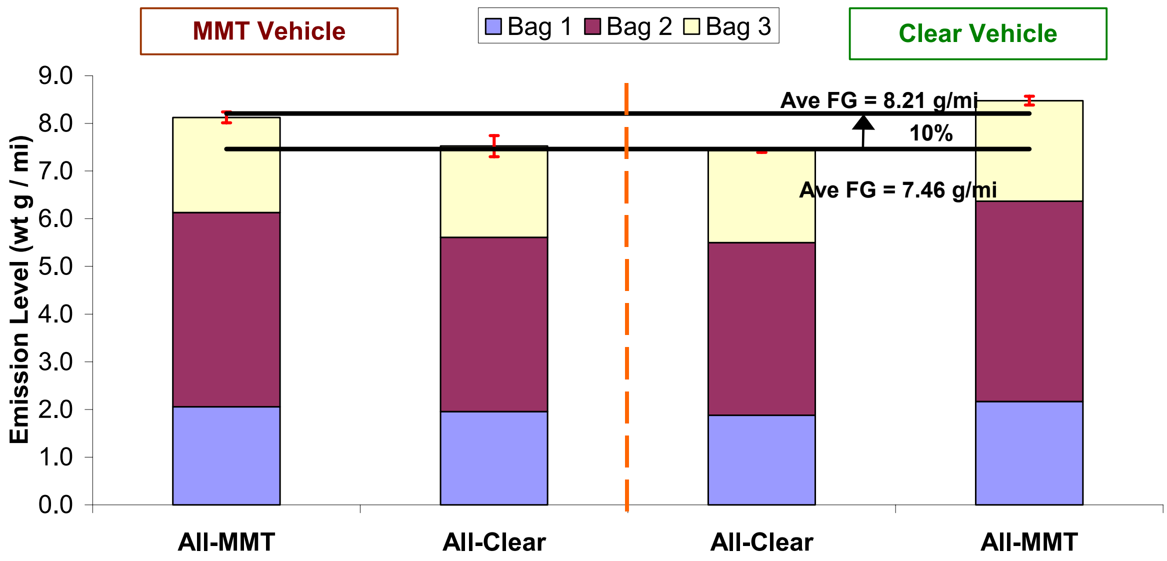


Figure 4. CO feedgas emissions of the MMT- and Clear-vehicle, as received and after complete parts swap.

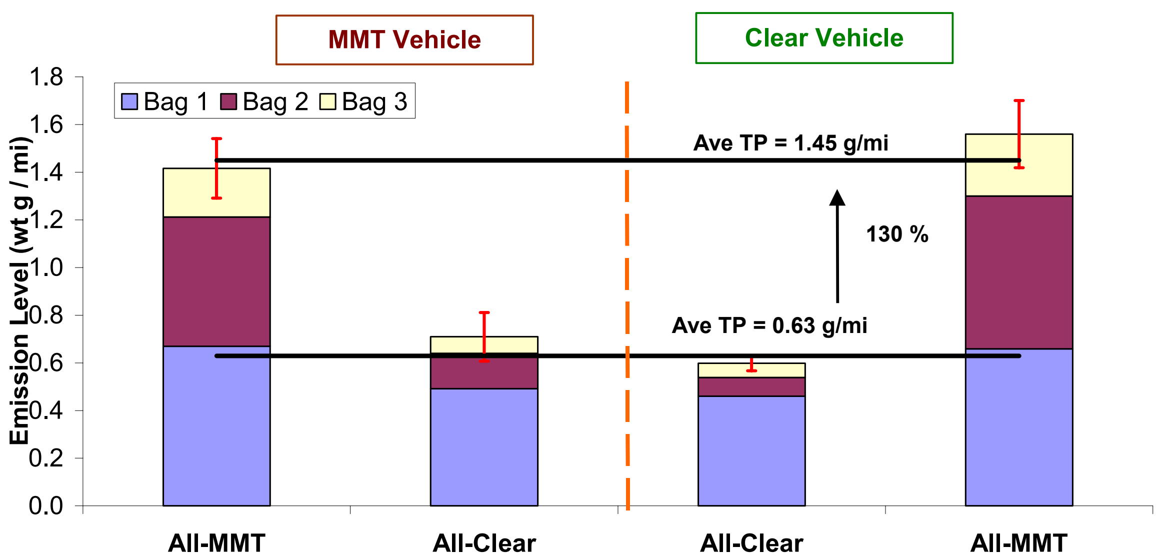


Figure 5. CO tailpipe emissions of the MMT- and Clear-vehicle, as received and after complete parts swap.

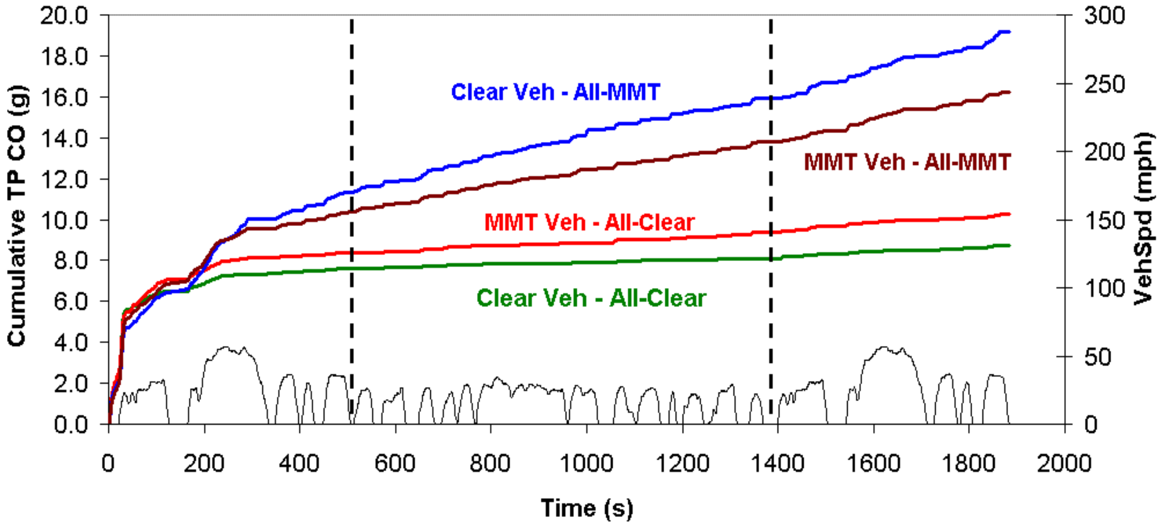


Figure 6. Cumulative CO tailpipe emissions of the MMT- and Clear-vehicle, as received and after complete parts swap. The dashed lines separate Bags 1, 2 and 3 of the FTP cycle.

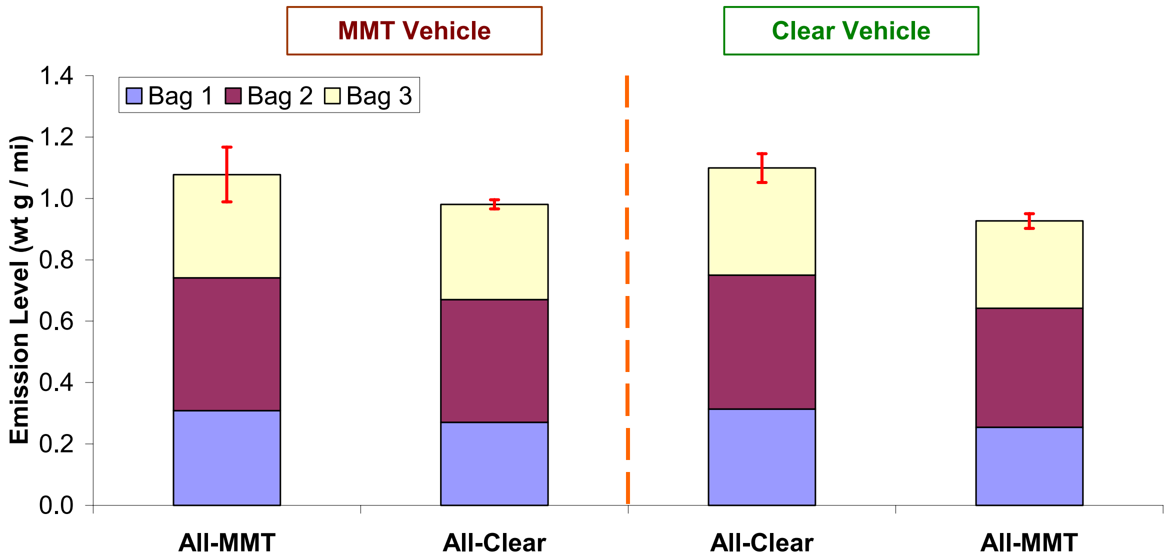


Figure 7. NOx feedgas emissions of the MMT- and Clear-vehicle, as received and after complete parts swap.

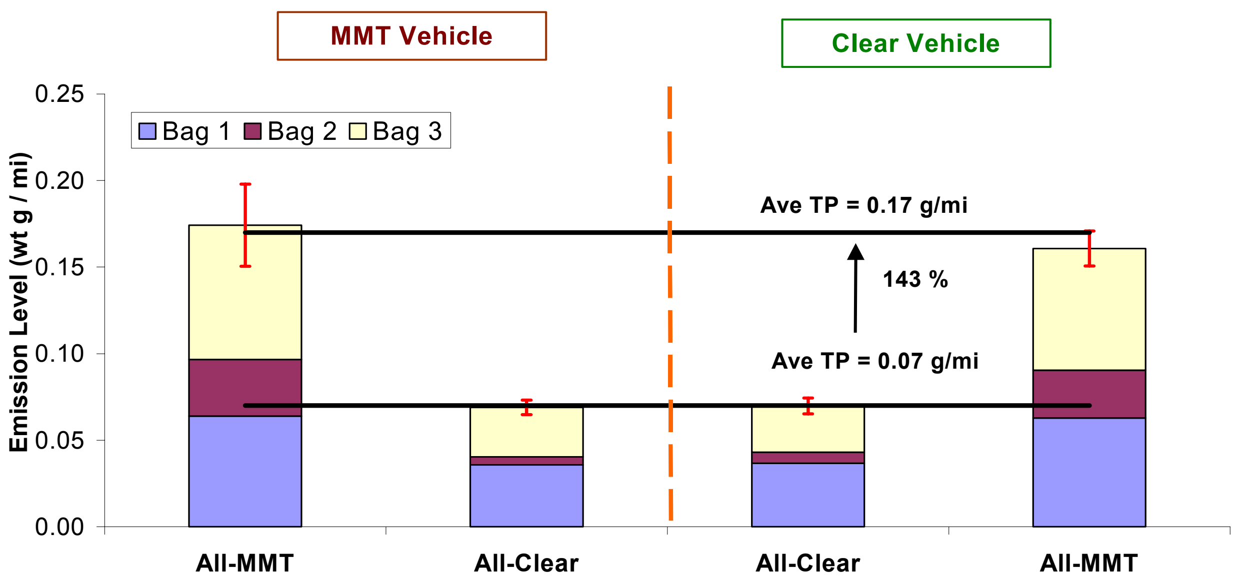


Figure 8. NOx tailpipe emissions of the MMT- and Clear-vehicle, as received and after complete parts swap.

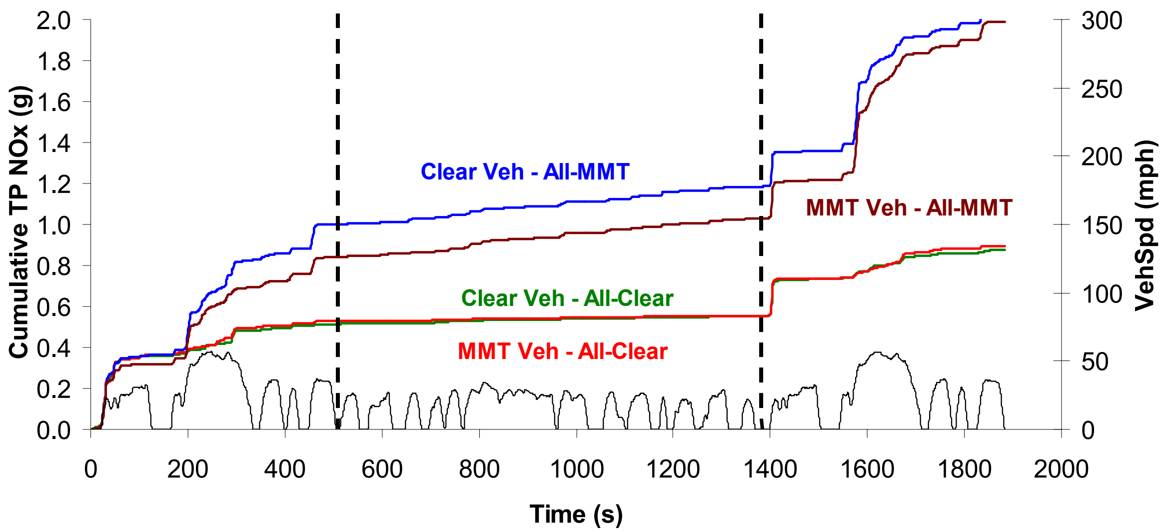


Figure 9. Cumulative NOx tailpipe emissions of the MMT- and Clear-vehicle, as received and after complete parts swap. The dashed lines separate Bags 1, 2 and 3 of the FTP cycle.

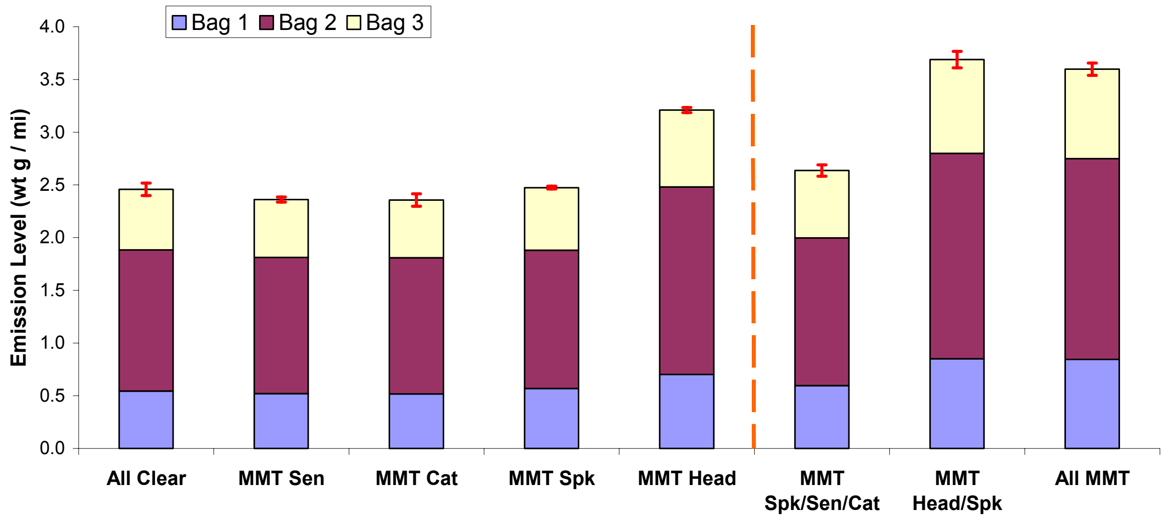


Figure 10. NMHC feedgas emissions from single and grouped components on the Clear vehicle.

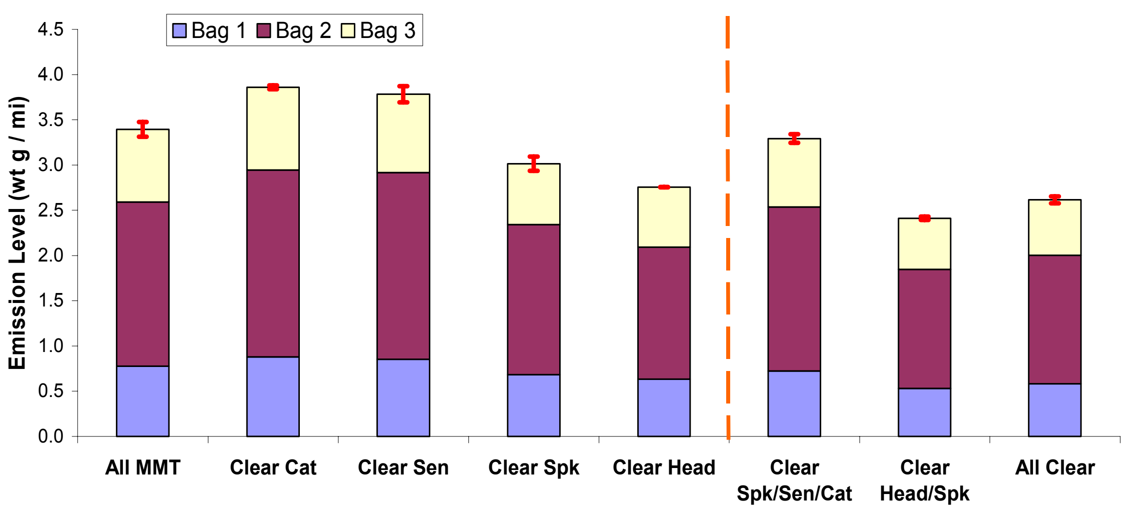


Figure 11. NMHC feedgas emissions from single and grouped components on the MMT vehicle.

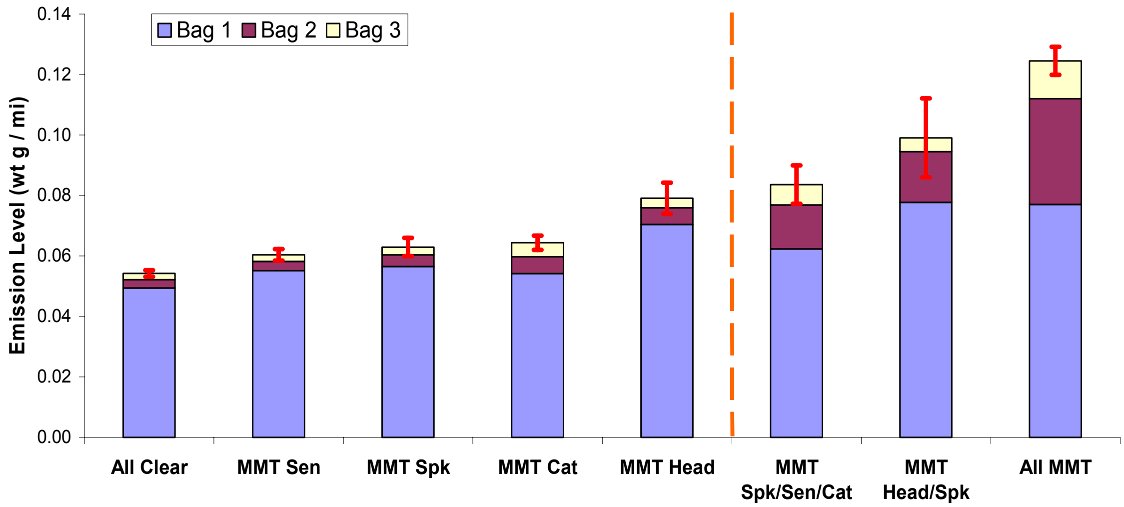


Figure 12. NMHC tailpipe emissions from single and grouped components on the Clear vehicle.

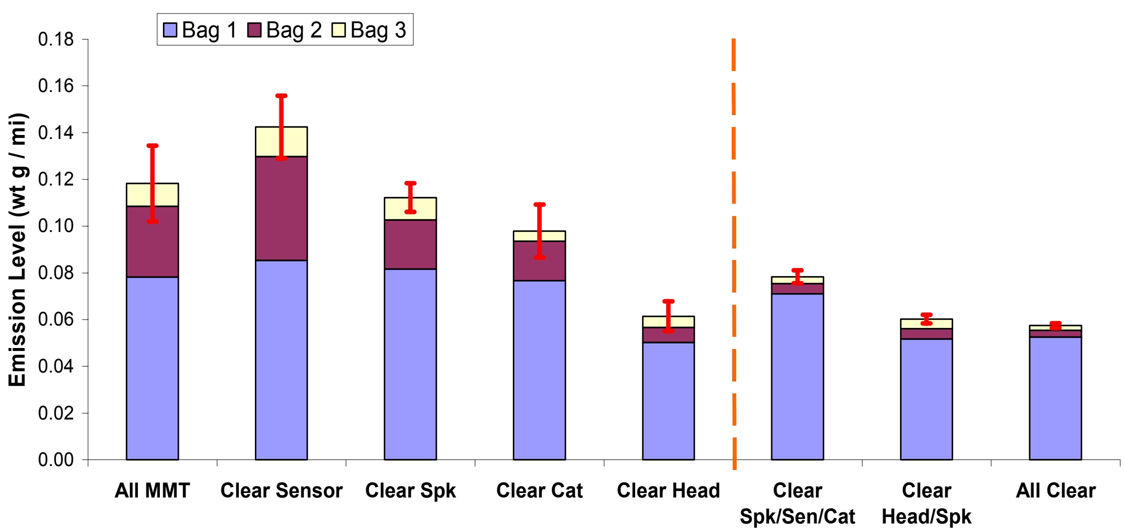


Figure 13. NMHC tailpipe emissions from single and grouped components on the MMT vehicle.

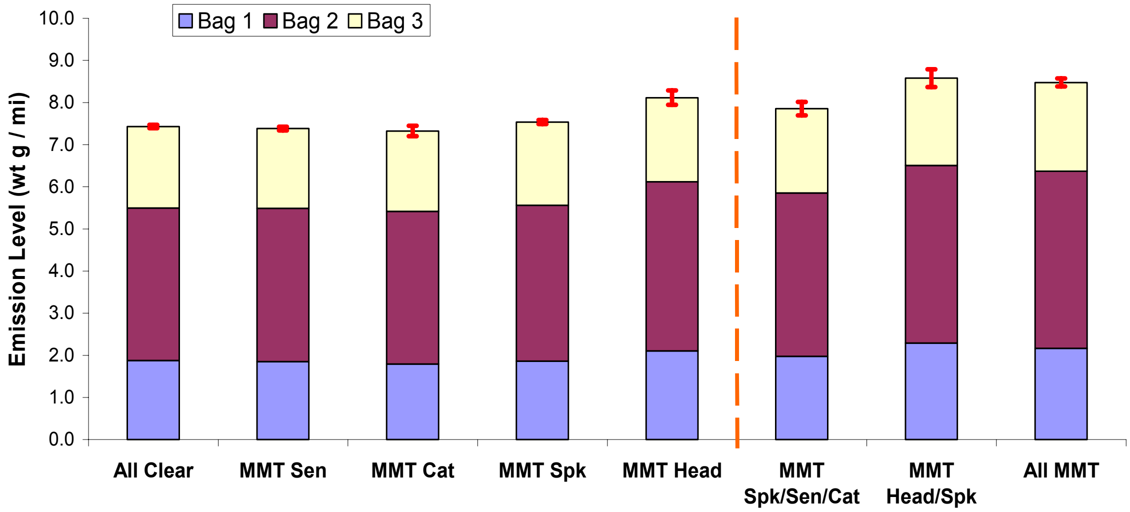


Figure 14. CO feedgas emissions from single and grouped components on the Clear vehicle.

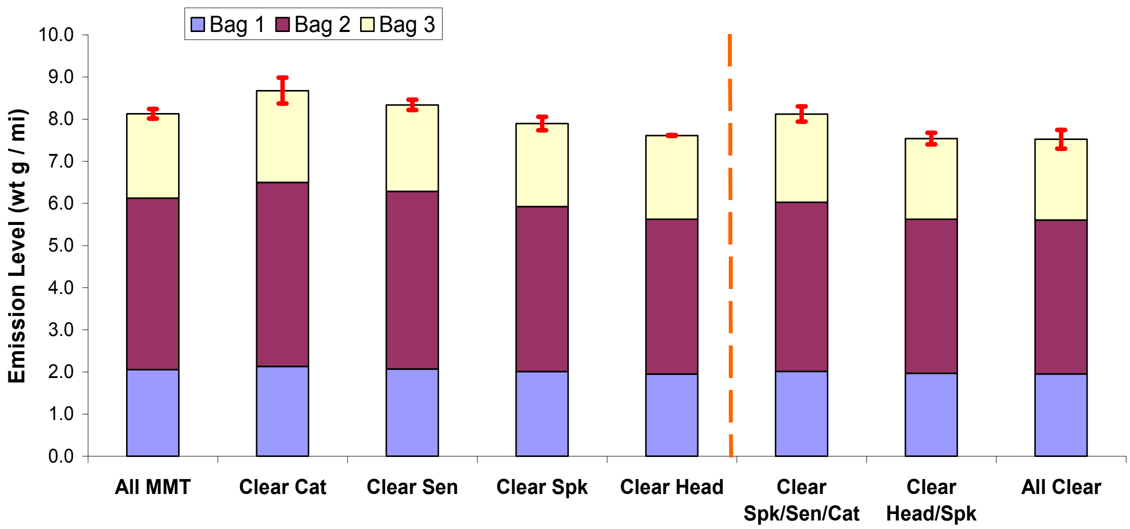


Figure 15. CO feedgas emissions from single and grouped components on the MMT vehicle.

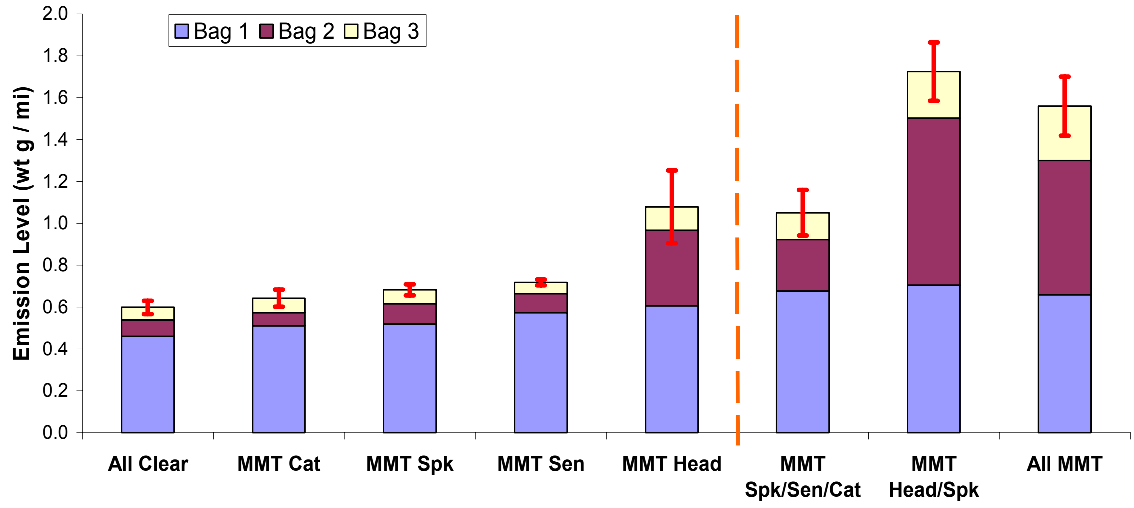


Figure 16. CO tailpipe from single and grouped components on the Clear vehicle.

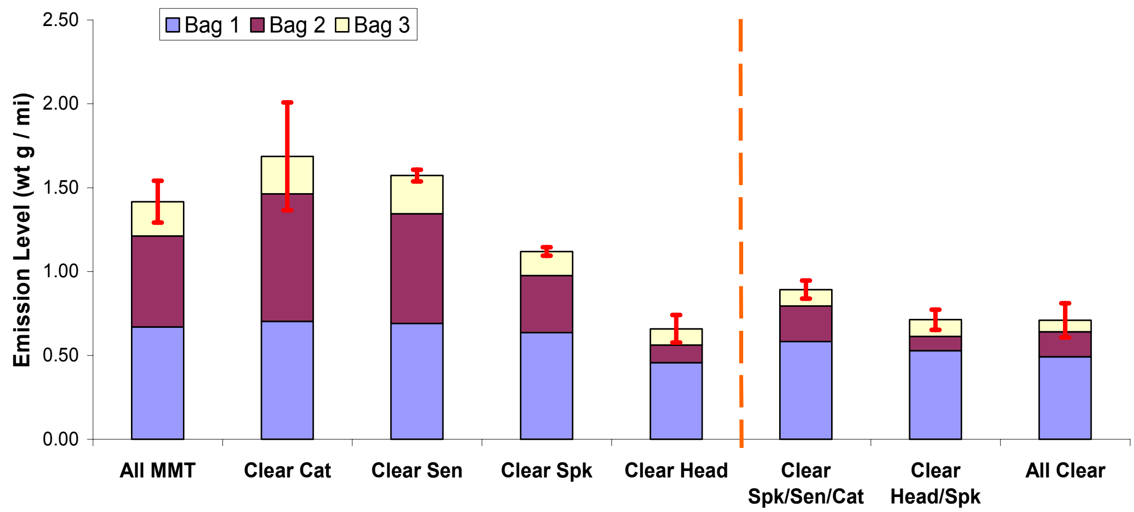


Figure 17. CO tailpipe from single and grouped components on the MMT vehicle.

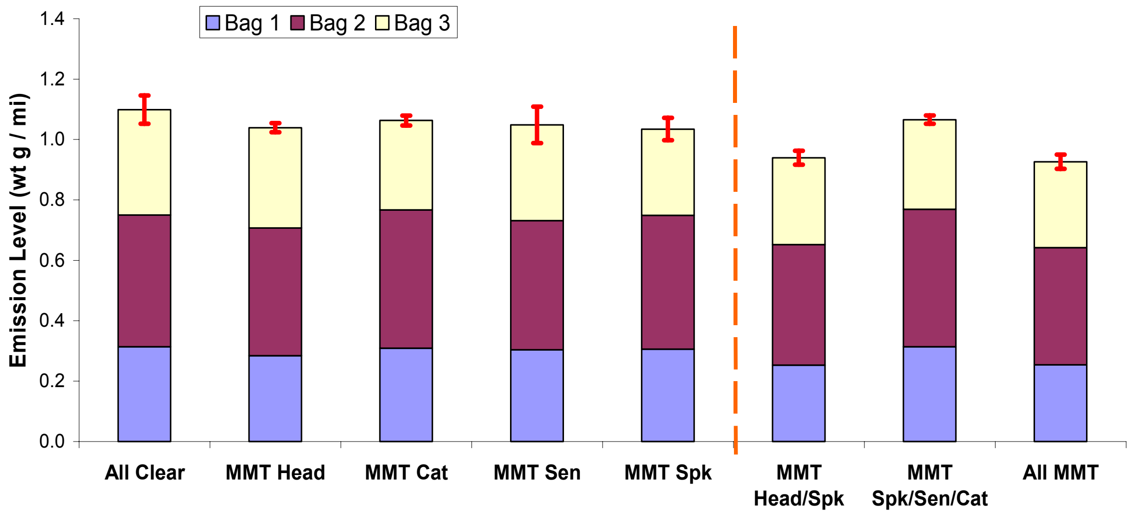


Figure 18. NOx feedgas from single and grouped components on the Clear vehicle.

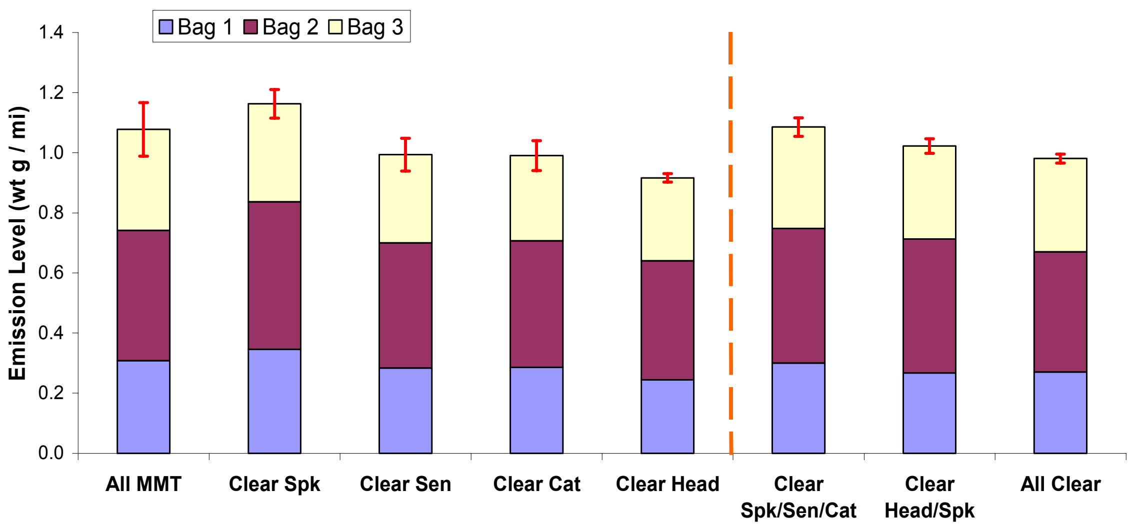


Figure 19. NOx feedgas from single and grouped components on the MMT vehicle.

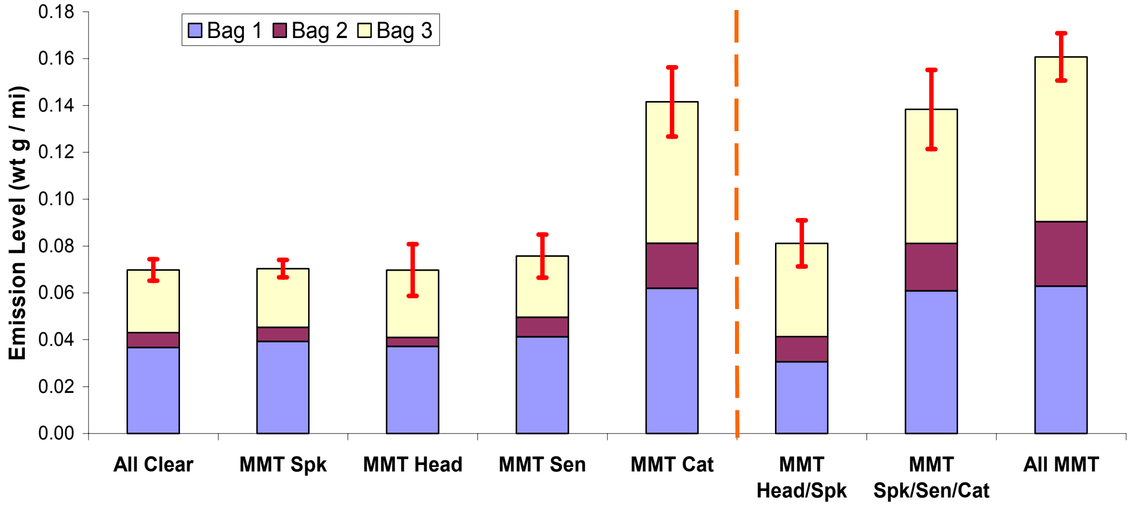


Figure 20. NOx tailpipe from single and grouped components on the Clear vehicle.

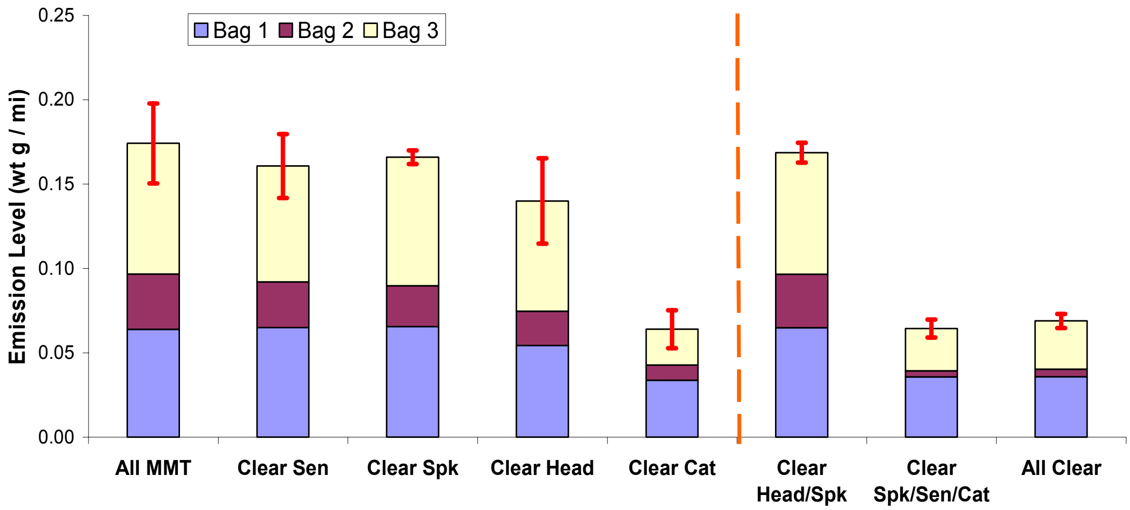


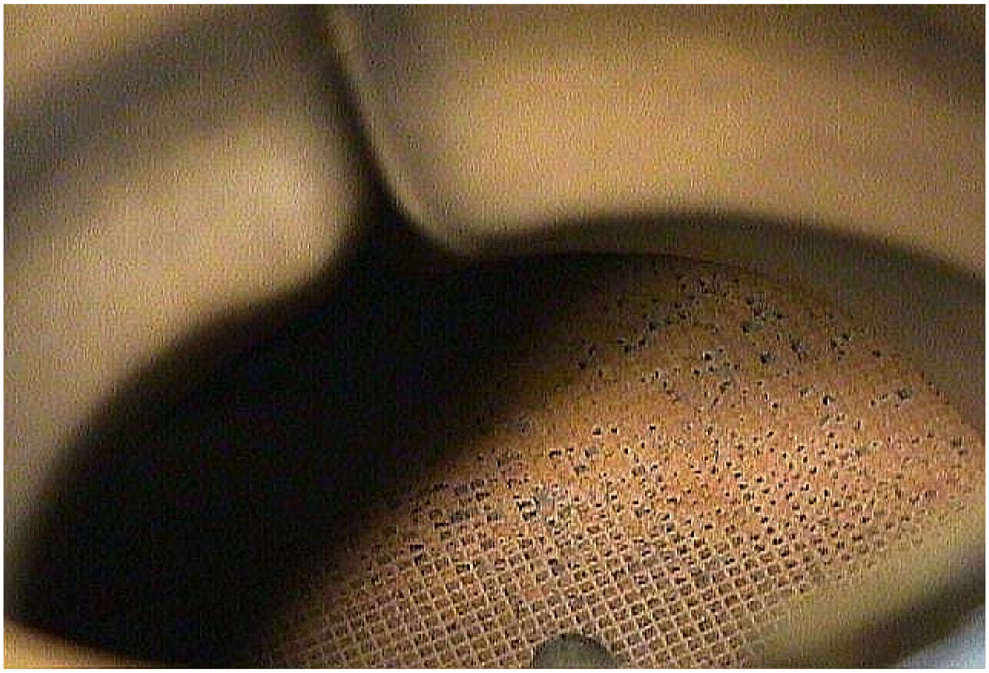
Figure 21. NOx tailpipe from single and grouped components on the MMT vehicle.

Clear (behind catalyst) | **Clear (in front of catalyst)** | **MMT (behind catalyst)** | **MMT (in front of catalyst)**

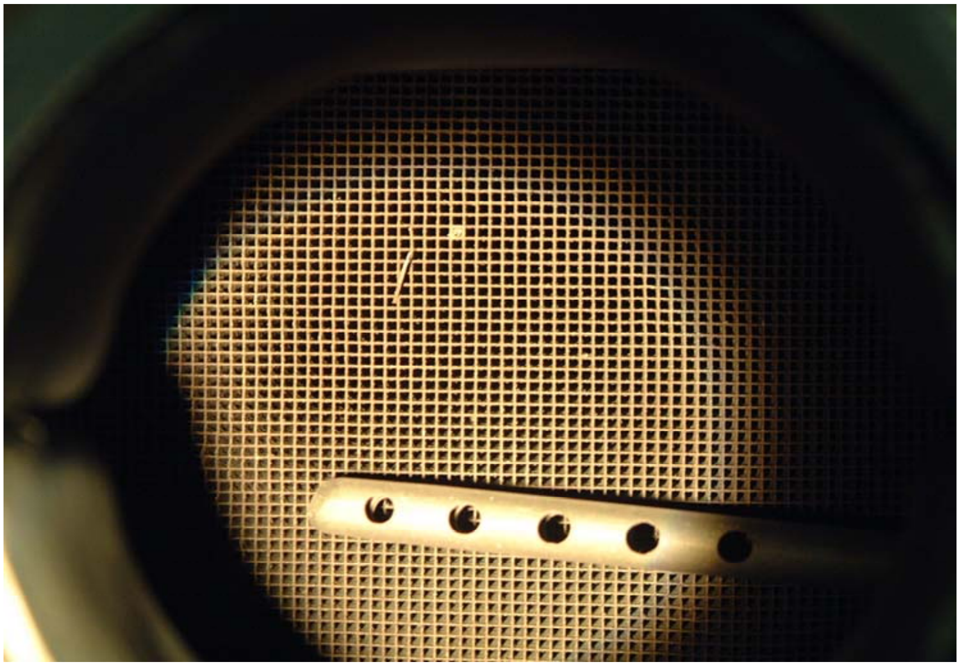
Figure 22. Front and rear HEGO sensors from the Clear- and MMT-vehicles.

Clear **MMT**

Figure 23. Spark plugs from the Clear- and MMT-vehicles.



a.) Catalyst from MMT Vehicle



b.) Catalyst from Clear Vehicle

Figure 24 a. and b. Digital photograph of catalyst front face from MMT- (a.) and Clear- (b) vehicle.

Clear - Head

MMT - Head

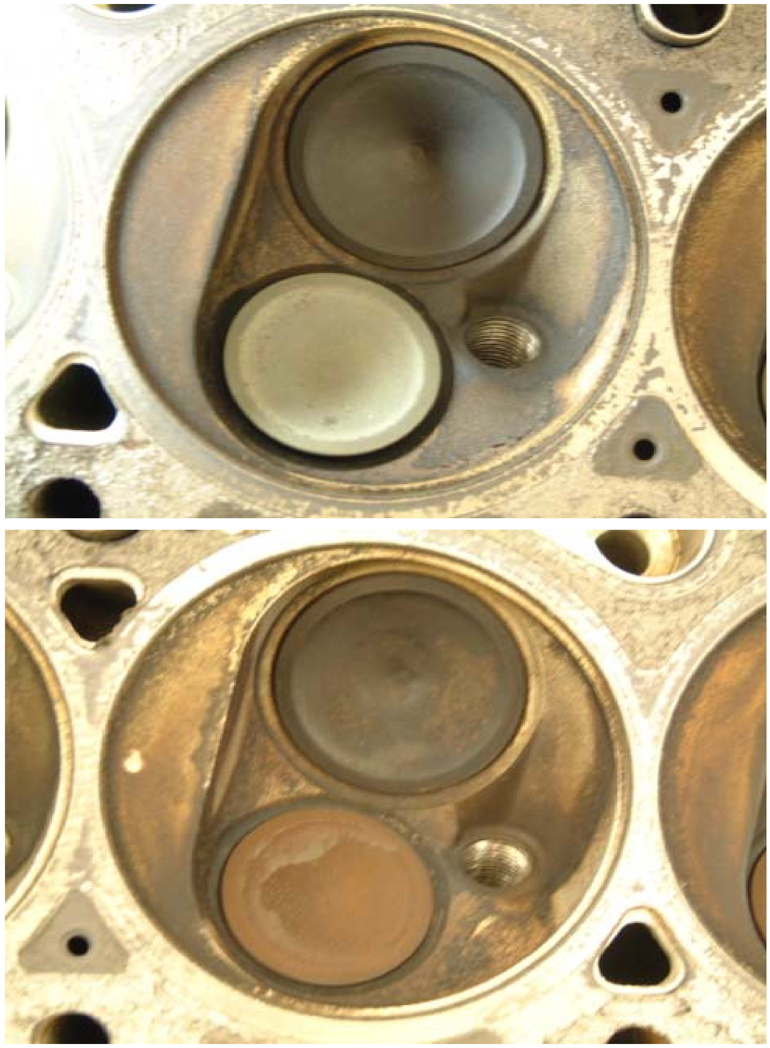


Figure 25. Intake and exhaust valves from Clear- and MMT-vehicles.

Clear - Head

MMT - Head

Figure 26. Exhaust valves on Clear- and MMT-vehicles.

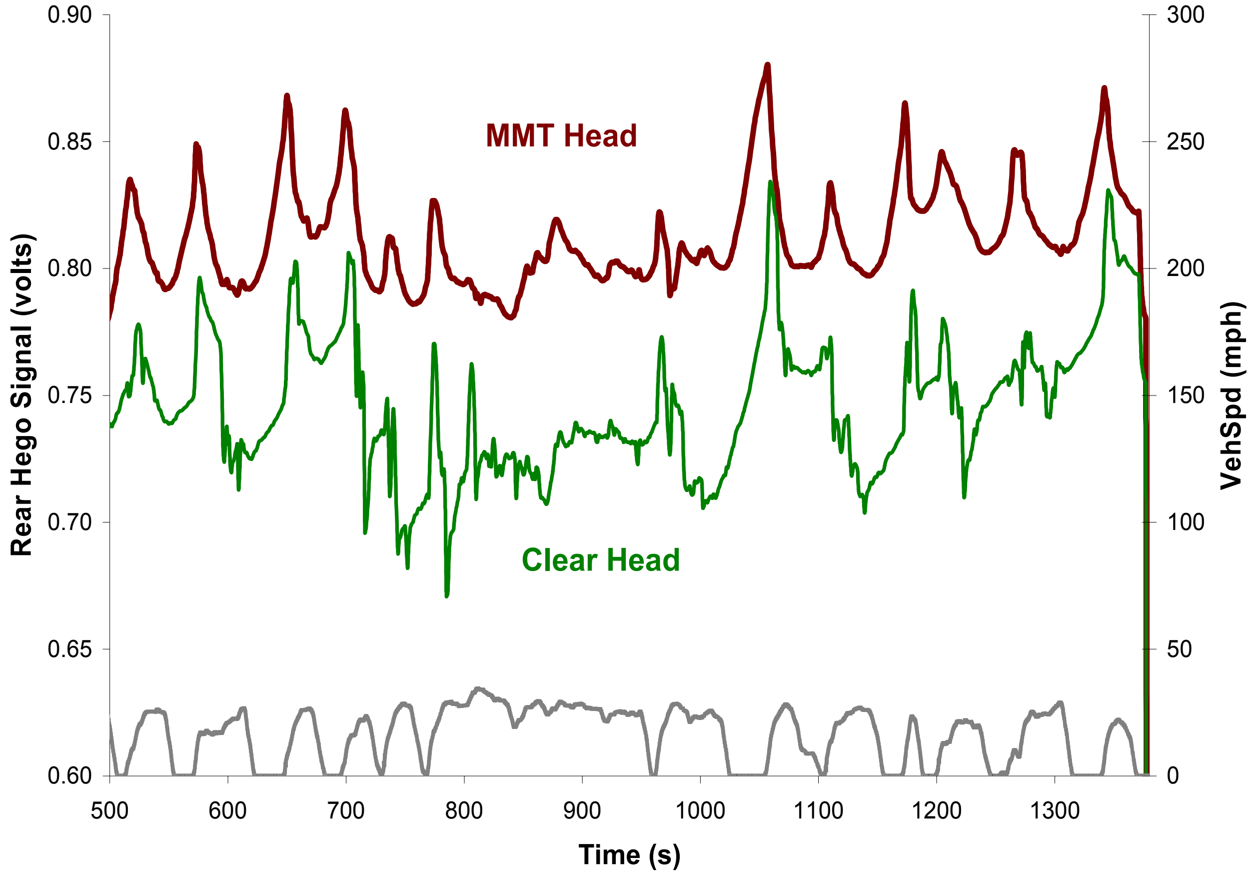


Figure 27. Average rear HEGO voltage – time traces during Bag 2 of FTP Cycle for all configurations with either Clear or MMT head. The vehicle speed trace is shown at the bottom of the figure.

APPENDIX 1. COMPARISON OF ALLIANCE AND FORD VERL TESTING ON MMT AND CLEAR VEHICLES.

MMT - Fueled Vehicle **Emission Testing Facility**

				General Motors (SAE 2002-01-2894)								
Vehicle	**Mileage Acc**	**Vehicle Mileage**		**Feedgas THC**	**Tailpipe THC**	**Tailpipe NMHC**		**Feedgas CO**	**Tailpipe CO**		**Feedgas NOx**	**Tailpipe NOx**
AE-16	MMT - Fuel	100K	**Average (2 Tests)**	2.78	0.114	0.091		7.21	1.028		1.24	0.216
			Std Dev	*0.09*	*0.001*	*0.000*		*0.02*	*0.002*		*0.01*	*0.016*
				Ford Motor								
			Average (9 Tests)	3.46	0.145	0.118		8.13	1.416		1.08	0.174
			Std Dev	*0.15*	*0.034*	*0.030*		*0.21*	*0.228*		*0.16*	*0.043*
			90% Conf.	*0.08*	*0.019*	*0.016*		*0.11*	*0.125*		*0.09*	*0.024*
			95% Conf.	*0.10*	*0.022*	*0.019*		*0.14*	*0.149*		*0.11*	*0.028*

Clear - Fueled Vehicle

				General Motors (SAE 2002-01-2894)								
Vehicle	**Mileage Acc**	**Vehicle Mileage**	**Test**	**Feedgas THC**	**Tailpipe THC**	**Tailpipe NMHC**		**Feedgas CO**	**Tailpipe CO**		**Feedgas NOx**	**Tailpipe NOx**
CE-16	Clear - Fuel	100K	**Average (2 Tests)**	1.99	0.049	0.044		6.60	0.449		1.27	0.105
			Std Dev	*0.00*	*0.001*	*0.001*		*0.02*	*0.016*		*0.00*	*0.003*
				Ford Motor								
			Average (9 Tests)	2.52	0.059	0.054		7.43	0.599		1.10	0.070
			Std Dev	*0.11*	*0.002*	*0.002*		*0.07*	*0.058*		*0.08*	*0.008*
			90% Conf.	*0.06*	*0.001*	*0.001*		*0.04*	*0.032*		*0.05*	*0.005*
			95% Conf.	*0.07*	*0.001*	*0.001*		*0.04*	*0.038*		*0.05*	*0.006*

APPENDIX 2. EMISSION TEST SUMMARY ON MMT VEHICLE

MMT Vehicle

CAT	SPARK	SENSOR	Engine Head	No. of Tests		Feedgas / Tailpipe Emissions							
						FG NMHC	TP NMHC		FG CO	TP CO		FG NOx	TP NOx
M	M	M	M	9	**Average**	3.39	0.118		8.13	1.416		1.08	0.174
					StdDev	0.15	0.030		0.21	0.228		0.16	0.043
					90% Conf.	0.08	0.016		0.11	0.125		0.09	0.024
M	C	M	M	3	**Average**	3.01	0.112		7.90	1.120		1.16	0.166
					StdDev	0.08	0.006		0.17	0.026		0.05	0.004
					90% Conf.	0.08	0.006		0.16	0.024		0.05	0.004
M	M	C	M	3	**Average**	3.78	0.142		8.34	1.573		0.99	0.161
					StdDev	0.09	0.014		0.13	0.037		0.06	0.020
					90% Conf.	0.09	0.013		0.12	0.035		0.05	0.019
C	M	M	M	3	**Average**	3.86	0.098		8.68	1.687		0.99	0.064
					StdDev	0.03	0.012		0.32	0.339		0.05	0.012
					90% Conf.	0.03	0.011		0.31	0.322		0.05	0.011
C	C	C	M	3	**Average**	3.29	0.078		8.12	0.893		1.09	0.064
					StdDev	0.05	0.003		0.19	0.057		0.03	0.006
					90% Conf.	0.05	0.003		0.18	0.054		0.03	0.005
M	C	M	C	3	**Average**	2.41	0.060		7.54	0.714		1.02	0.169
					StdDev	0.02	0.002		0.14	0.064		0.03	0.006
					90% Conf.	0.02	0.002		0.14	0.061		0.02	0.006
M	M	M	C	3	**Average**	2.76	0.061		7.61	0.658		0.92	0.140
					StdDev	0.002	0.007		0.01	0.087		0.02	0.027
					90% Conf.	0.002	0.006		0.01	0.082		0.01	0.025
C	C	C	C	3	**Average**	2.62	0.058		7.52	0.710		0.98	0.069
					StdDev	0.04	0.001		0.23	0.107		0.02	0.004
					90% Conf.	0.04	0.001		0.22	0.102		0.01	0.004

C = Clear Component
M = MMT Component

APPENDIX 2 (CONT.). EMISSION TEST SUMMARY ON CLEAR VEHICLE.

Clear Vehicle

CAT	SPARK	Sensor	Engine Head	No. of Tests		Feedgas / Tailpipe Emissions					
						FG NMHC	TP NMHC	FG CO	TP CO	FG NOx	TP NOx
C	C	C	C	9	Average	2.46	0.054	7.43	0.599	1.10	0.070
					StdDev	0.10	0.002	0.07	0.058	0.08	0.008
					90% Conf.	0.06	0.001	0.04	0.032	0.05	0.005
C	M	C	C	3	Average	2.47	0.063	7.54	0.683	1.03	0.070
					StdDev	0.01	0.003	0.05	0.027	0.04	0.004
					90% Conf.	0.01	0.003	0.05	0.026	0.04	0.004
C	C	M	C	3	Average	2.36	0.060	7.38	0.718	1.05	0.076
					StdDev	0.03	0.002	0.05	0.014	0.06	0.010
					90% Conf.	0.02	0.002	0.04	0.013	0.06	0.009
M	C	C	C	3	Average	2.36	0.064	7.32	0.642	1.06	0.141
					StdDev	0.06	0.002	0.13	0.043	0.02	0.016
					90% Conf.	0.06	0.002	0.13	0.041	0.02	0.015
M	M	M	C	3	Average	2.64	0.084	7.85	1.051	1.07	0.138
					StdDev	0.06	0.007	0.17	0.115	0.02	0.018
					90% Conf.	0.05	0.006	0.16	0.109	0.01	0.017
C	M	C	M	3	Average	3.69	0.099	8.58	1.726	0.94	0.081
					StdDev	0.08	0.014	0.23	0.148	0.02	0.010
					90% Conf.	0.08	0.013	0.21	0.141	0.02	0.010
C	C	C	M	3	Average	3.21	0.079	8.12	1.079	1.04	0.070
					StdDev	0.03	0.005	0.18	0.183	0.02	0.012
					90% Conf.	0.02	0.005	0.17	0.174	0.02	0.011
M	M	M	M	3	Average	3.60	0.124	8.48	1.559	0.93	0.161
					StdDev	0.06	0.005	0.10	0.148	0.03	0.011
					90% Conf.	0.06	0.005	0.09	0.141	0.02	0.010

C = Clear Component
M = MMT Component