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Effects of Organometallic Additives on Gasoline Vehicles: Analysis of Existing Literature

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COORDINATING RESEARCH COUNCIL, INC.

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FINAL REPORT

Effects of Organometallic Additives on Gasoline Vehicles: Analysis of Existing Literature

CRC Project E-114

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Acronyms and Abbreviations

AAM	Alliance of Automobile Manufacturers
ACEA	European Automobile Manufacturers' Association
ADA	Abgaszentrum der Automobilindustrie
A/F	Air/ Fuel Ratio
AIAM	Association of International Automobile Manufacturers
AIR	Air Improvement Resource, Inc.
AMA	U.S. Automobile Manufacturers Association
BET	Brunauer-Emmett-Teller theory
CAA	U.S. Clean Air Act
CADC	Common Artemis Driving Cycle
CARB	California Air Resources Board
CATARC	China Automotive Technology and Research Center
CC	Close coupled
CGSB	Canadian General Standards Board
CO	Carbon Monoxide
cpsi	Cells per square inch
CRC	Coordinating Research Council
CVMA	Canadian Vehicle Manufacturers' Association
EC	European Commission
EPA	Environmental Protection Agency
FTP	Federal Test Procedure
GMAC	General Motors Acceptance Corporation
HC	Hydrocarbon
HCD	High cell density
HCD-CC	High cell density-close coupled
HDCC	High density close coupled
HEGO	Heated exhaust gas oxygen (sensor)
ICCT	International Council on Clean Transportation
I&M (or I/M)	Inspection and maintenance
IM240	Specific I&M test procedure
LDV	Light-Duty Vehicle
LEV	Low Emission Vehicle
MECA	Manufacturers of Emission Controls Association
MIL	Malfunction indicator light
MMT	Methylcyclopentadienyl Manganese Tricarbonyl
Mn	Manganese
NCWM	National Conference on Weights and Measures
NEDC	New European Driving Cycle
NLEV	National Low Emission Vehicle
NMHC	Non-methane hydrocarbons
NMOG	Non-methane organic gases
NOx	Oxides of nitrogen
MOBILE5	EPA's model for mobile source emissions determination

MY	Model year
OBD	On-board diagnostics
OBD-II	On-board diagnostics
ON	Octane Number
PM	Particulate matter
RfC	Reference concentration
RFG	Reformulated gasoline
RPM	Revolutions per minute
SAE	Society of Automotive Engineers
SEPA	State Environmental Protection Administration (China)
SMA	Standard Mileage Accumulation
SRC	Standard Road Cycle
TEL	Tetraethyl Lead
THC	Total hydrocarbons
TLEV	Transitional LEV
TWC	Three-way catalyst
VOC	Volatile organic compounds
WOS	Web of Science
XRD	X-ray Dispersion
XRF	X-ray fluorescence spectroscopy

Executive Summary

ASTM requested that CRC undertake a literature study to evaluate the effects of organometallic components on gasoline vehicles to provide guidance in the ASTM D4814 fuel specification regarding appropriate concentration limits for organometallic additives in gasoline. Because all other organometallic additives are banned in the U.S., this literature study was undertaken to review and summarize the light-duty vehicle (LDV) impacts of using methylcyclopentadienyl manganese tricarbonyl (MMT) in gasoline. The review focuses on reports and publications describing MMT's effects upon engine and emissions system hardware, and how this may influence the performance and durability of such systems – including impacts on criteria pollutant emissions. Of particular interest are MMT's effects in modern, Tier 2 vehicles (and similar technology vehicles), which are equipped with advanced emissions control systems that include high cell density, close-coupled (HCD-CC) catalysts.

MMT was first introduced as a gasoline anti-knock additive in the late 1950's, although it did not find widespread usage in the U.S. until the mandated lead phasedown period that began in the mid-1970's. Since that time, MMT has been marketed globally by Ethyl Corporation (now Afton Chemical Corporation) and others. Throughout its history, MMT usage has been controversial. While useful as a lead-replacement octane booster, there are longstanding concerns that MMT may adversely affect the performance of catalytic emissions control systems. These concerns have grown as vehicle emissions control systems have become more sophisticated, in response to increasingly stringent performance, emissions and durability requirements.

While legal to use in some gasolines, current MMT usage in North America is very low, due to voluntary actions by fuel suppliers. Historically, MMT usage concentrations varied from 1/8 to 1/32 g Mn/gal – which corresponds to approximately 33 to 8 mg Mn/L. In many places where MMT is still allowed or in use, including Europe and China, lower concentration standards (2 mg Mn/L) have been introduced.

The starting point for this literature review was a database maintained by the National Conference on Weights and Measures (NCWM). This database includes approximately 75 technical papers, company reports, regulatory documents, and other items pertaining to the effects of MMT on vehicle performance, emissions, and emissions control systems. Some of these literature items have been peer reviewed, while others have not. In addition, the database contains many literature items that are not publicly available, and cannot be readily accessed through typical literature-searching techniques. In this review project, the NCWM database was supplemented with approximately 70 additional items of interest, which were identified by means of common literature searching methods.

From the mid-1970's through today, there have been numerous laboratory and field studies that investigated the effects of MMT on vehicle performance and emissions. While the issues of concern have varied somewhat over the years, they have generally centered on the inorganic combustion products of MMT (principally manganese oxides, sulfates, and phosphates), and how solid deposits of these products affect the long-term performance of engines and emissions control systems. In this report, we have focused our attention on studies involving modern, Tier 2 vehicle technologies (typically MY 2000 and later), while including a brief summary of earlier literature. More detailed information on these older technologies is provided in Appendix III to this report.

Most experimental programs described in the literature were conducted either by automakers or by Ethyl/Afton (or consortia that include one or both of these parties). Numerous programs have been executed – involving hundreds of vehicles covering wide ranges of model years, technology types, and testing conditions. In general, studies by the automakers have concluded that under certain test conditions, use of MMT is detrimental – contributing to catalyst plugging and increased emissions. In contrast, most studies by Ethyl/Afton have concluded that under typical operating conditions, usage of MMT does not cause harm, and does not contribute to exceedances of vehicle emissions standards.

In reviewing this literature, it is not our objective to interpret the findings and judge which studies may be more reliable than others. Rather, the objective is to summarize accurately what is reported in each relevant study. However, the stark differences in findings between most automaker studies and most Ethyl/Afton studies demand some explanation. Although there are several reasons for these opposing conclusions, two primary factors appear to dominate:

1. Differences in test cycles/conditions. Many of the automakers' test programs utilized rapid mileage accumulation procedures. Such accelerated tests are commonly conducted by automakers in an effort to more quickly identify potential problems in long-term customer service. The most frequently used durability test cycles were developed through a collaborative, public process, and are generally agreed to be suitable for accelerated mileage purposes. However, Ethyl/Afton maintain that such aggressive conditions are not representative of real-world situations, and they contribute to the appearance of effects that would not occur under milder conditions.

2. Basis for emissions comparisons. In several studies conducted and/or analyzed by Ethyl/Afton, it was stated that use of MMT did not contribute to exceedance of vehicle emissions standards. While concerned about these standards, the focus of most automaker studies has been on actual emissions increases caused by MMT – regardless of what standards are most appropriate for comparison. Generally, studies by the automakers refer to "certification" standards, while some studies by Ethyl/Afton refer to "in-use" standards.

While not clearly stated, it appears that the automakers and Ethyl/Afton approach the question of MMT's suitability from very different perspectives. The automakers are concerned about any condition that could lead to in-use consumer problems or damage to vehicles, and wish to ensure that vehicles comply with all requirements throughout the warranty period, the mandated regulatory period, and the vehicle's entire useful life. Ethyl/Afton seem more concerned about typical, or fleet-wide applications, and are interested in showing that MMT does not result in harm in these situations. These different perspectives have led to profoundly different interpretations, even when evaluating the same sets of experimental data.

The literature regarding the effects of MMT on gasoline vehicles is not entirely consistent. However, from review of the entire body of information, numerous observations and conclusions can be drawn. The most significant findings pertaining to Tier 2 vehicle technologies are summarized below.

- Modern Tier 2 vehicles, which began entering the U.S. fleet in the early 2000's, must comply with significantly more stringent emissions performance standards compared to previous technology vehicles. This is reflected in both the lower certification levels established for the four pollutant categories (HC, CO, NOx, and PM), and in the extended mileage accumulation period over which the standards apply. (Even more stringent standards will apply to Tier 3 vehicles.)

- To comply with Tier 2 standards, automakers have employed emissions control systems that include more active catalysts with higher cell densities, higher surface areas, and thinner cell walls. Furthermore, these catalysts are being mounted in configurations that are close coupled (CC) to the exhaust manifold, which allows for more rapid initial heating and higher overall catalyst temperatures. There is evidence that such high cell density, close coupled (HCD-CC) catalysts are more susceptible to adverse effects of MMT than earlier technologies.

- The close-coupled configuration of catalysts in Tier 2 vehicles not only promotes higher operating temperatures, but also causes sharper angles of incidence as the exhaust gases enter the catalyst. Higher catalyst operating temperatures promote both faster formation rates of Mn deposits, and creation of deposits that more readily adhere to catalyst surfaces. There is evidence that these higher temperature effects, coupled with higher cell density catalysts and sharper angles of incidence, increase plugging problems under certain operating conditions. There is also evidence that the rate of plugging increases with MMT concentration in the fuel.

- In some Pre-Tier 2 studies, increases in HC emissions from MMT-fueled vehicles were shown to be due in large part to engine deposits, rather than catalyst effects. However, with increased sensitivities of modern emissions control systems, and longer durability requirements for Tier 2 vehicles, there is concern that MMT usage may contribute to catalyst plugging, thereby reducing overall performance and increasing emissions of all pollutants.

- Evidence regarding the impacts of MMT on OBD systems is mixed. Although Mn deposits do occur on oxygen sensors, spark plugs, and other components, it is not clear to what extent this affects OBD performance. Some field and laboratory data suggest that impairment of OBD system components can occur with extended use of MMT.

- In-use Tier 2 vehicles in North America have not been subjected to long-term exposures to MMT. While MMT was widely used in Canadian gasoline when Tier 2 vehicles first entered the marketplace, it was voluntarily removed shortly thereafter (2003). Nevertheless, manufacturer data show that warranty rates in Canada for some vehicles with HCD-CC catalysts were higher than warranty return rates in the U.S. In addition, the rate of warranty returns in these particular models levelled off at a time that coincided with the phase out of MMT from Canadian gasoline.

- In-use surveys based on I/M data from the same time period as the Canadian experience described above did not show significant differences in failure rates between areas where MMT was used and areas where it was not. Similarly, I/M testing in areas of China that used MMT did not show unusual rates of emission failures.

- The relationships between MMT dosage levels and engine/emissions effects are not well defined. It is likely that these relationships vary with different technology vehicles, operating conditions, and consumer driving habits. Available data suggest that the adverse effects of catalyst plugging and increased emissions in Tier 2 vehicles are worsened as MMT concentrations increase – particularly upon long-term use. Some studies have related the extent of catalyst plugging to the total mass of Mn consumed in the fuel.

- Some vehicles appear to be more sensitive to adverse effects of MMT than other vehicles. Besides the specific type of HCD-CC catalyst being used, and its configuration with respect to the exhaust stream, driving behavior is likely an important contributing factor. Aggressive driving patterns leading to higher catalyst temperature will likely worsen the adverse effects of MMT.

- Based upon the experimental data reviewed here, there is credible evidence that under certain operating conditions, use of MMT in Tier 2 vehicles with HCD-CC catalysts can contribute to catalyst plugging, thereby impairing emissions control performance. These concerns could become more important with Tier 3 vehicles, which will have even more stringent emissions and durability requirements.

1 Introduction

Methylcyclopentadienyl manganese tricarbonyl (MMT; CAS number 12108-13-3) is an organometallic compound known to raise the octane rating of gasoline. The chemical formula of MMT is $C_9H_7MnO_3$, also written as $CH_3C_5H_4Mn(CO)_3$. The structure of MMT is shown in Figure 1. MMT has a boiling point of approximately 233 °C, a freezing point of 2 °C, and a molecular weight of 218.1, with manganese comprising 25.2% of its total mass. At room temperature, MMT is a liquid with low vapor pressure (4.7 x 10^{-2} mm Hg @ 20° C), low water solubility (70 mg/L @ 25 °C) and high solubility in hydrocarbon solvents.[1,2] In the gas phase, MMT is photochemically active, with an extremely short half-life of approximately 15 seconds.[3] Therefore, ambient exposures are not of concern.

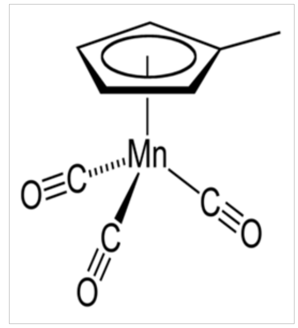

Figure 1. Chemical Structure of MMT

1.1 History of MMT Use

MMT was first marketed by Ethyl Corporation in 1959, as a supplement or replacement for tetraethyl lead (TEL).[4] It has been used in both leaded and unleaded gasoline, but did not find widespread use in the U.S. until the period of mandated lead phasedown, which began in 1974.[5] The MMT-based anti-knock package marketed by Ethyl was known as *HiTEC 3000*™ (and other similar product names). By 1976, MMT was used throughout the U.S., being present in approximately 40% of all gasoline, at a typical concentration of 12 mg Mn/gal.[5,6] [MMT dosage levels are commonly expressed as concentrations of Mn in gasoline. Several different units are used, including fractions of a gram/gal., mg/gal., and mg/L. Conversions among these units are shown in Table 1.]

Table 1. Unit Conversions for Common MMT Dosage Levels

1/8 g Mn/gal	0.1250 g Mn/gal	33.0 mg Mn/L
1/16 g Mn/gal	0.0625 g Mn/gal	16.5 mg Mn/L
1/32 g Mn/gal	0.0313 g Mn/gal	8.3 mg Mn/L
1/64 g Mn/gal	0.0156 g Mn/gal	4.1 mg Mn/L

The use of MMT in gasoline has been controversial over the past few decades. Several publications provide good chronologies of MMT's use in U.S. and Canadian gasolines.[7,8,9,10,11,12] A brief summary of this chronology is presented here.

In 1976, due to concerns regarding potential adverse effects on vehicle emissions and emissions control systems, the California Air Resources Board (CARB) issued a ban on the use of manganese-based additives in all gasoline. A waiver of this rule would be required to allow the use of MMT in California. To date, no such waiver has been requested, and the ban of MMT in California gasoline remains in effect.

The 1977 amendments to the U.S. Clean Air Act (CAA) permitted manganese additives to be used only in leaded gasoline although this Act also gave the EPA Administrator authority to waive the ban if the additive was shown to not cause or contribute to an exceedance of vehicle emission standards. In 1978, Ethyl Corporation applied for a waiver for the use of MMT in gasoline at concentrations of

8 and 16 mg Mn/L. (8 mg Mn /L is nominally equivalent to 1/32 g Mn/gal.) EPA denied the waiver application on the grounds that Ethyl failed to demonstrate that vehicle emissions or emission control devices would not be harmed.

In 1981, Ethyl Corporation submitted another waiver application to permit use of MMT at concentrations equivalent to 4 mg Mn/L (1/64 g Mn/gal). This application was also denied on the basis that Ethyl had failed to demonstrate that no emissions harm would result.

In 1990, additional CAA amendments were passed by Congress, conditionally banning the use of manganese-based additives in all reformulated gasoline (as opposed to conventional gasoline). A waiver may be granted if manganese is shown not to increase pollutant emissions through the completion of a waiver test program. Reformulated gasoline is required in those regions that experience the highest ozone concentrations in the U.S. (including all of California), as well as other areas that have voluntarily "opted-in" to the federal reformulated gasoline (RFG) program.

In 1990-1991, Ethyl submitted a new waiver application to permit use of MMT in gasoline at levels up to 8 mg Mn/L. Based upon the extensive set of emissions data presented by Ethyl, EPA concluded that MMT at this level would not cause or contribute to a failure of emissions control devices in use at that time. Nevertheless, the waiver request was denied due to concerns regarding potential health risks of airborne manganese.[A] (In 1993, EPA adopted a reduced inhalation reference concentration [RfC] for Mn of 0.05 $\mu g/m^3$.[13,8]) Ethyl appealed this decision on the grounds that EPA did not have the authority to make a ruling based on public health. In 1995, the U.S. Court of Appeals agreed with Ethyl's position, and ordered EPA to grant a waiver authorizing the use of MMT in conventional gasoline (not reformulated gasoline) at concentrations up to 8 mg Mn/L.

This waiver is still in effect today. However, since the late 1990's, all major refiners operating in the U.S. have voluntarily eliminated MMT from all their gasoline. Since that time, actual manganese levels in U.S. gasoline have been very low, although levels up to 8 mg Mn/L are still permitted by law, in non-reformulated gasoline.

The history of MMT usage in Canadian gasoline is different from the U.S. With the phase-out of leaded gasoline in the late 1970's, MMT found widespread usage in Canada. Although there was no legal limit on MMT concentrations, the Canadian General Standards Board (CGSB) established a voluntary standard of 18 mg Mn/L in 1978. The national mean concentration measured in Canadian gasoline in 1993 was 9 mg Mn/L.[14]

In 1997, due to concerns that MMT use could compromise the effectiveness of vehicles' on-board diagnostic (OBD) and emissions control systems, Canada passed the Manganese-Based Fuel Additives Act.[14,15] This Act prohibited the importation of MMT into Canada, and the trade of MMT

[A] Around this same time, EPA was involved in a separate regulatory process to reduce the reference concentration (RfC) for inhaled manganese. RfC represents an ambient concentration that is expected to have a negligible non-cancer health risk over a lifetime of exposure. Based upon epidemiological studies, the RfC value of 1.0 $\mu g\ Mn/m^3$ established in 1984 was reduced to 0.4 $\mu g/m^3$ in 1990, and further reduced to 0.05 $\mu g/m^3$ in 1993. EPA's derivation of this inhalation RfC for Mn is described in the literature. [Davis (1998) and Davis et al. (1998).]

between provinces. After legal challenge, pertaining to restrictions on commerce, this Act was rescinded, thus reverting to the CGSB voluntary MMT limit of 18 mg Mn/L in Canadian gasoline. However, just prior to implementation of Canadian-specific Tier 2 exhaust standards in 2004, all major Canadian refiners voluntarily eliminated MMT from their gasoline supply.[16] Since that time, actual manganese levels in Canadian gasolines have been very low, although the voluntary standard of 18 mg Mn/L is still in effect.

Several other countries also have established regulations regarding MMT in gasoline. A listing of these regulations (as of 2008) was provided in a report by the International Council on Clean Transportation (ICCT)[11] and the European Automobile Manufacturers' Association.[17] This information about allowable MMT levels, combined with more recent updates from the International Fuel Quality Center, is summarized below in Table 2.

Table 2. 2014 MMT Limits in Gasoline from Selected Countries [a]

Country/Region	Max. Mn Limit, mg/L
United States	
Conventional	8.3 [b]
Reformulated	Not allowed
California	Not allowed
Canada	18 [b]
European Union	2 [c]
Germany	Not allowed
China	
National	8 [d]
Beijing	2 [c]
Jiangsu	2 [c]
Shanghai	2 [c]
Russia	Not allowed
Latin America	
Argentina	8.3
Bolivia	18
Mexico	No limit
South Africa	
Unleaded	0
Pb replacement gasoline	36

Notes:

[a] MMT limits are constantly changing. This table represents values as of Jan., 2014.
[b] Fuel suppliers have voluntarily eliminated use of MMT
[c] 6 mg/L allowed prior to 2014
[d] 16 mg/L allowed prior to 2014

1.2 Combustion Products of MMT

Mn is a terrestrial, abundant element, and is essential for the human diet. The majority (up to 95%) of a person's total multimedia dose of Mn comes from food.[18,19] Yet, there are concerns about airborne Mn, as the impacts of exposure through inhalation are quite different from the impacts through ingestion.[20,14,21] Mn is somewhat unusual with respect to toxicity in that it is relatively non-toxic to humans, except for its effect on the brain.[22] High exposures to airborne Mn (such as in a ferromanganese plant occupational setting) can lead to a neuro-degenerative disease known as manganism, which has symptoms similar to those of Parkinson's disease.[14,23,24]

Combustion of gasoline containing MMT produces emissions of manganese oxides, including MnO, MnO_2, and Mn_3O_4, manganese phosphates and manganese sulfates. [25,26] These emissions are in the form of a fine particulate matter, which are typically red or brown in color. The particles were originally determined as having approximate size of 0.1-0.4 μm diameter,[3] while more recent work showed that a significant fraction of particles emitted at the tailpipe are larger than 0.5 μm, but almost all are in the respirable fraction (<5 μm).[27,28] While Mn_3O_4 was initially believed to be the dominant form of Mn particulate emissions, more recent work has shown that manganese sulfate and phosphate are major contributors, consisting of 70-90% of the respirable manganese emitted. [25,27,29,30]

Although the organometallic form of Mn is completely converted to inorganic manganese oxides during combustion of gasoline, not all of the combustion products are emitted from the vehicle. Attempts to determine emission rates of Mn have been made using direct dilution tunnel measurements and mass balance experiments.[14,28,31,32,33] Numerous studies have found that between 5 to 45% of the manganese in MMT-containing fuel is exhausted as particulate.[34,35,36] The remaining Mn is assumed to be left behind in the oil and on the engine and exhaust components. Mn-containing deposits have been found on numerous engine and exhaust components, including spark plugs, cylinder heads, catalysts, and oxygen sensors.[35,37,38] There are relatively little data regarding the emission rate of MMT from Tier 2 vehicles, though some have assumed similar emission rates as with pre-Tier 2 vehicles. [27]

1.3 Ambient Mn Levels

The disposition of Mn emissions in the atmosphere has been a topic of considerable interest, particularly in urban areas of Canada, where use of MMT has been significant. Some studies conducted near roadways suggest that elevated levels of Mn are found in soils and plants,[39,40,41] while other studies show mixed results.[42,43] Researchers compared Mn in $PM_{2.5}$ samples collected from the mid-1980's to mid-1990's as part of ambient monitoring networks in EPA-defined clean U.S. sites (National Parks), urban U.S. sites, and urban Canadian sites.[7] While wide ranges of values were found from each network, approximate concentrations for the clean U.S., urban U.S., and urban Canadian sites were 1, 3, and 12 ng/m^3, respectively. (For comparison, the RfC level is 50 ng/m^3.) These researchers also concluded that crustal contributions to ambient Mn concentrations are approximately 1-2 ng/m^3 in both the U.S. and Canada.

Because MMT was most widely used in Canadian gasolines, several studies of ambient Mn concentrations have focused on Canadian cities. Stable Mn concentrations were measured in Montreal from 1981 through 1990, despite increased use of MMT during this time.[44] This was followed by a sharp decline in ambient concentrations (by about 50%) from 1990 to 1992, which was attributed to the closing of a nearby ferromanganese plant, illustrating the importance that industrial sources can have. Several researchers have found correlations between traffic density and ambient Mn levels in Montreal.[45,46,47,48] It has also been shown that ambient Mn levels in Montreal declined once MMT was removed from gasoline.[49] A similar decrease in ambient fine particle Mn was noted in Australia following a decline in MMT usage.[50]

From a health perspective, personal exposure levels are more important than ambient concentrations. Several published studies have discussed human exposures to respirable Mn as determined by measurement and modeling in Montreal,[46] Toronto,[33,51,52,53] Indianapolis,[54] Sydney,[55] and elsewhere. Most studies show very low exposure levels, typically in the range of 0.01-0.02 μg/m^3, though considerably higher levels occur in some situations. There is little consensus regarding the potential health impacts of MMT usage in gasoline – even among regulatory agencies. For example, a 1996 paper by Health Canada researchers concluded: "Thus, exposure to respirable Mn is considered low for 98-99% of the population, and the contribution from the combustion of MMT in gasoline is not likely to represent a substantial health threat to Canadians."[56] At about the same time, a paper by EPA researchers concluded: "Given the information that is available at present and the uncertainties discussed here, a reasonable basis exists for concerns regarding potential public health risks, especially for susceptible subpopulations, if MMT were to be used widely in unleaded gasoline."[13]

1.4 Tier 2 Emissions Standards and Vehicle Technologies

The fate of MMT and Mn-containing particles is of particular concern within the engine and exhaust components of vehicles. Several studies have shown that between 5 to 45% of the Mn in fuels containing MMT is exhausted as particulate matter, while the remainder is left behind in the lubricant and as deposits on the engine and exhaust components.[35,36] Because these deposits build up over time, there is increasing concern that MMT will have a greater effect in advanced vehicles that are designed to meet increasingly stringent emission standards that must be maintained over a longer duration and distance.

Current Tier 2 and LEV II programs were phased-in beginning in 2004 by the U.S. EPA and CARB, respectively. Tier 2 standards are set up in bins, as shown in Table 3, which automakers can select from, but must maintain a fleet average consistent with Bin 5. These certification emission limits are verified via chassis dynamometer testing, and emission control components are monitored throughout the life of the vehicle via on board diagnostic (OBD) systems. European emissions standards, which are similar to the U.S. standards, are summarized in Table 4.

Table 3. U.S. Tier 2 Light-Duty Vehicle Exhaust Emissions Standards (in g/mi)

	Emission Limits at 50,000 miles					Emission Limits at 120,000 miles				
Bin	NO_x	NMOG	CO	PM	HCHO	NO_x	NMOG	CO	PM	HCHO
1	-	-	-	-	-	0	0	0	0	0
2	-	-	-	-	-	0.02	0.01	2.1	0.01	0.004
3	-	-	-	-	-	0.03	0.055	2.1	0.01	0.011
4	-	-	-	-	-	0.04	0.07	2.1	0.01	0.011
5	0.05	0.075	3.4	-	0.015	0.07	0.09	4.2	0.01	0.018
6	0.08	0.075	3.4	-	0.015	0.1	0.09	4.2	0.01	0.018
7	0.11	0.075	3.4	-	0.015	0.15	0.09	4.2	0.02	0.018
8	0.14	0.100	3.4	-	0.015	0.2	0.125	4.2	0.02	0.018

Table 4: Euro Light-Duty Vehicle Exhaust Emissions Standards

Year	HC (g/km)	CO (g/km)	NO_x (g/km)
2000 Euro 3	0.2	2.30	0.15
2005 Euro 4 *	0.1	1.00	0.08
2010 Euro 5/6 **	0.075	1.00	0.06

* Limit applicable for 100,000 km
** Limit applicable for 160,000 km

As regulations regarding emissions have evolved (shown in Table 5 and Figure 2), so too have components that control and reduce emissions of the exhaust gases: CO, NO_x, and hydrocarbons (HC). Reaching these emission levels requires a system approach that integrates advanced spark-ignition engines, advanced engine control strategies, clean fuels, clean lubricants, and advanced emissions control technologies.[57] Clean fuels have been implemented with respect to reduced sulfur, benzene, olefins and aromatics content, along with increased oxygenates.

Table 5: History of U.S. Federal Passenger Car Exhaust Emission Standards.
FTP Test Limits (g/mi). 50,000 mile limits, except as noted.

Model Year	Technology	CO	HC	NO_x	PM
1974	Pre-catalyst	28	3.0	3.1	
1975-1976	First Catalysts	15	1.5	3.1	
1977-1979	Oxidation Catalyst	15	1.5	2.0	
1980	Oxidation Catalyst	7.0	0.41	2.0	
1981-1993	Tier 0	3.4	0.41	1.0	0.20
1994-1999	Tier 1	3.4	0.25 [b]	0.4	0.08
1999-2003 [a]	NLEV	1.7-3.4	0.04-0.125 [b]	0.2-0.4	0.08
2004-Present [c]	Tier 2	2.1-4.2	0.01-0.125 [b]	0.02-0.20	0.01-0.02

[a] Range of standards for light duty vehicles
[b] NMOG
[c] 120,000 mile levels for Bin 2 - Bin 8

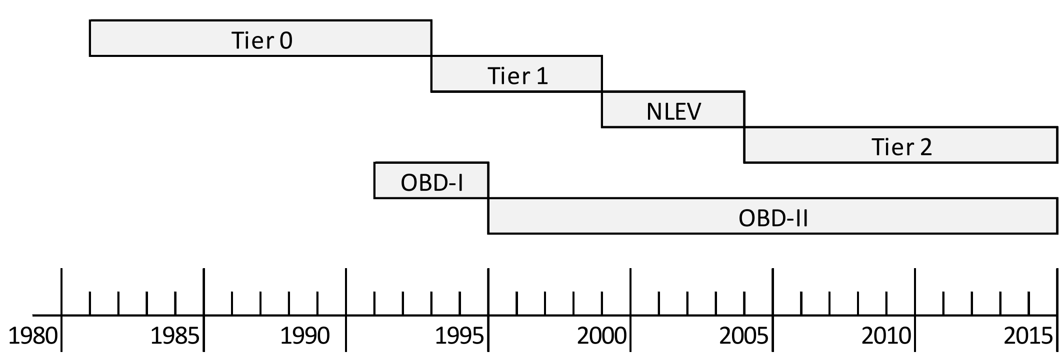

Figure 2: Approximate timeline of U.S. Federal light-duty vehicle emissions standards.
(Stated dates vary due to phase-in schedules, exemptions and other factors.)

Key emissions technologies that manufacturers have integrated into fleets for compliance with Tier 2/ LEV II include high cell density (HCD) substrates, close-coupled (CC) catalytic converters, advanced three-way catalysts (TWC), and other technologies shown in Table 6. Three-way catalysts (TWC), which are so-named because they reduce all three regulated gaseous emissions, have been the dominant emissions control technology on light duty vehicles since the early 1980's. TWCs are typically made up of highly dispersed precious metals (Pt, Pd, or Rh), along with promoters and stabilizers, on a high surface area aluminum oxide monolith to store and release oxygen for oxidation of CO and HC. In Tier 1 applications, monoliths typically had channel sizes that equate to 400 cells per square inch (cpsi). However, interest in improving conversion efficiencies has encouraged the development of HCD substrates, which provide more flow area with more surface area, and reduced thermal mass, which enables more rapid catalyst heat-up – a key to achieving low tailpipe emissions during cold-starts. Cell densities have increased to 600 - 900 cpsi, which provides large benefits in emissions performance.[57] To combat the high percentage of emissions that occur during cold-starts, catalytic converters have been moved closer to the exhaust systems in a close-coupled formation , enabling more rapid catalyst heat-up. These close-coupled configurations result in dramatic reductions of cold-start emissions, but also raise the maximum operating temperature of the catalyst, placing added demands on its thermal durability, particularly since the catalysts must operate for longer durations.

Table 6: Emissions Control Hardware and Techniques used to Meet Tier 2 Vehicle Standards. (From EPA [58])

Emissions Control Technologies	
Fast Light-Off Exhaust Gas Oxygen Sensor	Injection of Air into Exhaust
Universal Exhaust Gas Oxygen Sensor	Heat Optimized Exhaust Pipe
Retarded Spark Timing at Start-Up	Leak-Free Exhaust System
More Precise Fuel Control	Close-Coupled Catalyst
Faster Microprocessor	Improved Catalyst Washcoats
Individual Cylinder Air-Fuel Control	Increased Catalyst Volume and PGM Loading
Manifold with Low Thermal Capacity	Full Electronic Exhaust Gas Recirculation
Air-Assisted Fuel Injection	Engine Modifications

In addition to the catalysts themselves, the On-Board Diagnostic (OBD) system is responsible for monitoring vehicle emission control system components to ensure that emissions do not exceed 1.5 times the emissions standard. This is done through continuous monitoring of the oxygen storage capacity of the catalyst through upstream and downstream oxygen sensors. Degradation of the emissions monitoring system will trigger a malfunction indicator light (MIL) illumination to alert the consumer that repairs are necessary. The increasingly stringent emissions standards also require that OBD systems detect an increasingly small change in emissions over a longer period of time. This situation is expected to become even more challenging with Tier 3 vehicles.

Because of the sensitivities of these advanced catalyst systems, the Manufacturers of Emission Controls Association (MECA) has recommended strategies to integrate and optimize emissions technologies with advanced engine technologies, clean fuels and clean lubricants to ensure that the most stringent emissions standards are met.[57]

2 Project Objectives

The objectives of this project were to obtain, organize, summarize, and synthesize relevant literature information on the effects of methylcyclopentadienyl manganese tricarbonyl (MMT) on Model Year 2000 and newer gasoline vehicles. These objectives do not include interpretation of reported results, or judgement as to which reports are more reliable than others. The literature review focused on reported effects of MMT on engine and emissions control hardware, and how these effects may impact the durability and performance of such systems – including the impacts upon criteria pollutant emissions. Particular attention was paid to the effects in modern, Tier 2 vehicles (and similar technology vehicles), which are equipped with advanced emissions control systems, including high cell density, close-coupled (HCD-CC or HDCC) catalysts.

2.1 Literature Sources

The starting point for this literature review was a database being maintained by the National Conference on Weights and Measures (NCWM). At the beginning of the project, all stakeholders were asked to check this database and add other relevant references that were missing. As a result, the size of the database expanded significantly. The final NCWM database includes approximately 75 technical papers, regulatory documents, OEM statements, and other items pertaining to the effects of MMT upon vehicle performance, emissions, and emissions control systems.

To complement the literature included in the NCWM database, a systematic search was performed using two other databases: (1) SAE literature and (2) Web of Science (WOS). In both cases, combinations of search terms such as methylcyclopentadienyl manganese tricarbonyl, MMT, gasoline vehicles, emissions, after-treatment, and catalyst were used to identify items of interest. Through these means, several other relevant, publicly-available documents were uncovered. However, it should be noted that several of the reports and white papers included in the NCWM database are not publicly available. It is possible that additional relevant information sources exist that are not publicly available, and of which we are not aware.

Through these literature searching techniques, approximately 70 additional items of interest were identified beyond those already in the NCWM database, to create a database of about 145 items. This database was prepared as an Excel spreadsheet, which is provided to CRC as a deliverable of the E-114 Project. A hardcopy version of this database is included here as Appendix I. By reviewing abstracts of these literature items, we identified which ones addressed each of the following 12 topic areas:

1. History/overview of MMT usage
2. Gasoline octane enhancement by use of MMT
3. Emission rates of MMT
4. Effects of MMT on emissions of criteria pollutants
5. Effects of MMT on engine hardware
6. Effect of MMT on emissions control systems
7. Atmospheric concentrations of manganese: ambient and hot spots
8. Exposure assessments: ambient and hot spots
9. Deposition and environmental fate of MMT: road dust, water bodies

10. Measurement/characterization methodologies: ambient, emissions, and soils
11. Toxicity: *in vitro* and *in vivo*
12. Health effects

After classifying the literature into each of the topic areas, we further reviewed literature items that were relevant in topic areas 3 through 6, and assigned each a priority level of "low," "medium," or "high," to indicate the degree of relevance of each topic area with respect to the objectives of the project. "High" relevancy was assigned when detailed data and other information were provided for experimental studies on MY 2000 (and newer) vehicles, and for critical review papers; "medium" relevancy was assigned when detailed data were provided for experimental studies on older vehicles, and when the publication refers to data from other studies; "low" relevancy was assigned when the source discussed the topic of interest, but did not present any detailed experimental data.

Figure 3 shows a histogram of relevant publications in the database, subdivided into the groups/ sponsors responsible for the studies. The publications included here are those with ratings of "high" or "medium" relevancy with respect to the objectives of this work. These publications provide experimental data pertaining to the effects of MMT on vehicle emissions, engine components, and emissions control systems.

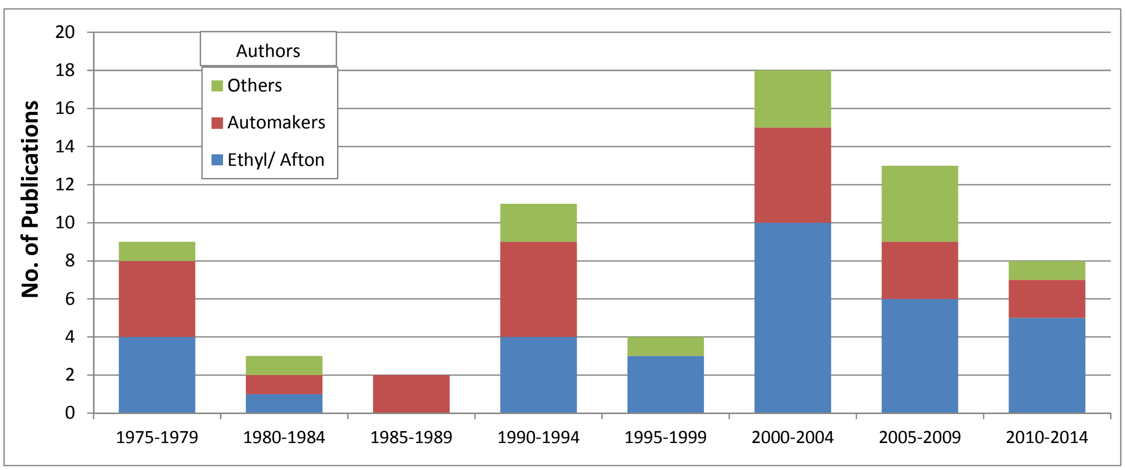

Figure 3: Number of publications or reports about MMT's effects on vehicles, published by Ethyl/Afton, automakers, or other organizations (research groups or government agencies).

Appendix II includes a listing of the most relevant, high and medium priority reports/papers addressing the impacts of MMT on gasoline vehicles. Brief summaries for each of these studies are provided in Appendix III. A general discussion of literature related to vehicle impacts prior to Tier 2 models is provided below, with more details on these individual studies provided in Appendix III. More detailed discussion of testing results from Tier 2 vehicles is also provided below.

3 Summary of Pre-Tier 2 Effects and Literature

3.1 Early MMT Literature (Before 2000)

Following the phase out of lead beginning in 1974, attention on MMT as an anti-knock additive grew, leading to research regarding its impacts. Much of the early work investigating the effects of MMT in gasoline was conducted by Ethyl Corporation and by various automakers, culminating in a 63-vehicle fleet study by CRC in 1979.[59] In addition, several related publications and reviews were provided by EPA. Following limitations imposed in the 1977 amendments to the Clean Air, much of the literature focused on efforts related to Ethyl's waiver applications to the EPA.[34,60,61,62] Concerns about the use of MMT were related to its interaction and effects on new oxidation and three way catalysts (TWC), as well as how it might affect the ability of vehicles to meet new emissions standards. As OBD systems were introduced, additional concerns arose about the effects of MMT on OBD system response. Both the automakers and Ethyl (along with other consortiums) conducted various vehicle fleet, engine and component studies to evaluate those effects, with the following general results:

- Emissions of hydrocarbons (HC) increased with use of MMT, while there was little or no effect on CO or NO_x. Increased HC was attributed to higher engine-out emissions related to manganese oxide deposits in the combustion chamber, on spark plugs and on oxygen sensors, but did not result from noticeable decreases in catalytic converter performance.[63]
- In some tests, MMT-fueled vehicles showed increases in catalyst performance, due to scavenging of catalyst poisons, such as phosphorus and zinc. [64] However, some studies by the automakers showed that catalyst efficiency decreased as exposure to Mn increased.[65,66,67]
- Fleet studies conducted by GM and CRC both showed that MMT could contribute to vehicles exceeding the new 0.41 g/mi HC emission standard,[68,59] while Ethyl concluded that MMT-fueled vehicles would still meet all applicable emissions standards.[69]
- Manganese oxides from combustion of MMT-containing fuels contribute to reddish-brown deposits that form on engine and exhaust components, including catalysts. Under severe operating conditions, these deposits can lead to catalyst plugging. However, plugging may not occur under less severe driving conditions.[70]
- Catalyst placement and exhaust temperatures were shown to have strong influences on how rapidly plugging occurs.[71] Deposits were less likely to form below 700°C while plugging speed increased by as much as 15-fold with a change in temperature from 705 to 843°C. [71]

3.2 Tier 1 (2000-2004)

In the early 2000's, the Alliance of Automobile Manufacturers (AAM) conducted a large fleet study to evaluate long-term effects of MMT. Much of the work during this time period was related to this fleet study. Also during this time, concerns about MMT's effect on OBD systems were growing. These works are summarized briefly below, and additional details can be found in Appendix III.

The AAM study was conducted in two parts over 6 years to evaluate the durability of 56 vehicles, each accumulating up to 100,000 miles. Part 1 was conducted to determine the long-term effects of

MMT on vehicle emissions and component durability, with the MMT-fueled portion of the fleet using a blend at 1/32 g Mn/gal.[72] Fuel effects and emissions varied across all vehicle models such that there was no consistent effect on any single emission category. However, statistical analysis of the fleet resulted in the conclusion that "the use of MMT in fuel is likely to increase both engine-out and tailpipe emissions of hydrocarbons and will cause some vehicles to fail exhaust emission certification standards within 50k miles."

Part 2 was conducted to address concerns regarding effects seen in the LEV vehicles during Part 1.[73,74] In Part 2, sixteen 1998 or 1999 California-certified LEVs (two pairs each of four models) accumulated 100k miles on a test track using the SMA cycle, with one vehicle from each pair utilizing fuel with 1/32 g Mn/gal MMT. Again, variations were seen in fuel effects on emissions from each vehicle model. At the conclusion of mileage accumulation, seven of eight MMT vehicles from four light-duty LEV models failed to meet emissions standards. The study concluded that MMT is expected to increase engine-out and tailpipe HC emissions, and may cause rapid degradation of catalytic converters at high mileage, causing breakthrough of CO, THC and NOx. Post-mortem laboratory analysis performed on one set of vehicles showed that manganese deposits on the valves and catalyst pores contributed to increased emissions.[75]

Ethyl responded to the AAM study, taking issue with various aspects of the test and presented their own evaluation of the data.[76,77,78,79] They noted that appropriate standards were not applied, and that all MMT-fueled vehicles met " in-use" emissions standards, which are defined for California LEV I criteria to be measured on average for engine families through testing of at least 10 vehicles for varying degrees of mileage intervals in which no more than 50% of the vehicles exceed emissions standards and that the fleet average does not exceed 1.3 times the emission limit. Ethyl's own analysis of different vehicle categories showed that fleet average compliance margins were not statistically different between MMT-treated and clear [B] gasoline for Tier 1, TLEV, or LEV fleets. Ethyl also pointed out how differences in octane rating from MMT vs. clear fuel could contribute to differences in emissions and vehicle performance.

4 Studies of Tier 2 Technologies

As emissions limits become more stringent, automakers increasingly rely on improved systems to monitor and control emissions. Larger emissions reductions can be achieved with high cell density catalysts (HCD) in a close-coupled configuration (HCD-CC or HDCC). Technologies have increased cell densities from the historically typical 400 cells per square inch (cpsi) to 600-900 cpsi. These HCD catalysts generally have thinner walls with increased surface area to improve conversion efficiency, and lower thermal mass to achieve operating temperatures more quickly. In addition, improved catalyst washcoats have enabled catalysts to withstand higher temperatures, allowing their placement closer to the exhaust manifold. Close-coupling enables quicker light-off due to higher exhaust gas temperatures, but also results in increased angles of incidence of the exhaust gas entering the catalyst.

[B] The term "clear" gasoline is typically used to indicate untreated or MMT-free gasoline.

With this evolving technology comes increased concern about catalyst plugging and fouling with the use of MMT. Higher surface area of the catalyst provides additional surfaces for deposits, which are clearly seen to form with use of MMT. Also, early work suggested that plugging by manganese oxide deposits can increase by as much as 15-fold with a change in temperature from 705°C to 843°C.[71] Therefore, close coupled catalysts with higher temperatures may be more susceptible to plugging. Additionally, the placement of close-coupled catalysts results in a sharper angle of incidence of gases onto the catalyst, which has been shown to increase the rate of plugging.[80]

Two different conditions are referred to as catalyst plugging: (1) channel obstruction and (2) pore-mouth blockage.[81] Channel obstruction occurs when deposits physically plug or obstruct the flow of exhaust streams through the honeycomb structure of the catalyst, resulting in a measurable pressure drop across the catalyst. Channel obstruction can also affect drivability of the vehicle, presumably due to higher backpressure. Pore-mouth blockage is a result of inhibition of mass transfer between the gas phase pollutants and the solid catalyst, and by blocking of active sites on the catalyst. This results in deterioration of conversion efficiency. Frequently, both conversion efficiency and pressure drops are measured when evaluating catalyst performance.

Many studies on Tier 2 vehicles have focused on how MMT and its deposits interact with the catalysts. Automakers have reported widespread failure of catalysts when using MMT in Tier 2 and similar vehicles.[82,83] In-use surveys conducted by Afton have not supported this observation.[84,85] However, these Canadian reviews were conducted at a time when the use of MMT in Canada was being voluntarily halted, so there was little opportunity for Tier 2 vehicles to accumulate substantial mileage with market fuels containing MMT. Meanwhile, surveys conducted in China have shown that MMT does not contribute to emission standard exceedances.[86] In addition to in-use surveys, other engine and catalyst testing in laboratory settings have been conducted, as well as a handful of fleet tests. The automakers generally conclude that MMT causes harmful effects on Tier-2 emissions control technologies, while studies performed or cited by Afton conclude that MMT does not contribute to the exceedance of applicable in-use emission standards. Some of these studies are briefly summarized below, with further detailed summaries available in Appendix III.

It should be noted that many of the studies described were those made available in the NCWM database, presumably by stakeholders. While some of the literature is published elsewhere in peer-reviewed journals, or are available through web searches, many studies are documented in technical reports or white papers that are not publicly available or retrievable through conventional literature or web searching approaches. Many of these studies have not been peer reviewed or vetted through other organizations and as such, their validity has not been widely accepted. It should be noted that much of the work from Afton that falls into this category has been submitted to the EPA as a condition of maintaining their fuel additive registration for mmt®. Also, several Afton reports make reference to additional studies or data that are not publicly available, nor were they included in the NCWM database, so they could not be included for review.

4.1 Regulated Emissions from Tier 2 Vehicles

Evaluations of regulated emissions from Tier 2 vehicles have been conducted by the automakers, Afton, and others - including the Chinese Environmental Protection Agency (SEPA). This includes various fleet and durability studies, as well as several engine studies with and without the use of

MMT. Many of these were conducted in Europe, or have a European focus, due to changes in regulations there. In late 2008, a ban on MMT was considered as part of the EU Fuel Quality Directive (Directive 2009/30/EC), but was later compromised to allow 6 mg Mn/L of fuel beginning in 2011 (further reduced to 2 mg Mn/L starting January, 2014). Article 8a of the Fuel Quality Directive requires that the European Commission (EC) conduct an assessment of the health and environmental risks of using metallic additives in fuel, and to develop a suitable test methodology.

In 2013, the EC issued a protocol describing the methodologies for evaluating effects of metallic fuel additives on emissions performance of light-duty vehicles, with the aim of generating data on regulated emissions, as well as speciation of emitted metals. [87] The methodology provides guidelines regarding the number of vehicles tested, the specific fuel type, requirements for fuel blending and storage throughout the test program, driving cycles used, mileage accumulation, intervals of emissions testing, and the methodology of calculating emissions effects with statistical significance. It also specifies additional testing to generate data regarding the instantaneous effects of metallic additives on emissions. The protocol calls for two phases of testing. In the first phase, a minimum of 24 vehicles (at least 4 models of different configurations with 6 vehicles of each model) must be "run-in" with no metallic additive, and emissions testing must be done to establish a baseline. Durability testing to 160,000 km is completed in Phase 2, during which emissions testing is conducted every 30,000 km.

4.1.1 Engine Studies

A laboratory study was conducted by a consortium of European automobile manufacturers (Audi, BMW, Daimler Chrysler, Porsche, and VW- referred to as the "Porsche Study"), in which two 2004 Porsche Carrera engines with complete exhaust gas systems (catalysts and oxygen sensors) were evaluated on an engine test bench to compare the use of MMT at 15 mg Mn/L to Super Plus gasoline in the European market.[88] The emissions control system in each set-up consisted of two 400 cpsi metal substrate catalysts for each of the two cylinder banks in the engine, arranged with short a distance between each other in a metal casing. Emissions testing was conducted after a 20-hour break-in, and after 100 and 179 hours of durability testing on the engine dyno. Results showed that MMT appeared to affect HC emissions, resulting in an increase of over 50% relative to the Super Plus engine after 179 hours of durability testing (equating to approximately 60,000 km based on fuel consumption). This increase was attributed primarily to increased engine out emissions, along with longer catalyst light off times of the MMT catalyst during EU cold start conditions. No fuel-specific effects were noted on CO or NO_x emissions. Additional testing of the components in a slave Porsche Carrera on a chassis dyno confirmed the engine test results, showing that EU-4 HC limits (0.1 g/mi) were exceeded by more than 10% with a strong influence due to increased engine-out emissions. A 5% loss of engine power and 3% decrease in maximum torque were also observed along with 6% higher exhaust gas back pressures and 5% higher specific fuel consumption. Evaluation of the components after testing showed visible Mn deposits present throughout the combustion chamber and exhaust system. The increase in engine-out HC emissions was attributed to these Mn deposits that were believed to accumulate fuel, which was subsequently exhausted as HC emissions, rather than being burned during combustion. Visible manganese deposits on the catalyst, as shown in Figure 4, were found to be responsible for the increased exhaust-gas backpressure and resulting torque and power loss. These deposits also resulted in a 25°C increase in light-off temperature of the starter catalysts, which explained the higher HC emissions. The oxygen sensors were not impaired, and MMT showed no effect on O_2 storage capacity.

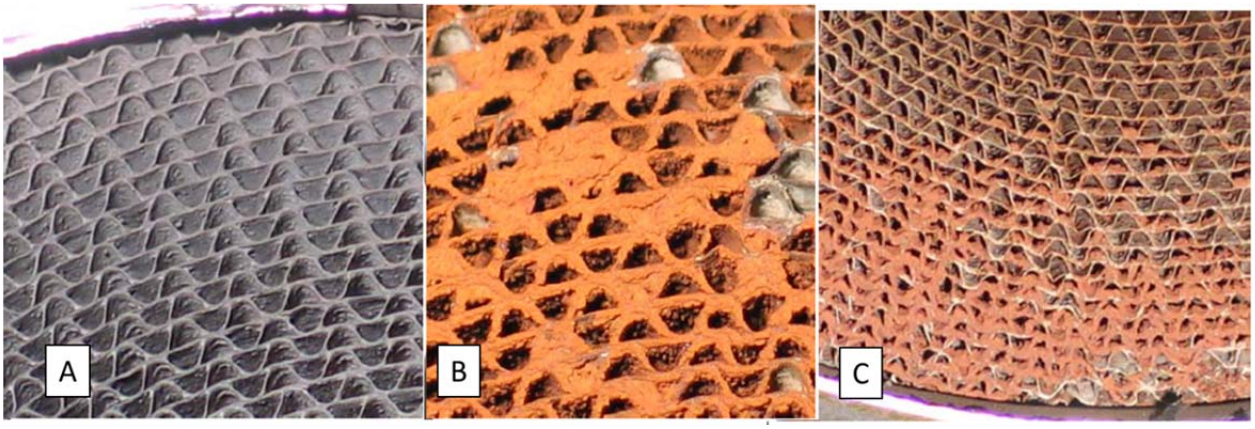

Figure 4: Color photographs of the front faces of the Porsche Carrera catalysts after durability testing. A) Starter catalysts with Super-Plus, B) Starter catalyst with Super Plus with MMT, C) Main catalyst with Super-Plus with MMT.

Afton responded to this study, claiming flaws in the test procedure contributed to the poor performance and increased emissions from the MMT vehicle. [89] They noted that the durability cycle used (which was reported to be favorable for MMT because the cycle's high engine loads and exhaust flows would limit the formation of deposits), was not representative of real-world driving, since in order to achieve the reported 60,000 km of driving, the average speed would have to be 400 kph. They also noted differences in fuel characteristics between the clear fuel and MMT-treated fuel. For example, the MMT-treated fuel had 2.3% higher density (0.7687 vs. 0.7514 kg/L), 430% higher sulfur (11.6 vs. 2.7 mg/kg) and 23% higher aromatics content (39.8 vs. 32.3 vol.%), all of which Afton state, could affect performance and emissions. However, the Porsche study states that the fuels were splash blended, so fuel qualities "differ only in regard to their manganese content." [90,91,92]

In addition, Afton concluded that the Euro-4 HC emissions limits were not exceeded since the emissions reported did not exceed the outlying emitter threshold limit (1.5 times the standard). They also point out that EU-specified testing protocols were not followed, which require testing a minimum of three vehicles and performing testing on a chassis dynamometer with regulation test fuels. While only one engine was tested using each fuel blend, the testing procedures followed in the Porsche study included chassis dynamometer testing with EU-Reference fuel following EU-Emission testing protocols after the 20-hour break in period and after 179-hours of durability testing. This test procedure resulted in the HC-emission limit exceedance in the MMT-engine. Although the Porsche study stated that the engine operation was identical between the two engines after the break-in period, Afton noted that a difference in exhaust temperatures of 15-30°C was seen during testing after the break-in phase, which they claim could contribute a 35-80% increase in the rate of catalyst deterioration. However, it appears that exhaust temperatures measured after 100 and 179 hour durability testing were more similar between the two engines.

4.1.2 Vehicle Studies

Several vehicle studies have been conducted on individual vehicles and on fleets of vehicles that meet Tier 2 or Euro 4 emission standards. These studies include: (1) a 2005 fleet study by Afton on

8-vehicles;[90] (2) six vehicle fleet assessment by the Chinese State Environmental Protection Agency (SEPA) in 2006, [93] (3) an ADA study on two VW vehicles; [94] (4) follow-on testing by Afton on a single VW vehicle;[95] (5) a 22-vehicle analysis on Euro 4 vehicles by Afton,[27] and (6) a fleet of U.S. vehicles conforming to Tier 2 standards.[96] Only one of the fleet studies conducted by Afton (Ref. no [90]) is reported in a publicly available SAE publication; other works were provided in the NCWM database, but were not publically available through database and web searches (e.g. [27,96]).

In a 2005 fleet study by Afton, results indicated that the use of MMT splash blended at 18 mg Mn/L had no significant effect on a vehicle's ability to meet applicable emissions standards.[90] In this study, an 8-car fleet of 2003 MY Euro 4 vehicles was evaluated over 100,000 km, with half the fleet operating on MMT-containing fuel. Each vehicle met the OBD threshold limit for NOx, CO and HC (shown as 0.6, 3.2, and 0.4 g/km, respectively), and all the MMT-fueled vehicles met the Euro 4 certification standards for CO and HC (1.0 g/mi and 0.1 g/mi, respectively). However, NO_x emissions exceeded Euro 4 certification standard (0.08 g/km) in several cases for both MMT and no-MMT vehicles, with more frequent exceedances by the MMT-free vehicles. It should be noted that the certification emissions standards used for comparison are the same Euro-4 certification standards used in the Porsche study[88], and shown in Table 4.

A 2006 study by the Chinese State Environmental Protection Agency (SEPA) was conducted on six imported vehicles rated to Euro 4 standards with 600 cpsi close-coupled TWC. Half of the fleet was tested at an MMT treat rate of 18 mg Mn/L. Durability testing to 80,000 km (50,000 miles) was completed using 28 driving modes to represent urban and highway driving, with 81.5% of the drive cycle achieving speeds above 80 kph (50 mph). This resulted in a calculated MMT consumption of 96.8 grams of Mn per vehicle over the durability testing. The report concludes that HC and CO emissions deteriorate with mileage for both groups, with the average of each measurement over various testing intervals meeting Euro 4 standards (0.1 and 1.0 g/km, respectively). Figures show that the HC and CO emissions from MMT vehicles are slightly higher than no-MMT vehicles. Likewise, NO_x emissions are reported to deteriorate with mileage for both vehicle groups, and it was reported that both vehicle groups exceeded the Euro 4 NO_x standard (0.08 gm/km).

In more recent testing conducted by ADA (Abgaszentrum das Automobilindustrie), two 2010 VW Eos with Euro 5 application were evaluated, one with a treat rate of 6 mg Mn/L compared to Euro 5 Reference fuel.[94] Durability testing over 160,000 km was done using the SRC conforming to EC Regulation 692/2008, with robotic driving on a chassis dynamometer at a rate of 1,650 km per day with only brief stops for re-fueling and engine checks for OBD faults (no other mention is made regarding MIL illumination or lack thereof during testing). Emissions were tested at periodic intervals, along with pressure drop measurements across the catalyst, exhaust temperatures, and oxygen storage capacity of the catalysts. Engine-out emissions were similar for the two vehicles throughout mileage accumulation, while tail-pipe measurements showed that Euro 5 emission limits were exceeded after 105k-km for THC, NMHC and NOx (shown as 0.1 g/km, 0.068 g/km, and 0.06 g/km, respectively) for the MMT vehicle, while all tailpipe emissions from the baseline vehicle were still well below the Euro 5 emission limits. The NOx and THC conversion rates of the MMT-catalyst also dropped sharply after 90,000 km due to deposit formation and mechanical plugging of the catalyst surface and cell channels by manganese oxides. Evidence for this plugging was provided by exhaust back pressure measurements of the catalyst. In addition, decreased oxygen storage capacity of the MMT catalyst was seen. Endoscopic images of the catalysts at various mileage intervals showed increasing amounts of plugging in the MMT- fueled vehicle, while no visible plugging was seen in the reference fuel vehicle as shown in Figure 5.

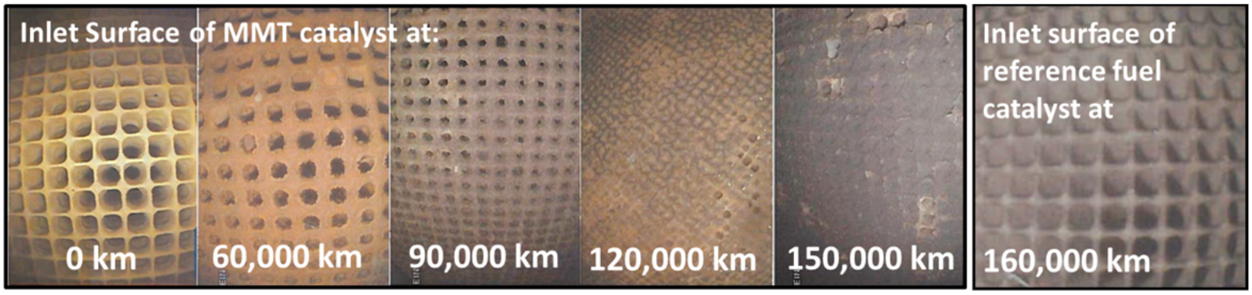

Figure 5: Color endoscopy images of 600 cpsi, close coupled catalyst from a VW Eos fueled with gasoline with 6 mg Mn/L over 150,000 km, compared to inlet surface from reference fuel catalyst after 160,000 km. Taken from Lohfink, 2014. [94]

Afton responded to the ADA study, saying that the conclusions were not warranted for two primary reasons.[95] First, although the cycle selected for testing conformed to EC protocols (p 28 says the SRC provides " a balanced mix of high and low exhaust gas temperatures, and can be considered the most suitable aging procedure." [87]), Afton stated that the manner in which it was applied for testing was too severe and did not reflect real-world operation, since mileage accumulation totaled in excess of 5,000 miles per week and the number of cold starts was very small. With such a severe pace of mileage accumulation, Afton maintained that the application of the SRC would produce higher than normal exhaust gas temperatures and reduce conditions that result in normal particle detachment mechanisms of manganese from exhaust components (this will be discussed in Section 4.2 on work by Roos[97] in which a "fuel cut" procedure was implemented to introduce particle detachment forces). Second, Afton disagreed with the conclusion that the vehicles exceed emission standards, stating that they should be compared to "in service conformity" standards rather than "type approval" standards. Afton explained that the Euro 5 "in-service conformity" performance standards define what constitute a "failure," and require that the two 2010 VW Eos vehicles not exceed 1.5 times that applicable type approval emission standard for 5 years or 100,000 km, whichever comes first. By those metrics, the MMT vehicles complied with the in-use standards despite mileage accumulation beyond 100,000 km. In their response to the ADA study, Afton reported results from their own test program on a single 2011 VW GTI vehicle, which conformed to US Tier 2 standards but had similar engine and exhaust components as the 2010 Eos such as a 600 cpsi three-way close coupled catalytic converter. They applied the SRC for mileage accumulation, but included one hour of engine off soak time after every four cycles (approximately 2 hours). After 120,000 miles, they reported that NOx, NMHC and CO emissions were all below "in-use" Tier 2 emission limits (which are reported to be the same 120,000 mi Bin 5 limits shown in Table 3). [95]

Afton has conducted multiple studies on fleets of vehicles in both the US and Europe, which are reported in unpublished white papers that were included in the NCWM database for review in this project. A 2014 report that was made available on the NCWM database discusses several of these fleet tests, and provides short reports as attachments. [86] This compilation of literature has been submitted to EPA as a condition of maintaining Afton's fuel additive registration for mmt®. This report reviews results of vehicle impacts over the past several decades and compiles results from

Afton's own testing programs on 27 Tier 2 and Euro 4/5 vehicles. The vehicles ranged from MY 2003 to 2007 and had catalyst technologies ranging from 400-900 cpsi, with some vehicles being tested to as high as 233,000 km. MMT treat rates were evaluated most frequently at 8.3 mg Mn/L, but ranged as high as 18 mg Mn/L. Afton reports that none of the MMT-fueled test vehicles failed to meet "in-use" emission standards and none experienced OBD MIL illumination resulting from fuel-related failures of catalytic converters, oxygen sensors or spark plugs. Other reports that are included as attachments to the main report provide additional testing details. In each case, MIL illumination is reported on a yes/no basis from OBD-II monitoring throughout mileage accumulation. In the majority of cases, no MIL illumination occurred, and for those cases in which it did occur, it resulted from issues not related to MMT. For several of the fleet tests, emissions compliance was reported on a yes/no basis, and the reports all conclude that none of the vehicles failed to meet appropriate in-use emissions standards.

One attachment to this report by Afton presents results from a 13-vehicle fleet certified to Tier 2 Bin-5 standards and tested to 120,000 miles (193,000 km).[96] The vehicles were tested on a variety of fuels, including several different commercially available fuels, gasoline with MMT at 8.3 mg Mn/L, and a rotating matrix of commercially available gasoline and two MMT-containing fuels at different concentrations (8.3 and 18 mg Mn/L). The report concluded that OBD-II systems functioned properly and did not indicate any MMT-related issues; parts swapping indicated little or no reduction in conversion efficiency of the catalysts for any regulated emissions; and "all vehicles met applicable in-use emissions standards," indicated on a yes/no basis. However, none of the measured data were presented in the report, with the exception of integrated emissions averages over the entire mileage accumulation in comparison to other fleet tests.

Another Afton report focused on the particulate measurements from a study they conducted in Europe on two vehicle fleets, named Europe 2012 and Europe 2013, which together totaled 22 vehicles.[98] The vehicles were each purchased second hand or drawn from for-hire fleets and tested on the Euro 5 regulatory emission cycle (NEDC and CADC) using reference fuel with MMT treat rates of 0, 6, or 18 mg Mn/L following EU protocol for the evaluation of metallic additives.[87] The study reported that all applicable emissions standards (the "type-approval" standard) met by the MMT-free fleet were also met by the MMT-fleet.

4.2 Interaction of Manganese Deposits on HCD-CC Catalysts and Particulate Matter

Observations throughout decades of testing MMT have clearly shown that over time, reddish-brown manganese deposits build-up on spark plugs, oxygen sensors and catalysts. However, some studies have shown improved catalyst efficiency when using MMT, due to its scavenging of phosphorus and sulfur, which ordinarily act as poisons to the catalyst. A reduction in phosphorus, zinc and sulfur contents in catalysts from MMT-fueled vehicles (at 75,000 miles or less) has been seen in studies by both Ethyl and automakers.[37,62,81] Given the longer durational requirements of Tier 2 emission standards, there is increased concern that more deposits are likely to build-up in the catalysts, resulting in greater pressure drops and drivability issues, as well as decreased catalytic performance.

PM results from a recent Afton study that was conducted on two fleets of vehicles capable of meeting Tier 3 and Euro 5 emission standards (which are described above as Europe 2012 and Europe 2013 fleets) showed that while particulate emissions from the MMT-fueled vehicles exceeded those of the

MMT-free vehicles in 15 out of 22 cases, all test vehicles met the Euro 5 "type approval" PM emission standard of 5 mg/km.[98] Another Afton study to characterize PM from Tier 2 technology vehicles showed that between 9 and 20% of total Mn in the fuel was exhausted from the tailpipe.[27] This range is consistent with previous studies (~ 12% in [34]; 13% in [36]; 27% in [99]; and 5-45% in [35]), which have also concluded that between 5 and 12 % remains in the oil, with the remainder in the engine and exhaust systems. This suggests that there is not a large increase in particle build up in the high cell density catalysts, despite their increased surface area. On the other hand, independent studies by both Afton[97] and Honda[80] have indicated that HCD-CC catalysts operating at high temperatures are more susceptible to plugging.

In the Honda Study (SAE 2007-01-1070), a parametric analysis was conducted to evaluate the influence of exhaust gas temperature, catalyst cell density, and exhaust system configuration on catalyst performance when used with MMT at 8.3 mg Mn/L.[80] Engine dynamometer testing was conducted at three different exhaust gas temperatures (600, 715, 805^{o}C) and 5 angles of incidence of the exhaust gas to the converter inlet surface (30^{o}, 45^{o}, 60^{o}, 70^{o}, and 90^{o}) using two different catalyst cell densities (400 and 600 cpsi) and three different catalyst layouts. All parameters studied were found to play a role in the rate of catalyst plugging. Higher cell density catalysts plugged more rapidly (at a constant exhaust temperature of 805^{o}C), although the influence of the exhaust manifold configuration was found to have a greater effect. As the angle of incidence became sharper (similar to close-coupled catalysts), the rate of plugging increased. At the sharpest angle of incidence (30^{o}), the converter became completely plugged after 275 hours of operation. Illustrations are provided in Figure 6.

These observations demonstrate that the angle of incidence has significant influence on how quickly deposits form and grow. With a sharper angle of incidence, the growth direction of deposits leads to easier cross-linking between cell walls resulting in more rapid plugging from the manganese oxides. Plugging speed also increased by 36% with an increase in temperature from 715^{o}C to 805^{o}C. This Honda study demonstrated that higher cell densities and close coupled catalysts, two of the key technologies utilized to meet more stringent standards, are more susceptible to plugging by MMT due to the layout and exposure to high temperatures, which results in a more adhesive behavior of the Mn_3O_4 deposits.

An Afton study was conducted and published about the same time, with similar parametric analysis conducted on 400, 600 and 900 cpsi catalysts in an engine test cell to evaluate exhaust gas temperatures (at 870^{o}C, 800^{o}C, and 750^{o}C) and different treat rates of MMT (8.3 and 18 mg Mn/L).[97] The results of this study largely supported the Honda findings, showing that increases in exhaust temperature, MMT treat rate, and catalyst cell density result in more rapid plugging of the catalyst, as measured by increased rate of pressure drop, shown in Figure 7 (Note the differences in time scales from Figure A and B). However, the study also demonstrated that introduction of a "fuel cut" procedure during the engine test cycle reduced the increased pressure drop (see Figure 8). During the fuel cut, fuel to the injectors was shut off for varying durations (20 seconds or 60 seconds) every five minutes while the engine was motored, producing temperature drops of almost 250^{o}C and 500^{o}C, respectively. This type of fuel cut procedure would require the engine to be turned off every five minutes, which is not expected to occur in real world driving conditions, but is meant to simulate natural particle detachment forces, such as thermal cycling from turning the vehicle on and off, thermal changes from acceleration and deceleration, and vibrations in normal operation.

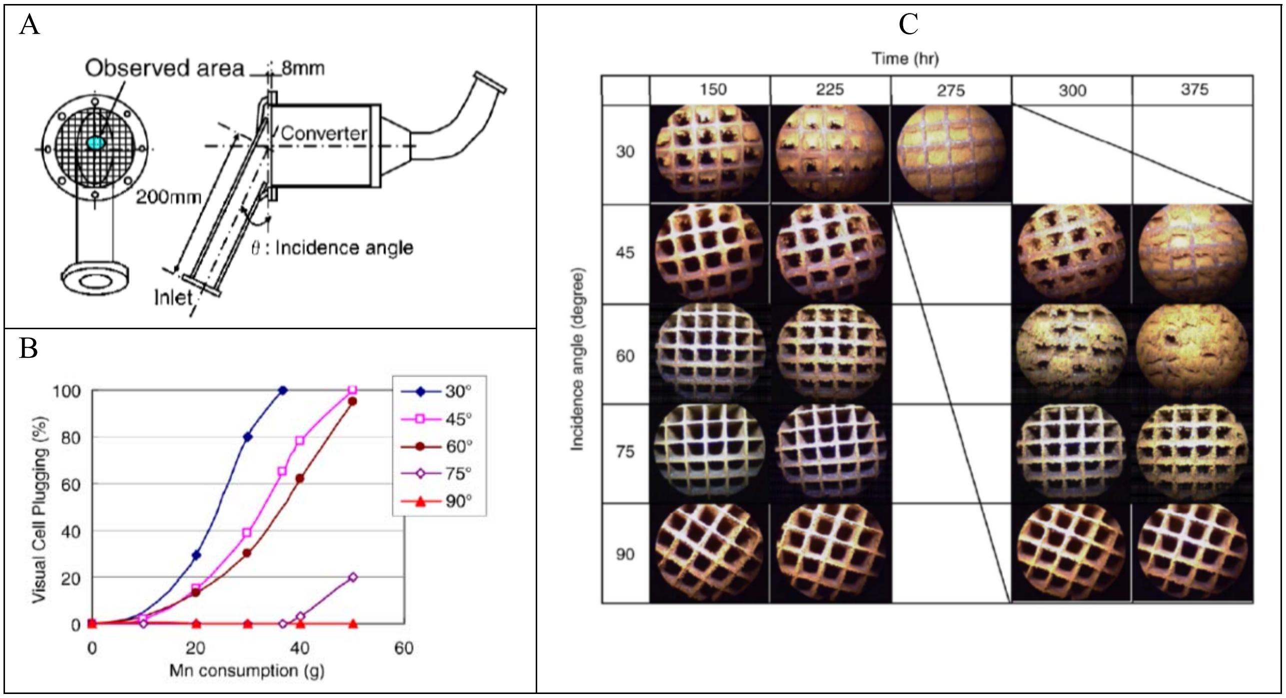

Figure 6: The angle of incidence (θ in Fig. "A") is specified by the inlet pipe and the converter surface. "B" shows the influence of the angle of incidence on plugging rate at 8.3 mg Mn/L at 805^{0}C. "C" shows color photographs of the variation of plugging time with incidence angle. Figures taken from Shimizu, 2007. [80]

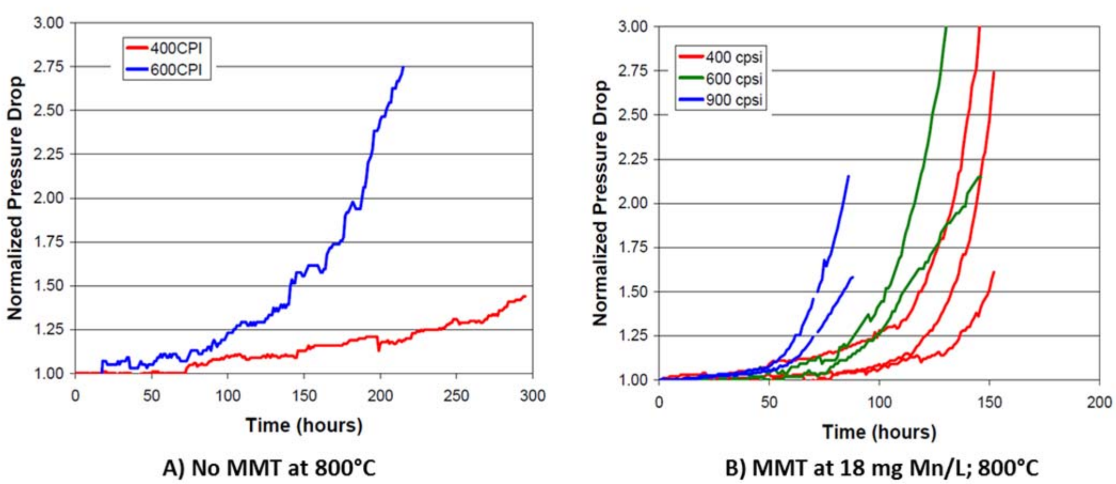

Figure 7: Changes in pressure drop across various cell density catalysts at 800°C without MMT (Fig. A) and with MMT at 18 mg Mn/L (Fig. B). Note the differences in time scales. (From Roos, 2007 [97])

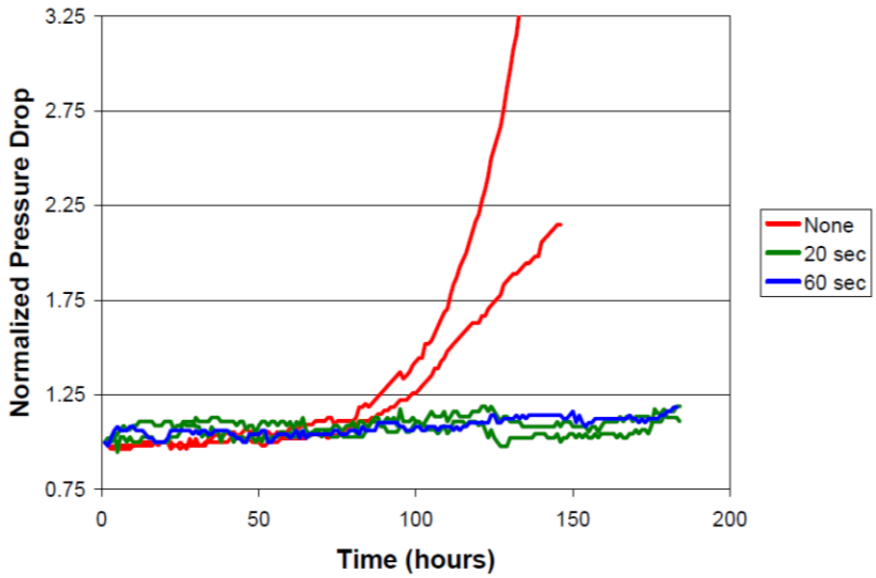

Figure 8: Changes in pressure drop across a 600 cpsi catalyst at 820^{0}C using fuel containing 18 mg Mn/L with and without fuel cut of various durations. (From Roos, 2007 [97])

More recent concerns about nanoparticles led to a study by Johnson Matthey, which demonstrated that the presence of metallic additives increased concentrations of nucleation mode particles relative to clear gasoline. Equal molar dosing of Mn and Fe (as Ferrocene – $FeCp_2$, Cp = C_5H_5) resulted in similar nanoparticle concentrations at the tailpipe.[100] Nanoparticle emissions were also found to increase as the dosing of Mn increased from 8.3 to 18 mg Mn/L.

4.3 In-use Studies and Surveys

Several in-use surveys have been conducted to compare data collected in U.S. and Canadian markets. It should be noted, however, that because the use of most MMT in Canada was halted in 2003, the time window for in-use evaluation of Tier-2 related vehicles was small. Therefore, much of the data from in-use surveys conducted by both automakers and Afton, which included vehicles ranging from MY 1996 to 2003, fall outside the Tier 2 scope of this work. However, it has been noted that some technologies used during this time were relevant to Tier 2, included a few early phase-in vehicles. In-use data by automakers focus on investigations of parts that were returned under warranty. MMT was frequently implicated as a source of harm based on visual inspection and laboratory testing. The in-use surveys conducted by Afton focused primarily on collection of OBD data from inspection and maintenance programs, and generally concluded that the use of MMT did not contributed to failures. Other more recent surveys have been conducted in China in which MY 2003 to 2006 vehicles were collected from in-use service and subjected to I/M emissions testing. These Chinese surveys, which evaluated over 250 vehicles, have not found any contribution of MMT to exceedance of emission standards. These surveys are further summarized below.

An abnormally high rate of catalytic converter replacement under warranty in Canada for the GM 2002 MY LL8 (a 4.2L in-line 6 cylinder engine) GMT 360/370 prompted an analysis by General Motors (this report was included in the NCWM database, but is not available through a web or literature search).[83] The engine and exhaust control systems of these GM vehicles were designed to be easily upgraded to Tier 2/ LEV 2 standards, utilizing a relatively close-coupled, 600 cpsi catalytic converter with an aggressive cold start heat-up strategy. Warranty data collected showed that the 2002 MY warranty replacement rates of catalysts in Canada peaked at 35 times those in the U.S. The analysis performed by GM included evaluation of returned catalysts from both Canada and the US (approximately 200 in each case). At that time, MMT was present in Canadian gasoline at levels of 5-15 mg Mn/L and not present in US gasoline. Analysis of the Canadian catalysts showed that failures were caused by partial plugging by Mn_3O_4 deposits in 93% of the cases. This plugging increased the flow restriction through the catalysts as indicated by backpressure measurements of 212 inches H_2O on average, whereas the normal range is expected to be around 7.5 inches H_2O. A photo of one of these catalysts is shown in Figure 9. The accumulation of these deposits led to degraded vehicle performance that was easily noticed by consumers, and in some cases, triggered a "service engine" light due to reduced emissions system efficiency detected by the OBD-II system. The study found that the rates of failure from deposits were not correlated with the odometer, and were more likely related to the operating temperature, which is dependent upon the driver and drive cycle.

Figure 9: Color photo of an early return of a Canadian GM 360/370 catalyst after 76,604 km. The inlet faces of both the inlet element (lower) and outlet element are pictured. Cold flow restriction was measured to be 197.6 in H_2O. Elemental analysis confirmed the reddish-brown deposits consisted mainly of Mn_3O_4.

The study also included emissions testing of 25 vehicles from U.S. markets and 24 vehicles from Canadian markets that had accumulated miles and were returned via the General Motors Acceptance Corporation (GMAC) lease program. Vehicles that previously had catalytic warranty issues or major engine repairs were excluded from testing. Average FTP emissions levels from the Canadian fleet were 119%, 175%, and 151% higher than the U.S. fleet for NMHC, CO, and NO_x, respectively. While all of the U.S. vehicles met the 50,000 mile certification standard, in the Canadian fleet, 7 vehicles exceeded the NMHC standard (0.10 g/mi), 1 vehicle exceeded the CO standard (4.2 g/mi), and 3 vehicles exceeded the NO_x standard (0.04 g/mi) at 50,000 miles. In addition, comparisons of engine-out emissions were not significantly different between the US and Canadian fleets, suggesting that Mn deposits in the engine are not a major contributor to the emissions differences. Cold flow restriction measurements across the catalysts produced an average of 8.7 inches H_2O in the U.S. fleet, while 20.0 inches H_2O was seen for the Canadian fleet, indicating flow restriction by Mn deposits. Example photos of the catalysts shown in Figure 10 illustrate visual plugging that coincides with an increased cold-flow restriction measurement. Analysis of the O_2 sensors showed no differences in performance between the fleets, although Mn deposits were visible on the surfaces of the Canadian fleet sensors. This study concluded that MMT vehicles have substantially higher emissions and higher rates of failure.

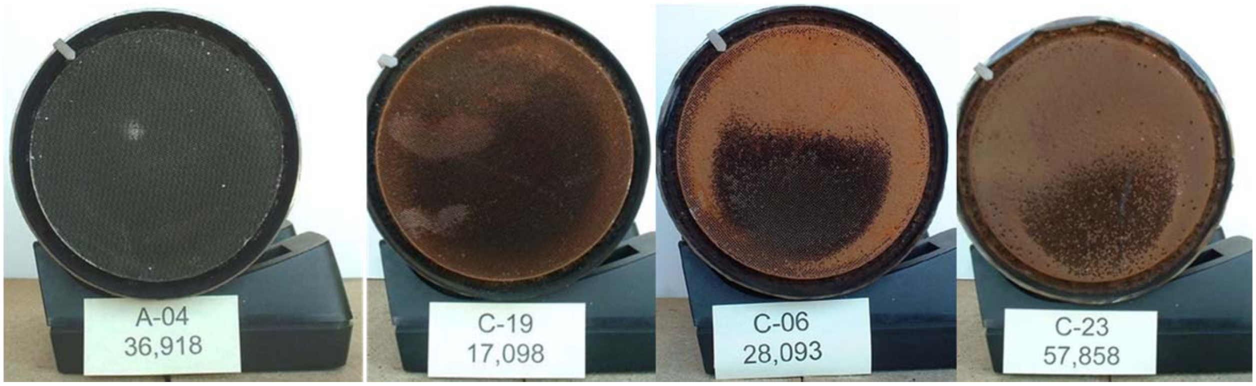

Figure 10: Color photos of exhaust catalyst inlet faces from in-use survey of GM 360/370 vehicles. A-04 is a typical inlet element from a US vehicle; C-19 is a low-restriction (9.4 in H_2O at 100 g/s) element from a Canadian Vehicle; C-06 is an average restriction (21 in H_2O) element from a Canadian vehicle; and C-23 is a high-restriction (81.7 in H_2O) element from a Canadian vehicle.

At an emission control conference in 2004, a consortium of automakers reported on consumer complaints in Canada regarding high fuel consumption, lack of power, and increased OBD alerts, as well as widespread failure of catalysts and emission control components.[82]

To investigate these claims, Afton conducted several in-use surveys. In one such study, they collected compliance data from various Inspection and Maintenance (I&M) programs using IM240 testing in British Columbia, Canada (where MMT was in use) and in Wisconsin, Arizona, and Illinois (where MMT was not in use) from 1996 to 2003, when MMT was phased out in Canada.[85] In a comparison of failure rates between all models in which data were collected, no significant differences were found. The authors explained that differences in cutpoints (e.g., the emissions measurement that defines a pass/fail) existed between the different I/M programs. To accommodate these differences, the test results were adjusted to the cutpoints in regions having less stringent cutpoints to provide a pass/fail result. The study concluded that IM240 testing does not detect deterioration of emissions control systems or components caused by MMT. The study also separately evaluated MY 2000 and 2001 Tier 2-capable vehicles in Canada. While these data could not be compared to U.S. data because of a shift to OBD testing rather than IM240 testing, failure rates of the 2000 and 2001 MY vehicles (first tested in 2002 and 2003) were low overall, at 0.1% and 0.3%, respectively. However, mileage rates for the vehicles were also low, having been in use for only two years at the time of testing, with the 2000 fleet having average mileage accumulation of 21,500 mi.

In the same study, Afton also focused on vehicles with HCD catalysts, comparing failure rates at the two-year test mark of all 2001 Honda Civics (which were equipped with 600 cpsi close-coupled catalysts) to 2000 Honda Civics (equipped with 400 cpsi catalysts) from the British Columbia Air Care I&M program. Since MMT was phased-out mid-2003, the data were restricted to the initial 6-months of data accumulation for both vehicle types. Results showed that the failure rate from 2,815 MY2001 Civics (600 cpsi) tested in the first 6 months of 2003 was much lower than that from 2,593 MY2000 Civics (400 cpsi) tested in the first six months of 2002 (~0.1% vs. ~1.6%). In addition, the

2001 Civics had lower failure rates than the average of all 2001 models (about 0.4%). A number of these vehicles also had high mileage accumulation, so vehicles with mileage in excess of 60,000 km were compared. Only 0.5% of high-mileage 2001 Civics failed, while 2.8% of the 2000 Civics failed. It was concluded that there is no I&M evidence to substantiate concerns that the use of MMT causes emissions failures.

A second survey was conducted by Afton to compare OBD and maintenance issues on MY 2001 and later vehicles when using MMT in three different markets.[84] A phone survey was conducted in Regina, Canada (where MMT was in use) and in Minneapolis, MN, and Denver, CO (where no MMT was used) to collect data regarding the frequency of MIL illumination and resulting repairs. A fuel survey of seven service stations in Regina was also conducted, with MMT concentrations found to range from 3.3 to 13.4 mg Mn/L in six stations, and one station having none. While the authors noted that differences could occur from factors other than fuel (such as climate, maintenance culture, engine calibrations, etc.), they found no statistically significant differences in rates of MIL illumination, or in the frequency or type of repairs. When looking specifically at repairs for components that come into contact with the fuel or its combustion products, the survey results showed that spark plugs displayed the highest rates of repair, but were twice as frequent in U.S. markets. The total rate of catalytic converter repair was low, totaling 11 in all markets. Although 6 out of the 11 occurred in Regina, the authors report that the repairs were primarily due to recall or warranty issues, and concluded that there was no statistically significant difference between markets.

Afton has also reported on the results of several in-use surveys conducted in Chinese markets that use MMT (Appendix 4 in [86]) None of the surveys, which were conducted by both Afton and the China Automotive Technology and Research Center (CATARC), found any emissions impacts associated with the use of MMT. In one such attachment, a presentation given at a CRC workshop, Afton presented emissions compliance data from 150 MY 2005 and 2006 taxis in Beijing, China, where MMT was widely used at up to 8 mg Mn/L.[101] All vehicles were certified to Euro 3 / Euro 4 standards with variable mileage up to 160,000 km. Each vehicle was tested using the Beijing I/M emissions test procedure. 146 of the 150 vehicles passed emissions testing, with the four failures occurring from VW Jettas in the same mileage bin (40-80k-km). The presentation concludes that all vehicles were operating properly on Beijing area specification fuels.

The final attachment (Attachment 7 in Appendix 4 of [86]) includes a paper presented at a 2010 Fuels and Lubes Conference by CATARC. In this study, emission control system performance was measured for 108 light duty State II certified vehicles of various makes and models procured around China with mileage ranging from 40,000 to 100,000 km (MY range is not reported, however State II was implemented between 2003 and 2004). The vehicles were first subjected to Type I emissions testing "as-is", which resulted in 75% of the vehicles meeting State II standards (0.5 g/km THC + $NO_{x,}$, 2.1 g/km CO). Routine repairs were then completed on the failing vehicles (not including exhaust components), resulting in only 10 remaining failures, none of which were due to a single pollutant. Following emissions testing, additional laboratory analysis was conducted on 18 selected catalysts, chosen to reflect a balance of high and low emitters with a range of mileage accumulation. XRF analysis of catalyst surfaces showed correlations between Pb and Zn concentrations and emissions performance, while no such correlation was found with Mn. The report concluded that most vehicles met emission standards, including many with high mileage. The failures were attributed primarily to improper maintenance and repair routines. For those that failed because of catalyst reasons, the major contributor was thermal aging, with Pb or Zn poisoning having a lesser effect. Mn did not negatively affect performance or emissions.

4.3.1 Sierra Research Report on Manufacturer Survey and Afton Response

In anticipation of a review by the Canadian government on MMT, a survey of automakers was conducted in which eighteen manufacturers were asked if any vehicles using advanced emissions control systems they had sold in Canada prior to MY2004 had experienced catalyst plugging or deterioration associated with MMT. While the review was never completed after the use of MMT was voluntarily halted, the data collected during the survey was provided as blinded reports and summarized in a 2008 report by Sierra Research.[12] Nine of the surveyed manufacturers, who collectively represented 86% of the total light-duty sales in Canada in 2006, responded that adverse impacts from the use of MMT were seen in select vehicles with Tier 2-like exhaust systems. A summary of the information from the nine blinded manufacturer reports is provided in Table 7, taken from the Sierra Report.

Table 7: Summary of Canadian Vehicle Models Adversely Affected by MMT, as Reported in Blinded Manufacturers' Reports. (Table 11-2 from Sierra Research Report. [12])

Table 11-2
Sources of Evidence of Adverse MMT® Impacts on Exhaust Emissions, Operation, and Performance of In-Use Canadian Vehicles with Advanced Emission Control Technologies and Systems

MFR	Warranty Claims	In-Use Vehicle Inspection	Laboratory Testing	Emissions Testing	Number of Models Impacted by MMT® Identified	Model Years
A	Yes	Yes	No	No	1	1999
C	Yes	Yes	Yes	Yes	4	2000-2002
D	Yes	Yes	Yes	Yes	2	2003
I	No	Yes	No	No	1	2002
J	Yes	Yes	Yes	Yes	7	2002-2003
K	Yes	Yes	Yes	Yes	1	2003
L	No	Yes	Yes	Yes	3	2001
M	Yes	Yes	Yes	Yes	5	2001-2003
O	No	No	Yes	No	1	2001

The information in Table 7 indicates that twenty-five vehicle models from MY 1999-2003 from these nine manufacturers experienced adverse impacts from the use of gasoline containing MMT. It should be noted that these impacts were not all identified via high warranty claim rates, and some impacts were identified through manufacturer testing or other types of evaluations on parts returned for other reasons or on individual or small fleets of vehicles. A total of 11 of the vehicles identified were reported to have higher warranty rates in Canada compared to the US. In many cases, the manufacturers performed additional evaluations of the catalysts that were returned under warranty. At the very least, typically a visual inspection was performed that indicated some degree of plugging by reddish-brown or orange deposits, which allowed the manufacturer to attribute at least some of the warranty claim increases to the use of MMT.

Through our own investigation of the blinded manufacturer reports, we have compiled Table 8 to compare the effects reported on individual vehicles and indicate what level of testing was performed on each vehicle or vehicle fleet. Vehicles that experienced warranty claims are highlighted in yellow. Vehicles that were reported to experience adverse effects identified through other testing but were not reported to experience high warranty claims are highlighted in blue. In addition to the 25 models in Table 7 that were reported to have evidence of adverse effects, 6 models were assigned numbers in the blinded reports but were reported to have experienced no adverse effects up to that time, bringing the total to 31 models as shown in Table 8. In addition to these, several manufacturers mentioned other vehicles that utilized HDCC catalysts or Tier-2 relevant systems in which no known effects were seen. For example, Manufacturer D reported an additional 5 models, Manufacturer K reported an additional 4 models, and Manufacturer O reported on six models, all with HDCC systems that sold prior to 2004, but did not experience MMT-related issues (bringing the total number of vehicles reported by these manufacturers to 46 by our count). However, most of the manufacturers noted that many of the vehicle models with HDCC systems that did not experience issues were likely not exposed to MMT for a long enough duration before MMT was halted in Canada. For example, Manufacturer J reported a qualitative analysis on over 70 catalysts that showed deposits on 4 out of 5 models (J-4 through J-8) although no increase in warranty claims was noted. Similarly, Manufacturer K reported that the additional 4 models mentioned above with HDCC systems were not relevant because they were too new to accumulate mileage before MMT was removed.

Combined, the nine manufacturers reported that 11 vehicles experienced higher warranty claims for converter replacement in Canada compared to the US. Several manufacturer reports (C, D, J and M) show plots of return rates or comparisons of return rates to the U.S (comparison of return rates are noted in Table 8). However, citing confidentiality of the warranty information, quantification of the actual rate of return is not reported. While warranty rates can be higher in Canada compared to the U.S. due to more severe conditions, Manufacturer J investigated this claim, and showed catalyst warranty repair rates were 35 times higher in one particular situation, while other warranty repairs were only about 1.4 times higher. Although several manufacturers noted that not all warranty claims were attributable to the use of MMT (e.g., M-1 experienced high warranty rates for other reasons), there were typically higher claim rates in Canada compared to the U.S, ranging from 3 to 20 times higher.

In most cases, manufacturers reported that visual inspection of the catalysts returned under warranty confirmed reddish-brown or orange deposits that contributed to plugging of the catalyst cells. An example from Manufacturer D is shown in Figure 11. Further, many of the manufacturers conducted some level of laboratory analysis on the deposits that confirmed the deposits were primarily Mn_3O_4. Therefore, the discrepancies between warranty claims in the U.S. and Canada were attributed to the use of MMT. In addition, several of the manufacturers (C, D, J, and M) reported a decline or levelling-off of catalyst-related warranty claims that coincided with the removal of MMT from Canadian fuel. An example of the decline is pictured in Figure 12 from Manufacturer M reporting.

Table 8: Summary of manufacturer data reported on individual testing and claims for Canadian vehicles identified in Sierra Research Report

Model	MY	Certification	Catalyst Description	Warranty Claims[1]	No. of vehicles[3]	Visual Inspection	Other Testing
A-1	1999	Tier 1	400 cpsi, not HDCC	Yes	3	Yes*	None
A-2	2000	NLEV-ULEV	600 cpsi, HDCC	No		No	None
C-1a	2000-01	LEV I	600 cpsi, HDCC in MY 2000; add'l 400 cpsi in MY2001	Yes (20 x)	NQ	Yes **	Lab, Emissions on returned catalyst
C-1b	2002	ULEV I	900 cpsi	Yes (12x)	NQ	Yes**	None
C-2	2002	LEV 1	900 cps + 600 cpsi M configuration	Yes (6 x)	NQ	Yes **	None
C-3	2002	LEV I	2-900 cpsi with 400 cpsi downstream	Yes (12 x)	NQ	Yes **	Laboratory
D-1	2003	T2B7	HDCC with 400 cpsi	Yes	NQ	Yes **	Emissions testing on returned catalyst; Engine Dyno testing on catalyst; Durability testing on new D-1
D-2	2003	T2B8	HDCC with 400 cpsi	No	NQ	No	Durability testing
I-1	2002	NLEV (LEV)	600 cpsi HDCC with 400 cpsi under floor	No	5	Yes*	None
J-1	2002-03	NLEV (LEV)	600 cpsi, mid under floor, 16 in from exhaust manifold	Yes (35x)	NQ	Yes**	See GM 360, Emissions testing on 24 cats returned under warranty
J-2	2003	LEV I	600 cpsi with add'l downstream under floor. (1 AWD, two-2WD)	Yes (AWD-37x)	NQ		7 in-use vehicles underwent emissions testing
J-3	2001-02	LEV I	400 cpsi, close coupled	N/A		Yes*	Lab analysis indicates plugging by Mn
J-4	2001-02	NLEV (LEV)	350 cpsi catalyst	No	20	Yes*	No
J-5	2001-02	NLEV (LEV)	400 cpsi warm up catalyst	No	20	Yes**	No
J-6	2001-03	Tier 1	Dual close-coupled 400 cpsi, located 16 in downstream	No	14	Yes*	No
J-7	2001	NLEV	600 cpsi located 24 in downstream	No	16	Yes *	No
J-8	2002-03	NLEV	600 cpsi located 9 in downstream	No	2	Yes	No
K-1	2003	NLEV (LEV)	600 cpsi, 17 cm downstream, 80 mm diameter	Yes	NQ	Yes**	Lab/emissions testing on returned catalysts; Durability, engine dyno testing on 1 new vehicle, 1 engine
K-2	2003		600 cpsi, 44 cm downstream, 103 cm diameter.	No			Durability testing on one new
L-1	2001	NLEV (LEV)	600 cpsi, single close coupled	No	1	Yes	Durability, Emissions
L-2	2001	NLEV (LEV)	600 cpsi, two close coupled, either side of V	No	3	Yes	Durability, Emissions on in-use catalysts
L-3	2004	T2B5	600 cpsi	No	NA	No	Durability testing on one vehicle
M-1	2001-03	ULEV	600 cpsi, manifold mounted HDCC	Yes [2]	NQ	Yes**	Lab, Durability on two production vehicles
M-2	2002-03	T2B5	dual bed 600 cpsi mid-under floor, HDCC	Yes (3 x)	NQ	Yes**	Durability on two production vehicles
M-3	2002	T2B5	600 cpsi, dual brick	No		No	Durability on two production vehicles
M-4	2002	T2B5	dual brick, 900/400 cpsi with perpendicular exhaust inlet	No		No	Durability on two production vehicles
M-5	2003	T2B5	900/400 , mid under floor, HDCC	No		No	No
M-6	2003	T2B5	900/400 , mid under floor, HDCC	No		No	Durability on two production vehicles
M-7	2003	T2B5	900 cpsi, HDCC on each exhaust bank, with single 350 cpsi under floor	No		No	Durability on two production vehicles
M-8	2003	T2B5	900 cpsi, HDCC each bank w/ single 350 cpsi under floor	No		No	Durability on two production vehicles
O-1	2001	ULEV	600 cpsi	No	20		

¹ A "Yes" indicates that higher warranty claims were seen in Canada compared to the US. Number in parentheses indicates increased rate of Canadian warranty claims
² M-1was reported to have other warranty issues, however, higher rates in Canada were attributed to the use of MMT based on visual inspection of catalysts.
3 "NQ" indicates not quantified.
* Visual inspection reported reddish-brown deposits, no obvious plugging
** Visual inspection reported reddish-brown deposits AND plugging

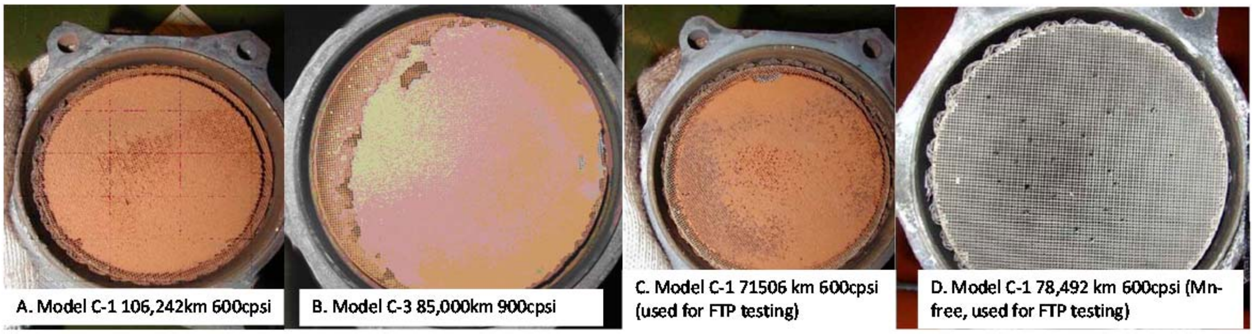

Figure 11. Color photos illustrating plugging of A) 600 cpsi and B) 900 cpsi Catalysts from Manufacturer C used in Canada. Catalysts shown in C and D were those used for emission testing comparison. "C" was visually assessed to be 90% plugged. "D" is a typical USA catalyst taken from a vehicle driven in an MMT-free area.

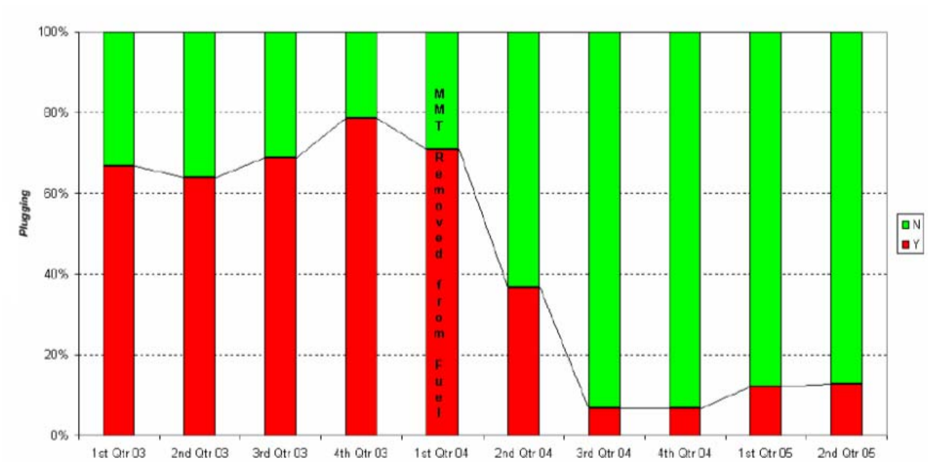

Figure 12. Ratio of catalytic converters from MY 2001-2003 M-1 models returned through warranty that were observed to have surface plugging or restricted flow. (Through June 30, 2005.)

As shown in Table 8, several manufacturers reported data from their own testing programs that consisted of emissions and/or durability testing. In addition, several of the manufacturers reported on further "in-use" evaluation (e.g., Manufacturer J, whose report appears to be the same as the GM report already summarized). These results are summarized in Appendix III for each manufacturer. In general, durability and emissions testing were reported on either a single model or a small fleet of vehicles. In some cases, additional emissions testing was completed on the converters that were returned under warranty. These test results confirmed that plugging caused drivability issues and MIL illumination in some vehicle models. Emissions testing showed that plugged catalysts resulted in increases that could be seen in all three regulated gaseous pollutants. Additional "in-use" surveys were conducted by Manufacturer M, who acquired 70 Canadian vehicles of a model having high warranty claims. Catalyst plugging ranged from 2 to 80%. Extent of plugging correlated with NOx and THC emissions.

Based on the blinded manufacturer reports as well as additional literature summary, the Sierra Research Report concluded that vehicles equipped with close-coupled catalysts or HDCC catalysts appear to be affected more frequently than under-floor catalysts, and that exhaust system geometry and exhaust gas dynamics play a role in plugging. In addition, high exhaust gas or peak catalyst temperatures (800°C or more) are more frequently associated with plugging. The amount of MMT consumption also affects plugging, with increased consumption leading to a higher degree of plugging. However, because vehicles with advanced emissions control technologies were only just being implemented while MMT was being phased out in Canada, the ultimate impacts cannot be determined, and the effects seen in the survey are characterized by Sierra Research as being only the "tip of the iceberg."

Afton prepared a response to the Sierra Report which was included as Appendix 6 to their report "Seeking Local Solutions."[86] Afton points out that several articles were missed and should be reflected in the conclusions from the literature review summary. However, their primary response regards the conclusions drawn from the blinded manufacturer reports. Afton points out that the report is not peer reviewed and that its confidential nature and lack of quantification of warranty claims makes the results difficult to validate.

Afton also points out that other factors can contribute to catalyst plugging besides MMT, and that the conclusion that high-cell density catalysts are more susceptible to plugging by MMT is highly selective. In support of this statement, Afton performed an investigation of catalytic converter performance in the U.S. and collected hundreds of HDCC catalysts from recyclers across the country. They observed that many of these catalysts had obstructed pores for reasons un-related to MMT. Several example photographs are provided in Figure 13.

Figure 13. Color photographs of plugged catalysts collected from catalysts recyclers in the U.S. Analysis on a 2001 Honda Civic Converter (673) showed deposits are primarily Ca, P, and Zn (14.4%, 12.2%, 11%, respectively). Other examples included Nissan Catalysts from California (730) and from Texas (664), and GM catalysts from Washington (503), and Texas (530). (Numbered catalysts are from left to right)

Afton also stated that the conclusion made in the Sierra report that MMT is not compatible with HDCC catalysts is unwarranted. They pointed out that of the 45 models identified by all manufacturers, 36 models experienced no warranty claims (Note that by our count, 11 out of 46 models experienced warranty claims). Therefore, Afton argued that the "majority" of 2000-2004 vehicles with advanced vehicle emission control systems did not experience problems, and those that did were at unquantified levels and could possibly have been attributed to other warranty issues. Afton concluded that the Sierra report supports the demonstration that MMT is a beneficial fuel additive.

Afton also disagreed with the conclusion in the Sierra report that catalyst plugging becomes pronounced beyond a "threshold" brick temperature of 800^{0}C. They pointed out that the brick temperature for model O-3 was reported to reach 1000^{0}C, yet that model didn't experience any plugging or warranty issues. Therefore, they maintain that temperature differences between models are not a root cause of plugging. Afton also noted that only a small fraction of the manufacturers who reported their own emissions and durability testing followed "normal" test procedures.

In addition, Afton hypothesized that model M-1 was the 2001 Honda Civic. Based on their own analysis, Afton determined that 2001 Honda Civic models produced for sale in Canada had a different engine calibration than those produced for sale in the U.S. They found that certification data for the different engine calibrations showed projected emissions to vary by 200 to 500%. In addition, they noted that the 2001 Honda Civic had other reports of widespread failure and warranty issues not associated with the use of MMT (supported with service bulletins included as Attachment 1 in Appendix 6 of [86]). (Note that manufacturer M reported there were other warranty issues associated with this catalyst. However, a discrepancy in warranty claims in Canada and the U.S. was attributed to plugging by MMT based on visual inspections). Afton also pointed out that differences in warranty programs existed between the US and Canada, and therefore warranty claims were not comparable. In one case, Manufacturer J reported that differences in warranty systems restricted comparisons of warranty rates. In other reports, it is not clear that differences in warranty programs were taken into consideration.

4.4 Reviews of Other Works

4.4.1 Arcadis Review

Following protocols set forth by the EC methodology, Arcadis conducted an evaluation of data from other previously conducted fleet studies, as listed below.[102] (Note, this paper by Arcadis appears as an Appendix to an unknown report. It is included in the NCWM database, but is not publicly available. Also, several test programs described in the Arcadis paper are not included in the literature database.) The analysis of data was conducted in two parts that coincide with the EU protocol: (1) a comparison of instantaneous emissions which is completed by comparing MMT and MMT-free fuels, and (2) durability testing. In addition, analysis of particulate matter was performed.

In Phase I, statistical analysis of results from 54 vehicles evaluated in 5 different programs was conducted. The programs that included instantaneous emissions measurements are the following:

- AVL 1997 – unknown test program, not included in literature
- U.S. 2013 – unknown test program, not included in literature
- Europe 2012 [98] (previously discussed)
- Europe 2013 [98] (previously discussed)
- EPA 1998 - unknown test program, likely includes waiver application data

Arcadis performed statistical analysis on all Tier 2 and similar vehicles (excluding Program 5 above), concluding that vehicle type and drive cycle had significant impacts on the instantaneous regulated emissions while the level of Mn content (0, 8.3 or 18 mg Mn/L) did not have any impact. In general, the report concludes that "No adverse instantaneous effects of any significance to regulated tailpipe emissions were measured by the EU protocol. However, some vehicles with some technologies on some drive cycles did exhibit different behavior for MMT vs. MMT-free fuels." The summary of instantaneous emissions from individual vehicles from each of the different test programs is shown in Figure 14. The results are mixed, with higher emissions from MMT fuels in some cases, and lower emissions in others.

Phase 2 of the EC protocol specifies durability testing. Arcadis's Phase 2 analysis included results from three separate tests: (1) AAM Part 2, [73] (2) Europe Euro 4 (study by Afton [90]), and (3) U.S. Tier 2 (study by Afton [96]). Mileage accumulation in these programs ranged from 80,000 km to 160,000 km. Arcadis calculated the emissions compliance for each program as the average integrated emissions over the lifetime of the vehicle below the applicable emission standard. This compliance was determined for vehicles in two mileage bins (above and below 80,000 km). Of the 15 different cases assessed, both sets of vehicles had similar compliance margins; only in one case was the difference between the MMT and MMT-free fleets statistically significant. However, in 11 out of 15 cases, total compliance margins for the MMT-fueled fleet were lower than for the MMT-free fleet.

The integrated emissions for the combined MMT and MMT-free fleets were also compared. The combined integrated NOx emissions were 11% higher from the MMT-free fleet, while HC emissions were 16% higher from the MMT fleet. An analysis of the OBD MIL illumination occurrences was also performed, showing that MMT did not result in more frequent MIL illuminations. The report concluded that the use of MMT at the treat rates evaluated had no impact on deterioration of vehicle emissions control systems, did not cause material differences in vehicle emission levels, and did not impact the vehicles' ability to meet emissions standards.

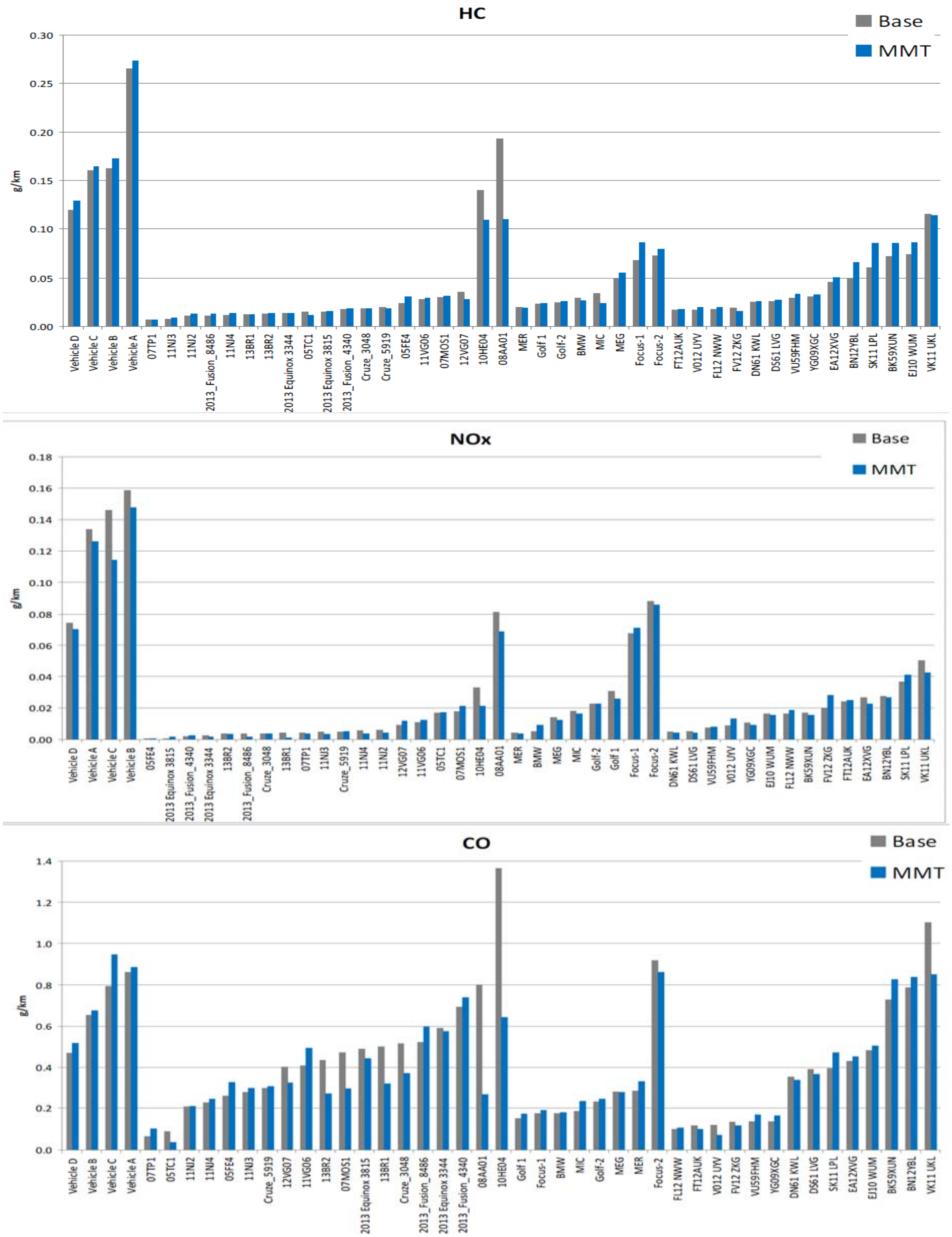

Figure 14: Instantaneous Emissions measurements from 4 different test programs.[102]

5 Summary and Conclusions

In this project, we have obtained, organized, and summarized literature information related to the effects of MMT as a gasoline additive on vehicle emissions, engines, and exhaust control systems. This work was requested of CRC by ASTM to provide guidance in the ASTM D4814 fuel specification regarding appropriate concentration limits for organometallic compounds in gasoline, and focused primarily on the effects of MMT on modern Tier 2 and similar technology vehicles. Much of the literature reviewed was included in the NCWM Organometallics Committee database, with additional items added via literature and journal searches. Several of the items included in the NCWM database were from private sources and are not available to the public, nor have they been peer reviewed.

The scope of this work was to summarize relevant literature items and to synthesize information to create an overview report that outlines the major issues, and presents evidence for specific effects of MMT on engines, exhaust system components and emissions. This did not include development of a complete database that fully documents the effects seen within each study. Detailed summaries of "high" and "medium" priority studies (e.g., those that directly evaluated the impacts of MMT on vehicle emissions, engines or emissions control system components), are provided in Appendix III.

Numerous MMT studies have been reported over the past several decades, with most conducted by one of two parties: (1) automakers or (2) Afton Chemical Corporation (previously known as Ethyl), a producer of MMT. The conclusions presented across the range of studies are not consistent. Studies conducted by automakers tend to focus on emissions measurements and component effects after long-term exposures to MMT, sometimes under more severe operating conditions. These studies note that reddish-brown deposits characteristic of manganese oxides tend to build up on engine parts, spark plugs, oxygen sensors, and catalysts; and often conclude that harmful effects are seen on engines and emissions control components. In particular, long term exposures to MMT can result in catalyst plugging that contributes increased emissions and, in some cases, results in exceedances of emissions standards. These results are frequently supported with photographic evidence of catalyst plugging showing visible reddish-brown or orange deposits that are most often noted to be Mn_3O_4. In addition, automakers have reported that catalyst exposures to MMT, such as those experienced in Canada before the use of MMT was phased-out, resulted in increased warranty issues related to catalyst plugging and drivability complaints by consumers.

On the other hand, studies conducted by Ethyl/Afton conclude that when used in typical service, MMT does not cause problems or result in exceedances of applicable emissions limits. Much of their recent work has focused on I/M emissions testing and OBD-II analysis. From such work it is concluded that the relevant emissions standards are not exceeded as a result of MMT use. In addition, Ethyl/Afton has repeatedly disagreed with the methodologies, results and conclusions presented by the auto industry. Their three primary objections are as follows:

> (1) Some testing drive cycles used by the automakers are too severe, and are not representative of actual in-use driving. High temperatures associated with "severe" driving cycles have been shown to increase the rate of catalyst plugging by manganese deposits. Afton maintains that less severe conditions would reduce the rates of plugging. (The automakers maintain that the most frequently used durability test cycles were developed through a collaborative, public process, and are generally agreed to be suitable for accelerated mileage accumulation purposes.)

(2) In determining the emissions effects of MMT usage, test results should be evaluated against "in-use" or "applicable" emissions standards, rather than against "design" or "certification" emission standards. The in-use testing requirements referred to by Afton are different between the US and the EU. For Tier 2, Afton refers to the U.S. Tier 2 in-use verification test program criteria that no more than 50% of a fleet of at least 10 vehicles should exceed 1.3 times the certification standard. For Euro 4, 5 and 6, Afton refers to "In service conformity" requirements that emissions from a test group not exceed 1.5 times the applicable type-approval emission standard.

(3) Because of the octane boost provided by MMT, test fuels with and without MMT should be blended to different compositions. However, it should be noted that simple MMT dosing into gasoline has been the rule, not the exception, for test programs conducted by both Ethyl/Afton and the automakers.

These three arguments pertain especially to controlled laboratory or fleet test programs, but are not as relevant to in-use operations, such as occurred during the Canadian experience with MMT in NLEV and Tier 2 vehicles. This experience is documented in a 2008 report that includes a survey of emissions and performance results from automakers that had Tier 2-type technologies in the Canadian market while MMT was still in use. This survey revealed that several manufacturers experienced higher catalyst-related warranty claims in Canada as compared to the U.S. While not all vehicles using advanced emission control strategies relevant for Tier 2 (e.g. high cell density, close coupled catalysts) experienced noticeable effects from use of MMT, several manufacturers reported that warranty rates were 3 to 35 times higher in Canada for some vehicles as compared to the U.S. These manufacturers also noted that the large disparity between U.S. and Canadian warranty rates diminished once MMT was eliminated from Canadian gasoline.

Emissions

Increases in HC emissions have been seen throughout the history of testing MMT, even at relatively low mileage (<50,000 miles). Early analysis suggested that increased HC emissions were due primarily to Mn_3O_4 deposits on cylinder heads and valves, causing a fuel-rich shift. More recent post mortem analysis and component switching after extended mileage accumulation (>100,000 miles) have indicated that both oxygen sensors and catalysts also play a role in increased HC emissions from MMT-fueled vehicles with longer durational requirements.

The effects of MMT on CO and NOx emissions are less clear, although beneficial impacts have been seen in some early model emission control systems. These benefits were attributed to improved catalyst conversion efficiencies resulting from manganese's ability to scavenge catalyst-poisoning elements such as S, P, Pb, and Zn. However, testing programs utilizing long mileage accumulation periods (>100,000 miles) have demonstrated increased emissions of CO and NO_x with use of MMT. This is attributed to more extensive build-up of Mn deposits on the catalyst over time, contributing to catalyst plugging, which results in emissions increases due to reduced catalyst efficiencies and higher exhaust gas space velocities.

OBD systems and sensors

Most laboratory studies have shown that MMT has little effect on the catalyst's oxygen storage capacity, or the performance of O_2 sensors and OBD systems. While there certainly are deposits that build up on these systems, it is not clear that they have strong adverse impacts on OBD functionality or result in reduced

OBD response. Investigations of IM240 data and use of consumer surveys do not indicate that MMT has caused widespread problems with OBD systems.

Catalyst Plugging

Long before concerns of high cell density (HCD) catalysts arose, some of the earliest work showed evidence of catalyst plugging by Mn-deposits. While this early work was conducted using much higher concentrations of MMT than currently contemplated, more recent engine dynamometer studies have shown that plugging rate increases with higher exhaust gas temperatures. Increasing catalyst temperatures from approximately 700 °C to 850 °C has been shown to increase the rate of catalyst plugging by a factor of 15. This is attributed to both increased production of the particulate species Mn_3O_4, and the higher adhesive behavior of deposits at such elevated temperatures. Plugging time has also been shown to be inversely proportional to the Mn concentration in the fuel, over the range of 8-33 mg Mn/L. In at least one case, adverse impacts have been seen using MMT at concentrations as low as 6 mg Mn/L. Laboratory testing by both Afton and the automakers has shown that plugging occurs more rapidly with high cell density catalysts and with higher temperatures.

Tier 2 Concerns

Modern Tier 2 vehicles (and similar technology vehicles in Europe and elsewhere) must comply with significantly more stringent emissions performance standards compared to previous technology vehicles. This is reflected in both the lower certification levels established for the four pollutant categories (HC, CO, NOx, and PM), and in the extended mileage accumulation period over which the standards apply. To comply with Tier 2 standards, automakers employ emissions control systems that include more active catalysts with higher cell densities, higher surface areas, and thinner cell walls. Furthermore, these catalysts are mounted in configurations that are close coupled (CC) to the exhaust manifold, allowing for more rapid initial heating and higher overall catalyst temperatures.

All of these emissions control system enhancements raise concerns regarding the use of MMT. The higher operating temperatures may be expected to promote faster formation rates of Mn_3O_4, and the creation of deposits that more readily adhere to the catalyst surface. The higher cell densities used in Tier 2 catalysts may be expected to worsen plugging issues. The close-coupled configurations result in exhaust gases entering Tier 2 catalysts with a sharper angle of incidence, which has been shown to exacerbate plugging. Finally, the long-term emissions durability requirements for Tier 2 vehicles (and even more severe requirements for Tier 3) raise concerns about gradual degradation of catalyst efficiency, adverse impacts on OBD systems, and potential exceedances of exhaust emissions standards.

Tier 2 Results

When looking exclusively at the Tier-2 relevant body of literature, recent research has been dominated by Afton, although much of this work is not publically available. The published Tier 2 work can be divided into three categories: (1) vehicle and engine studies involving durability testing with and without MMT to assess effects on emissions and exhaust components, (2) in-use surveys in which vehicles that have accumulated mileage under normal consumer use are evaluated, and (3) various types of laboratory studies.

Laboratory studies conducted by both the automakers (Honda[80]) and Afton[97] confirm that high temperatures, high cell densities, and close coupling of catalysts (resulting in higher angles of incidence of the exhaust to the catalyst), are more likely to result in plugging by MMT. However, Afton has also shown that introduction of particle detachment conditions (demonstrated as a fuel-cut) can reduce the formation of plugging particles.[97]

Vehicle fleet and engine studies conducted by the automakers generally conclude that MMT causes harm through catalyst plugging, increased emissions, or both. The automakers' test programs generally focus on actual emissions increases, not just exceedances of emissions standards. However, various automakers' test programs have shown different results. For example, the results of one engine study showed a strong increase in HC emissions with MMT, but almost no change in CO or NO_x.[88] Comparisons of tail-pipe and raw engine-out emissions indicated that the HC increase with MMT was primarily due to engine differences, with less contribution from the catalyst (except during cold-start conditions.) In another study, significant differences in HC, CO, and NO_x were observed when comparing MMT fleets (in Canada) vs. no-MMT fleets (in the U.S.).[83] In this case, engine out emissions between fleets were similar, so the tailpipe differences were attributed to plugging in the catalysts. Similarly, an auto industry study using two VW vehicles showed no differences in engine-out emissions of CO, THC and NO_x, yet significant differences in tailpipe emissions, which were attributed to catalyst plugging by MMT.[94]

On the other hand, vehicle and engine studies conducted by Afton conclude that MMT does not cause emissions standards to be exceeded. Afton studies generally use mileage accumulation cycles that are less severe than those used in the automaker studies. In addition, they focus on comparisons to appropriate in-use emission standards, rather than on actual emissions increases. In some cases, Afton has shown data in which small emissions increases are observed when using MMT, but these increases have not resulted in exceedances of standards.

Fewer vehicle studies have been conducted by third parties, with only a single study by the China SEPA reporting on Tier-2 relevant vehicles (Euro 4 vehicles). In this case, vehicles were subjected to relatively low mileage accumulation (50,000 miles). MMT usage was found to increase emissions of HC and CO, although the Euro 4 standards were met in each case. NO_x emissions were comparable between the MMT and no-MMT cases, but many of these vehicles exceeded the Euro 4 NO_x standard.

Likewise, in-use surveys have been conducted by automakers, Afton, and third parties; with different conclusions being drawn. Both Afton and the automakers conducted surveys in Canada, focusing on Tier 2 relevant vehicles during the time of the voluntary phase out of MMT (in 2003). The automakers focused their reporting (in Sierra Research 2008 report and GM report) on comparisons of warranty claims between the U.S and Canada. While the actual numbers of warranty claims were not indicated, the rate of claims was reported to be 3-35 times higher in Canada than in the U.S. for several vehicle models. Based on visual inspection and/or laboratory analysis of the catalysts, the manufacturers attributed failures to catalyst plugging by manganese deposits. Several manufacturers reported on further "in-use" testing of additional vehicles or catalysts that had exhibited high warranty claims. Both GM and Manufacturer M (in the Sierra Research report) showed that increased emissions correlated with plugging by Mn deposits. In some cases, this plugging caused exceedances of emissions standards.

In-use surveys conducted by Afton in Canada focused on investigations of I/M program data and consumer reports of MIL failures. From these studies, they concluded that MMT does not contribute to increased failure rates.

While these Canadian surveys were limited due to the phase-out of MMT, other in-use surveys have been conducted in China by Afton and a CATARC. Combined, these surveys have evaluated nearly 250 vehicles using I/M testing procedures, and have concluded that MMT does not contribute to exceedances of emission standards.

Although it is not possible to identify a particular technology type, design, or layout that is most affected by MMT, it appears that some vehicles are more susceptible to problems than others. It is also likely that consumer driving habits are an important contributing factor. Based upon the experimental data reviewed here, there is credible evidence that all of the above-mentioned problems can occur in Tier 2 vehicles – especially with long-term use that allows for greater manganese accumulation in the catalyst. In particular, the in-use Canadian experience with Tier 2-type vehicles clearly demonstrated that use of MMT can cause consumer problems in select cases. While speculative at this point, it is reasonable to believe that similar issues would be of concern with future Tier 3 vehicles.

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98. Afton Chemical Corporation; Evalutation of the Impact of Gasoline Containing the MMT(R) Fuel Additive on Particulate Matter Emissions in Vehicles Designed to Meet Euro 5 Emission Standards and Implications for the New U.S. Tier 3 PM Emission Standards. 2014.

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101. Cunningham, L.J., H. Shao, and M.W. Meffert; In-Use Emissions Compliance of 2005 and 2006 Model Year Taxis in Beijing, China. 18th CRC On-Road Vehicle Emissions Workshop San Diego 2008.

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List of Appendices

APPENDIX I. CRC-114 Literature Database

Ref. No	Critical Ref.	Info. Source [a]	Literature Type	Primary Author	Date	Title	Citation	Sponsor or Primary Author Affiliation	Test Program	Category (for Sorting)	Relevance by Topic Area: 1 History	2 Octane	3 Emissions	4 Criteria Pollutants	5 Engines	6 Exhaust System	7 Atmos. Conc.	8 Exposure	9 Fate	10 Measurement	11 Toxicity	12 Health
1	Y	61. NCWM	Paper	Faggan, J.E.	1975	An Evaluation of Manganese as an Antiknock in Unleaded Gasoline	SAE Paper 750925	Ethyl		Emissions, Engine, Exhaust				M		M						
2	Y	101. SAE	Paper	Moran, J.B.	1975	The Environmental Implications of Manganese as an Alternate Antiknock	SAE Paper 750926	E.P.A		Health, Environment	X					M		X			X	X
3	Y	35. NCWM	Paper	Benson, J.D.	1977	Manganese Fuel Additive (MMT) Can Cause Vehicle Problems	SAE Paper 770655	General Motors Research		Engines, Exhaust				M	M	M						
4	Y	60. NCWM	Paper	Lenane, D.L.	1977	MMT- A Further Evaluation	SAE Paper 770656	Ethyl		Emissions, Engine, Exhaust				M		M						
5	Y	102. SAE	Paper	Faix, L.J.	1978	A Study of the Effects of Manganese Fuel Additive on Automotive Emissions	SAE Paper 780002	General Motors Corp.		Emissions			X	M	M	M						
6	Y	59. NCWM	Paper	Lenane, D.L.	1978	Effect of MMT on Emissions from Production Cars	SAE Paper 780003	Ethyl		Emissions				M		M						
7	Y	36. NCWM	Paper	Furey, R.L. and Summers, J.C.	1978	How MMT Causes Plugging of Monolithic Converters.	SAE Paper 780004	General Motors Research		Exhaust						H						
8	Y	103. SAE	Paper	Lichtenstein I.E.	1978	MMT Plugging of Oxidation Catalysts on Ceramic and Metal Supports During Engine Dyno Studies of Catalyst Durability	SAE Paper 780005	Matthey Bishop, Inc.		Exhaust						M						
9	Y	29. NCWM	Report	CRC	1979	CRC MMT Field Test Program	CRC Report No. 503	CRC		Emissions, Exhaust			X	M	M	M						
10	Y	104. SAE	Paper	Carlson, R.R.	1979	Conduct of Mileage Accumulation and Emissions Testing for the CRC/MMT Program	SAE Paper 790703	Systems Control, Inc.	CRC 1979	CRC 1979				M	M	M						
11	Y	105. SAE	Paper	Benson, J.D.	1979	Results of the Coordinating Research Council MMT Field Test Program	SAE Paper 790706	CRC	CRC 1979	CRC 1979			M	M	M	M						
12	Y	106. SAE	Paper	Wallace, J.S.	1979	Effects of MMT on Exhaust Emissions	SAE Paper 790707	EPA	1978 Waiver	Exhaust			M	M								
13	Y	107. SAE	Paper	Hughmark, G.A.	1980	A Statistical Analysis of the Effect of MMT Concentration on Hydrocarbon Emissions	SAE Paper 800393	Ethyl	Emissions	Emissions			M	M		M						
14	Y	108. SAE	Paper	Williamson, W.B.	1982	Effects of Fuel Additive MMT on Contaminant Retention and Catalyst Performance	SAE Paper 821193	Ford	Emissions	Emissions						M						
15	Y	109. SAE	Paper	Duncan, J.	1984	Combustor Study of the Deactivation of a Three-Way Catalyst by Lead and Manganese	SAE Paper 841408	EPA	Exhaust	Exhaust						M						
16	Y	28. NCWM	Report	CGSB Working Group	1986	An Assessment of the Effect of MMT on Light-Duty Vehicle Exhaust Emissions in the Canadian Environment	Prepared by Working Group under the jurisdiction of the CGSB Gasoline and Alternative Automotive Fuels Committee	CGSB	Emissions	Emissions			X	M								
17	N	110. SAE	Paper	Hilden, D.L.	1986	The Effect of Manganese Fuel Additive and Exhaust Gas Recirculation on Diesel Particulate Emissions	SAE Paper 860621	General Motors Research Labs.	Emissions, Particulate	Emissions, Particulate				L								
18	N	27. NCWM	Report	Hotz, M.C.B.	1986	Lead in Gasoline; Alternatives to Lead in Gasoline	The Royal Soc. of Canada, Suppl. Report. The Commission on Lead in the Environment. February 1986	The Commission on Lead in the Environment	Review	Review						L						X
19	N	247. WOS	Paper	Abbott, P.J.	1987	Methylcyclopentadienyl Manganese Tricarbonyl (Mmt) in Petrol - the Toxicological Issues.	Sci.Total Environ., 67,(2-3), 247-255. 1987.	Australian National Health and Research Council	Health, Environment	Health, Environment				NA	NA	NA		X			X	X
20	N	111. SAE	Paper	Hazra, A.K.	1987	Recent Developments in Motor Vehicle Pollution Control in Canada	SAE Paper 871074	Environment Canada	Health, Environment	Health, Environment				NA	NA	NA						
21	Y	112. SAE	Paper	Hurley, R.G.	1989	Characterization of Automotive Catalysts Exposed to the Fuel Additive MMT	SAE Paper 890582	Ford	Exhaust	Exhaust						M						
22	Y	14. NCWM	Paper	Lenane, D.L., et al	1990	Effect of a Fuel Additive on Emission Control Systems	SAE Paper 902097	Ethyl	1990 Waiver Application	Exhaust, Engine				M	M	M						
23	Y	62. NCWM	Docket		1990		EAP Air Docket A-90-16		1990 Waiver Application	Docket				M	M	M						
24	Y	37. NCWM	Paper	Hammerle, R.H., et al	1991	Particulate Emissions from Current Model Vehicles Using Gasoline with Methylcyclopentadienyl Manganese Tricarbonyl	SAE Paper 912436	Ford Motor Company	Particulates	Particulates				M								X
25	Y	38. NCWM	Paper	Hurley, R.G. et al	1991	The Effect on Emissions and Emission Component Durability by the Fuel Additive Methylcyclopentadienyl Manganese Tricarbonyl (MMT)	SAE Paper 912437	Ford Motor Company	Emissions, Exhaust	Emissions, Exhaust						M						
26	Y	63. NCWM	Docket		1991		EPA Air Docket A-91-46		Docket	Docket				M	M	M						
27	N	246. WOS	Newsletter	Esper, G.A.;	1992	EPA's Denial of Use of Mmt in Unleaded Gasoline.	J.Air Waste Manage.Assoc., 42,(3), 250-250. 1992.		Regulation	Regulation				L		L						
28	Y	113. SAE	Paper	Hurley, R.G.	1992	The Effect of Mileage on Emissions and Emission Component Durability by the Fuel Additive Methyldcyclopentadienyl Manganese Tricarbonyl (MMT)	SAE Paper 920730	Ford	1991 Ford	Emissions, Exhaust, Particulate				M	M	M						
29	Y	114. SAE	Paper	Hammerle, R.H.	1992	Effect of Mileage Accumulation on Particulate Emissions from Vehicles Using Gasoline with Methylcyclopentadienyl Manganese Tricarbonyl	SAE Paper 920731	Ford	1991 Ford	1991 Ford			X	M								
30	N	26. NCWM	Register	E.P.A	1993	Fuels and Fuel Additives; Extension of Time and Finding Concerning Fuel Additive Waiver Application	Federal Register, Vol. 58, No. 235. Thursday, Dec. 9, 1993	none	Regulation	Regulation	X											
31	Y	115. SAE	Paper	Hubbard, C.P.	1993	The Effect of MMT on the OBD-11 Catalyst Efficiency Monitor	SAE Paper 932855	Ford	Exhaust	Exhaust				M	M	M						
32	Y	64. NCWM	Docket		1993		EPA Air Docket A-93-26		Docket	Docket				M	M	M						

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											1 History	2 Octane	3 Emissions	4 Criteria Pollutants	5 Engines	6 Exhaust System	7 Atmos. Conc.	8 Exposure	9 Fate	10 Measurement	11 Toxicity	12 Health
33	Y	13. NCWM	Paper	Aradi, et. Al	1994	The Physical and Chemical Effect of Manganese Oxides on Automobile Catalytic Converters	SAE Paper 940747	Ethyl	1990 Waiver (plus Escorts)	Exhaust						M				X		
34	Y	25. NCWM	Paper	Lenane, D.L., et al	1994	Emissions Results from a 48-car test evaluation of MMT performance additive	The Science of Total Environment, 146/147 (1994) 245-251	Ethyl	1990 Waiver Application	Emissions, Engine				M	M	M						
35	N	241. WOS	Paper	Loranger, S. and J. Zayed;	1994	Manganese and Lead Concentrations in Ambient Air and Emission Rates from Unleaded and Leaded Gasoline Between 1981 and 1992 in Canada - A Comparative-Study.	Atmos.Environ., 28,(9), 1645-1651. 1994.	Health and Welfare Canada	Health, Environment	Health, Environment								X				
36	N	244. WOS	Paper	Loranger, S., J. Zayed, and E. Forget;	1994	Manganese Contamination in Montreal in Relation with Traffic Density	Water Air and Soil Pollution, 74,(3-4), 385-396	Canadian Petroleum Products Inst., Ethyl, Environment Canada, Environment Quebec	Health, Environment	Health, Environment							X					
37	N	243. WOS	Paper	Lynam, D.R., G.D. Pfeifer, B.F. Fort, G.L. Terhaar, and D.P. Hollrah;	1994	Atmospheric Exposure to Manganese from Use of Methylcyclopentadienyl Manganese Tricarbonyl (Mmt) Performance Additive.	Sci.Total Environ., 147, 103-109. 1994.	Ethyl	Health, Environment	Health, Environment			X				X	X				
38	Y	12. NCWM	Paper	Roos, J.W., et al.	1994	The Effect of Manganes Oxides on OBD-II Catalytic Converter Monitoring	SAE Paper 942056	Ethyl	1990 Waiver, OBD analysis (plust add'l catalysts)	Exhaust						M						
39	N	24. NCWM	Report	Wood, G., Egyed, M.	1994	Risk Assessment for the Combustion Products of Methylcyclopentadienyl Manganese Tricarbonyl (MMT) in Gasoline	Environmental Health Directorate	Health Canada	Health, Environment	Health, Environment	X							X				X
40	N	245. WOS	Paper	Zayed, J., M. Gerin, S. Loranger, P. Sierra, D. Begin, and G. Kennedy;	1994	Occupational and Environmental Exposure of Garage Workers and Taxi Drivers to Airborne Manganese Arising from the Use of Methylcyclopentadienyl Manganese Tricarbonyl in Unleaded Gasoline	American Industrial Hygiene Association Journal, 55,(1), 53-58	Health and Welfare Canada	Health, Environment	Health, Environment								X		X		X
41	N	242. WOS	Paper	Loranger, S. and J. Zayed;	1995	Environmental and Occupational Exposure to Manganese - A Multimedia Assessment	International Archives of Occupational and Environmental Health, 67,(2), 101-110	Natural Sci. Engineering Research Council of Canada, Environ. Canada, and Environ. Quebec	Health, Environment	Health, Environment							X					
42	N	239. WOS	Paper	Loranger, S., J. Zayed, and G. Kennedy;	1995	Contribution of Methylcyclopentadienyl Manganese Tricarbonyl (Mmt) to Atmospheric Mn Concentration Near Expressway - Dispersion Modeling Estimations.	Atmos.Environ., 29,(5), 591-599. 1995.	Natural Sci. Engineering Research Council of Canada, Environ. Canada, and Environ. Quebec	Health, Environment	Health, Environment							X					
43	N	240. WOS	Paper	Lytle, C.M., B.N. Smith, and C.Z. Mckinnon;	1995	Manganese Accumulation Along Utah Roadways - A Possible Indication of Motor-Vehicle Exhaust Pollution.	Sci.Total Environ., 162,(2-3), 105-109. 1995.	BYU	Health, Environment	Health, Environment									X	X		
44	N	238. WOS	Paper	Egyed, M. and G.C. Wood;	1996	Risk assessment for combustion products of the gasoline additive MMT in Canada.	Sci.Total Environ., 189, 11-20. 1996.	Health Canada	Health, Environment	Health, Environment							X	X				
45	N	20. NCWM	Waiver Docket	Ethyl Corporation	1996	Subject Matter Index for Wide Range of Tests and Evaluations on the Effects of the HiTEC 3000 ® Performance Additive Sponsored or Submitted by Ethyl Corp. to the US EPA.				List of References				L	L	L						L
46	N	55.3. NCWM	Report	Maxwell, R.	1996	Review and Assessment of AAMA/AIAM Test Program Protocol for Investigation of the Effect of MMT Fuel Additive on Vehicle Emissions Levels and Onboard Diagnostics System Performance	Final Report, Oct. 2, 1996. Report No. REM-MMT-96-01	AAMA	AAM, 2002	AAM, 2002				L	L	L						
47	N	58.1. NCWM	Report	Compilation	1997	Characterization of Manganese Particulates from Vehicles Using MMT Fuel	A Compilation of Results from Studies performed by: Lawrence Livermore Nat'l Lab., Southwest Research Inst., Univ. of Minn., Research Triangle Inst., Ethyl Res. and Develop.	Ethyl	1992/ 1993 Test Fleet, Particulate measurements	Emissions, Particulate				L								
48	N	235. WOS	Paper	Frumkin, H. and G. Solomon;	1997	Manganese in the U.S. gasoline supply.	American Journal of Industrial Medicine, 31,(1), 107-115. 1997.	Emory University	Health, Environment	Health, Environment											X	X
49	N	237. WOS	Paper	Loranger, S. and J. Zayed;	1997	Environmental contamination and human exposure to airborne total and respirable manganese in Montreal.	J.Air Waste Manage.Assoc., 47,(9), 983-989. 1997.	U. Montreal	Health, Environment	Health, Environment							X	X				
50	Y	11. NCWM	Paper	Roos, J.W., Scull, H.M., Dykes, K.L., Hotchkiss, A.R., Grande, D.G., Lenane, D.L.	1997	Evaluation of On-Board Diagnostic Systems and the Impact of Gasoline Containing MMT	SAE Paper 972849	Ethyl	OBD analysis	Exhaust						M						
51	N	236. WOS	Paper	Wallace, L. and T. Slonecker;	1997	Ambient air concentrations of fine (PM2.5) manganese in US national parks and in California and Canadian cities: The possible impact of adding MMT to unleaded gasoline.	J.Air Waste Manage.Assoc., 47,(6), 642-652. 1997.	EPA	Health, Environment	Health, Environment	X						X					
52	N	234. WOS	Paper	Davis, J.M., A.M. Jarabek, D.T. Mage, and J.A. Graham;	1998	The EPA health risk assessment of methylcyclopentadienyl manganese tricarbonyl (MMT)	Risk Analysis, 18,(1), 57-70	EPA	Health, Environment	Health, Environment								X				X
53	N	232. WOS	Paper	Davis, J.M.;	1998	Methylcyclopentadienyl manganese tricarbonyl: Health risk uncertainties and research directions.	Environ.Health Perspect., 106, 191-201. 1998.	EPA	Health, Environment	Health, Environment	X							X			X	X
54	N	23. NCWM	Statement	Gov't of Canada	1998	Government of Canada Statement on MMT		Canada	Regulation	Regulation	X											
55	N	233. WOS	Paper	Veysseyre, A., K. van de Velde, C. Ferrari, and C. Boutron;	1998	Searching for manganese pollution from MMT anti-knock gasoline additives in snow from central Greenland.	Sci.Total Environ., 221,(2-3), 149-158. 1998.	Commission of European Communities and Switzerland	Health, Environment	Health, Environment									X			
56	N	227. WOS	Paper	Ardeleanu, A., S. Loranger, G. Kennedy, G. L'Esperance, and J. Zayed	1999	Emission rates and physico-chemical characteristics of Mn particles emitted by vehicles using methylcyclopentadienyl manganese tricarbonyl (MMT) as an octane improver	Water Air and Soil Pollution, 115, (1-4), 411-427	U. Montreal	Health, Environment	Health, Environment			X							X		

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57	N	228. WOS	Paper	Clayton, C.A., E.D. Pellizzari, C.E. Rodes, R.E. Mason, and L.L. Piper	1999	Estimating distributions of long-term particulate matter and manganese exposures for residents of Toronto, Canada	Atmos. Environ. , 33,(16), 2515-2526	Ethyl	Health, Environment	Health, Environment							X	X				
58	N	51. NCWM	Paper	Colmenares, C., et al	1999	Analysis of manganese particulates from automotive decomposition of methylcyclopentadienyl manganse tricarbonyl	Applied Surface Science, 151 (1999) 189-202	Ethyl	1992/ 1993 Test Fleet, Particulate measurements	Particulates				L		L						
59	N	231. WOS	Paper	Lyznicki, J.M., M.S. Karlan, and M.K. Khan;	1999	Manganese in gasoline	J. of Occupational and Environ. Medicine, 41,(3), 140-143	American Medical Association	Health, Environment	Health, Environment	X							X			X	X
60	N	229. WOS	Paper	Pellizzari, E.D., C.A. Clayton, C.E. Rodes, R.E. Mason, L.L. Piper, B. Fort, G. Pfeifer, and D. Lynam;	1999	Particulate matter and manganese exposures in Toronto, Canada	Atmos. Environ., , 33,(5), 721-734	Ethyl	Health, Environment	Health, Environment							X	X		X		
61	N	224. WOS	Paper	Ressler, T., J. Wong, and J. Roos;	1999	Manganese speciation in exhaust particulates of automobiles using MMT-containing gasoline	Journal of Synchrotron Radiation, 6, 656-658	Ethyl	Health, Environment	Health, Environment										X		
62	N	225. WOS	Paper	Zayed, J., A. Vyskocil, and G. Kennedy;	1999	Environmental contamination and human exposure to manganese - contribution of methylcyclopentadienyl manganese tricarbonyl in unleaded gasoline	International Archives of Occupational and Environmental Health, 72,(1), 7-13	U. Montreal	Health, Environment	Health, Environment			X				X	X	X			
63	N	226. WOS	Paper	Zayed, J., B. Hong, and G. L'Esperance;	1999	Characterization of manganese-containing particles collected from the exhaust emissions of automobiles running with MMT additive	Environ. Sci. Technol. , 33,(19), 3341-3346	U. Montreal	Health, Environment	Health, Environment			X							X	X	
64	N	230. WOS	Paper	Zayed, J., J. Pitre, M. Rivard, and S. Loranger;	1999	Evaluation of pollutant emissions related to the use of MMT in gasoline	Water Air and Soil Pollution, 109,(1-4), 137-145	U. Montreal	Emissions	Emissions								X				
65	N	223. WOA	News clipping		1999	Health effects testing required on gasoline additive MMT	C&EN, Feb. 15, 1999		Health, Environment	Health, Environment												X
66	N	222. WOS	Paper	Bhuie, A.K., D. McLaughlin, and D.N. Roy;	2000	Exposure of urban ecosystems to Mn and Pb contaminants from gasoline additives beside a major highway in the Greater Toronto Area, Canada	Forestry Chronicle, 76,(2), 251-258	Faculty of Forestry and the Inst. of Environ. Studies; Ethyl	Health, Environment	Health, Environment									X	X	X	
67	N	221. WOS	Paper	Crump, K.S.;	2000	Manganese exposures in Toronto during use of the gasoline additive, methylcyclopentadienyl manganese tricarbonyl	J. of Exposure Analysis and Environ. Epidemiology, 10,(3), 227-239	Ethyl	Health, Environment	Health, Environment							X	X				
68	N	57. NCWM	Paper	Meffert, M.W.	2000	Analysis of Nitrous Oxide Emissions from Light Duty Passenger Cars	SAE Paper 2000-01-1952	Ethyl	Emissions	Emissions				L								
69	N	47. NCWM	Paper	Ressler, T., et al	2000	Quantitative Speciation of Mn-Bearing Particulates Emitted from Autos Burning (Methylcyclopentadienyl)manganese Tricarbonyl-Added Gasolines Usings XANES Spectroscopy	Environ. Sci. Technol. 2000, 34, 950-958	Ethyl	Particulates	Particulates										X		
70	Y	52. NCWM	Paper	Roos, J.W.	2000	Characterization of Combustion Products from the Fuel Additive MMT	AWMA 93rd Annual Conf. and Exhibition, Salt Lake City, June 18-22, 2000	Ethyl		Emissions, Particulate				H				X				
71	Y	19. NCWM	Paper	Roos, J.W., et al.	2000	A Systems Approach to Improved Exhaust Catalyst Durability: The Role of the MMT Fuel Additive	SAE Paper 2000-01-1880	Ethyl	Exhaust	Exhaust						H						
72	N	220. WOS	Paper	Bhuie, A.K. and D.N. Roy;	2001	Deposition of Mn from automotive combustion of methylcyclopentadienyl manganese tricarbonyl beside the major highways in the greater Toronto area, Canada.	J.Air Waste Manage.Assoc., 51,(9), 1288-1301. 2001.	Ethyl	Health, Environment	Health, Environment									X	X		
73	N	219. WOS	Paper	Molders, N., P.J. Schilling, J. Wong, J.W. Roos, and I.L. Smith;	2001	X-ray fluorescence mapping and micro-XANES spectroscopic characterization of exhaust particulates emitted from auto engines burning MMT-Added gasoline	Environ.Sci.Technol., 35,(15), 3122-3129.	Ethyl	Health, Environment	Health, Environment										X		
74	N	217. WOS	Paper	Pellizzari, E.D., C.A. Clayton, C.E. Rodes, R.E. Mason, L.L. Piper, B. Fort, G. Pfeifer, and D. Lynam;	2001	Particulate matter and manganese exposures in Indianapolis, Indiana	J. Exposure Analysis and Environmental Epidemiology (2001) 11, 423-440	Ethyl	Health, Environment	Health, Environment								X				
75	N	218. WOS	Paper	Zayed, J.;	2001	Use of MMT in Canadian gasoline: Health and environment issues	American Journal of Industrial Medicine, 39,(4), 426-433	U. Montreal	Health, Environment	Health, Environment			X	L			X	X			X	X
76	Y	1.1. NCWM	Paper (and supporting info)	AAM	2002	The Impact of MMT on Vehicle Emissions and Durability- Part 1: A Joint Study by the Alliance of Automobile Manufacturers, The Association of International Automobile Manufacturers, and The Canadian Vehicle Manufacturers Association.	MMT Program Part 1 Report- July 29, 2002	AAM, AIAM, CVMA	AAM 2002, Part 1	AAM 2002, Part 1				H	H	H						
77	Y	1.2. NCWM	Paper (and supporting info)	AAM	2002	The Impact of MMT on Vehicle Emissions and Durability- Part 2: A Joint Study by the Alliance of Automobile Manufacturers, The Association of International Automobile Manufacturers, and The Canadian Vehicle Manufacturers Association.	MMT Program Part 2 Report- July 29, 2002	AAM, AIAM, CVMA	AAM 2002, Part 2	AAM 2002, Part 2				H	H	H						
78	N	9. NCWM	Press Release/ Presentation	AIAM	2002	New Auto Study Finds Fuel Additive Causes Vehicle Emission Failures		Association of International Automobile Manufacturers (AIAM)	AAM, 2002	AAM, 2002	X		X	L	L							
79	Y	250. Web	Report	Air Improvement Resources, Inc.	2002	Effects of MMT in Gasoline on Emissions from On-Road Motor Vehicles in Canada	Final Report submitted to Canadian Vehicle Manufacturers Association, and Association of International Automobile Manufacturers of Canada. Nov. 11, 2002	Canadian Vehicle Manufacturers Association	Emissions	Emissions				M								

APPENDIX I. CRC-114 Literature Database

												Relevance by Topic Area												
Ref. No	Critical Ref.	Info. Source [a]	Literature Type	Primary Author	Date	Title	Citation	Sponsor or Primary Author Affiliation	Test Program	Category (for Sorting)	1 History	2 Octane	3 Emissions	4 Criteria Pollutants	5 Engines	6 Exhaust System	7 Atmos. Conc.	8 Exposure	9 Fate	10 Measurement	11 Toxicity	12 Health	
80	N	214. WOS	Paper	Audrey, S., L. Takser, M. Andre, S. Martin, M. Donna, S.A. Genevieve, B. Philippe, H. Georgette, and H. Guy;	2002	A comparative study of manganese and lead levels in human umbilical cords and maternal blood from two urban centers exposed to different gasoline additives.	Sci.Total Environ., 290,(1-3), 157-164. 2002.	U. Montreal	Health, Environment	Health, Environment								X					
81	Y	116. SAE	Paper	Benson, J.D.	2002	The impact of MMT gasoline additive on exhaust emissions and fuel economy of low emission vehicles	SAE Paper 2002-01-2894	Alliance of Automobile Manufacturers (AAM)	AAM 2002- Part 2	AAM 2002- Part 2				H									
82	N	215. WOS	Paper	Gerber, G.B., A. Leonard, and P. Hantson;	2002	Carcinogenicity, mutagenicity and teratogenicity of manganese compounds.	Critical Reviews in Oncology Hematology, 42,(1), 25-34. 2002.	Catholic University of Louvain	Health, Environment	Health, Environment											X		
83	N	216. WOS	Paper	Keiloun, M., F. Yang, Y.K. Chau, F. Gagnon, B. Bouyahi, M. Rivard, G. Kennedy, L. Normandin, and J. Zayed;	2002	Exposure of gas station attendants to methylcyclopentadienyl manganese tricarbonyl (MMT) used in gasoline.	Water Air and Soil Pollution, 141,(1-4), 155-163. 2002.	U. Montreal	Health, Environment	Health, Environment								X		X			
84	Y	10. NCWM	Report	Lyons, J.M	2002	Impacts Associated with the Use of MMT as an Octane Enhancing Additive in Unleaded Gasolines- A Critical Review	Sierra Reasearch, Report Num: SR02-07-01	Canadian Vehicle Manuf. Assoc.; Assoc. of Int'l Auto. Manuf. of Canada (AIAMC)	Review	Review	X		X	H	H						X	X	
85	Y	22. NCWM	Paper	Roos, J.W., et al.	2002	Reformulating Gasoline for Lower Emissions Using the Fuel Additive MMT ®	SAE Paper 2002-01-2893	Ethyl	Emissions	Emissions				H									
86	Y	56. NCWM	Paper	Roos, J.W.	2002	A peer-reviewed critical analysis of SAE Paper 2002-01-2894 , "The impact of MMT gasoline additive on exhaust emissions and fuel economy of low emission vehicles."	SAE Paper 2002-01-2903	Ethyl	AAM 2002	AAM 2002				H	H	H							
87	N	117. SAE	Paper	Xiong, C.	2002	Investigation on the Stability of MMT Anti-knock Additive	SAE Paper 2002-01-2895	Beijing POL Research Institute	Properties	Properties				NA	NA	NA							
88	N	213. WOS	Paper	Bankovitch, V., G. Carrier, C. Gagnon, L. Normandin, G. Kennedy, and J. Zayed;	2003	Total suspended particulate manganese in ambient air in Montreal 1981-2000.	Sci.Total Environ., 308,(1-3), 185-193. 2003.	U. Montreal	Health, Environment	Health, Environment							X						
89	Y	54. NCWM	Paper	Cunningham, L.J., et al	2003	AAM/AIAM Fleet Test Program: Analysis and Comments	SAE Paper 2003-01-3287	Ethyl	AAM 2002	AAM 2002				H	H	H							
90	Y	55.2. NCWM	Report	Environ International Corporation	2003	AAM Study Statistical Analysis	Prepared for Ethyl Corporation	Ethyl	AAM 2002	AAM 2002				H	H	H							
91	Y	55.1. NCWM	Report	Ethyl Corporation	2003	A Critical Analysis of the Alliance of Automobile Manufacturer' MMT Study: Separating Fact From Fiction		Ethyl	AAM 2002	AAM 2002				H	H	H							
92	Y	211. WOS	Paper	Geivanidis, S., P. Pistikopoulos, and Z. Samaras;	2003	Effect on exhaust emissions by the use of methylcyclopentadienyl manganese tricarbonyl (MMT) fuel additive and other lead replacement gasolines	Sci.Total Environ., 305,(1-3), 129-141. 2003.	Ethyl	Emissions	Emissions	X			H		H							
93	N	5. NCWM	Presentation		2003	Demo Panel Data _120409							X	L		L				X			
94	N	212. WOS	Paper	Zayed, J., A. Guessous, J. Lambert, G. Carrier, and S. Philippe;	2003	Estimation of annual Mn emissions from MMT source in the Canadian environment and the Mn pollution index in each province.	Sci.Total Environ., 312,(1-3), 147-154. 2003.	U. Montreal	Health, Environment	Health, Environment			X										
95	N	6. NCWM	Manual	Accord	2004	2004 Honda Accord Owner's Manual	Vehicle owners manual	Honda	N/A	N/A					L								
96	Y	34. NCWM	Report	Blumberg, K., and Walsh, M.P.	2004	Status Report Concerning the Use of MMT in Gasoline	Report to International Council on Clean Transportation, Sept., 2004	ICCT	Review	Review		X		L	L	L					X	X	
97	Y	53. NCWM	Report	Afton Chemical Co.	2004	Afton Chemical Corporation's (Afton) Comments on the International Council on Clean Transportation (ICCT) Status Report on MMT®			Review, Response	Review, Response				M	M	M							
98	N	209. WOS	Paper	Dobson, A.W., K.M. Erikson, and M. Aschner;	2004	Manganese neurotoxicity	Redox-Active Metals in Neurological Disorders, 1012, 115-128	NIH	Health, Environment	Health, Environment										X			
99	Y	45. NCWM	Presentation	Global Auto Industry	2004	MMT's Impact on Vehicles; The Perspective of Global Auto Industry	Beijing China, Nov. 2004	GM, Ford, Daimler Chrysler, Volkswagen, Honda, Toyota	Engines, Exhaust	Engines, Exhaust	X				M	M							
100	Y	31. NCWM	Paper	McCabe, R.W.; DiCicco, D,M.; et al	2004	Effects of MMT® Fuel Additive on Emission System Components: Comparison of Clear- and MMT ®- fueled Escort Vehicles from the Alliance Study	SAE Paper 2004-01-1084	Ford Motor Company	AAM 2002	AAM 2002			X	H	H	H							
101	N	210. WOS	Paper	Pfeifer, G.D., J.M. Roper, D. Dorman, and D.R. Lynam;	2004	Health and environmental testing of manganese exhaust products from use of methylcyclopentadienyl manganese tricarbonyl in gasoline.	Sci.Total Environ., 334, 397-408. 2004.	Ethyl	Health, Environment	Health, Environment	X						X	X	X	X			
102	Y	251. Web	Presentation	Schindler, K.P.	2004	Impact of MMT on Vehicle Emission Performance	Asian Vehicle Emission Control Conference 2004 (AVECC)	Volkswagen						H		H							
102.5	N	208. WOS	Paper	Bhuie, A.K., O.A. Ogunseitan, R.R. White, M. Sain, and D.N. Roy;	2005	Modeling the environmental fate of manganese from methylcyclopentadienyl manganese tricarbonyl in urban landscapes.	Sci.Total Environ., 339,(1-3), 167-178. 2005.	Ethyl	Health, Environment	Health, Environment			X						X				

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Ref. No	Critical Ref.	Info. Source [a]	Literature Type	Primary Author	Date	Title	Citation	Sponsor or Primary Author Affiliation	Test Program	Category (for Sorting)	Relevance by Topic Area: 1 History	2 Octane	3 Emissions	4 Criteria Pollutants	5 Engines	6 Exhaust System	7 Atmos. Conc.	8 Exposure	9 Fate	10 Measurement	11 Toxicity	12 Health
103	Y	118. SAE	Paper	Boone, W.P.	2005	Effect of MMT Fuel Additive on Emission System Components: Detailed Parts Analysis from Clear and MMT-Fueled Escort Vehicles from the Alliance Study	SAE Paper 2005-01-1108	Ford Motor Company	AAM 2002- Part 2	AAM 2002- Part 2				M	H							
104	N	207. WOS	Paper	Cohen, D.D., B.L. Gulson, J.M. Davis, E. Stelcer, D. Garton, O. Hawas, and A. Taylor;	2005	Fine-particle Mn and other metals linked to the introduction of MMT into gasoline in Sydney, Australia: Results of a natural experiment	Atmos Environ, 39,(36), 6885-6896	Australian Research Council; U.S EPA	Health, Environment	Health, Environment			X				X			X		
105	Y	18. NCWM	Paper	Cunningham, L.J., et al	2005	Assessing High-Cell Density Catalyst Durability with MMT ® Fuel Additive in Severe Driving Conditions	SAE Paper 2005-01-3840	Afton Chemical Corporation	Tier 2	Exhaust						H						
106	N	21. NCWM	Letter	Gagne, L.P.	2005	Re. General Review of Emission-Related Notices of Defect and Recalls (Canada and U.S.)		Environment Canada	Exhaust	Exhaust						L						
107	Y	44. NCWM	Report	Richter, H.	2005	Influence of Ash-Forming Gasoline Additives such as MMT® on Exhaust Emissions and Performance Characteristics of PC-Engines		Porsche	Exhaust, Emissions, Engine	Exhaust, Emissions, Engine			X	H	H	H					X	X
108	Y	48. NCWM	Report	Afton Chemical Co.	2005	Response to a New Automobile Industry-Sponsored Test of the Effects of MMT® in Vehicles Designed to Meet Euro IV Emission Standards		Ethyl	Tier 2	Exhaust, Response				R								
109	Y	50. NCWM	Report	Afton Chemical Co.	2006	A Report on the Results of Alternative Tier 2 Testing For the Characterization of Particulate from Vehicles Using the Gasoline Additive MMT® in the Fuel	Final Report Submitted to the U.S. E.P.A. Docket ID: EPA-HQ-OAR-0074-0164	Afton Chemical Corporation	Tier 2	Emissions, Particulate												
110	N	205. WOS	Paper	Boudia N, Halley R, Kennedy G, Lambert J, Gareau L, Zayed J.	2006	Manganese concentrations in the air of the Montreal (Canada) subway in relation to surface automobile traffic density	Sci. Total Environ; 2006; 366:143-147	U. Montreal	Health, Environment	Health, Environment							X					
111	Y	74. NCWM	Report	D' Aniello, Michael.	2006	Adverse Effects of MMT-Doped fuel on 2002-3 MY LL8 GMT360/370	GM Research	General Motors Research	In-use survey	Survey				H		H						
112	N	206. WOS	Paper	Gulson B, Mizon K, Taylor A, Korsch M, Stauber J, Davis JM, Louie H, Wu M, Swan H.	2006	Changes in manganese and lead in the environment and young children associated with the introduction of methylcyclopentadienyl manganese tricarbonyl in gasoline - preliminary results	Environmental Research 2006; 100:100-114	Macquarie University	Health, Environment	Health, Environment							X	X		X		
113	Y	16. NCWM	Paper	Meffert, M.W.	2006	Evaluation of Factors Affecting Vehicle Emission Compliance Using Regional Inspection and Maintenance Program Data	SAE Paper 2006-01-3406	Afton Chemical Corporation	Compliance	Compliance						M						
114	Y	17. NCWM	Paper	Roos, J.W., et al.	2006	A Survey of American and Canadian Consumer Experience- The Performance of Late Model Year Vehicles Operating on Gasoline With and Without the Gasoline Fuel Additive MMT ®	SAE Paper 2006-01-3405	Afton Chemical Corporation	Compliance	Compliance					M	M						
115	N	204. WOS	Paper	Finkelstein MM, Jerrett M.	2007	A study of the relationships between Parkinson's disease and markers of traffic-derived and environmental manganese air pollution in two Canadian cities	Environmental Research 2007; 104:420-432	Canada Institutes for Health Research; U.S. EPA	Health, Environment	Health, Environment								X				X
116	Y	15. NCWM	Paper	Roos, J.W., et al.	2007	The Interaction of MMT Combustion Products with the Exhaust Catalyst Face	SAE Paper 2007-01-1078	Afton Chemical Corporation	Tier 2	Exhaust						H						
117	Y	2. NCMW	Paper	Shimizu, C. et al	2007	Parametric Analysis of Catalytic Converter Plugging Caused by Manganese-Based Gasoline Additives	SAE Paper 2007-01-1070	Honda	Exhaust	Exhaust						H						
118	N	203. WOS	Paper	Walsh MP.	2007	The global experience with lead in gasoline and the lessons we should apply to the use of MMT	American Journal of Industrial Medicine 2007; 50:853-860		Health, Environment	Health, Environment	X			L		L						X
119	N	3. NCMW	Repeat of #2		2007				N/A	N/A												
120	Y	8. NCWM	Report	Lyons, J.M	2008	Impacts of MMT® Use in Unleaded Gasoline on Engines, Emissions Control Systems, and Emissions.	Sierra Reasearch, Report Num: SR2008-08-01	Canadian Vehicle Manufacturers Assoc.; Assoc. of Int'l Auto. Manufactures of Canada	Review	Review	X	X	X	H	H							
121	Y	33. NCWM	Report	ACEA	2009	ACEA Position on Metal Based Fuel Additives	ACEA Report, Nov. 16, 2009		Review	Review	X			M	M	M						X
122	N	46. NCWM	Report	ACEA	2009	A repeat of NCWM #33 (above)																
123	N	4. NCWM	Comments	AIAM	2009	AIAM Comments on Nevada Department of Agriculture Proposed Repeal of MMT Ban in Gasoline	Dec. 9, 2009	AIAM	N/A	N/A	X				L	L						
124	Y	42. NCWM	Report	Minjares, Ray; Walsh, Michael	2009	Methylcyclopentadienyl Manganese Tricarbonyl (MMT): A Science and Policy Review	ICCT 2009 MMT Report	ICCT	Review	Review	X			M	M	M					X	X
125	N	43. NCWM	Letter	Walsh, M.	2009	Letter to Nevada Department of Agriculture	From ICCT	ICCT	Letter	Letter					L	L						

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126	Y	49. NCWM	Report	Afton Chemical Co.	2010	mmt® and the Precautionary Principle: Insights to a Recent ICCT Paper on mmt. A Response to the International Council on Clean Transporation;s (ICCT) Report Entitled "Methylcyclopentadienyl Manganese Tricarbonyl (MMT): A Science and Policy Review" Jan. 2009		Afton Chemical Corporation	Review, Response	Review, Response				M	M	M						
127	Y	32. NCWM	Paper	Gidney, J.T., et al	2010	Effect of Organometallic Fuel Additives on Nanoparticle Emissions from a Gasoline Passenger Car	Environmental Science and Technology. Vol. 44, No. 7, 2010	Johnson Matthey	Emissions, Particulate	Emissions, Particulate				H								
128	N	201. WOS	Paper	Oudijk G.	2010	The Rise and Fall of Organometallic Additives in Automotive Gasoline	Environ. Forensics 2010; 11:17-49	NA	History	History	X	X										
129	N	202. WOS	Paper	Joly A,	2011	Reduced Atmospheric Manganese in Montreal Following Removal of Methylcyclopentadienyl Manganese Tricarbonyl (MMT)	Water Air and Soil Pollution 2011; 219:263-270	U. Montreal	Health, Environment	Health, Environment							X	X		X		
130	N	41. NCWM	Blog	Minjares, Ray	2012	Update: MMT	ICCT MMT 2012 Update		Review	Review	X				L	L						X
131	Y	71. NCWM	Report (Appendix)	ARCADIS	2013	Assessment of the impact of mmt® (HiTEC® 3000) Additive on the Emissions Performance of Vehicles: Input to the Risk Assessment of the mmt® Fuel Additive. Appendix A			Emissions, Exhaust, Particulate	Emissions, Exhaust, Particulate				H	H	H						
132	N	7. NCWM	Table	Dolmatz, S.	2013	Fuel and Fuel Additive Statements from Owner's Manuals, 2001-2003		N/A	N/A	N/A					L							
133	N	67. NCWM	Protocol	European Commission	2013	Protocol for the Evaluation of Effects of Metallic Fuel-Additives on the Emissions Performance of Vehicles.			Regulation	Regulation				L	L	L						
134	N	65. NCWM	Report	MECA	2013	LEV III and Tier 3 Exhaust Emission Control Technologies for Light-Duty Gasoline Vehicles		Manufacturers of Emission Controls Association	N/A	N/A						L						
135	N	68. NCWM	Report	Mudgal, S.,	2013	Development of a risk assessment for health and environment from the use of metallic addtives and a test methodology for that purpose: Final Report	Report to European Commision, DG Clima. Feb. 11, 2013 by BIO Intelligence Service	European Commission	Health, Environment	Health, Environment								X			X	X
136	N	75. NCWM	Letter	ACEA	2014	DG CLIMA Committee on Fuel Quality - 27 January, 2014: Draft Commission proposal concerning FQD Article 8a - Mn limit		ACEA	ACEA comments rejecting the use of MMT													
137	N	69. NCWM	Presentation	ACEA	2014	Information on the necessity of a ban on metallic additives in petrol	Draft presentation	European Automobile Manufacturers Association	Health, Environment	Health, Environment						L						
138	Y	40. NCWM	Report	Afton Chemical Co.	2014	Seeking Local Solutions to Global Challenges: HiTEC®3000 (mmt®)1 Fuel Additive as an Option for Optimizing Global Energy Supply	Afton Chemical Corporation, Feb. 2014	Afton Chemical Corporation	Engines, Exhaust	Engines, Exhaust	X	X			H	H						X
139	Y	73. NCWM	Report	Afton Chemical Co.	2014	Evaluation of the Impact of Gasoline Containing MMT® Fuel Additive on Particulate Matter Emissions in Vehicles Designed to Meet Euro 5 Emission Standards and Implications for the New U.S. tier 3 PM Emission Standards	Afton Chemical Corporation, Technical Report, July 2014	Afton Chemical Corporation	Emissions, Particulate	Emissions, Particulate				H	H	H						
140	N	70. NCWM	Presentation	ARCADIS	2014	EU Fuel Quality Directive (FQD) 2009/30/EC and mmt® (methylcyclopentadienyl manganese tricarbonyl)	Presented to the EU Commision, Jan. 27, 2014		Presentation	Presentation				L	L	L		X				X
141	Y	39. NCWM	Paper	Lohfink, C., et al	2014	Influence of Metal-Based Additives in Gasoline Fuel on the Exhaust Gas Emission System Components Over Useful Life Period Using the Example of Manganese-Containing Additive	SAE Paper 2014-01-1380	ADA Abgaszentrum der Automobilindustrie (volkswagen)	Exhaust	Exhaust			X			H						
142	Y	72. NCWM	Report	Afton Chemical Co.	2014	A Critical Review of the SAE Paper Titled "Influence of Metal-Based Additives in Gasoline Fuel on the Exhaust Gas Emission System Components Over Useful Life Period Using the Example of Manganese-Containing Additive" (SAE 2014-01-1380)	Afton Chemical Corporation, Technical Report, Sept. 2014	Afton Chemical Corporation	Response, Emissions	Response, Emissions				H	H	H						
143	N	66. NCWM	Presentation	MECA	2014	Vehicle Emission Standards Drive Technology Deployment: High Cell Density Substrates		Manufacturers of Emission Controls Association	N/A	N/A						L						
144	N	30. NCWM	Picture																			

NCWM = current database maintained by NCWM
WOS = Web of Science Search
SAE = SAE search

H = High Relevancy: and other information are provided in report for studies on vehicle year 2000 and later, or for critical reviews.
M = Medium Relevancy: when the source addresses the topic area and refers to existing data, but does not provide new data to support the findings.
L = Low Relevancy: given when the source only generally mentions the topic without reference.

APPENDIX II. Critical References from CRC-114 Literature Database

Ref. No.	Info. Source	Literature Type	Primary Author	Date	Title	Citation	Sponsor or Primary Author Affiliation	Test Program	Category (for Sorting)
1	61. NCWM	Paper	Faggan, J.E.	1975	An Evaluation of Manganese as an Antiknock in Unleaded Gasoline	SAE Paper 750925	Ethyl		Emissions, Engine, Exhaust
2	101. SAE	Paper	Moran, J.B.	1975	The Environmental Implications of Manganese as an Alternate Antiknock	SAE Paper 750926	E.P.A		Health, Environment
3	35. NCWM	Paper	Benson, J.D.	1977	Manganese Fuel Additive (MMT) Can Cause Vehicle Problems	SAE Paper 770655	General Motors Research		Engines, Exhaust
4	60. NCWM	Paper	Lenane, D.L.	1977	MMT- A Further Evaluation	SAE Paper 770656	Ethyl		Emissions, Engine, Exhaust
5	102. SAE	Paper	Faix, L.J.	1978	A Study of the Effects of Manganese Fuel Additive on Automotive Emissions	SAE Paper 780002	General Motors Corp.		Emissions
6	59. NCWM	Paper	Lenane, D.L.	1978	Effect of MMT on Emissions from Production Cars	SAE Paper 780003	Ethyl		Emissions
7	36. NCWM	Paper	Furey, R.L. and Summers, J.C.	1978	How MMT Causes Plugging of Monolithic Converters.	SAE Paper 780004	General Motors Research		Exhaust
8	103. SAE	Paper	Lichtenstein I.E.	1978	MMT Plugging of Oxidation Catalysts on Ceramic and Metal Supports During Engine Dyno Studies of Catalyst Durability	SAE Paper 780005	Matthey Bishop, Inc.		Exhaust
9	29. NCWM	Report	CRC	1979	CRC MMT Field Test Program	CRC Report No. 503	CRC		Emissions, Exhaust
10	104. SAE	Paper	Carlson, R.R.	1979	Conduct of Mileage Accumulation and Emissions Testing for the CRC/MMT Program	SAE Paper 790703	Systems Control, Inc.	CRC 1979	CRC 1979
11	105. SAE	Paper	Benson, J.D.	1979	Results of the Coordinating Research Council MMT Field Test Program	SAE Paper 790706	CRC	CRC 1979	CRC 1979
12	106. SAE	Paper	Wallace, J.S.	1979	Effects of MMT on Exhaust Emissions	SAE Paper 790707	EPA	1978 Waiver	Exhaust
13	107. SAE	Paper	Hughmark, G.A.	1980	A Statistical Analysis of the Effect of MMT Concentration on Hydrocarbon Emissions	SAE Paper 800393	Ethyl	Emissions	Emissions
14	108. SAE	Paper	Williamson, W.B.	1982	Effects of Fuel Additive MMT on Contaminant Retention and Catalyst Performance	SAE Paper 821193	Ford	Emissions	Emissions
15	109. SAE	Paper	Duncan, J.	1984	Combustor Study of the Deactivation of a Three-Way Catalyst by Lead and Manganese	SAE Paper 841408	EPA	Exhaust	Exhaust
16	28. NCWM	Report	CGSB Working Group	1986	An Assessment of the Effect of MMT on Light-Duty Vehicle Exhaust Emissions in the Canadian Environment	Working Group under jurisdiction of CGSB Gasoline and Alternative Auto. Fuels Committee	CGSB	Emissions	Emissions
21	112. SAE	Paper	Hurley, R.G.	1989	Characterization of Automotive Catalysts Exposed to the Fuel Additive MMT	SAE Paper 890582	Ford	Exhaust	Exhaust
22	14. NCWM	Paper	Lenane, D.L., et al	1990	Effect of a Fuel Additive on Emission Control Systems	SAE Paper 902097	Ethyl	1990 Waiver Application	Exhaust, Engine
23	62. NCWM	Docket		1990		EAP Air Docket A-90-16		1990 Waiver Application	Docket
24	37. NCWM	Paper	Hammerle, R.H., et al	1991	Particulate Emissions from Current Model Vehicles Using Gasoline with Methylcyclopentadienyl Manganese Tricarbonyl	SAE Paper 912436	Ford Motor Company	Particulates	Particulates
25	38. NCWM	Paper	Hurley, R.G. et al	1991	The Effect on Emissions and Emission Component Durability by the Fuel Additive Methylcyclopentadienyl Manganese Tricarbonyl (MMT)	SAE Paper 912437	Ford Motor Company	Emissions, Exhaust	Emissions, Exhaust
26	63. NCWM	Docket		1991		EPA Air Docket A-91-46		Docket	Docket
28	113. SAE	Paper	Hurley, R.G.	1992	The Effect of Mileage on Emissions and Emission Component Durability by the Fuel Additive Methyldcyclopentadienyl Manganese Tricarbonyl (MMT)	SAE Paper 920730	Ford	1991 Ford	Emissions, Exhaust, Particulate
29	114. SAE	Paper	Hammerle, R.H.	1992	Effect of Mileage Accumulation on Particulate Emissions from Vehicles Using Gasoline with Methylcyclopentadienyl Manganese Tricarbonyl	SAE Paper 920731	Ford	1991 Ford	1991 Ford
31	115. SAE	Paper	Hubbard, C.P.	1993	The Effect of MMT on the OBD-11 Catalyst Efficiency Monitor	SAE Paper 932855	Ford	Exhaust	Exhaust
32	64. NCWM	Docket		1993		EPA Air Docket A-93-26		Docket	Docket
33	13. NCWM	Paper	Aradi, et. Al	1994	The Physical and Chemical Effect of Manganese Oxides on Automobile Catalytic Converters	SAE Paper 940747	Ethyl	1990 Waiver (plus Escorts)	Exhaust
34	25. NCWM	Paper	Lenane, D.L., et al	1994	Emissions Results from a 48-car test evaluation of MMT performance additive	The Sci. of Total Environment, 146/147 (1994) 245-251	Ethyl	1990 Waiver Application	Emissions, Engine

APPENDIX II. Critical References from CRC-114 Literature Database

Ref. No.	Info. Source	Literature Type	Primary Author	Date	Title	Citation	Sponsor or Primary Author Affiliation	Test Program	Category (for Sorting)
38	12. NCWM	Paper	Roos, J.W., et al.	1994	The Effect of Manganes Oxides on OBD-II Catalytic Converter Monitoring	SAE Paper 942056	Ethyl	1990 Waiver, OBD analysis (plus add'l catalysts)	Exhaust
50	11. NCWM	Paper	Roos, J.W., Scull, H.M., Dykes, K.L., Hotchkiss, A.R., Grande, D.G., Lenane, D.L.	1997	Evaluation of On-Board Diagnostic Systems and the Impact of Gasoline Containing MMT	SAE Paper 972849	Ethyl	OBD analysis	Exhaust
70	52. NCWM	Paper	Roos, J.W.	2000	Characterization of Combustion Products from the Fuel Additive MMT	AWMA 93rd Annual Conf. & Exhibition, Salt Lake City, June 18-22, 2000	Ethyl		Emissions, Particulate
71	19. NCWM	Paper	Roos, J.W., et al.	2000	A Systems Approach to Improved Exhaust Catalyst Durability: The Role of the MMT Fuel Additive	SAE Paper 2000-01-1880	Ethyl	Exhaust	Exhaust
76	1.1. NCWM	Paper (and supporting info)	AAM	2002	The Impact of MMT on Vehicle Emissions and Durability- Part 1: A Joint Study by the Alliance of Automobile Manufacturers, The Association of International Automobile Manufacturers, and The Canadian Vehicle Manufacturers Association.	MMT Propgram Part 1 Report- July 29, 2002.	AAM, AIAM, CVMA	AAM 2002, Part 1	AAM 2002, Part 1
77	1.2. NCWM	Paper (and supporting info)	AAM	2002	The Impact of MMT on Vehicle Emissions and Durability- Part 2: A Joint Study by the Alliance of Automobile Manufacturers, The Association of International Automobile Manufacturers, and The Canadian Vehicle Manufacturers Association.	MMT Propgram Part 2 Report- July 29, 2002.	AAM, AIAM, CVMA	AAM 2002, Part 2	AAM 2002, Part 2
79	250. Web	Report	Air Improvement Resources, Inc.	2002	Effects of MMT in Gasoline on Emissions from On-Road Motor Vehicles in Canada	Canadian Vehicle Manufacturers Assoc., and Assoc. of Int'l Automobile Manufacturers of Canada. Nov. 11, 2002	Canadian Vehicle Manufacturers Association	Emissions	Emissions
81	116. SAE	Paper	Benson, J.D.	2002	The impact of MMT gasoline additive on exhaust emissions and fuel economy of low emission vehicles	SAE Paper 2002-01-2894	Alliance of Automobile Manufacturers (AAM)	AAM 2002- Part 2	AAM 2002- Part 2
84	10. NCWM	Report	Lyons, J.M	2002	Impacts Associated with the Use of MMT as an Octane Enhancing Additive in Unleaded Gasolines- A Critical Review	Sierra Reasearch, Report Num: SR02-07-01	Canadian Vehicle Manufacturers Assoc.; Assoc. of Int'l Auto. Manufactures of Canada (AIAMC)	Review	Review
85	22. NCWM	Paper	Roos, J.W., et al.	2002	Reformulating Gasoline for Lower Emissions Using the Fuel Additive MMT ®	SAE Paper 2002-01-2893	Ethyl	Emissions	Emissions
86	56. NCWM	Paper	Roos, J.W.	2002	A peer-reviewed critical analysis of SAE Paper 2002-01-2894 , "The impact of MMT gasoline additive on exhaust emissions and fuel economy of low emission vehicles."	SAE Paper 2002-01-2903	Ethyl	AAM 2002	AAM 2002
89	54. NCWM	Paper	Cunningham, L.J., et al	2003	AAM/AIAM Fleet Test Program: Analysis and Comments	SAE Paper 2003-01-3287	Ethyl	AAM 2002	AAM 2002
90	55.2. NCWM	Report	Environ International Corporation	2003	AAM Study Statistical Analysis	Prepared for Ethyl Corporation	Ethyl	AAM 2002	AAM 2002
91	55.1. NCWM	Report	Ethyl Corporation	2003	A Critical Analysis of the Alliance of Automobile Manufacturer' MMT Study: Separating Fact From Fiction		Ethyl	AAM 2002	AAM 2002
92	211. WOS	Paper	Geivanidis, S., P. Pistikopoulos, and Z. Samaras;	2003	Effect on exhaust emissions by the use of methylcyclopentadienyl manganese tricarbonyl (MMT) fuel additive and other lead replacement gasolines	Sci.Total Environ., 305,(1-3), 129-141. 2003.	Ethyl	Emissions	Emissions
96	34. NCWM	Report	Blumberg, K., and Walsh, M.P.	2004	Status Report Concerning the Use of MMT in Gasoline	Report to Int'l Council on Clean Transportation, Sept., 2004	ICCT	Review	Review
97	53. NCWM	Report	Afton Chemical Co.	2004	Afton Chemical Corporation's (Afton) Comments on the International Council on Clean Transportation (ICCT) Status Report on MMT®			Review, Response	Review, Response
99	45. NCWM	Presentation	Global Auto Industry	2004	MMT's Impact on Vehicles; The Perspective of Global Auto Industry	Beijing China, Nov. 2004	GM, Ford, Daimler Chrysler, Volkswagen, Honda, Toyota	Engines, Exhaust	Engines, Exhaust
100	31. NCWM	Paper	McCabe, R.W.; DiCicco, D.W. et al	2004	Effects of MMT® Fuel Additive on Emission System Components: Comparison of Clear- and MMT ®- fueled Escort Vehicles from the Alliance Study	SAE Paper 2004-01-1084	Ford Motor Company	AAM 2002	AAM 2002
102	251. Web	Presentation	Schindler, K.P.	2004	Impact of MMT on Vehicle Emission Performance	Asian Vehicle Emission Control Conference 2004 (AVECC)	Volkswagen		

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Ref. No.	Info. Source	Literature Type	Primary Author	Date	Title	Citation	Sponsor or Primary Author Affiliation	Test Program	Category (for Sorting)
103	118. SAE	Paper	Boone, W.P.	2005	Effect of MMT Fuel Additive on Emission System Components: Detailed Parts Analysis from Clear and MMT-Fueled Escort Vehicles from the Alliance Study	SAE Paper 2005-01-1108	Ford Motor Company	AAM 2002- Part 2	AAM 2002- Part 2
105	18. NCWM	Paper	Cunningham, L.J., et al	2005	Assessing High-Cell Density Catalyst Durability with MMT ® Fuel Additive in Severe Driving Conditions	SAE Paper 2005-01-3840	Afton Chemical Corporation	Tier 2	Exhaust
107	44. NCWM	Report	Richter, H.	2005	Influence of Ash-Forming Gasoline Additives such as MMT® on Exhaust Emissions and Performance Characteristics of PC-Engines		Porsche	Exhaust, Emissions, Engine	Exhaust, Emissions, Engine
108	48. NCWM	Report	Afton Chemical Co.	2005	Response to a New Automobile Industry-Sponsored Test of the Effects of MMT® in Vehicles Designed to Meet Euro IV Emission Standards		Ethyl	Tier 2	Exhaust, Response
109	50. NCWM	Report	Afton Chemical Co.	2006	A Report on the Results of Alternative Tier 2 Testing For the Characterization of Particulate from Vehicles Using the Gasoline Additive MMT® in the Fuel	Final Report Submitted to the U.S. E.P.A. Docket ID: EPA-HQ-OAR-0074-0164	Afton Chemical Corporation	Tier 2	Emissions, Particulate
111	74. NCWM	Report	D' Aniello, Michael.	2006	Adverse Effects of MMT-Doped fuel on 2002-3 MY LL8 GMT360/370	GM Research	General Motors Research	In-use survey	Survey
113	16. NCWM	Paper	Meffert, M.W.	2006	Evaluation of Factors Affecting Vehicle Emission Compliance Using Regional Inspection and Maintenance Program Data	SAE Paper 2006-01-3406	Afton Chemical Corporation	Compliance	Compliance
114	17. NCWM	Paper	Roos, J.W., et al.	2006	A Survey of American and Canadian Consumer Experience- The Performance of Late Model Year Vehicles Operating on Gasoline With and Without the Gasoline Fuel Additive MMT ®	SAE Paper 2006-01-3405	Afton Chemical Corporation	Compliance	Compliance
116	15. NCWM	Paper	Roos, J.W., et al.	2007	The Interaction of MMT Combustion Products with the Exhaust Catalyst Face	SAE Paper 2007-01-1078	Afton Chemical Corporation	Tier 2	Exhaust
117	2. NCMW	Paper	Shimizu, C. et al	2007	Parametric Analysis of Catalytic Converter Plugging Caused by Manganese-Based Gasoline Additives	SAE Paper 2007-01-1070	Honda	Exhaust	Exhaust
120	8. NCWM	Report	Lyons, J.M	2008	Impacts of MMT® Use in Unleaded Gasoline on Engines, Emissions Control Systems, and Emissions.	Sierra Reasearch, Report Num: SR2008-08-01	Canadian Vehicle Manufacturers Assoc.; Assoc. of Int'l Auto. Manufactures of Canada (AIAMC)	Review	Review
121	33. NCWM	Report	ACEA	2009	ACEA Position on Metal Based Fuel Additives	ACEA Report, Nov. 16, 2009		Review	Review
124	42. NCWM	Report	Minjares, Ray; Walsh, Michael	2009	Methylcyclopentadienyl Manganese Tricarbonyl (MMT): A Science and Policy Review	ICCT 2009 MMT Report	ICCT	Review	Review
126	49. NCWM	Report	Afton Chemical Co.	2010	mmt® and the Precautionary Principle: Insights to a Recent ICCT Paper on mmt. Response to the Int'l Council on Clean Transporation's (ICCT) Report Entitled "Methylcyclopentadienyl Manganese Tricarbonyl (MMT): A Science and Policy Review" Jan. 2009		Afton Chemical Corporation	Review, Response	Review, Response
127	32. NCWM	Paper	Gidney, J.T., et al	2010	Effect of Organometallic Fuel Additives on Nanoparticle Emissions from a Gasoline Passenger Car	Environmental Science and Technology. Vol. 44, No. 7, 2010	Johnson Matthey	Emissions, Particulate	Emissions, Particulate
131	71. NCWM	Report (Appendix)	ARCADIS	2013	Assessment of the impact of mmt® (HiTEC® 3000) Additive on the Emissions Performance of Vehicles: Input to the Risk Assessment of the mmt® Fuel Additive. Appendix A			Emissions, Exhaust, Particulate	Emissions, Exhaust, Particulate
138	40. NCWM	Report	Afton Chemical Co.	2014	Seeking Local Solutions to Global Challenges: HiTEC®3000 (mmt®)1 Fuel Additive as an Option for Optimizing Global Energy Supply	Afton Chemical Corporation, Feb. 2014	Afton Chemical Corporation	Engines, Exhaust	Engines, Exhaust
139	73. NCWM	Report	Afton Chemical Co.	2014	Evaluation of the Impact of Gasoline Containing MMT® Fuel Additive on Particulate Matter Emissions in Vehicles Designed to Meet Euro 5 Emission Standards and Implications for the New U.S. Tier 3 PM Emission Standards	Afton Chemical Corporation, Technical Report, July 2014	Afton Chemical Corporation	Emissions, Particulate	Emissions, Particulate
141	39. NCWM	Paper	Lohfink, C., et al	2014	Influence of Metal-Based Additives in Gasoline Fuel on the Exhaust Gas Emission System Components Over Useful Life Period Using the Example of Manganese-Containing Additive	SAE Paper 2014-01-1380	ADA Abgaszentrum der Automobilindustrie (volkswagen)	Exhaust	Exhaust
142	72. NCWM	Report	Afton Chemical Co.	2014	A Critical Review of the SAE Paper Titled "Influence of Metal-Based Additives in Gasoline Fuel on the Exhaust Gas Emission System Components Over Useful Life Period Using the Example of Manganese-Containing Additive" (SAE 2014-01-1380)	Afton Chemical Corporation, Technical Report, Sept. 2014	Afton Chemical Corporation	Response, Emissions	Response, Emissions

Appendix III: Summaries of Key Literature

CONTENTS

OVERVIEW

This Appendix provides summaries of publications and reports on the effect of MMT on engine, emissions, and exhaust components of vehicles. Any literature that was found to be relevant to this topic was designated by a “high” or “medium” relevancy, as outlined in Appendix I to this report. Studies that were earlier than MY 2000 were given a relevancy no higher than medium, while any publication reporting on the effects of MMT on vehicle components after MY 2000 may be designated as “high” relevancy. Those with medium relevancy designation (e.g. publications between 1970-1999) have a general summary with fewer details about the vehicles and testing cycles. Studies with high relevancy designation have more details, including a table which details the sponsor of the study, the vehicle fleet description, the test protocol and mileage accumulation, the catalyst technology and emissions testing protocol. The fields that were not described in detail in each individual study are left blank or removed from the table.

1 SUMMARY OF EARLY STUDIES (PRIOR TO TIER 2)

Note: Since these early studies have been designated as having only “medium” relevancy, a general summary of each study is provided with fewer details about the vehicles and testing cycles.

1.1 Studies Conducted in the 1970’s

1.1.1 Ref. No. 01: Faggan, J.E., 1975. An Evaluation of Manganese as an Antiknock in Unleaded Gasoline (SAE 750925)

In this paper, Ethyl Corporation presented results of early testing with MMT at concentrations of 0.125 g Mn/gal (33 mg Mn/L), demonstrating benefits of the use of MMT. They concluded that the data from extensive road and dynamometer engine tests showed that MMT is compatible with vehicle operation, provides benefits for valve guide and seat wear, decreases emissions of polynuclear aromatics, and does not lessen the effectiveness of catalysts. They also found that catalyst plugging did occur with MMT under severe conditions, which would cause rapid catalyst deterioration, whether or not manganese was present. Under typical driving condition, no plugging was observed. It was also concluded that most of the manganese is converted to Mn_3O_4 in the exhaust.

1.1.2 Ref. No. 02: Moran, J.B., 1975. The Environmental Implications of Manganese as an Alternate Antiknock (SAE 750926)

This review was performed by the EPA to inform themselves about relevant environmental and health impacts of using manganese as a fuel additive. While much of the work was focused on health-related issues, it was concluded from the review that the use of Mn in gasoline would result in increased emissions of hydrocarbons.

1.1.3 Ref. No. 03: Benson, J.D., 1977. Manganese Fuel Additive (MMT) Can Cause Vehicle Problems (SAE 770655)

Sponsor/ Author Affiliation	General Motors
Study Type	Primary- Fleet Study
Vehicle Test Fleet Description	Two 1976 Oldsmobile Cutlasses equipped with bead-type underfloor converters and three 1977 Chevrolet Novas equipped with monolithic manifold and bead-type underfloor converters
Mn Concentration	0.034 g Mn/l (0.129 g Mn/gal) and 0.017 g Mn/L (0.064 g Mn/gal)
Baseline Fuel	
Test Protocol	Mileage accumulation on a chassis dyno with severe R007 driving schedule
Mileage Accumulation	Four cars accumulated 80,000 km (50,000 miles), but tests were terminated on the fifth car at 64,000 km (40,000 mi) due to repeated plugging of the monolithic converter
Emission Test Protocol	
Catalyst Technology	

Summary: In this study, which used a severe driving schedule (it was pointed out that the R007 cycle is more severe than the emissions certification schedule), MMT caused plugging of monolithic converters located close to the exhaust manifold, partial plugging of an underfloor bead converter, an increase in HC emission from the engines, and excessive spark plug deposits. It was also found that the use of MMT enhanced catalytic converter oxidizing activity.

1.1.4 Ref. No. 04: Lenane, D.L. 1977. MMT – A Further Evaluation (SAE 770656)

This work provided a progress report of results from fleet testing that was underway at the time (additional results are discussed in Lenane, 780003), with several of the cars having been tested to 20,000 miles or less. Further fleet testing results are discussed below.

1.1.5 Ref. No. 06: Lenane, D.L. 1978. Effect of MMT on Emissions from Production Cars (SAE 780003)

This paper summarized Ethyl Corporation's work on two vehicle fleets to evaluate emissions over 50,000 miles with pairs of vehicles operating on either base fuel or with MMT treat rates of 1/8, 1/16 or 1/32 g Mn/gal. At the time of the publication, 16 vehicles from one fleet using 1/16 g Mn/gallon, and 10 pairs of vehicles from the second fleet with a treat rate of 1/8 g Mn/gallon had completed mileage accumulation using an EPA accumulation cycle. Statistical analysis of the fleet data showed little differences in stabilized engine-out emissions between clear and MMT vehicles. Some small differences seen in tailpipe HC emissions were caused mostly from abnormally high HC emissions in one MMT vehicle.

1.1.6 Ref. No. 05: Faix, L.J. 1978. A Study of the Effects of Manganese Fuel Additive on Automotive Emissions (SAE 780002)

A vehicle fleet test was performed by GM to further evaluate MMT effects on emission control systems after early studies (Benson, Lenane) suggested increases in HC emissions. All engines tested were designed to conform with stricter (for the time) emission standards of 0.41 g/mi HC, 3.4 g/mi CO, and

2.0 g/mi NO_x. The test program included 12 dynamometer engines and thirty-one vehicles which accumulated the equivalent of over 2.5 million miles of test data using the AMA Certification Mileage Accumulation Cycle. MMT levels were at 1/8 g Mn/ gal.

Both engine and tailpipe HC emissions increased to the extent that they were more than double the final emission levels of the clear-fueled vehicles, and exceeded the emission standards before 15,000 miles (while the clear-fueled vehicles met the emission limit). The deterioration of HC was about the same using 1/8 or 1/16 g Mn/ gal, and attempts to recalibrate to meet the emission standards were unsuccessful. Increased HC emissions were attributed to Mn_3O_4 deposits in the combustion chambers. There was little to no effect on methane, CO, or NO_x. No effect on catalytic conversion efficiency was seen, and no maintenance requirements developed.

1.1.7 Ref. No. 07: Furey, R.L. and Summers, J.C. 1978. Effect of MMT on Emissions from Production Cars (SAE 780004)

To investigate the mechanism of converter plugging by MMT seen in other studies (Benson, SAE 770655), GM conducted an engine dynamometer study to investigate some of the variables that could have an effect, including manganese concentration, exhaust gas temperature, A/F ratio and exhaust O_2 content, and exhaust particulate size. Based on the data, the mechanism of plugging was suggested to be Mn_3O_4 particles that are formed at high temperatures impinging on the surface of the catalyst. While the particles were found to be quite small (~0.01 µm diameter), and were expected to pass through the catalyst, the flow direction of the exhaust gases was found to impact the catalyst surface, which, if the particles or catalyst were at or above the melting or sintering temperature of the particles, would result in particles sticking to the catalyst. These plugging deposits may not form below 700^0C, but plugging speed increased by as much as 15-fold with a change in temperature from 705 to 843^0C. The exhaust gas temperature and concentration of MMT had significant effects on plugging rate, and plugging time was inversely proportional to the concentration of MMT in the fuel.

1.1.8 Ref. No. 08: Lichtenstein, I.E and Mundy, J.P., 1978. MMT Plugging of Oxidation Catalysts on Ceramic and Metal Supports During Engine Dyno Studies of Catalyst Durability (SAE 780005).

Engine dynamometer durability studies of oxidation catalysts showed that MMT causes manganese deposits that affect catalyst performance for HC and CO. The severity of these effects is related to the level of MMT, the cell density, and engine aging time. An engine dyno cycle with high temperatures (>1500°F) resulted in severe clogging and loss of catalyst functionality with Mn as low as 0.06 g/gal (1/16)

1.1.9 Ref. No. 12: Wallace, J.S. and Garbe, R.J. 1979. Effects of MMT on Exhaust Emissions (SAE 790707)

The EPA performed a statistical analysis of data resulting from Ethyl Corporation's 1978 waiver application testing program, along with other available data from literature to determine the effects of MMT on 1) O_2 sensors used in TWC-equipped vehicles, 2) catalyst efficiency and enhancement, 3) combustion chamber deposits, 4) fuel economy, and 5) catalyst plugging. The results showed that:

1) With 88-99% confidence, both 1/32 and 1/16 g Mn/gal MMT-fueled vehicles had increased HC emissions.
2) With 98% confidence, MMT caused or contributed to failure of vehicles to meet emission standards.
3) No statistically significant, adverse effects were seen on NO_x or CO.
4) MMT is suspected of having adverse effects on O_2 sensors.
5) Catalyst enhancement is seen when using MMT, but it does not overcome adverse effects.
6) No instantaneous effect is seen on fuel economy.
7) Limited information regarding combustion chamber deposits indicate they result in increased HC emissions.
8) There is increased potential for catalyst plugging under severe conditions, which may be seen in a small number of vehicles under high load.

1.2 CRC MMT Field Test Program

1.2.1 Ref. No: 09: CRC, 1979. CRC MMT Field Test Program

1.2.2 Ref. No. 10: Carlson, R.R., et al. 1979. Conduct of Mileage Accumulation and Emission Testing for the CRC/MMT Program. (SAE 790703)

1.2.3 Ref. No. 11: Benson, J.D. et al. 1979. Results of Coordinating Research Council MMT Field Test Program. (SAE 790706)

The results of the first large-scale fleet testing program to investigate the effects of MMT are presented in several related publications, listed above. The results are all described together in the summary below:

Sponsor/ Author Affiliation	CRC
Study Type	Primary
Vehicle Test Fleet Description	63 Vehicles, in 3 fleets with 7 models each, each designed to meet 1977-1978 California Emission standards of 0.41 g/mi HC, 9.0 g/mi CO and 1.5 g/mi NOx.
Mn Concentration	1/32 and 1/16 g Mn/gal
Baseline Fuel	Chevron certification fuel (Clear) for mileage accumulation; Indolene clear for emissions testing.
Test Protocol	Mileage accumulation on Riverside International Raceway Track, up to 19 hours/ day
Mileage Accumulation	50,000 mi
Emission Test Protocol	duplicate EPA certification tests at 0.3k, 5k, 10k, 15k, 22.5k, 30k, 37.5k, 45k; and 50k miles. Both engine out and tailpipe emissions were measured.
Catalyst Technology	2 models (out of seven) had three-way catalysts, 5 models had conventional oxidation catalysts

Summary: A CRC task force was put together to investigate concerns that MMT use would result in exceeding 0.41 g/mi HC standards. The primary objective was to evaluate effects on HC emissions under two different concentrations of MMT, with secondary objectives to determine effects on catalytic converter plugging, catalyst conversion efficiency, oxygen sensor life and spark plug life. A statistical analysis of results from the entire fleet determined that engine-out HC emissions increased with the MMT-containing fuels, and that the increase was proportional to the MMT concentration in the fuel. The mileage at which the tailpipe HC emissions exceeded California emission standards was significantly reduced with the MMT fuels. At 50k miles, the fleet average difference in HC emissions relative to clear fuel were 0.48 g/mi and 0.79 g/mi for the 1/32 and 1/16 blend MMT fuels, respectively. The study also showed that MMT had no statistically significant effects on CO or NOx emissions. Catalyst pressure drop measurements indicated that no catalyst plugging occurred with any of the fuels, but the two vehicle models equipped with TWC systems experienced a decreased life of the oxygen sensor, which resulted in a marked increase in tailpipe HC and CO emissions. It was found with at least 98% confidence that MMT caused or contributed to failure of vehicles to meet the emission standards. However, the sample size was too small and limited the degree of confidence for cars equipped with TWC.

1.2.4 Ref. No. 13. Hughmark, G.A. and Sobel, B.A. 1980. A Statistical Analysis of the Effect of MMT Concentration on Hydrocarbon Emissions (SAE 800393)

Ethyl performed its own statistical analysis of the data generated with the 1979 CRC fleet study, along with data from other studies conducted by Ford, GM, and Ethyl. The analysis excluded data from the CRC study on Pontiacs and Volvos, due to the effects seen on the O_2 sensors and both engine-out and tailpipe emissions. In their statistical analysis of HC emissions, Ethyl divided the data into low-mileage and high-mileage phases since the engine-out HC emissions seemed to increase initially and then level off. It was concluded that while engine-out HC emission increase linearly with MMT concentration in the fuel, there is also a linear increase in catalytic converter efficiency up to 15,000 miles with increases in MMT concentration.

1.3 Studies Conducted in the 1980's

1.3.1 Ref. No 14. Williamson, W.B. and Gandi, H.S. 1982. Effects of Fuel Additive MMT on Contaminant Retention and Catalyst Performance (SAE 821193)

Ford Motor company performed a post-mortem analysis on TWCs from a Ford fleet of vehicles operated for 50,000 miles on 0.125 g Mn/gal (33 mg/L). The analysis found that significantly less P and Zn contaminants were on catalysts of vehicles fueled with MMT than without, suggesting that the Mn_3O_4 formed during combustion of Mn serves as a scavenger in the exhaust. Beneficial effects were supported by results of a laboratory study using a range of 0.016 to 0.157 g Mn/gal. The optimum levels of MMT were suggested to be in the lower range (e.g. < 0.03 g Mn/gal) where benefits of reduced contaminant retention are seen, but disbenefits of increased HC feedgas levels, adverse engine deposits and catalyst plugging are minimal.

1.3.2 Ref. No. 15: Duncan, J. and Braddock, J.N. 1984. Combustor Study of the Deactivation of a Three-Way Catalyst by Lead and Manganese (SAE 841408)

This study was conducted with the EPA to evaluate the activity and durability of a platinum-rhodium TWC as a function of lead and manganese fuel levels using a pulse-flame combustor. Simulations were performed for the equivalent of 24,000 miles. While lead causes the most rapid deterioration of a TWC, loss of the 80% three-way conversion window occurred at 13,500 miles using fuel with MMT at 0.0625 g Mn/gal. This occurred at 9,000 miles and 22,500 miles for lead and base fuels, respectively.

1.3.3 Ref. No. 21. Hurley, R.G. et al. 1989. Characterization of Automotive Catalysts Exposed to the Fuel Additive MMT (SAE 890582)

Ford characterized catalysts that were exposed to MMT after mileage accumulation ranging from 22,000 to 43,000 miles using XRF, XRD, optical microscopy, SEM, electron microprobe, and visual inspection. The catalysts were removed from Canadian consumer vehicles under warranty. It was assumed that all vehicles were operated using gasoline that met the Canadian standard of 1/16 g Mn/gal. Characterization results showed that a thick layer (5-20 microns) of Mn_3O_4 covered the surface of the catalysts, which resulted in increased mass transfer resistance. Catalyst efficiency was also reduced, and the light-off temperatures and conversion of NO, CO and HC was found to decrease as exposure to MMT increased.

1.4 1990-1993 Ethyl Waiver Application Publications and Follow-On Reporting

Waiver application testing conducted in 1990 was on a fleet of 48 vehicles, described below: Subsequent publications and reports described below are based on testing of the same vehicles shown in this table.

Additional vehicle testing was performed and submitted to the EPA in 1993. This fleet consisted of 44 vehicles.

<table>
<tr><td>Sponsor/ Author Affiliation</td><td>Ethyl Corporation</td></tr>
<tr><td>Study Type</td><td>Waiver Application testing</td></tr>
<tr><td>Vehicle Test Fleet Description</td><td>48 vehicles: 6 cars each of 8 models representing 53% of the U.S. sales in 1988, identified as:
TABLE 1
Summary of Ethyl Test Fleet Cars
<table>
<tr><th>Car Identification</th><th>Engine Cyl/Config.</th><th>Engine Displ., L</th><th>Percentage of 1988 Production</th></tr>
<tr><td>C</td><td>4/L</td><td>2.0</td><td>5.7</td></tr>
<tr><td>D</td><td>6/V</td><td>3.0</td><td>1.9</td></tr>
<tr><td>E</td><td>4/L</td><td>1.9</td><td>5.5</td></tr>
<tr><td>F</td><td>8/V</td><td>5.0</td><td>7.2</td></tr>
<tr><td>G</td><td>4/L</td><td>2.5</td><td>4.2</td></tr>
<tr><td>H</td><td>6/V</td><td>2.8</td><td>12.9</td></tr>
<tr><td>I</td><td>6/V</td><td>3.8</td><td>9.3</td></tr>
<tr><td>T</td><td>6/V</td><td>3.0</td><td>6.6</td></tr>
<tr><td></td><td></td><td></td><td>53.3</td></tr>
</table>
(Table from Lenane, SAE 902097)</td></tr>
<tr><td>Mn Concentration</td><td>0.03125 g Mn/ gal (1/32 g Mn/gal; 8.3 mg Mn/L)</td></tr>
</table>

Baseline Fuel	Howell EEE
Test Protocol	
Mileage Accumulation	75,000 miles with 1,000 mile break in
Emission Test Protocol	FTP testing at 5,000 mile intervals
Catalyst Technology	variable, with close-coupled arrangement – mostly Tier 1 vehicles

1.4.1 Ref No. 22: Lenane, D.L. 1990. Effect of a Fuel Additive on Emission Control Systems (SAE 902097)

1.4.2 Ref No. 23: EPA Air Docket A-90-16: Ethyl 1990 Waiver Submission Contents

The emissions results included in the 1990 waiver submission were also published in Lenane, D.L. SAE 902097. The results of the two reports are summarized together here.

Summary: As part of their 1990 Waiver application, Ethyl designed this test program with input from the EPA regarding the size of the test fleet, the mileage accumulation, the statistical analysis performed, and other aspects of testing.

Each car in the fleet was first driven 1,000 miles on base fuel, which was followed by FTP testing to rank and pair vehicles. 75,000 miles of accumulation was performed over a two year period, during which necessary and appropriate maintenance regimes were followed. Data generated from the test were subjected to multiple statistical analyses, and the mean integrated results are shown below. With use of the MMT fuel, reductions in CO and NO_x were seen, while HC emission increased slightly. However, it was concluded that the small increase in HC emissions would not cause or contribute to failure of the emission control system to meet emission standards.

Mean integrated emissions:

Emissions	Thousand Mile Interval	Delta (MMT-Clear) g/mi
HC	50	.018
	75	.018
CO	50	-0.09
	75	-0.22
NOx	50	-0.07
	75	-0.11

In addition, Ethyl performed checks on the durability of the emission components. A 50,000 mile check showed no statistical difference in the performance of the oxygen sensors. An evaluation of the catalytic performance showed that, between 50 and 75 thousand miles, the additive enhanced the ability of the catalyst to convert NO_x, had a small benefit in converting HC, but no benefit in converting CO. Back pressure testing performed after 75,000 miles to determine plugging of the catalyst also showed no statistically significant difference between the groups of vehicles fueled with or without MMT. Additional focused testing on models with close-coupled catalyst configurations was performed on new catalysts for 30,000 miles. This resulted in similar and constant back pressure for both vehicles, indicating no catalyst plugging.

Additional testing was performed to determine the amount of manganese emitted from the test fleets to estimate airborne Mn concentrations. PM was measured after 75,000 miles of accumulation, and the MMT fleet showed an average of .003 g/mi less PM emitted. The manganese in the particulate represented about 0.39% of the manganese input to the engine by the fuel.

1.4.3 Ref. No. 33: Aradi, A.A., et al. 1994. The Physical and Chemical Effect of Manganese Oxides on Automobile Catalytic Converters. (SAE 940747)

Sponsor/ Author Affiliation	Ethyl Corporation
Study Type	Waiver application testing-follow on reporting
Vehicle Test Fleet Description	In addition to vehicles from the 1988 fleet testing, 4 1991 Ford Escorts were also evaluated for a total of 22 vehicles as shown: Car Model — Number of Cars — Number of Monoliths 1.9 L Ford Escort — 6 — 6 3.8 L Ford Taurus — 6 — 6 2.8 L GM Buick Century — 6 — 6 3.8 L GM Buick Century — 2 — 2 5.0 L Ford Crown Victoria — 2 — 4
Mn Concentration	1/32 g Mn/gal (as used in the test fleet of waiver application)
Baseline Fuel	Howell EEE
Test Protocol	Evaluate catalytic converter efficiencies on slave dynamometer
Mileage Accumulation	Vehicles in the 1988 fleet accumulated 75,000 miles as part of waiver application testing; the 1991 Ford Escorts accumulated 24,000 miles
Emission Test Protocol	Catalysts were paired with a slave engine on a dynamometer; Catalyst cores were evaluated using a pulse flame combustor and via laboratory analysis.
Catalyst Technology	Ford Escorts had Pd/Rh formulations; the rest of 1988 fleet had Pt/Rh formulations.

Summary: Further evaluation of the catalysts from vehicles that had accumulated miles during Ethyl's 1988 fleet testing as part of their waiver application was done, along with catalysts from 1991 Ford Escorts that had accumulated 24,000 miles. The Escorts were included due to high HC emissions seen previously. Catalytic conversion efficiencies were evaluated using slave-engine dynamometer testing, then evaluating cores by laboratory analysis (B.E.T surface area measurements, SEM, and XRF) and using a pulse flame combustor with a synthetic exhaust gas.

Slave-engine dynamometer testing of the catalysts resulted in only one vehicle having significant differences: the 1988 Ford Crown Victoria showed higher conversion efficiencies with the MMT fuel for all three pollutants (HC, CO, NO_x). The MMT 2.8L GM Buick had lower HC efficiency and the MMT 3.8L GM Buick had lower CO conversion efficiency, but as a fleet, statistical analysis indicated no adverse effect on catalyst conversion efficiency from the use of MMT. The '91 Ford Escorts with 24,000 miles did not show statistically significant differences between MMT and clear fuel.

Additionally, back pressure measurements across the catalysts indicated no differences with MMT. This, along with consistent conversion efficiencies, was taken to indicate that manganese oxide deposits do not plug catalytic converters.

Surface area measurements of the catalyst cores, evaluated in different sections (inlet third, middle third, outlet third) revealed small differences of surface area in the clear and MMT-fueled catalysts. The 2.8L Buick Centuries and the 3.0 L Ford Taurus showed higher surface area in the first 1/3 of the MMT-fueled catalyst, while the Dodge Dynasty and Escorts showed lower surface area. However, the opposite was seen in the last 1/3 of the catalyst for each of the vehicles, so that the Centuries and Tauruses had lower surface area in the final 1/3 and the Dynasties and Escorts had higher surface area. A mean of the entire fleet indicated that the inlet surface area was higher for additive-exposed catalysts.

XRF analysis of the catalysts showed that manganese concentrations were highest on the front face of the catalyst, although, emissions results showed these deposits did not adversely affect the catalyst. Lower phosphorous and zinc deposits were also noted on the MMT-catalysts.

The authors concluded that manganese oxide deposits do not deactivate the catalyst or adversely affect its performance.

1.4.4 Ref. No. 34: Lenane, D.L. et al. 1996. Emissions results from a 48-car test evaluation of MMT performance additive (Sci. Tot. Env. 146/147)

Sponsor/ Author Affiliation	Ethyl Corporation
Study Type	Waiver Application testing – Follow on Reporting

General Summary/ Overview: The publication presents follow-on results of the same 48-car testing protocol performed by Ethyl as part of their 1990 waiver application described above. The discussions of emission results testing and component testing are essentially the same as those presented in SAE Paper No. 902097, but further express results in comparison to emission standards, and show results of further PM testing.

The mean integrated HC emissions were the same as presented previously: 0.018 g/mi higher for MMT-fueled vehicles over the entire test interval. Statistical analysis of the fleet showed average HC emissions remained below the standard (0.41 g HC/mi), although some models (with both fuels) exceeded the criteria. Differences in CO emissions were small, but slightly lower CO was seen for the MMT-fueled vehicles at higher mileage (from 40-75k mi). However, on a fleet average basis, both groups of vehicles exceeded the standard of 3.4 g/mi beginning at about the 40,000 mile mark. Both groups met the NOx standard of 1.0 g/mi, although the MMT fleet had about a 20% reduction in NOx emissions compared to the base-fueled fleet beginning at 5,000 mi.

Some questions about differences in laboratory results of PM emissions prompted additional laboratory correlation testing to determine the percentage of Mn emitted as particulate. A previous report by EPA found that use of MMT dramatically increased PM emissions. This laboratory comparison showed that the EPA test tunnel had a high concentration of chlorofluorocarbon refrigerant, which contributed to increases in PM due to chloride, and was an anomalous result. It was also concluded that 12% of the Mn in the fuel was exhausted as airborne particulate (rather than 0.39% as reported previously).

1.4.5 Ref. No 32: EPA Air Docket A-93-26: Ethyl Resubmission of Additional Test Results for 1991 Waiver Application

Sponsor/ Author Affiliation	Ethyl Corporation
Study Type	1993 Fleet Testing Results
Vehicle Test Fleet Description	44 Vehicles comprised of paired vehicles of the following 1992/1993 Model Year: 1. 1992 Crown Victoria, 4.6L 2. 1992 Buick Regal, 3800cc 3. 1992 Ford Mustang, 5L 4. 1993 Toyota Camry, 2.2L 5. 1993 Oldsmobile Achieva, 2.3L 6. 1993 Honda Civic TLEV, 1.5L 7. 1993 Ford Escort, TLEV, 1.9L 8. 1993 Dodge Shadow, 2.5L
Mn Conc.	1/32 g Mn/gal (8.3 mg Mn/L)
Baseline Fuel	Chevron ULCQ
Test Protocol	Periodic FTP emissions testing
Mileage Accumulation	Up to 65,000 miles of accumulation (in the document dated July 15, 1993- although it appears vehicles were subsequently tested to 100,000 miles, and additional tests were performed in later documentation not provided).
Emission Test Protocol	FTP
Catalyst Technology:	

Summary: The most recent material provided in the docket for the 1993 submission of additional test results was dated July 15, 1993, although the program continued on for additional testing, which is reported in later publications. At 65,000 miles, as reported here, no effect on CO emissions was seen; a statistically significant reduction in NO_x emissions occurred, and a slight increase in HC emissions, although the differences were not statistically significant. Ethyl concluded that use of MMT reduced regulated emissions. They also concluded that the results of testing completed by Ford on their 1991 Escort appear to be anomalous.

1.4.6 Ref. No: 38. Roos, J.W., 1994. The Effect of Manganese Oxides on OBD-II Catalytic Converter Monitoring (SAE 942056)

Sponsor/ Author Affiliation	Ethyl Corporation
Study Type	1993 Fleet Testing Results
Vehicle Test Fleet Description	Results are stated to be from 6-1993 Toyota Camrys; 4-1992 Ford Crown Victorias, although the table below is used to describe the analysis conducted on catalysts.

Table 1. Catalysts used in this study.

Catalyst	Aging	Fuel	Catalyst Location
Crown Victoria Front right	100K miles	MMT	Close Coupled
Crown Victoria Front right	100K miles + 16 hrs 1300°C	MMT	Close Coupled
Crown Victoria Front right	100K miles	Base	Close Coupled
Crown Victoria Front right	100K miles + 16 hrs 1300°C	Base	Close Coupled
Crown Victoria	new		
Honda	100K miles	MMT	Close Coupled
Honda	100K miles + 5 hrs 1150°C	MMT	Close Coupled
Honda	100K miles + 10 hrs 1150°C	MMT	Close Coupled
Honda	100K miles + 34 hrs 1150°C	MMT	Close Coupled
Honda	100K miles	Base	Close Coupled
Honda	100K miles + 5 hrs 1150°C	Base	Close Coupled
Honda	100K miles + 10 hrs 1150°C	Base	Close Coupled
Honda	100K miles + 34 hrs 1150°C	Base	Close Coupled
Toyota	100K miles	MMT	Underbody
Toyota	100K miles + 24 hrs 1300°C	MMT	Underbody
Toyota	100K miles	Base	Underbody
Toyota	100K miles + 24 hrs 1300°C	Base	Underbody

Mn Conc.	1/32 g Mn/gal (8.3 mg Mn/L)
Baseline Fuel	Chevron ULCQ
Test Protocol	Catalysts and oxygen sensors from vehicles used in Waiver application testing were evaluated in slave vehicle tests. Some catalysts underwent additional aging, as shown in the table. Catalyst conversion efficiency, O_2 storage capacity and the dual catalyst monitor method were evaluated in a laboratory set-up using catalyst cores and synthetic exhaust.
Mileage Accumulation	100,000 miles during durability fleet testing
Emission Test Protocol	FTP using slave vehicle
Catalyst Technology	See table

Summary: This SAE paper presents follow-on results from Ethyl's 1993 waiver application addressing concerns about the effects of MMT on OBD systems. Emissions, catalyst conversion efficiency and oxygen sensors were evaluated to determine if the use of MMT alters the functionality of the components.

Slave vehicle testing was used to evaluate the catalysts and oxygen sensors from 6-1993 Toyota Camrys and 4-1992 Ford Crown Victorias (part of the 92/93 fleet vehicle testing) after 100k miles of accumulation with either base fuel or MMT fuel). FTP testing indicated average conversion efficiencies for THC, CO and NOx were better for MMT catalysts compared to the base fuel catalysts for both Crown Vics and Camrys. NO_x emissions from the Camrys were slightly higher with the MMT catalyst but lower in the Crown Vics. THC and CO emissions were lower from both vehicle types with the MMT catalyst. Evaluation of the oxygen sensors was done by comparing the mean emissions between tests with base sensors and MMT-aged sensors with original equipment. Results showed no emissions difference, indicating that use of MMT did not affect the operation of the O_2 sensors.

Catalyst cores were removed and evaluated in a laboratory setting. The cores were tested with new heated exhaust gas oxygen (HEGO) sensors, synthetic exhaust gas, and a set space velocity. Testing was set up similarly between the two types of catalysts from the different vehicle models, and showed that MMT did not adversely affect the O_2 sensors or degrade the O_2 storage capacity of the catalyst. The base and MMT catalysts followed the same general correlation between oxygen storage and hydrocarbon conversion efficiency.

Since previous work had shown that manganese oxide deposits build up preferentially on the front part of the catalyst, catalyst cores were shortened and evaluated. Results showed that the oxygen storage capacity relationships were the same between the base and MMT catalysts, indicating that deposits do not affect the oxygen storage capacity; and therefore do not affect the emission system components that influence catalyst monitor response by OBD.

1.4.7 Ref. No. 50: Roos, J.W. et al. 1997, Evaluation of On-Board Diagnostic Systems and the Impact of Gasoline Containing MMT (SAE 972849)

Sponsor/ Author Affiliation	Ethyl Corporation
Study Type	Primary
Vehicle Test Fleet Description	Two 1994 Ford 4.6L Thunderbirds
Mn Concentration	1/32 g Mn/gal (8.3 mg Mn/L)
Baseline Fuel	
Test Protocol	
Mileage Accumulation	65,000 mi
Emission Test Protocol	
Catalyst Technology	Thermally aged catalysts to set off MIL

Summary: The purpose of this study was to evaluate how MMT might affect OBD systems to result in an MIL illumination. First, new catalysts were thermally degraded using a high RPM cycle on a mileage accumulation dyno, followed by 50,000 miles of accumulation with MMT fuels. Catalyst performance was then evaluated via investigation of catalyst monitor response, oxygen storage capacity, and the correlation between oxygen storage capacity and converter efficiency. The study found that MMT did not contribute to the catalyst's O_2 storage capacity and did not corrupt the correlation between O_2 storage capacity and HC conversion efficiency or the response to the O_2 sensor.

1.4.8 Ref. No. 70: Roos, J.W., et al. 2000, Characterization of Combustion Products from the Fuel Additive MMT. (AWMA, June 2000)

Sponsor/ Author Affiliation	Ethyl Corporation
Study Type	Primary
Vehicle Test Fleet Description	18 Vehicles with previously accumulated mileage from emissions test fleet. Much of the results focused on particle measurements from a 1997 Ford Taurus with 40k miles.

Table 2. Test Vehicles used for Characterization of MMT Combustion Products.

Vehicle	Engine	Test Mileage	Fuel Economy (mpg)	Fuel Sulfur (ppm)	Tests
1992 Buick Regal	3.8 L V6	68,000	19	40	1
1992 Buick Regal	3.8 L V6	68,000	18	40	1,2
1993 Ford Escort	1.9 L I4	63,000	27	40	1
1993 Ford Escort	1.9 L I4	63,000	27	40	1,2
1993 Honda Civic TLEV	1.5 L I4	103,000	44	40	1,2
1993 Toyota Camry	2.2 L I4	103,000	23	40	1,2,5
1997 Ford Taurus A	3.0 L V6	40,000	22	335	1,2
1997 Ford Taurus B	3.0 L V6	40,000	22	335	1,2,3,4,5

1. Particulate sizing
2. Manganese speciation
3. Volatile and semi-volatile manganese compound evaluation
4. Manganese emission rate evaluation
5. Camry was also tested with a pipe in place of original catalyst. Taurus was also tested with an inactive catalyst in place of original catalyst.

Mn Concentration	8.3 mg Mn/L (1/32 g Mn/gal)
Baseline Fuel	
Test Protocol	See measurements from each vehicle in table
Mileage Accumulation	Variable, as shown in table.
Emission Test Protocol	UDDS with dilution tunnel
Catalyst Technology	

Summary: This study focused on particulate emissions and speciation of manganese from testing during mileage accumulation of the 92/93 Fleet (from the '93 waiver application information) along with a 1997 Ford Taurus. A series of tests were also conducted to detect volatile manganese.

Analysis of results found that approximately 13% of the manganese consumed during the UDDS was emitted from the vehicle, and most of this was found in the $PM_{2.5}$ fraction. This was very similar to results of previous studies. Speciation of the particles indicated that most of the manganese is in the form of divalent manganese; overall phosphate and sulfate were the dominate forms of the Mn. No volatile emissions of Mn were found. Additionally, the presence of an active three-way catalyst served to lower the particulate emissions. The study also showed that vehicle design and mileage accumulation had little impact on the distribution of manganese in different particle sizes.

A comparison of $PM_{2.5}$ results from other fleet studies based on driving cycles is provided in the paper. Another study in 1994 (Lynum, Ref. No. 37) showed that MMT not emitted in the exhaust is found in the engine components and oil. In 3-light duty trucks accumulating 20,000 miles on a test cycle designed to maximize Mn emissions, about 27% of the Mn was emitted in the exhaust, 12% was in the oil, 35% was in the engine, manifolds, exhaust pipe, and mufflers (most in the exhaust and mufflers), and 15-18% in the catalyst.

1.4.9 Ref. No. 71: Roos, J.W., et al. 2000 A Systems Approach to Improved Exhaust Catalyst Durability: The Role of the MMT Fuel Additive. (SAE 2000-01-1880)

Sponsor/ Author Affiliation	Ethyl Corporation
Study Type	Related to Waiver Application Testing
Vehicle Test Fleet Description	2 of each- 1992 Ford Crown Vic, 1993 TLEV Honda Civic, 1993 Toyota Camrys
Mn Concentration	8.3 mg Mn/L (1/32 g Mn/gal)
Baseline Fuel	Chevron ULCQ

Test Protocol	After emissions testing, catalyst cores were removed and subjected to conversion efficiency testing using simulated exhaust gas blends and analyzed using PIXIE or ICP/MS
Mileage Accumulation	100,000 miles after break in
Emission Test Protocol	For catalyst testing: Duplicate FTP testing for catalysts of Crown Vic and Camry in mileage accumulation vehicle, Civics in a slave vehicle.
Catalyst Technology	

Summary: Subsequent to mileage accumulation on vehicles during waiver application testing, three pairs of catalysts from vehicles with high mileage were analyzed to evaluate performance and deposits of Phosphorous and Manganese. FTP testing was first performed on the vehicles, followed by testing of catalyst cores using exhaust gas blends and laboratory analysis.

FTP testing showed that the MMT catalysts as a group displayed better CO and NO_x conversion, while conversion of HC was better in two out of three vehicles. The catalyst activity measured through exposure of catalyst cores to custom exhaust blends again showed some variability for HC activity between the vehicle models, while average CO activity was about 2.5% better for MMT vehicles, and NO_x activity was similar. Analysis of the cores showed that the front sections of the catalysts contained the highest Mn in the MMT catalysts, and the highest levels of Phosphorous in both catalysts. However, phosphorous deposition was lower for the MMT catalysts, suggesting that the formation of $MnPO_4$ during combustion acts to scavenge the phosphorous so that it is no longer available to deposit onto the catalyst. The deposition of Mn does not adversely affect the catalyst.

1.5 Ford 1991 Study

Ford conducted an 8-vehicle study with 1991 vehicles as described in the table. The results from this study were presented in a series of publications, each of which is summarized below.

Sponsor/ Author Affiliation	Ford Motor Co.
Study Type	Primary
Vehicle Test Fleet Description	4- 1991 production Escorts, 4- 1991 Explorers with 1993 production prototype engines
Mn Concentration	1/32 (0.029 g Mn/gal mentioned in SAE 912436)
Baseline Fuel	Chevron UL/CQ Unleaded
Test Protocol	5% city, 5% gravel, 20% rural, 70% highway, public roads with average speed 54 mph (all vehicles with routine scheduled maintenance)
Mileage Accumulation	105,000 mi (with first 5,000 miles of break in, 100k of mileage accumulation on test fuel).
Emission Test Protocol	5k, 20k, 55k, 85k, 105k Emissions testing using Indolene Clear on FTP (CVS-C/H excluding heat build and evaporative tests in the same chassis test cell), replicated 6 times per vehicle at each mileage interval; PM testing done using mileage accumulation fuel on a series of six repeated 3-phase tests to accumulate sufficient particulate. Regulated emissions were measured simultaneously.
Catalyst Technology	Escorts with single close mounted 92 in^3 TWC; Explorers with 2 underbody 75 in^3 TWC with two O_2 sensors.

1.5.1 Ref. No. 24: Hammerle, R.H., et al. 1991, Particulate Emissions from Current Model Vehicles Using Gasoline with Methylcyclopentadienyl Manganese Tricarbonyl (SAE 912436)

Summary: This interim report of the 1991 Ford Study presented results for particulate measurements taken at 5,000, 20,000 and 55,000 miles.

Results showed that 6-45% of the manganese used in the fuel was emitted as particulate matter, and that the total particulate matter emitted increased with mileage accumulation. It was hypothesized that the increase with mileage accumulation was due to an initial build up and subsequent stabilization of Mn-deposits. Total particulate mass emissions were generally between 0-2.0 mg/mi higher than for MMT-free vehicles, with an average of roughly 2 mg/mi for MMT-free fuel and 5 mg/mi for MMT fuel. These rates are well below the 80 mg/mi standard. 8% (5-11%) of the Mn was found in the engine oil. 50-80% of the Mn was unaccounted for in this study. It was concluded that this remaining Mn may be stored in the engine, catalyst and exhaust systems.

1.5.2 Ref. No. 25: Hurley, R.G., et al. 1991. The Effect on Emissions and Emission Component Durability by the Fuel Additives Methylcyclopentadienyl Manganese Tricarbonyl (MMT) (SAE 912437)

Summary: This interim report of the 1991 Ford Study presented results for exhaust gas measurements taken at 5,000, 20,000 and 55,000 miles.

Emissions testing was conducted on both feedgas and tailpipe samples. A modified paired t-test and statistical evaluation of all results indicated that MMT had a detrimental effect for both feedgas and tailpipe emissions of HC at both 15,000 and 50,000 miles. This was true for the entire fleet, as well as for the individual pairs of vehicles. On a fleet basis, a beneficial effect of MMT on CO emissions was seen through 50,000 miles. A beneficial effect of MMT was also seen on NO_x emissions at 15,000 miles, but the effect was detrimental at 50,000 miles. However, these CO and NO_x effects were not consistent between individual vehicle pairs.

1.5.3 Ref. No 28: Hurley, R.G. et al., 1992. The Effect of Mileage Emissions and Emission Component Durability by the Fuel Additive Methylcyclopentadienyl Manganese Tricarbonyl. (SAE 920730)

Summary: After completion of 105,000 miles of accumulation, a final paper on the effect on emissions and emission component durability was published, which included the initial analysis up to 50,000 miles. The detrimental effect of MMT on HC emissions seen in the interim report to 55,000 miles continued to 100,000 miles, and increased as mileage was accumulated. However, the MMT effects on CO and NO_x emissions were inconclusive.

In this work, a series of component switching tests were done in which the exhaust system components (HEGO sensors and catalysts) from the MMT-fueled vehicles were installed into the non-MMT vehicles and FTP emissions testing was performed in triplicate. When the MMT-fueled components were switched into the non-MMT vehicle, increases in HC emissions were observed, indicating impairment of both the oxygen sensors and the catalysts. In addition, a 15 micron thick layer of Mn_3O_4 was observed on the surface of the housing for the O_2 sensor.

Laboratory characterization of the catalysts showed manganese concentrations were higher at the inlet of the catalysts. In the Escorts, 6 wt.% of the manganese concentration was on the inlet of the catalyst, decreasing to 2 wt.% and 0.6 wt.% at the middle and outlet of the brick, respectively. In the Explorers, higher concentrations were seen on the first brick, with 2 wt.% on the inlet and 1 wt.% on the exit, while the second brick contained 1 wt.% and 0.4 wt.% on the inlet and exit, respectively. Other contaminants (such as Pb, S, P, Zn and Ca) were lower on the MMT exposed catalysts.

1.5.4 Ref. No. 29: Hammerle, R.H. et al., 1992. Effect of Mileage Accumulation on Particulate Emissions from Vehicles Using Gasoline with Methylcyclopentadienyl Manganese Tricarbonyl. (SAE 920731)

Summary: This publication focused on PM emissions from the emissions testing performed throughout the Ford Study. The paper presents follow-on results from SAE 912436 which presented interim PM measurements up to 55,000 miles of testing. While PM emissions from the MMT fuel were generally higher up to 55,000 miles, as reported previously (SAE Paper No. 912436), emissions from both the MMT and MMT-free vehicles dipped at 85,000 miles, and seemed to level off by 105,000 miles. Total PM emissions were up to 1.6 mg/mi higher from MMT vehicles vs. MMT-free vehicles. During the complete testing, anywhere from 5-45% of the Mn in the fuel was emitted as particulate matter, while 8% was found to be in the engine oil.

1.5.5 Ref. No. 31: Hubbard, C.P., et al. 1993, The Effect of MMT on the OBD-II Catalyst Efficiency Monitor. (SAE 932855)

To evaluate the deposition of Mn on catalysts, Ford carried out an additional laboratory analysis study on the catalysts from the Escorts used in the 1991 Ford Study, along with several other catalysts. This analysis involved measuring oxygen storage capacity of catalysts that had been aged in mileage accumulation tests, as well as oven-aged catalysts -- with or without MMT.

X-ray diffraction confirmed that Mn deposited onto the catalyst during combustion of MMT-containing fuels is mainly Mn_3O_4, which provides for an increased level of oxygen storage capacity in the catalyst. In addition, the response from the HEGO sensors is reduced. Together, the catalyst monitor’s ability to determine a malfunctioning catalyst is compromised.

1.6 Tier 1 Vehicles

1.6.1 Ref. No. 85: Roos, J.W. et al. 2002, Reformulating Gasoline for Lower Emissions Using the Fuel Additive MMT® (SAE 2002-01-2893)

Sponsor/ Author Affiliation	Ethyl Corporation
Study Type	Primary
Vehicle Test Fleet Description	Nine- 1997 Ford Crown Victorias, 4.6L designed to meet Tier 1
Mn Concentration	8.3 mg Mn/L (RFG-MMT) used RFG-1 with MTBE and lower ON streams to meet ON.
Baseline Fuel	RFG-1 is RFG blended with MTBE; RFG-3 is RFG with ethanol; all fuels are blended to the same ON.

Test Protocol	SMA mileage accumulation cycle
Mileage Accumulation	80,000 km (plus 16,000 km of break-in with Chevron gasoline; total 96,000 km.)
Emission Test Protocol	FTP testing with accumulation fuel and emission test fuel at the beginning and end of mileage accumulation.
Catalyst Technology	Close coupled (Tier 1)

Summary: In this work, Ethyl compared emissions systems performance of a fleet of vehicles with MMT blended fuel to other fuel formulations with like ON ratings. Their primary conclusion is that MMT provides improved emission system performance, which degrades quickly when using MTBE or ethanol as an oxygenate.

In Part 1 of this report, Ethyl presents the results of testing a fleet of nine vehicles, three vehicles each using one of three different fuel formulas blended to the same ON using MTBE, ethanol, or MMT and MTBE. Emissions testing was performed after a 16,000 km break-in period using a certification fuel, and again after 80,000 km of mileage accumulation. The HC and NOx emissions from each of the fleets were statistically similar, while the CO emissions from the MMT fleet were lower than the non-MMT fleets. Emissions from all fleets remained below applicable emission standards. The non-MMT fuels also displayed greater loss of HC and CO cold start conversion efficiency by the catalyst compared to the MMT fleet.

In Part 2, an additional six fuel types were tested in the nine vehicles. These different fuel formulations yielded similar changes in emissions levels in all three fleets. Additional testing was then done to evaluate emissions from the RFG-1 and RFG-MMT fuels. During this testing, the MMT fleet emitted significantly lower levels of HC, CO, NOx, benzene, N_2O and NH_3.

1.6.2 Ref. No. 92: Geivanidis, et. al. 2003. Effect on Exhaust Emissions by the Use of Methylcyclopentadienyl Manganese Tricarbonyl (MMT) Fuel Additive and Other Lead Replacement Gasolines.

<table>
<tr><td>Sponsor/ Author Affiliation</td><td>Ethyl Corporation</td></tr>
<tr><td>Study Type</td><td>Primary</td></tr>
<tr><td>Vehicle Test Fleet Description</td><td>Four vehicles:
<table>
<tr><th>Vehicle Description</th><th>Mileage (km)</th><th>Emission Std.</th></tr>
<tr><td>1. 1992 BMW 318i, with Catalyst</td><td>90,509</td><td>Euro 1</td></tr>
<tr><td>2. 2000 Opel Corsa with Catalyst</td><td>3,380</td><td>Euro 4</td></tr>
<tr><td>3. 1989 Seat Ibiza, no catalyst</td><td>141,767</td><td>ECE 1504</td></tr>
<tr><td>4. 1985 VW Golf II</td><td>159,350</td><td>ECE 1504</td></tr>
</table></td></tr>
<tr><td>Mn Concentration</td><td>Evaluated a total of 6 different leaded and unleaded replacement fuels: (LRG-1) super leaded gasoline in the EU market, (LRG-2) Unleaded gasoline containing MTBE and aromatics as RON boosters; (LRG-3)- LRG-2 with lowered MTBE compensated with MMT at 18 mg/L; (ULG-1 = LRG-4) avg. unleaded gasoline available in the market at time of testing; (ULG-2) LRG-3 MMT at 18 mg/L but with lower MTBE and lower RON; and (LRG-5 = ULG-3) ULG-1 with MMT splash blended to 18 mg/L.</td></tr>
</table>

Baseline Fuel	N/A
Test Protocol	Evaluate immediate effects on exhaust emissions of different fuel characteristics.
Mileage Accumulation	Variable, see table
Emission Test Protocol	Chassis dyno measurements on NEDC cycle; Catalyst equipped vehicles tested with each of the 3 ULG fuels described, Non-catalyst equipped vehicles were tested with each of the 5 LRG fuels.
Catalyst Technology	See vehicle description table.

Summary: This study was carried out to test the immediate emissions effects of different lead alternative gasoline blends. Regulated emissions, two non-regulated pollutants, and vehicle performance were measured on two catalyst equipped vehicles and two non-catalyst equipped vehicles. The different ULG fuels did not have any measurable effects on the emissions from catalyst vehicles or on fuel consumption. CO emissions from the 1992 BMW exceeded emissions standards with all of the ULG fuels, while the remaining pollutant emissions from both vehicles met the standards. There was no measureable effect on formaldehyde or benzene emissions.

Testing of the non-catalyst equipped cars on the 5 different LRG fuels (two of which had MMT at 18 mg/L) produced inconsistent results. The authors concluded that it was not possible to identify consistent trends and that no effect of the fuel type could by established. However, all of the testing resulted in emissions that were below or only marginally above the relevant emissions standards. Additionally, for the non-catalyst equipped vehicles, the shift from leaded to unleaded fuels resulted in an increase in benzene and formaldehyde emissions, attributable to the increased aromatics content of the lead replacement fuels.

1.7 AAM 2002 Study and Related Publications

1.7.1 Ref. No: 76 – Part 1 of the Alliance of Automobile Manufacturers Study on the Impact of MMT on Vehicle Emissions and Durability

Sponsor/ Author Affiliation	Alliance of Automobile Manufacturers
Study Type	Primary Study
Vehicle Test Fleet Description	40 vehicles, 10 models in 20 matched pairs

Table 2
Description of Test Vehicles

Make	Year	Model	Engine	No. Cyl.	Catalyst	Calib.
GM	1996	S10 Blazer #	4.3L	V6	1-UF	Tier 1
	1997	Cavalier	2.2L	L4	1-UF	TLEV
	1997	Saturn	1.9L DOHC	L4	CC+UF	TLEV
Daimler Chrysler	1996	Intrepid @	3.3L	V6	2-CC	TLEV
	1996	Neon @	2.0L	L4	1-CC	TLEV
	1996	Caravan @#	3.3L	V6	1-CC	TLEV
Ford	1997	Escort	2.0L	L4	1-CC	TLEV
	1996	Crown Victoria	4.6L	V8	2-CC+2-UF	TLEV
Honda	1996	Civic	1.6L	L4	1-CC	LEV
Toyota	1996	Corolla @	1.8L DOHC	L4	1-UF	Tier 1

@ 1997 OBD II system
\# Light-duty truck to accumulate mileage with 510 lb of ballast

Mn Conc.	1/32 g Mn/gal (8.3 mg Mn/L)
Baseline Fuel	Clear
Test Protocol	Test Track driving following SMA Cycle
Mileage Accumulation	50,000
Emission Test Protocol	FTP testing at 4, 15, 25, 35, and 50- thousand miles using California Phase 2 emissions certification test fuel without MMT. Both engine out and tailpipe emissions were tested.
Catalyst Technology	variable

Summary: The Study design was reviewed by an independent consultant from EPA (Maxwell Report, Appendix of Part 1 report, Report No. REM-MMT-96-01), who stated that the "emissions testing part is a well-designed program," and that the "Program design of using vehicles operating in pairs…will minimize variables and should allow statistically significant conclusions." The study found the following emissions effects of the MMT-containing fuel:

Emission	Tailpipe (avg. and statistical significance)	Engine Out
NMHC	13% higher between 4-50k mi. (avg., statistically significant)	Not statistically analyzed
THC	14% higher between 4-50k mi. (avg.)	
CO	6% higher between 4-50k mi. (statistically significant only at 50k mi.)	Same with both fuels
NO	10% lower between 4-50k mi. (statistically significant only at 50k mi.)	1% lower
CO_2	Varied 1% or less between 15-35 k mi.	
Cold CO –THC	12% higher	

Fuel economy was also found to be 0.1-0.5 mpg lower with MMT-fueled vehicles throughout the 50k interval (statistically significant only at 15 and 35k mi). Actual on-road fuel economy was about 0.2 mpg lower. Exhaust valve leakage (apparently due to manganese-containing deposits on the valve seats) occurred with one MMT-fueled model (Honda Civic), and spark plug misfire occurred in two MMT-fueled vehicles of one model (Chevy Cavalier) - likely due to Mn deposits on the spark plugs. The Honda Civics (one of the LEV models) running on MMT failed to meet emission certification limits for HC within 50k miles (and in-use limits at 75k mi).

The study concluded that “the use of MMT in fuel is likely to increase both engine-out and tailpipe emissions of hydrocarbons and will cause some vehicles to fail exhaust emission certification standards within 50 k miles.”

1.7.2 Ref. No 77; Part 2 of the Alliance of Automobile Manufacturers Study on the Impact of MMT on Vehicle Emissions and Durability - LEV Vehicles

1.7.3 Ref. No. 81: Benson J.D. and Dana, G. 2002. The Impact of MMT Gasoline Additive on Exhaust Emissions and Fuel Economy of Low Emission Vehicles (LEV). (SAE 2002-01-2894)

The results of Part 2 of the AAM study were presented in a final report, as well as in the SAE publication. The two will be summarized together in this section.

Sponsor/ Author Affiliation	Alliance of Automobile Manufacturers
Study Type	Primary
Vehicle Test Fleet Description	Two pairs of 5 LEV models: 4 each of the vehicles in two matched pairs from the following table, along with the Honda Civics from Part 1:

Table 1
Description of Test Vehicles

Make	Year	Model	Engine	No. Cyl.	Catalyst	Calib.
Volkswagen	1999	Beetle	2.0L	4	1-UF	LEV
Plymouth	1998	Breeze	2.0L	4	1-CC	LEV
Ford	1998	Escort	2.0L	4	1-CC	LEV
Chevrolet	1999	Tahoe	5.7L	8	2-UF	LEV

Mn Conc.	1/32 g Mn/ gal (8.3 mg Mn/L)
Baseline Fuel	Clear
Test Protocol	Test track using customer-type driving cycle; SMA cycle
Mileage Accumulation	75-100,000 miles
Emission Test Protocol	FTP testing at 4/15/25/35/50/75, and 100 k miles
Catalyst Technology	See table

Summary: The AAM study was extended in Part 2 to further evaluate how MMT would affect LEV-certified vehicles. In Part 2, sixteen 1998 or 1999 California-certified LEV’s (two pairs each of four models) accumulated 100k miles (using a SMA cycle on a test track) with one vehicle from each pair utilizing fuel with 1/32 g Mn/gal MMT. Emissions testing was performed at 4, 15, 25, 35, 50, 75, and 100k miles following similar protocols as in Part 1. The LEV vehicles from Part 1 (the Honda Civics) were included in the statistical analysis of results up to 75k miles.

The results from all vehicles were combined and a statistical analysis was performed to determine significant effects (meaning to a 5% significance level). Seven of the eight MMT-fueled vehicles exceeded NMOG emission certification standards, while only one of the clear-fueled vehicles exceeded the standard. At the end of the program, NMOG, CO, NOx and CO_2 emissions were all statistically significantly higher for the MMT-fueled vehicles.

Emissions effects of MMT-containing fuel:

Emission	Tailpipe	Engine	Notes
HC (between 4-100k mi)	9% higher	15 % higher	Both were significantly higher after 100 k mi
CO	Similar for first 75k miles, at 100k mi, CO was 14% higher	3% higher at 100 k miles	Differences were significant at 100 k miles
NO_x	Lower for first 75k miles, 24% higher at 100 k miles	No significant effect thru 100 k miles	
CO_2	Higher	Higher	Both higher throughout after 25k miles.

Other effects: Catalyst breakthrough of THC, CO and NOx was significantly higher for MMT fueled vehicles at 100 k miles. A/F ratios of the engine-out exhaust were consistently lower (fuel rich) for MMT-fueled vehicles beyond 15k miles. Engine out oxygen was consistently higher beyond 4000 miles for MMT fueled vehicles, suggesting a fuel-rich shift in air-fuel ratio.

City fuel economy was lower for all MMT fueled vehicles at mileages above 25,000 miles. On-road fuel economy measured during 100 k miles was lower by 0.6 mpg (6.3%) for MMT vehicles. Seven of the eight MMT vehicles from four light-duty LEV models (including the Civics from Phase 1) failed to meet emissions standards.

General conclusions: MMT is expected to increase engine-out and tailpipe HC emissions, and may cause rapid degradation of catalytic converters at high mileage, causing breakthrough of CO, THC and NOx.

1.7.4 Ref. No. 86: Roos, J.W., et al. 2002, A Peer-Reviewed Critical Analysis of SAE Paper 2002-01-2894 “The Impact of MMT Gasoline Additive on Exhaust Emissions and Fuel Economy of Low Emission Vehicles (LEV).” (SAE 2002-01-2903)

Ethyl responded to Part 2 of the AAM study and its related SAE publication in this SAE publication in 2002. They maintained that the mileage accumulation cycle used in the AAM study is not representative of consumer driving, being much more severe, and more similar to cycles that are used to age vehicle- or emission system components. They claimed that this cycle would more than double the deterioration rates of the catalyst compared to severe consumer use. Additionally, they pointed out the independent reviewer of the test protocol (Maxwell) had noted that the proposed mileage accumulation cycle was too severe.

Ethyl also noted that comparisons of fleet emissions from the AAM study were made to “certification standards,” rather than to “in-use standards.” When compared to appropriate in-use standards, all of the MMT vehicles passed, rather than 7 of 8 vehicles failing. [Note: “in-use standards” that Ethyl uses refers to criteria that a test fleet does not exceed 1.3 times the applicable standard with no more than 50% of the vehicles failing, following California LEV I Emission standards] Afton’s own analysis showed that on a fleet basis, no statistically significant differences occurred with any of the measured emission points, and confirmed that OBD and emission system performance were not harmed by MMT.

It was also pointed out that the differences in emissions and conversion efficiencies at 100,000 miles were driven by the Ford Escort fleet tested. Ethyl noted that these differences could be attributed to a series of mechanical problems, and pointed out inconsistencies in maintenance records, claiming that the MMT-fleet and the base fleet were given unequal treatment.

1.7.5 Ref. No. 91: Ethyl, 2003. A Critical Analysis of the Alliance of Automobile Manufacturer's MMT Study: Separating Fact From Fiction

1.7.6 Ref. No. 89: Cunningham, L.J, et al., 2003. AAM/AIAM Fleet Test Program: Analysis and Comments (SAE 2003-01-3287)

Ethyl hired Environ to evaluate and conduct statistical analysis on the results from the AAM study, and issued a report and an SAE publication on the findings. The summaries of these are included here. Many of the arguments presented in the previous paper (SAE 2002-01-2903) are duplicated here. However, additional statistical analyses of the results were also included.

After additional statistical analysis by Environ, Ethyl concluded that the results of the AAM study were misrepresented in three principal ways. First, the vehicle emissions were compared to inappropriate standards, and that all of the MMT-fueled vehicles met appropriate emissions standards. Second, inappropriate statistical analyses were applied to the data. Third, the AAM study misrepresented facts, particularly those regarding vehicle maintenance schedules.

Ethyl/ Environ issues with the test protocol:

In review of the test protocol used, Ethyl/Environ reiterated some concerns about the drive cycle and the severe mileage accumulation that were used, stating that "the accumulation procedure resulted in emission system deterioration more than twice the rate of the most extreme fraction observed with typical drivers." (From Environ Report) They provided an example showing that some severe driving cycles age vehicles by a factor of 2.5 (i.e., each mile driven is the equivalent of 2.5 miles of consumer use). By this metric, test vehicle emissions measured at 50k miles could reasonably be compared to 100k emissions standards.

The report also addressed inconsistencies in maintenance practices, claiming that at least three of the vehicle pairs showed preferential treatment of base-fueled vehicles (e.g. beneficial maintenance was performed on clear-fueled vehicles, while no maintenance was performed on MMT-fueled vehicles, or emissions changes were not linked to maintenance issues with MMT-fueled vehicles).

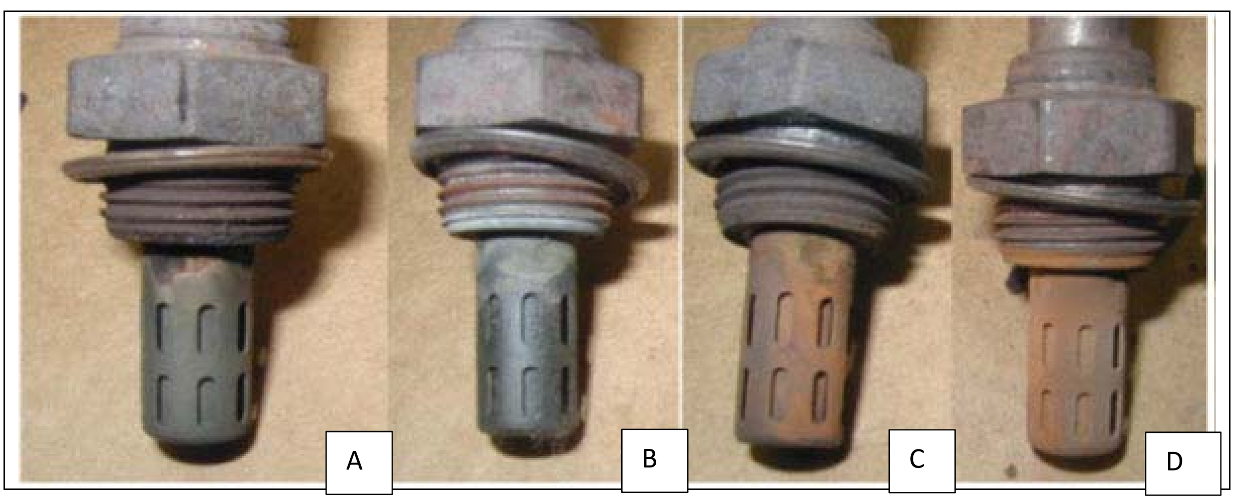
Ethyl also stated that "AAM inexplicably compare individual vehicle results against certification emissions standards even though certification standards only apply to 'new' motor vehicles." When the emissions of the LEV fleet are compared to the in-use emission standards, they easily comply. [Note: "in-use" as described here refers to test criteria in which a vehicle fleet of at least 10 vehicles is measured on average, and no more than 50% of the vehicles should exceed 1.3 times the emission limit.] It was also noted that differences in octane rating from MMT vs. clear fuel can contribute to emissions differences.

Environ conducted a separate statistical analysis, stating that the pairwise approach used in the AAM study failed to provide a direct estimate of variability within vehicle models. Statistical analyses were subdivided into vehicle type; 36 different statistical analyses for the Tier 1 vehicles showed no statistically significant difference in emissions.

1.7.7 Ref. No 100: McCabe, R.W., DiCicco, D.M, et al. 2004. Effects of MMT Fuel Additive on Emission System Components: Comparison of Clear- and MMT- fueled Escort Vehicles from the Alliance Study (Ford Post Mortem Analysis). (SAE 2004-01-1084)

Sponsor/ Author Affiliation	Ford Motor Company (SAE Paper 2004-01-1084)
Study Type	Secondary- Post Mortem Analysis of Escorts from AAM study
Vehicle Test Fleet Description	2- 1998 LEV Ford Escorts from AAM study
Mn Concentration	1/32 g Mn/gal (8.3 mg Mn/L)
Baseline Fuel	
Test Protocol	Mileage accumulation on SMA cycle (see AAM Part 2)
Mileage Accumulation	100 k miles
Emission Test Protocol	FTP cycle with systematic parts swapping
Catalyst Technology	400 cpsi (62 cells/cm^2), close coupled, 1.66L volume

Summary: Ford performed an additional analysis on one set of the Ford Escort vehicles from the Alliance study by systematically swapping parts and performing an additional 60 FTP emissions tests. The engine cylinder heads, spark plugs, O_2 sensors, and catalysts were swapped individually and in groups to identify the components that were responsible for the higher emissions seen in the Alliance study after 100,000 miles of accumulation. Within 90% confidence limits, all of the emissions difference between the MMT and clear-fueled vehicles could be accounted for by the parts selected for analysis. This study showed that: (1) increases in both engine out and tailpipe NMHC were attributable to the cylinder head and spark plugs (although OBD codes were not registered for misfire during emissions testing), (2) increases in CO were attributable to the MMT cylinder head, and (3) increases in NOx were attributed to the catalyst. Photographic evidence of the parts showed Mn deposits on the valves and spark plugs, and indicated that approximately 20% of the catalyst channels were blocked during high gas flow events.



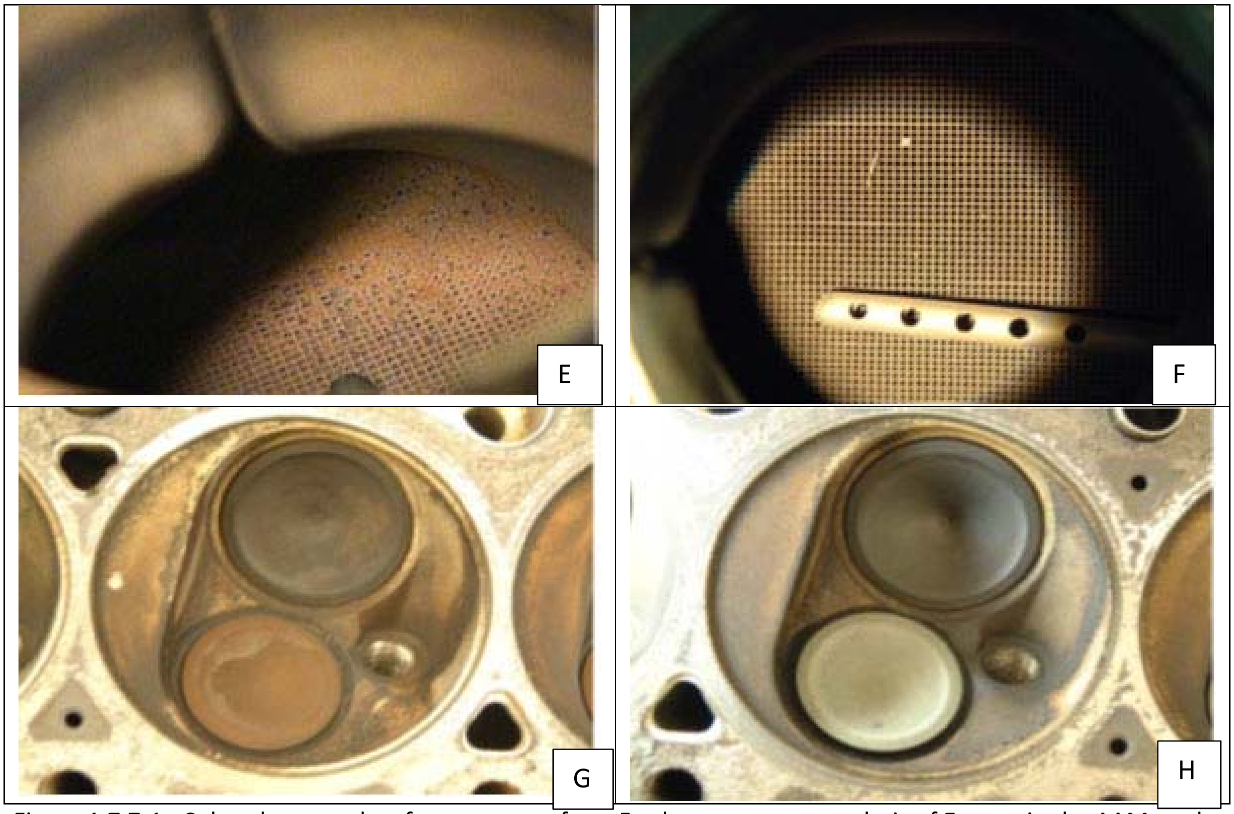


Figure 1.7.7-1: Color photographs of components from Ford post-mortem analysis of Escorts in the AAM study. "A" and "B" are HEGO sensors from behind and in front of the catalyst of the clear-fueled Escort, respectively. "C" and "D" are HEGO sensors from the rear and front of the MMT-fueled catalyst, respectively. "E" is the catalyst from the MMT vehicle with 20% plugging of channels, "F" is the catalyst from the clear-fueled vehicle. "G" and "H" are the cylinder head with inlet and exhaust valves from the MMT and clear-fueled vehicles, respectively.

1.7.8 Ref. No. 103: Boone, W.P., 2005. Effect of MMT Fuel Additive on Emission System Components: Detailed Parts Analysis from Clear and MMT-Fueled Escort Vehicles from the Alliance Study. (SAE 2005-01-1108)

Sponsor/ Author Affiliation	Ford Motor Company
Study Type	Secondary- Post Mortem Analysis of Escorts from AAM study
Vehicle Test Fleet Description	2- 1998 Ford Escorts from AAM Study
Mn Concentration	1/32 g Mn/ gal (8.3 mg Mn/L)
Baseline Fuel	
Test Protocol	Mileage accumulation on SMA cycle (see AAM Part 2)
Mileage Accumulation	100,000 mi
Emission Test Protocol	FTP cycle with systematic parts swapping
Catalyst Technology	400 cpsi (62 cells/cm^2), close coupled, 1.66L volume

Summary: This 2005 study provided follow on from the Ford Post-mortem analysis of the Ford Escorts evaluated in the AAM study (SAE Paper No. 2004-01-1084). Further analysis of the cylinder head, spark plugs, oxygen sensors and catalysts was performed to identify the reasons for each part's role in affecting emissions increases experienced in the AAM study. In addition, laboratory analysis (XRD and EDX) was conducted on the intake and exhaust valves, the fuel injectors, and EGR valves from the cylinder head to characterize deposits. In addition to the post-mortem results published in SAE Paper No. 2004-01-1084, the study concluded that the HEGO (O_2) sensors and spark plugs had Manganese deposits on them, although neither affected the vehicle emissions or performance. The Mn-deposits on the catalyst also did not affect the HC or CO emissions. The study found that the increase in NMHC emissions were primarily due to leakage through the exhaust valves, resulting in increased feed gas levels. The observed increases in CO were due to rich shifts in the air/fuel ratio, attributable to deposits on the intake and exhaust valve coats. The increase in NOx emissions observed from the vehicles during the AAM testing was attributed to blockage of channels in the catalyst with Mn-containing material. The blocked channels resulted in increased space velocity, which caused higher Nox breakthrough

1.7.9 Ref. No. 79: Air Improvement Resource, 2002. Effects of MMT in Gasoline on Emissions from On-Road Motor Vehicles in Canada

Summary: AIR used emissions results from the AAM 2002 Part 1 and Part 2 studies to model on-road emissions in Canada from 1995-2020. The emissions analyses were done by grouping the vehicles used in Part 1 and Part 2 into like categories and performing a statistical analysis of the results. The emissions were input to EPA's MOBILE5 model to project two cases of MMT use with 100% market penetration (current market penetration of MMT was at 90%). Case 1 was at a base MMT concentration of 0.031 g Mn/gal (the amount used in the AAM study) at 100% penetration. In Case 2, the MMT use was adjusted to reflect the average Canadian concentration. Model projections predicted that by 2010, fleet-wide Nox emissions would be lower when MMT is used, but VOC and CO would increase. However, by 2020, all emissions would be higher if MMT were used. The study concluded that if MMT were not discontinued before NLEV and Tier 2 vehicles come into widespread use, VOC, CO and Nox emissions in Canada may be significantly higher than anticipated in Environment Canada's planning inventories. Furthermore, use of MMT could significantly increase costs for vehicle owners and manufacturers due to adverse impacts on emissions control systems.

2 SUMMARY OF STUDIES RELATED TO TIER 2 AND SIMILAR TECHNOLOGIES

2.1 Fleet and Engine Studies by Afton

2.1.1 Ref. No. 105: Cunningham, L.J. et al. 2005, Assessing High-Cell Density Catalyst Durability with MMT® Fuel Additive in Severe Driving Conditions. (SAE 2005-01-3840)

Sponsor/ Author Affiliation	Afton Chemical Corporation
Study Type	Primary
Vehicle Test Fleet Description	2 pairs of 2003 VW Passats and Opel Corsas (8 vehicles)
Mn Concentration	18 mg Mn/L
Baseline Fuel	Locally supplied unleaded gasoline
Test Protocol	Severe service; mixed city and highway driving in and around Barcelona, Spain with additional high-speed driving on a test track.
Mileage Accumulation	100,000 km with 7,000 km of break in using base fuel.
Emission Test Protocol	ECE/EUDC at 20k, 40k, 60k, 80k, and 100k- km

Catalyst Technology	Certified to Euro 4 standards; High cell density (>400 cpsi) close-couple manifold mounted.

Summary: Afton conducted this test to determine the emission system durability of vehicles equipped to meet Euro 4 standards. Mileage accumulation included mixed city and highway driving as well as on a test track to represent severe driving for European standards. Vehicles were first paired so that average emissions were as close as possible after the break-in period.

Emissions results: Results showed that the emissions systems performed well. Each of the vehicles easily met the OBD threshold for NO_x, CO and HC, and all the MMT®-fueled vehicles met the Euro 4 certification standards for all regulated pollutants. A vehicle-by-vehicle comparison can be made from the data presented in the publication figures. These figures show that the base-fueled vehicles exceeded performance standards for NO_x more frequently than did the MMT-fueled vehicles. However, HC emissions were slightly higher for the MMT-fueled vehicles, and CO emissions increased more for the MMT-fueled vehicles as mileage increased.

The authors concluded that MMT is compatible with vehicles equipped with HCD/CC catalysts, and that all vehicles easily met in-service emissions standards and remained well below the OBD threshold. It was also concluded that the results of this study are comparable to previous test programs conducted in the 1980's and 1990's, and demonstrate that MMT has not adversely affected evolving emission control technologies, as illustrated in the figure below, taken from the report.

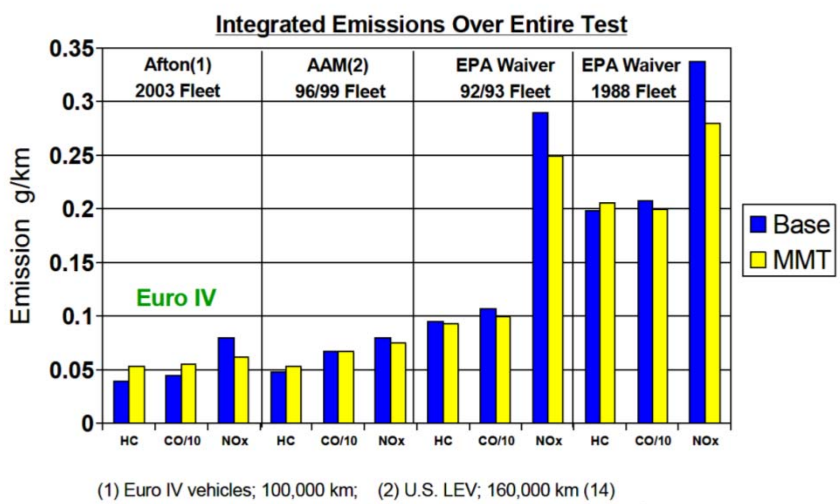


Figure 2.1.1-1: Integrated emissions over various test programs. (Note that the data portrayed from the AAM fleet reflects Afton's own analysis and interpretation of the data set.)

2.1.2 Ref. No. 109: Afton, 2006. A Report on the Results of Alternative Tier 2 Testing for the Characterization of Particulate from Vehicles Using the Gasoline Additive MMT® in the Fuel.

Sponsor/ Author Affiliation	Afton Chemical Corporation
Study Type	Primary
Vehicle Test Fleet Description	Two-2003 Corollas (ULEV) with 600 cpsi catalysts; Two-2003 Chevy Silverado 2WD pickups (Tier 1-LDV) with 400 cpsi under floor; Two-

	1997 Tauruses (Tier 1, with 66k mi).
Mn Concentration	0.03125 g Mn/gal (1/32 g Mn/gal; 8.3 mg Mn/L)
Baseline Fuel	Halterman HF-04337 EE fuel with 30 ppm sulfur
Test Protocol	SMA mileage accumulation on dyno
Mileage Accumulation	50,000 (+ add'l 5k break in.)
Emission Test Protocol	5k, 25k, 50k, Particulate (PM 2.5, 10, and TSP) on emissions dyno using REM01 / REP05 cycle
Catalyst Technology	

Summary: Afton conducted this testing to measure manganese emission rates and better characterize particulate speciation of Mn-tailpipe emissions from Tier 2 vehicles. This was done in response to a request from EPA to determine how much manganese is exhausted from the vehicle, and the chemical form of that manganese.

The atomic percentages of Mn collected on $PM_{2.5}$ filters ranged from 0.4 to 3.8, in comparison to 0.8-1.9 determined in an earlier Afton study conducted in 1997. This accounts for about 1-5% of the manganese in the fuel that is emitted as respirable particulate, with the bulk of the Mn emitted as TSP. In total, 9-20% of the Mn in the fuel is emitted from the tailpipe (with an average of about 13.3%) , which is mainly manganese phosphates (in the form of Hureaulite [$Mn_5(PO_4)_2(PO_3OH)_2 \cdot 4H_2O$]) with smaller amounts of $MnSO_4$ and Mn_3O_4. Therefore, it was concluded that 86.7% remains in the engine and exhaust systems.

2.1.3 Ref. No. 116: Roos, J.W. et al. 2007, The Interaction of MMT Combustion Products with the Exhaust Catalyst Face. (SAE Paper No. 2007-01-1078)

Sponsor/ Author Affiliation	Afton Chemical Corp.
Study Type	Primary with review of other studies (mostly Ethyl studies)
Vehicle Test Fleet Description	1996 Honda Civic LEV (with 400 cpsi catalyst), 2003 Honda Civic and Toyota Corolla ULEV vehicles (with 600 cpsi cat) (all with previously accumulated mileage between 75-100k); Engine Test Procedure: Ford 4.6L V8 engine on dyno test cell, paired with new catalysts using 400, 600, 900 cpsi with two different quantities of Mn
Mn Concentration	Mn concentration: 8.3 and 18 mg Mn/L
Baseline Fuel	Chevron ULCQ
Test Protocol	Vehicle test procedure performed on a chassis dyno using first 505 seconds of UDDS cycle to simulate cold start and AAM cycle (used as mileage accumulation cycle in AAM study) for high temperature severity. In the Engine testing procedures, exhaust gas temperatures and pressure drop across the catalyst were measured. A repeating cycle of 5 min of steady state operation at a baseline exhaust temperature (820°C) with a one minute fuel cut (to simulate throttle closing or vehicle stopping as a particle detachment event)
Mileage Accumulation	Up to 300 hours
Emission Test Protocol	None
Catalyst Technology	400, 600, 900 cpsi

Summary: This paper provides background on the historical changes of catalytic converters, and references effects of MMT on historical catalysts (many of the studies referenced were from Ethyl/

Afton). It also explains why manganese-containing particles should not affect monolithic catalysts. For example, the mass median size of manganese-containing particles is around 0.5 µm, leading to particle to catalytic cell opening ratios of 1:2200 and 1:1900 for 400 cpsi and 600 cpsi catalysts, respectively. Therefore, the opening should not prevent passage of particulates. The authors also state that the thinner walls of higher cpsi catalysts provide less surface area on the catalyst face for particles to collect (although, this statement seems to be counter-presented later in the paper, as experimental work shows that higher cpsi catalysts exhibit more rapid pressure drop). The paper also reports that only about 1-6% of the manganese is deposited as particles on the catalyst face, and that this deposit improves catalyst efficiency due to a reduction in phosphorous poisoning.

The vehicle testing procedure was used to investigate mechanisms of MMT combustion product interactions with the catalyst by measuring exhaust gas temperatures under different types of vehicle operation for ULEV and LEV vehicles. This vehicle testing portion concluded that peak temperatures were higher using the "AAM" cycle, and that ULEV vehicles tested did not generally operate at higher exhaust gas temperatures than the LEV vehicle, even under severe operating conditions.

Following this testing, new catalysts were evaluated in an engine test cell, coupled with a Ford 4.6L V8 engine. New 400 and 600 cpsi catalysts were from the 1996 and 2003 Honda Civics, respectively, and 900 cpsi catalysts were evaluated from a 2003 Ford Crown Victoria while measuring the pressure drop across the catalyst. Parametric analysis was conducted to evaluate the effects of MMT concentration (at 8.3 or 18 mg Mn/L) and exhaust gas temperature (750^{o}C, 800^{o}C and 870^{o}C) on each of the three different catalyst cell densities. Baseline experimentation at a constant temperature showed that the elimination of particle detachment forces (such as thermal cycling from turning the vehicle on and off, thermal changes from acceleration and deceleration and vibrations in normal vehicle operation) result in pressure increase even without MMT, and that higher cell density converters experience a higher rate of particle impact that results in an increased rate of pressure drop. Similar testing on a 400 cpsi catalyst with MMT at 18 mg/L showed increased pressure drop with a shorter duration in comparison to no MMT, with an exponential rise after about 100 hours. However, when a fuel cut procedure was included in the test cycle to simulate a particle detachment force, the pressure drop increase associated with either fuel blend is reduced dramatically to almost no increase over 160 hours of testing for both 400 and 600 cpsi catalysts when MMT was used. The fuel cut, which occurred every 5 minutes for either 20 or 60 seconds, reduced the exhaust gas temperature by about 250^{o}C and 500^{o}C, respectively.

The effects on catalysts of different densities were also evaluated at a set temperature of 800^{o}C, using MMT at 18 mg Mn/L, and no detachment forces. Higher cell density catalysts plugged much more rapidly than lower cell density, with the 900 cpsi catalyst reaching a doubling of pressure drop at about 75 hours while the 600 and 400 cpsi catalysts reached the same metric at 110 and 130 hours, respectively. This result was consistent with those seen in the Honda study, and it was noted that rates were similar when no MMT was used. Two figures are provided below for comparison. Note the differences in scale. Comparison of treat rates of MMT, however, indicated that increasing the treat rate from 8.3 to 18 mg Mn/L doubles the rate at which an increase in converter pressure drop is observed for both 400 and 600 cpsi converters. An analysis on exhaust temperatures also showed strong correlations, with doubling in pressure drop measured at 60 hours, 130 hours and 230 hours each at temperatures of 870°C, 800°C, and 750°C when using MMT at 18 mg Mn/L. The study concluded that in the absence of particle detachment forces, catalyst cell density, MMT concentration and exhaust gas temperature all have an effect on catalyst plugging (measured by pressure drop). However, when sufficient particle detachment forces are introduced, an increase in pressure drop is not measured.

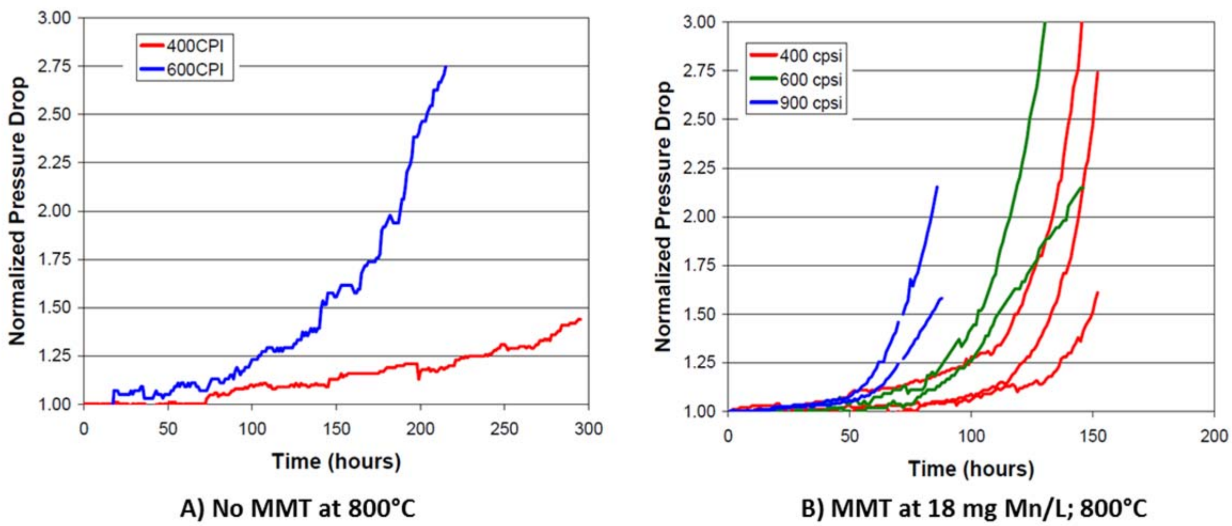


Figure 2.1.3-1: Changes in pressure drop across various cell density catalysts at 800°C without MMT (Fig. A) and with MMT at 18 mg Mn/L (Fig. B). Note the differences in time scales. (From Roos et al., 2007)

2.2 Automaker Studies

2.2.1 Ref. No. 99: AAM, 2004, MMT's Impact on Vehicles: The Perspective of the Global Auto Industry.

Summary: This presentation was given in Beijing in 2004, and is a compilation of the auto industry's perspective on the use of MMT at that time. None of the references discussed in the presentation are cited. The presentation first gives a brief history of the use of MMT and the evolution of exhaust emission systems up to Tier 2.

The presentation discusses complaints about problems from MMT's use in Canada, and describes many consumer complaints about higher fuel consumption, lack of power, increase in OBD alerts, and a higher number of vehicles needing new catalysts (again, this information is not referenced). Manufacturers found that catalyst failure rates are much higher in Canada than in the U.S., indicating significant impacts on real-world emissions and costs to the consumers. They also claim that impacts become more severe as vehicle technologies advance and that failures in catalysts occur much more rapidly with LEV or Euro 3 emission control systems. They forecast that increased use of high cell density/close-coupled (HCD/C)C catalysts will be more likely to plug from higher exhaust temperatures because Mn_3O_4 forms under these conditions (≥715°C).

The presentation also summarizes results from the AAM study in 2002 (primarily focused on Part 2 results from LEVs) and concludes with recommendations that China conduct its own MMT study.

2.2.2 Ref. No. 102: Schindler, 2004. Impact of MMT on Vehicle Emission Performance

Summary: This highly cited presentation provides a summary of the Volkswagen experience in China at the Asian Vehicle Emission Control Conference in Beijing in April, 2004. The presentation provides little background on the test program and no supporting information. It was reported that endurance tests in China caused spark plug fouling, catalyst plugging, Mn deposits in exhaust system and combustion chambers, deposits and wear on piston rings and grooves, and poisoning of the lambda sensor. The results were supported primarily with photographs used in the presentation. It was concluded that adverse effects seen with use of MMT are contrary to air quality objectives, and that MMT should be banned.

2.2.3 Ref. No. 117: Shimizu, C. et al., 2007. Parametric Analysis of Catalytic Converter Plugging Caused by Manganese-Based Gasoline Additives. (SAE 2007-01-1070)

Sponsor/ Author Affiliation	Honda
Study Type	Primary
Vehicle Test Fleet Description	Engine dynamometer testing
Mn Concentration	8.3 mg Mn /L (1/32 g Mn/gal)
Baseline Fuel	
Test Protocol	parametric analysis using engine dynamometer testing at constant speed and constant load
Mileage Accumulation	
Emission Test Protocol	
Catalyst Technology	

Summary: In this study by Honda, engine dynamometer testing was done to evaluate the influence of exhaust gas temperature, catalyst cell density, exhaust system configuration and manganese on catalytic converter deposits and plugging. Engine dynamometer testing was conducted at three different exhaust gas temperatures (600, 715, 805^{0}C) and 5 angles of incidence of the exhaust gas to the converter inlet surface (30^0, 45^0, 60^0, 70^0, and 90^0) using two different catalyst cell densities (400 and 600 cpsi) and three different catalyst layouts. All three parameters studied were found to play a role in the rate of catalyst plugging. Higher cell density catalysts plugged more rapidly (at a constant exhaust temperature of 805^{0}C), although the influence of the exhaust manifold configuration was found to have a greater effect. As the angle of incidence became sharper (similar to close-coupled catalysts), the rate of plugging increased. At the sharpest angle of incidence (30^0), the converter became completely plugged after 275 hours of operation.

These observations demonstrate that the angle of incidence has significant influence on how quickly deposits form and grow. With a sharper angle of incidence, the growth direction of deposits leads to easier cross-linking between cell walls resulting in more rapid plugging from the manganese oxides. Plugging speed also increased by 36% with an increase in temperature from 715^{0}C to 805^{0}C. This Honda study demonstrated that higher cell densities and close coupled catalysts, two of the key technologies utilized to meet more stringent standards, are more susceptible to plugging by MMT due to the layout and exposure to high temperatures, which results in a more adhesive behavior of the Mn_3O_4 deposits. It was concluded that a close-coupled catalytic converter layout exposed to high temperature exhaust with high cell density configuration is more prone to plugging by MMT.

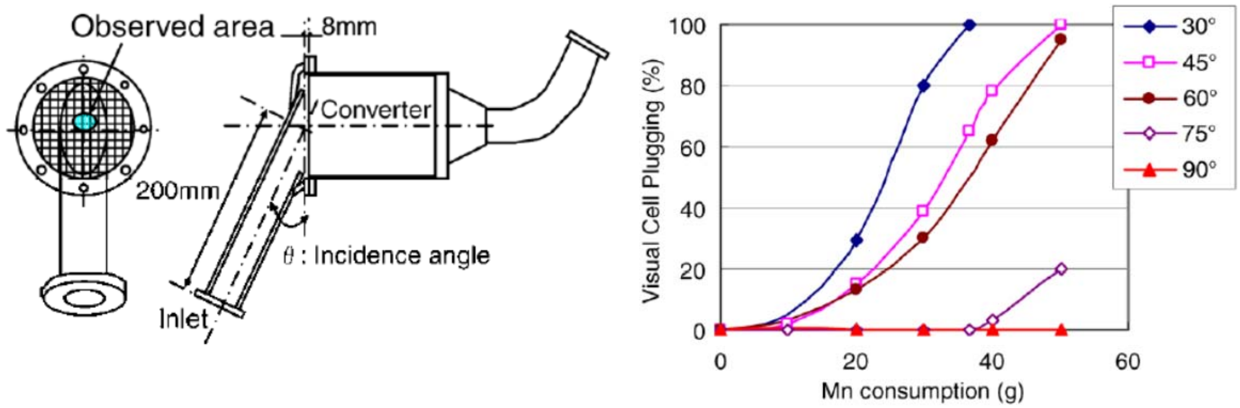


Figure 2.2.3-1: Layout of catalytic converter with exhuast inlet and incidence angle; observed rate of plugging with different angle of incidence.

2.2.4 Ref. No. 127: Gidney, J.T. et al., 2010. Effect of Organometallic Fuel Additives on Nanoparticle Emissions from a Gasoline Passenger Car. (Johnson Matthey Study) (Env. Sci. & Pol. Vol. 44)

Sponsor/ Author Affiliation	Johnson Matthey
Study Type	Primary
Vehicle Test Fleet Description	Single 1.6L 4 Cylinder SI engines meets Euro Stage 3 emissions standards from 2000-2005
Mn Concentration	8.3 and 18 mg Mn/L (Also, Fe at 8.4 mg/L and Pb at 31.3 mg/L)
Baseline Fuel	Standard gasoline with 50 ppm Sulfur
Test Protocol	Chassis-dyno testing
Mileage Accumulation	Vehicle previously had 11,000 mi (17,703 km). Then fitted with new TWC and driven 4000 miles using mixed driving patterns before present testing.
Emission Test Protocol	ECE and EUDC
Catalyst Technology	

Summary: This study evaluated particle sizes in exhaust from vehicles fueled with low levels of Pb, Fe and Mn organometallic additives. The study showed that the presence of metal-containing species increased particle concentrations in the nucleation mode, where most of the number emissions are found. Higher amounts of manganese increased particle concentrations, resulting in higher number concentration than use of Fe or Pb.

2.3 Porsche Study and Response by Afton

2.3.1 Ref. No: 107: Richter, H., 2005. Influence of Ash-Forming Additives such as MMT ® on Exhaust Emissions and Performance Characteristics of PC-Engines (Porsche Study)

Sponsor/ Author Affiliation	Porsche
Study Type	Primary "Porsche Study"

Vehicle Test Fleet Description	2- 2004 Porsche Carrera Engines
Mn Concentration	15 mg Mn/L
Baseline Fuel	Super Plus (with detergent additives)
Test Protocol	Engine dynamometer testing; 20 hour conditioning on Durability Test Cycle
Mileage Accumulation	179 hours of endurance testing (equating to ~60,000 km based on the amount of fuel consumed)
Emission Test Protocol	EU emission test on engine test bench with super plus after 20-hour break-in, after 100 hours of durability, and after 179 hours of durability. Also, vehicle testing on rolls after break in and after 179 hours of durability using EU-Ref fuel on the MMT vehicle only
Catalyst Technology	two 400 cpsi catalysts arranged as cascade with short distance between each other  Figure: Porsche Carrera catalyst layout

A laboratory study was conducted by a consortium of European automobile manufacturers (Audi, BMW, Daimler Chrysler, Porsche, and VW- referred to as the "Porsche Study"), in which two 2004 Porsche Carrera engines with the complete exhaust gas systems were evaluated on an engine test bench to compare the use of MMT at 15 mg Mn/L to Super Plus gasoline in the European market. The emission control system in each vehicle consisted of two 400 cpsi metal substrate catalysts for each of the two cylinder banks in the engine, arranged with a short distance between each other.

Emission testing was conducted on the identical engines after a 20-hour break in period using Super Plus with no-MMT, then after 100 hours of durability testing on clear or MMT fuel, then after a total of 179 hours or durability testing. The 179 hours of durability testing was conducted using a 1-hour test including engine idle, low load, and high load freeway driving, which was assumed to be favorable for MMT since its relatively high engine loads and exhaust gas-flow would not favor the formation of deposits. It was estimated that according to the amount of fuel consumed, 179 hours of durability testing corresponded to 60,000 km of driving. Maximum exhaust temperatures of the cycle ranged between 310^{o}C at idle (10 min) and 910^{o} C at high load (30 min). The maximum temperatures in the washcoat of the starter catalyst was about 1075°C with both fuels. Vehicle testing was also conducted on rolls after break in and after 179 hours of durability using EU-Ref fuel on the MMT engine only in a Porsche Carrera.

After the initial 20-hour break-in, emission and performance testing on the engines showed similar behavior. After 100-hours of durability testing, the MMT and base fueled engines showed similar emissions behavior. The CO and NO_x in particular did not show any fuel-specific changes.   However, after 179-hours of testing, the HC emissions were more than 50% higher when using MMT compared to Super Plus, exceeding the Euro IV standard. This increase was attributed to increase in manganese-oxide deposits on the combustion chamber walls and spark plugs due to significant differences in engine-out emissions (compared to those measured after the catalytic converter, 30% higher engine out emissions when using MMT compared to Super plus). Measurements taken in the first phase of the EU test cycle (ECE test) also showed higher HC exhaust emissions after 179 hours, indicating that MMT deposits contributed to slow lighting-off during cold starts.

Additional testing of the MMT-engine after 179-hours of testing was conducted by first installing the catalyst and oxygen sensors in a Porsche Carrera vehicle and testing on a chassis dyno to test the thermal ageing and deactivation of the catalysts. Comparison between the MMT and SuperPlus catalysts showed only a small difference in HC emissions (about 10%). Subsequently, the MMT-engine was installed along with its respective catalyst and oxygen sensors (this did not occur for the base fueled engine). This vehicle testing confirmed the engine exhaust tests, showing that HC emissions increased by 54%, relative to the base testing, exceeding the EU-4 limit by 11%. Comparison between the MMT engine and slave engine tests showed a strong influence of increased emissions resulting from the engine. A 5% loss of engine power and 3% decrease in maximum torque were observed, along with 6% higher exhaust gas back pressures and 5% higher specific fuel consumption. The oxygen sensors were not impaired, and MMT showed no effect on O_2 storage capacity, but Mn deposits were present throughout the combustion chamber and exhaust system, as illustrated in the figures below.

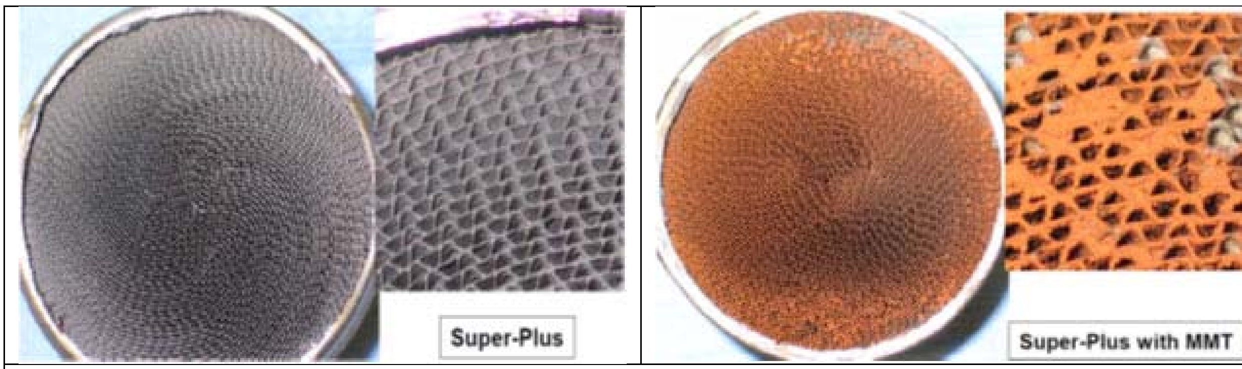


Figure 2.3.1-1: Color photographs of the Front face of the starter catalysts after durability testing with Super-Plus without and with MMT. Analyses performed showed Mn content of 6.4% in the washcoat of the front face catalyst and 1.7% in that of the main catalysts. Catalysts with Super-Plus with no MMT had no Mn deposits in the catalyst coatings.

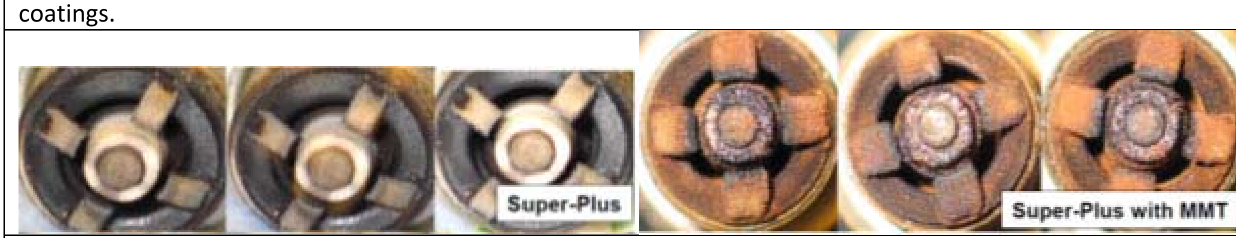


Figure 2.3.1-2: Color photographs of spark plugs after endurance testing

2.3.2 Ref. No: 108: Afton Chemical Co., 2005. Response to New Automobile-Industry Sponsored Test of the Effects of MMT® in Vehicles Designed to Meet Euro-IV Emission Standards

Summary: In response to the 2005 study published by Porsche, Afton prepared this report claiming errors in the testing that was performed, which caused increased emissions from the engines fueled with MMT after 179 hours of durability testing. Their arguments are as follows:

1. The durability cycle chosen is not representative of real world driving. Although in the report it was stated that the cycle selected was expected to be favorable for MMT and did not favor the build-up of Mn-deposits on the catalyst, Afton maintained that the cycle is not representative of real world driving conditions. For a 179-hour test to result in approximately 60,000 km of travel (assuming 17% time at idle), a driver would have to drive an average speed of 400 kph.

2. It was pointed out that the emissions standards that were exceeded for HC are type approval standards, not in-service conformity standards. In service conformity requirements in the EU, as described by Afton, preclude testing of any vehicle that has been subjected to overly sever service. In addition, in-service conformity defines "outlying emitters" that exceed 1.5 times the type approval standard. The Porsche did not exceed this threshold limit.

3. The fuels with and without MMT appeared to have different characteristics. In most other studies, fuel spec comparisons show slight differences in ON, but no significant difference in other fuel properties. In the Porsche study, there are differences in many other fuel properties. For example, the MMT-treated fuel had 2.3 % higher density (0.7687 vs. 0.7514 kg/L), 430% higher sulfur (11.6 vs. 2.7 mg/kg) and 23% higher aromatics content (39.8 vs. 32.3 vol.%).

4. The two Porsche engines experienced different exhaust temperatures during break-in testing. Due to a 15-30^{o}C higher temperature seen for the MMT engine, the MMT catalyst likely experienced higher thermal degradation, which could contribute a 35%-80% increase in the rate of catalyst deterioration.

2.4 In-Use Surveys

2.4.1 Ref. No: 113: Meffert, M.W., 2006. Evaluation of Factors Affecting Vehicle Emissions Compliance Using Regional Inspection and Maintenance Program Data. (SAE 2006-01-3406)

Sponsor/ Author Affiliation	Afton Chemical Corporation
Study Type	Primary
Vehicle Test Fleet Description	In use vehicle I/M program
Mn Concentration	British Columbia average in Canada (1996-2003)
Baseline Fuel	Wisconsin, Arizona, Illinois Average in U.S (zero)
Test Protocol	Comparison of I/M data from IM240 testing

Summary: This work focused on comparing compliance of inspection and maintenance (I/M) data using IM240 testing cycles in Canada (BC) and the US (Wisconsin, Arizona, Illinois) between 1996 (when OBD-II and Tier 1 standards were implemented) through 2003 (when MMT was phased out in Canada). Based upon failure rate comparisons between the two regions, it was concluded that MMT is compatible with vehicles having advanced emission control technologies. The study evaluated the I/M data using different criteria:

First, Afton focused on 1998 Honda Civics and 1999 Proteges, which had high I/M failure rates. This illustrated that IM240 testing is capable of identifying vehicles that have component or performance issues. However, because the failure rates were similar between the two regions, these failures should not be attributed to use of MMT in Canada. The study also compared failure rates among all 1996+ models. This comparison included about 100,000 vehicles in BC, 150,000 in Wisconsin, and 350,000 in Illinois. No consistent, significant differences in failures rates were found among these vehicles. This was taken to indicate that MMT did not affect operation or deterioration of emissions control systems or components.

Afton also evaluated vehicles that were included in the 2002 AAM study, by pulling those specific make/ model/year vehicles from the I/M database. A comparison of all 1996 vehicles, which had an average mileage accumulation of 60-k miles, showed that the failure rate in Wisconsin was higher than that in BC (3.23% vs. 2.23%). 1998 Ford Escorts also had a higher failure rate in the US (1.9% in Wisconsin vs. 1.1% in BC). A separate evaluation of 1996 Ford Crown Victorias was performed, since many of these vehicles are used for taxis or police cars. After removing taxis (those accumulating greater than 25-k miles per year), failure rates were similar (note, average mileage ~65k miles). The failure rates of the taxis were much higher in Canada than in the US (73% vs. 33%), albeit with mileage accumulation almost twice as high in Canada.

The study also focused on vehicles that were capable of meeting Tier 2 standards, and compared model year 2000 and 2001 “Tier 2-capable” vehicles (although these data could not be compared to US data because of a shift to OBD testing). 2000 MY vehicles tested in 2002 (with 21,500 average mileage accumulation) had a failure rate of 0.1%. 2001 MY vehicles tested in 2003 had a failure rate of 0.3% (after excluding Audi A4, which had an extremely high failure rate, attributed to other major defects). Average mileage was not provided for the 2001 MY vehicle fleet.

Finally, Afton focused on evaluation of HCD/CC catalyst vehicles in Canada, comparing failure rates (at the two year test mark) between 2001 Honda Civics (600 cpsi catalyst) with 2000 Honda Civics (400 cpsi catalyst). Since MMT was phased-out mid-2003, the data were restricted to the first 6-months of testing for both vehicles. The data showed that the failure rate for the 2001 Civics was much lower than the 2000 Civics after two years of use (~0.1% vs. ~1.5%), as well as much lower than the average of all 2001 models (about 0.4%)- See Figure 3 in the paper. A number of these vehicles also had high mileage accumulation, so vehicles with mileage in excess of 60,000 km were compared. Only 0.5% of 2001 Civics failed, while 2.8% of the 2000 Civics failed. (Note that the 2001 Civic was hypothesized by Afton to be the M-1 vehicle reported in the Sierra Report that was noted to have high warranty claim rates in Canada- See Section 3.3)

2.4.2 Ref. No. 114: Roos, J.W, et al. 2006: A Survey of American and Canadian Consumer Experience- The Performance of late Model Year Vehicles Operating on Gasoline With and Without the Gasoline Fuel Additive MMT® (SAE 2006-01-3405)

Sponsor/ Author Affiliation	Afton Chemical Corporation

Study Type	Primary- Market Survey
Vehicle Test Fleet Description	337 Vehicles in Regina, CA; 350 vehicles each in Minneapolis, MN and Denver, CO.
Mn Concentration	In Canada, between 0 and 13.4 mg Mn/L;
Baseline Fuel	US fuel without MMT
Test Protocol	Consumer Phone Surveys
Mileage Accumulation	Variable with fleet averages of 46,000 km in Regina, CA; 66,000km in Minneapolis; 55,000 km in Denver
Emission Test Protocol	NA
Catalyst Technology	Survey focused on 2001 and later/ Tier 2 vehicles

Summary: In response to automakers' claims that the use of MMT causes failures of new HCD/CC catalysts in newer/ Tier 2 vehicles, Afton conducted a public survey in three cities, focusing on vehicles from 2001 and later. Phone surveys were conducted in Regina, Saskatchewan Canada (where MMT was routinely used) and in Minneapolis and Denver (where no MMT was used). (A fuel survey was also conducted at 7 refueling stations in Regina, with MMT concentrations found to range from 3.3 to 13.4 mg Mn/L at 6 stations, and no MMT was found at one station.) To compare OBD and maintenance issues between MMT and no-MMT use, the survey questions focused on the frequency of MIL illumination and the resulting repairs. While the authors noted that factors other than fuels (such as climate, maintenance culture, engine calibrations, etc.) could be important, they found no statistical differences in the rates of MIL illumination or the frequency and type of repairs among the three locations. In fact, when looking specifically at repairs for components that come into contact with the fuel or its combustion products, the survey results showed that spark plugs displayed the highest rates of repair, but were twice as frequent in U.S. markets. The total rate of catalytic converter repair was low, totaling 11 in all markets. Although 6 out of the 11 occurred in Regina, the authors report that the repairs were primarily due to recall or warranty issues, and they concluded that there were no statistically significant differences among markets.

2.4.3 Ref. No 111: D'Aniello, M. 2006, Adverse Effects of MMT-Doped Fuel on 2002-3 MY LL8 GMT 360/370

Sponsor/ Author Affiliation	General Motors
Study Type	Primary- Survey
Vehicle Test Fleet Description	190 US returns and 212 Canada returns of catalysts under warranty; Survey of 25 US vehicles and 24 Canada vehicles, randomly selected from lease returns (without history of converter or engine problems) All vehicles were 2002 Chevy Trailblazers or GMC Envoys
Mn Concentration	Canadian fuel average (5-15 mg Mn/L)
Baseline Fuel	US fuel average- no MMT
Test Protocol	Evaluation of warrantied catalysts; FTP testing of vehicles
Mileage Accumulation	Avg. US fleet (of 25 vehicles) = 39,800 miles (18,800-66,700 miles) Avg. Canadian fleet (of 24 vehicles) = 37,600 miles (7,700-84,800 mi)
Emission Test Protocol	FTP testing
Catalyst Technology	600 cpsi

An abnormally high rate of catalytic converter replacement under warranty in Canada(7.9% in Canada compared to 0.3% warranty replacement in the U.S.) for the GM 2002 MY LL8 (a 4.2L in line 6 cylinder engine) GMT 360/370 (a mid-sized truck) prompted an investigation by GM. This report was included in the NCWM database (and has similarities between Manufacturer J in the Sierra Report- see Section 3.3.2), but was not available through a web or literature search. The engine and exhaust control systems of these vehicles were designed to be easily upgraded to Tier 2/ LEV 2 standards, utilizing a relatively close-coupled, 600 cpsi catalytic converter with an aggressive cold start heat-up strategy. The analysis included evaluation of 212 catalysts returned in Canada and 190 catalysts returned in the US. Problems with the Canadian catalysts (where MMT use ranged from 5-15 mg Mn/L) were found to be caused primarily by partial plugging with Mn_3O_4 deposits (in 199 out of 212 cases). An analysis of flow restriction through the Canadian catalysts showed the average restriction in the returned catalysts was 212 inches H_2O, whereas the normal range is expected to be around 7.5 inches H_2O. The accumulation of these deposits led to degraded vehicle performance and low fuel economy that was easily noticed by consumers and in some cases, triggered a "service engine" light due to reduced emissions system efficiency detected by the OBD-II system. The study also found that manganese oxide failure was not correlated with the odometer, and is related to the operating temperature, which is dependent upon the driver and drive cycle. For example, customers who operate vehicles at high speeds (70-85 mph) or for trailer towing may experience higher rates of deposit collection. The primary failure in US returns was broken inlet catalyst elements (in 96 cases), excessive operating temperatures (in 30 cases), and exhaust system noise (in 53 cases). None of the converters in the US market displayed deposits of Mn_3O_4, and the US failure modes were in line with those generally observed for all GM catalytic converter types.

In conjunction with the analysis of returned catalysts, an emissions survey was conducted on in-use vehicles that had accumulated mileage under real-world circumstances, and were subsequently returned via the General Motors Acceptance Corporation (GMAC) lease program. Emissions testing was conducted on 25 vehicles from US markets and 24 vehicles from Canadian markets, excluding any vehicles that had previously had catalyst warranty issues or major engine repairs. All were model year 2002 Chevrolet Trailblazers or GMC Envoys with the 2002MY GMT360 configuration. FTP emissions testing produced average results of 0.076/ 0.645/ 0.169 NMHC/ CO/ NO_x in g/mile for the US fleet. All US vehicles met LDT2 NLEV 50,000 mile certification standards with a compliance of 76%/15%/42%, respectively, as expected from the engineering and certification work done during development of the vehicles. Emissions from the vehicles collected in the Canadian markets were much higher at 0.090/1.131/0.255 g/mi. On average, the emissions met 50,000 mile standards with a compliance of 90%/26%/64%. However, 7 vehicles exceeded the 50,000 mi NMHC standard, 1 vehicle exceeded the 50,000 mile CO standard, and 3 vehicles exceeded the 50,000 mile NO_x standard.

The comparisons of engine-out emissions were not significantly different between the US and Canadian fleets, suggesting that manganese deposits in the engine (under relatively low average miles) is not a major contributor to the emission differences. Cold flow restriction measurements across the catalysts produced an average of 8.7 inches H_2O in the US fleet, while 20.0 inches H_2O was seen for the Canadian fleet, indicating flow restriction by Mn-deposits. Analysis of high- and low-restriction sub-groups showed that Canadian vehicles with low-restriction performed similarly to US vehicles, while those with high-restriction had significantly higher tailpipe emissions. Relative to the US sample, the Canadian sample displayed higher tailpipe emissions for each regulated component and higher deterioration rates as a function of odometer. Laboratory analysis of the catalytic converters showed high deposits of Mn in the Canadian sample, albeit with lower deposits of phosphorous. Analysis of the O_2 sensors showed no differences in performance from either fleet, although Mn-deposits were visible on the surfaces of the Canadian fleet. The study concluded that MMT vehicles have substantially higher emissions and higher rates of failure.

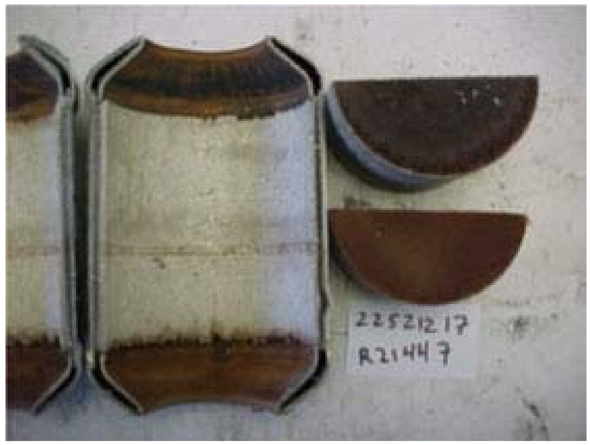


Figure 2.4.3-1Figure: Photo of catalyst inlet brick returned under warranty in Ontario, Canada after 76,604 km. The inlet face (lower portion) is heavily contaminated with reddish-brown deposits identified mainly as Mn_3O_4 by XRF. The outlet face (upper portion) does not have visible deposits. Cold flow restriction for this particular part was measured to be 197.6 inches H_2O at 100 g/s (26 times the average).

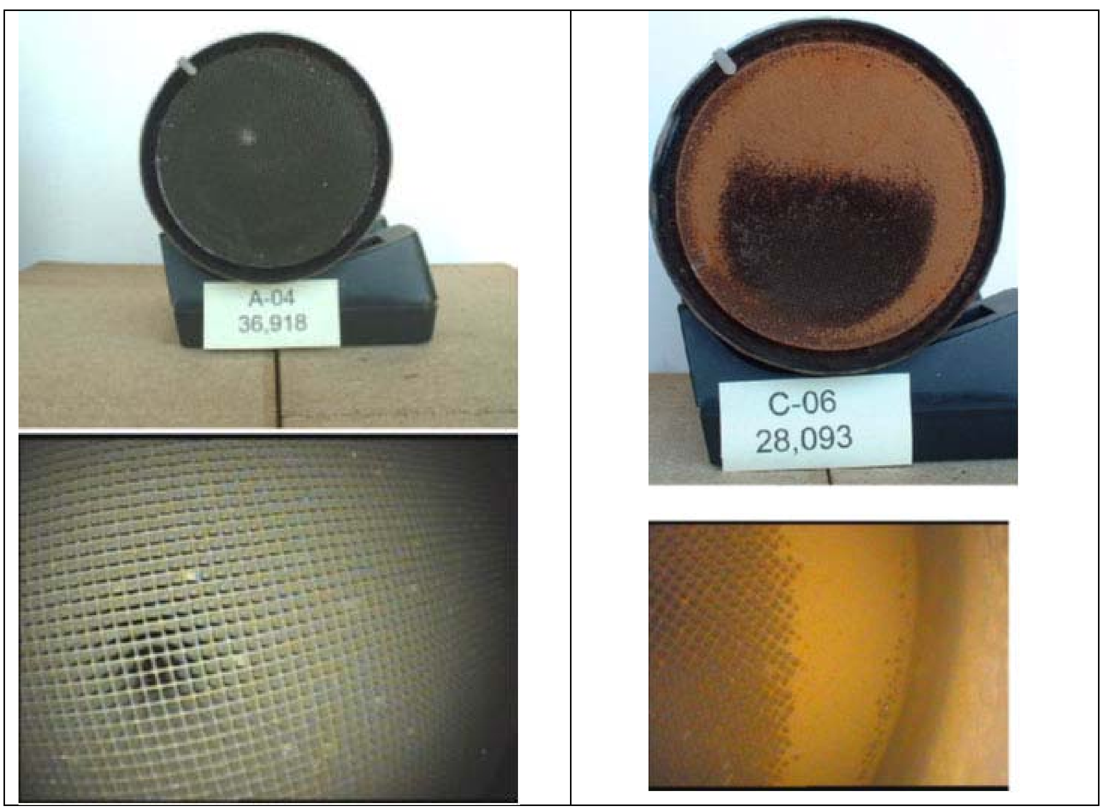


Figure 2.4.3-2: Color Photographs of typical US vehicle inlet element, inlet face (left) and photographs of an average restriction (21 inches H_2O) Canadian Vehicle Inlet Element inlet face (right)

2.5 ADA Study (Abgaszentrum de Automobilindustrie) and Afton Response

2.5.1 Ref. No. 141: Lohfink C., et al., 2014. Influence of Metal Based Additives in Gasoline Fuel on the Exhaust Gas Emission System Components Over Useful Life Period Using the Example of Manganese-Containing Additive. (SAE 2014-01-1380)

Sponsor/ Author Affiliation	ADA
Study Type	Primary
Vehicle Test Fleet Description	Two-2010 Volkswagen Eos equipped with downsized DISI engine (VW 1.4L TSI, 90kW) with Euro 5 application
Mn Concentration	6 mg Mn/ L
Baseline Fuel	Euro 5 Reference fuel
Test Protocol	Standard Road Cycle (emissions durability procedure from US EPA) on a chassis dyno driven by a robot; 1650 km/ day for 5 days/week; routine maintenance schedules followed every 30k mi.
Mileage Accumulation	160,000 km
Emission Test Protocol	NEDC (New European Drive Cycle) tests; every 30k km (with a 3k-km run in) exhaust analysis over fixed intervals of 30k-km; measuring engine out and tailpipe emissions.
Catalyst Technology	Close coupled TWC, 600 cpsi converter with Euro 5 application

Summary: This test program measured pressure drop across the catalyst, exhaust temperatures, and oxygen storage capacity of the catalysts, along with frequent emissions testing over the duration of the 160k-km accumulation using the SRC cycle. Throughout mileage accumulation, only brief stops to re-fuel and check the engine (for OBD faults, although no mention of OBD illumination or lack thereof is mentioned in the remainder of the document) were made. The number of cold-starts during mileage accumulation were considered negligible. Over the test program, engine out raw emissions were comparable between both vehicles, but tailpipe emissions changed dramatically with mileage accumulation. Tailpipe CO, THC, NMHC, and NOx emissions increased up to 130k-km, then decreased slightly between 130-160k-km, before finally increasing to highest level. Euro 5 emission limits were exceeded after 105k-km for THC, NMHC and NOx for the MMT vehicle while all tailpipe emissions from the baseline vehicle were well below the Euro 5 emission limit values, with a negligible increase in THC, NMHC and NOx emissions due to thermal aging of the catalyst over the entire endurance run. The NOx and THC conversion rates of the catalyst dropped sharply after 90k-km due to deposit formation and mechanical plugging of the catalytic surface and cell channels of the catalytic converter by manganese oxides. Evidence of this plugging was supported by exhaust back pressure measurements of the catalyst. Measurements also showed that MMT decreased the oxygen storage capacity of the catalyst over time. Endoscopic images of the catalyst surface taken throughout mileage accumulation showed steady build-up of brown deposits typical of manganese oxides on the MMT vehicle, while none were found on the reference vehicle catalyst.

[Note: The Euro 5 standards used to compare with measured tailpipe emissions in this paper are: 1000 mg CO/km; 100 mg THC/km, 68 mg NMHC/km; 60 mg NOx/km (80 for Euro 4); and 4.5 mg PM/km.]

Figure 2.5.1-1: Color photographs of inlet surfaces of MMT catalysts at various mileage intervals, taken with an endoscopic camera, compared to inlet surface of reference catalyst after 160,000 miles.

Post analysis after 160,000 km endurance run showed manganese deposits penetrated 3.8 mm into the catalyst surface, and analysis showed that much of the reddish-brown components were manganese with some typical ash from the engine oil. Up to 200 ppm of manganese was detected in the engine oil.

2.5.2 Ref. No. 142: Afton, 2014. A Critical Review of SAE Paper titled "Influence of Metal-Based Additives in Gasoline Fuel on the Exhaust Gas Emission System Components Over Useful Life Period Using the Example of Manganese-Containing Additive (SAE 2014-01-1380)". [1]

Sponsor/ Author Affiliation	Afton Chemical Corporation
Study Type	Review/ Response to ADA study with additional test work
Vehicle Test Fleet Description	2011 VW GTI with engine and emissions controls similar to 2010 VW Eos, certified to U.S. Tier 2, which are close to Euro 5.
Mn Concentration	6 mg Mn/L
Baseline Fuel	Clear fuel
Test Protocol	SRC with two hours run time and 1 hour off soak time; operating 16 hours per day, 7 days per week.
Mileage Accumulation	120,000 mi
Emission Test Protocol	
Catalyst Technology	600 cpsi close-coupled TWC

Summary: This is Afton's response to ADA's VW Eos Study above. For two primary reasons, Afton claimed that the conclusions are not warranted. First, they noted that the conditions used to accumulate mileage were too severe (5,000 miles/week), and do not reflect real world operation - noting that the cycle used conforms to the EC protocol for evaluating metallic additives, but only if it

[1] Due to identified errors, Afton requested that this report be removed from the NCWM database. However, as of June 9, 2015, the report remained within the database.

does not produce higher exhaust temperatures. (In draft EC protocols, p 28 says the SRC provides "… a balanced mix of high and low exhaust gas temperatures, and can be considered the most suitable aging procedure."). Cold starts, which are "negligible" in the cycle applied by VW, and other operations of real world conditions can have substantial impacts on how manganese particulates interact (Afton has shown this in SAE 2007-01-1078). Other tests have also shown that under "normal" or "real world" conditions, MMT is fully compatible with advanced emissions control systems. Afton also mentioned that the emissions standards presented the ADA paper are design standards rather than in-service conformity standards (as shown in the table below, a 1.5 multiplier).

Design Standards vs. In-Use standards (g/km)

Standard	THC	NMHC	CO	NOx	PM
Design Standard (compared in VW paper)	.100	0.068	1.000	0.060	0.50 (.05 corrected!)
In-Use standards	0.150	0.102	1.500	0.090	0.075

The second reason given for dismissing the ADA results is that the history of the test vehicles is questionable, and there appeared to be a bias between the vehicles before the start of testing. Comparison of the data tables shows that CO from the reference vehicle was about 150 mg/km higher, while NOx and PM from the MMT vehicle were about 8 mg/km and 1.5 mg/km higher, respectively (the vehicles were not well matched). In addition, the initial oxygen storage capacity of the MMT catalyst was about 10% lower than the MMT-free catalyst.

Afton then conducted an experimental test program to acquire its own results using a single 2011 VW GTI, and showed that NOx, NMHC and CO emissions were all below "in-use limits."

2.6 Other Vehicle Studies and Reviews

2.6.1 Ref. No. 138: Afton, 2014. Seeking Solutions to Global Challenges: HiTEC®3000 (mmt®) Fuel Additive as an Option for Optimizing Global Energy Supply

This compilation of work by Afton reviews health and vehicle impacts of MMT over the past several decades. The report and several hundred pages of attachments has been reported to the EPA as a condition of maintaining Afton's fuel additive registration for MMT. Several of the attachments are publications discussed elsewhere in this summary report while the report itself and others of the attachments are not available via web searches.

Information regarding testing conducted [presumably] by Afton on 2003 and later model year vehicles, including low emission vehicle technologies identified as necessary to meet Tier 2 and Euro 4/5 emissions standards is summarized in the main body of the report. The report notes that none of the MMT-fueled test vehicles failed to meet in-use emission standards as indicated by lack of MIL illumination, and none reported fuel-related failures of catalytic converters, oxygen sensors or spark plugs attributable to MMT. As noted in Table 5 from the report (shown below), catalyst technologies ranged from 400-900 cpsi, with some vehicles accruing mileage as high as 233,000 km. MMT was used most frequently tested at 8.3 mg Mn/L, but was evaluated as high as 18 mg/ L. Converter failure or catalyst plugging is reported on a yes/no basis, with none of the catalysts reported as experiencing either. Further details on these vehicles are provided in Appendix 3 to the report, which are briefly summarized below.

Table 5
Manganese Consumption in *mmt* Vehicle Fleet Tests

Model Year and Make	Mileage	Converter Cell Density	Manganese Consumption[a]	Converter Failure/Plugging?
2007 Impala	100K km	400 cpsi	90 grams	No
2007 TrailBlazer	80K km	600 cpsi	75 grams	No
2007 Caravan	100K km	600 cpsi	85 grams	No
2007 Charger	100K km	600 cpsi	50 grams	No
2007 Fusion	100K km	900 cpsi	35 grams	No
2007 Civic	100K km	600 cpsi	55 grams	No
2007 Odyssey	100K km	900 cpsi	45 grams	No
2007 Elantra	100K km	400 cpsi	65 grams	No
2007 Altima	100K km	400 cpsi	70 grams	No
2007 Camry	100K km	600 cpsi	35 grams	No
2007 Prius	194K km	900 cpsi	80 grams	No
2007 Yaris	100K km	600 cpsi	50 grams	No
2005 Corolla[b]	100K km	600 cpsi	120 grams	No
2005 Corolla[c]	194K km	600 cpsi	105 grams	No
2005 Corolla[d]	194K km	600 cpsi	115 grams	No
2005 Accord[b]	100K km	600 cpsi	140 grams	No
2005 Accord[c]	194K km	600 cpsi	125 grams	No
2005 Accord[d]	194K km	600 cpsi	135 grams	No
2005 Explorer[b]	194K km	900 cpsi	220 grams	No
2005 Explorer[c]	194K km	900 cpsi	100 grams	No
2005 Agila	80K km	600 cpsi	95 grams	No
2004 Regal	196 K km	600 cpsi	135 grams	No
2004 Regal	100K km	600 cpsi	150 grams	No
2004 Camry	100K km	600 cpsi	75 grams	No
2003 Corolla	233K km	600 cpsi	130 grams	No
2003 Corsas	100K km	600 cpsi	125 grams	No
2003 Passat	100K km	>500+ cpsi	150 grams	No

[a]Explorer, , Charger, Odyssey, 2004 Camry, 2007 Camry and Fusion models have twin close-coupled converters; these models actually consumed twice the amount of manganese listed on a whole vehicle basis.
[b] 18 mg Mn/liter
[c] 8.3 mg Mn/liter
[d] Rotating (0 mg Mn/liter, 8.3 mg Mn/liter, and 18 mg Mn/liter)

In total, there are six appendices to this report, each with attachments, as listed below in Table 2.6.1-1, which includes additional details about the number of pages of each attachment and if and where it is further summarized in this report. Several of the items were already included and summarized in this appendix. Those reports are noted. Additionally, several other papers that were presented at conferences were included as attachments. Each of these is further summarized in its own section, as noted in the table. Some of the attachments are Afton technical reports that are not available via a web or literature search. Those reports are summarized within this section, as noted in Table 2.6.1-1.

Table 2.6.1-1. Attachments to the “Seeking Solutions to Global Challenges” Report

	Section Report	Document Type	Date	# of Pages	How Handled in DRI Report
2	Appendix 1: Use of mmt Fuel Additive (HiTEC® Octane Booster) Reduces Petrol Aromatic Content and Toxic Benzene Emissions	Afton Report	?	6	Not dated, no author or information gives this a low priority ranking
3	Appendix 2: In Their Own Words	Afton	?	13	Not reviewed; deals

		Report			with health effects
4	Appendix 3: Compilation of mmt Vehicle Test Programs			1	
5	Appendix 3, Attachment 1: Evaluation of the Compatibility of Gasoline Containing the MMT Fuel Additive in U.S. Tier 2 Vehicles	Afton Report	2012	12	Section 2.3.1.1
6	Appendix 3, Attachment 2: North American Tier 2 Vehicle Durability Test Fleet Compatibility Evaluation with MMT-Containing Gasoline	Afton Report	2012	4	Section 2.6.1.1
7	Appendix 3, Attachment 3: Vehicle Durability Testing in 2007 Model Year Vehicles Certified to North American Tier 2 Emissions Standard	Afton Report	2010	4	Section 2.6.1.1
8	Appendix 3, Attachment 4: Alternative Tier 2 Specification Testing: Assessing the Performance of the 2003 ULEV Toyota Corolla and 2003 and 1997 Vehicles Certified to Federal Tier 1 Emissions Standards	Afton Report	2009	4	Section 2.6.1.1
9	Appendix 3, Attachment 5: Emissions Effects of MMT for Light-Duty Vehicles	Pub: *Res. Environ. Sci.*	2006	8	See Section 2.6.2
10	Appendix 3, Attachment 6: Assessing High-Cell Density Catalyst Durability with MMT Fuel Additive in Severe Driving Conditions	SAE 2005-01-3840	2005	11	See Section 2.1.1
11	Appendix 4: Compilation of mmt In-Use Vehicle Test Programs				
12	Appendix 4, Attachment 1: Evaluation of Factors Affecting Vehicle Emission Compliance Using Regional Inspection and Maintenance Program Data	SAE 2006-01-3406	2006	15	See Section 2.4.1
13	Appendix 4, Attachment 2: A Survey of American and Canadian Consumer Experience – The Performance of Late Model Year Vehicles Operating on Gasoline with and Without the Gasoline Fuel Additive MMT	SAE 2006-01-3405	2006	21	See Section 2.4.2
14	Appendix 4, Attachment 3: Solicitor client privileged information: Review of emissions-related Notices of Defects and Recalls	e-mail	2005	4	Low priority ranking; not summarized
15	Appendix 4, Attachment 4: Analysis of the Durability of In-Use Tier 2 Vehicles in an Area with MMT Containing Gasoline	Afton Report	2010	2	See Section 2.6.1.2
16	Appendix 4, Attachment 5: In-Use	Afton	2008	16	See Section 2.6.1.2

	Emissions Compliance of 2005 and 2006 Model Year Taxis in Beijing, China	Presentation			
17	Appendix 4, Attachment 6: Durability Analysis of In-Use Hyundai Elantras in Tianjin, China	Afton Report	2009	3	See Section 2.6.1.2
18	Appendix 4, Attachment 7: Survey and Analysis of In-Use Vehicle Emissions Performance in China	CATARC Report	2010	22	See Section 2.6.1.2
19	Appendix 5: Compilation of mmt Laboratory Testing				
20	Appendix 5, Attachment 1: Experimental Study of Influence of Gasoline Fuel with MMT on Aging Performance of Three-Way Catalyst	Tsinghua U. Report	2011	12	See Section 2.6.1.3
21	The Interaction of MMT Combustion Products with the Exhaust Catalyst Face	SAE 2007-01-1078	2007	18	See Section 2.1.3
22	Appendix 6: A New Sierra Research Paper on mmt Fails to Discredit the Clear Benefits of mmt and Its Compatibility with Vehicle Performance	Afton Report	?	20	See Section 3.3.3
23	Appendix 6, Attachment 1: Comparing the Old to the New: An Assessment of Advanced Emission Control Technology Necessary to Meet Stringent Tier 2 Emission Standards in the U.S.	Afton Report	?	3	See Section 3.3.3
24	Appendix 6, Attachment 2: Catalytic Converters Fail for Reasons Unrelated to mmt	Afton Report	>2008	7	See Section 3.3.3
27	Appendix 6, Attachment 3: Assessing Warranty Programs in Canada and the U.S.: Factors that Must Be Considered in Any Comparison of U.S. and Canadian Experience (multiple appendices attached)	Afton Report	?	9	Not addressed/ out of scope
28	Appendix 6, Attachment 4: An Engineering Assessment of the 2001 Honda Civic: Defects and Operational Factors that Could Impact the Performance of the Civic's Emission Control System in Consumer Use in North America (multiple Appendices attached)	Afton Report	?	15	Not addressed/ out of scope
37	Appendix 6, Attachment 5: Competing Science and Competing Interests: Making Sense of the MMT Debate	Kevin Fast	2009	18	Not addressed

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2.6.1.1 Appendix 3 to "Seeking Local Solutions…"Compilation of Vehicle Test Programs

Further details on testing of the vehicle test programs summarized in the main report are given as Attachments in Appendix 3:

Appendix 3, Attachment 1. Afton, 2012: Evaluation of the Compatibility of Gasoline Containing the MMT® Fuel Additive in U.S. Tier 2 Vehicles

This 2012 un-published report presented results from a thirteen vehicle fleet certified to Tier 2 Bin-5 standards tested to 120,000 miles (193,000 km) on a cycle representative of severe consumer driving, averaging approximately 45 mph. (NOTE: these vehicles were summarized Table 5 in the above section and include the 2005 Corollas, Accords and Explorers.) Four Accords and Corollas were tested on a variety of fuels: two were tested each using a different commercially available fuel, one was tested using, gasoline with MMT at 8.3 mg Mn/L, and one each of the Accords and Corollas were tested using a rotating matrix of commercially available gasoline and two MMT-containing fuels at different concentrations (8.3 and 18 g Mn/L. Note: It is not clear if the 2005 Accord and 2005 Corrolla tested to 100k km on 18 g Mn/L were included in this program as they are not mentioned within but appear to be lumped with the other vehicles tested in the program in Table 5 above). Three Explorers were operated on three different commercially available gasolines, one at 8.3 mg Mn/L and one at 18 mg Mn/L. Emissions testing was conducted at 0, 25k, 50k, 62.2k, 75k, 90k, 105k, and 120k mi. using FTP procedure with US06 on all vehicles at 120k mi. Post-mortem component testing was completed by swapping catalysts and/or O_2 sensors onto a slave vehicle. The report concluded that OBD-II systems functioned properly and did not indicate any MMT-related issues; parts swapping indicated little to no reduction in conversion efficiency of the catalysts for any regulated emissions; and all vehicles met applicable emissions standards, which were reported on a yes/no basis. However, no data were presented in the report with the exception of Figure 2.6.1-1 below, which shows integrated emissions averages over the entire mileage accumulation in comparison to other fleet tests. Afton's analysis consisted primarily of their own fleet data, along with several additional studies, and included the 1979 CRC study ("pre-Tier 0, 1979"), their 1990 and 1993 Waiver submissions ("Tier 0, 1988" and "Tier 0, TLEV, 1993", respectively), the AAM study results from Part 2 ("LEV, 2002"), previous work with Euro 4 vehicles by Cunningham "Euro 4, 2005", from a SEPA study (the Chinese regulatory agency) on Euro 4 vehicles tested to 80,000 km (in a Chinese journal, not included in the database), and from their evaluation of Tier 2 vehicles. The figure shows that in both the recent Euro 4 studies and the Tier 2 study, CO and HC emissions from the MMT-fleet exceeded those of the base fleet, although all vehicles still met appropriate emissions standards.

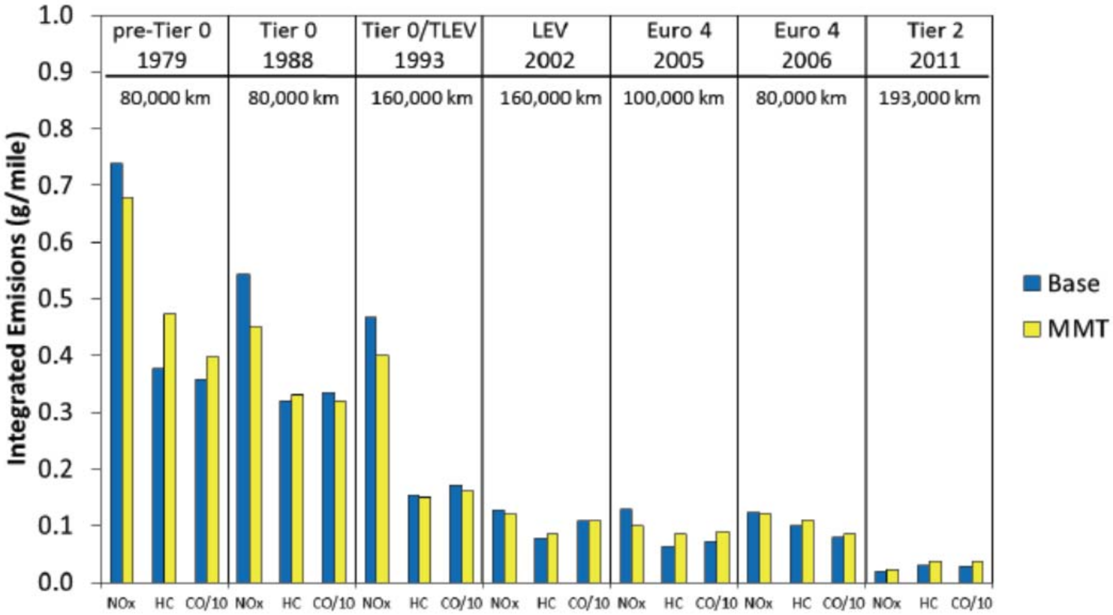


Figure 2.6.1-1 Integrated emission results from historical fleet testing as reported by Afton. Note that the figure includes data from other studies not conducted by Afton and represents their own interpretation of the data.

Appendix 3, Attachment 2: "North American Tier 2 Vehicle Durability Test Fleet Compatibility Evaluation with MMT® Containing Gasoline." Afton Chemical Corporation Technical Report, March 2012.

> This 4 page report details the testing of two 2004 Regal and two 2004 Camry fleets that were tested up to 120,000 mi. The testing performed included monitoring OBD II response when fueled at 8.3 mg Mn/L vs. no MMT. No vehicles experienced MIL illuminations for exhaust emission control components including catalysts, oxygen sensors and spark plugs. Emissions data were not reported.

Appendix 3, Attachment 3: "Vehicle Durability Testing in 2007 Model Year Vehicles Certified to North American Tier 2 Emission Standards." Afton Technical Report, 2010.

> This 4-page report details the testing of the twelve-2007 vehicles listed in Table 5 from the main report. The vehicles were each operated with MMT at 8.3 mg Mn/L for up to 100,000 km. Mileage accumulation was halted on the Trailblazer after an MIL illumination showed two codes- one related to low catalyst efficiency and one to throttle position. Afton reported that a mechanic linked the code to a heavily fouled throttle body. With that exception, the rest of the vehicles did not experience any OBD illumination. FTP emissions testing was conducted, and no emissions failures were reported. Emissions reporting was provided on a yes/no basis, without data.

Appendix 3, Attachment 4: "Alternative Tier 2 Speciation Testing: Assessing the Performance of the 2003 ULEV Toyota Corolla and 2003 and 1997 Model Year Vehicles Certified to Tier 1 Emission Standards." Afton Chemical Corporation, 2009.

This 4 page report details the results from testing Tier 1 and ULEV vehicles. Two 2003 Corollas were evaluated to 240,000 km and 225,000 km. Two Silverados were evaluated to 80,000 km and two Tauruses to 192,000 km with MMT at 1/32 g Mn/gal. The drive cycle used had average speeds of 57 mph and max speed of 80 mph on a dyno up to 80,000 miles. The Corollas continued to accumulate mileage on the road. None of the vehicles experienced any MIL illumination during testing and no drivability or non-scheduled maintenance issues were reported. Emissions data were not reported.

2.6.1.2 Appendix 4 to "Seeking Local Solutions…" Compilation of mmt in-use test programs

Appendix Four of the report includes seven attachments reporting on in-use vehicle test programs as listed in Table 2.6.1-1. Several that are not described elsewhere are summarized here.

Attachment 4, "Analysis of Durability of In-Use Tier 2 Vehicles in an Area with MMT® containing gasoline"(Feb. 2009):

In New Mexico, where MMT was in wide use, with an average concentration of around 4.0 mg Mn/L until it was discontinued in 2007, Afton acquired twenty-four 2002-2005 MY vehicles certified to Tier 2 Bins 4 or 5. Via CARFAX history and OBD evaluations, no vehicles reported drivability issues or history of OBD illumination or trouble codes. FTP emissions testing indicated that all vehicles met applicable "in-use emissions standards

Attachment 5, "In-use emission compliance of 2005 and 2006 model year taxis in Beijing, China," Cunningham, L.J. et. All. Presented at the 18th CRC On-Road Vehicle Emissions Workshop, San Diego (March 31,2008).

This Power Point presentation (cited as a poster) reports on emissions compliance of 2005 and 2006 MY taxis in Beijing China, where MMT was reported as widely used up to 8 mg MN/L. 150 vehicles (half Hyundai Elantras with 400 cpsi catalysts and Half VW Jettas with 600 cpsi catalysts, 30% reported from MY 2005 with remaining as MY 2006) certified to Euro III / Euro IV standards with variable mileage were subjected to emissions testing. 146/150 vehicles passed steady state Beijing I/M emissions testing, with the four VW Jettas failing all in the same mileage bin (40-80k-km). The presentation concludes that all vehicles were operating properly on Beijing area specification fuels.

Attachment 6, "Durability Analysis of In-use Hyundai Elantras in Tianjin, China," China Automotive Technology and Research Center (2009).

This report summarizes the results of 3 Hyundai Elantras (two taxis, one personal) that were acquired from service for testing. Fuel tested from 9 suppliers in Tianjin showed an average MMT concentration of 7.6 mg Mn/L, with 8 of 9 stations containing at least 5 mg Mn/L. The vehicles had mileage ranging from 49,000 km to 63,000 km. All vehicles were reported to have met applicable emission standards.

Attachment 7-Survey and Analysis of In-Use Vehicle Performance in China." Li-Mengliang. Asia Fuels and Lubes Conference, Singapore. March 2010.

Emission control system performance was measured for 108 light duty State II certified vehicles of various makes and models procured around China with mileage ranging from 40,000 to 100,000 km. After initial Type I emissions testing on the vehicles "as-is", 75% of the vehicles met State II standards (0.5 g/km THC + NO_{x}, 2.1 g/km CO). After routine repairs were completed on the failing vehicles (not including exhaust components), only 10 vehicles continued to fail. Failures were not consistent with a single pollutant. In addition, no strong correlation between mileage and emissions was seen for the entire fleet, which was considered to be due to the difference between makes and models. An analysis on three vehicles of the same make and model did show a very strong correlation between mileage and emissions.

Following emissions testing, additional laboratory analysis was conducted on 18 selected catalysts, chosen to reflect a balance of high and low emitters with a range of mileage accumulation. BET surface area measurements, which show collective thermal exposure, had the highest correlation with vehicle emissions performance, particularly for CO emissions. All of the catalysts analyzed that had passed CO State II limits had BET surface area above 17.5 m^2/gram, while the worst performing catalyst also had the lowest BET surface area at 6.2m^2/g. Further XRF results showed correlations between Pb and Zn and emissions performance. In general, when both Pb and Zn were high, emissions were also generally higher. However, one catalyst had very high Pb and Zn, but low emissions. Further analysis showed deposits of Ca and Mg that were hypothesized to help prevent poisoning of Pb and Zn. No correlation between high amounts of Mn on the catalysts and emissions could be determined. Additionally, high levels of Mn did not correspond to low BET surface areas, which supports that Mn did not affect spark plugs or thermal exposure.

Four State IV certified vehicles of the same make and model were procured from Tianjin. The vehicles had mileages of 50k, 70k, 140k, and 150k-km. (It is unclear if this analysis might be related to those described in Appendix 6, above.) Emissions testing as received showed a strong correlation with mileage, with the lowest three mileage vehicles meeting State IV in use standards. Analyses performed on the catalysts (one close coupled and one underfloor for each vehicle) from the 70k and 150k-km vehicles, showed that the lower mileage close coupled catalyst had 15% higher precious metal content, which was attributed to stripping or thermal degradation in the high mileage catalyst. The higher mileage catalyst also showed clear signs of poisoning with 6% Pb content. No discussion of Mn content was included.

The report concluded that most vehicles met emission standards despite many exceeding the required durability limit. For those that didn't meet the limit, the primary reason for failures could be attributed to improper maintenance and repair routines. For those that failed because of catalyst reasons, the major contributed is thermal aging, with Pb or Zn poisoning having a lesser effect. Mn did not negatively affect performance or emissions.

2.6.1.3 Appendix 5 to "Seeking Local Solutions…" Compilation of mmt Laboratory testing

Appendix 5, Attachment 1. "Experimental Study of Influence of Gasoline Fuel with MMT on Aging Performance of Three Way Catalyst." Chen Tun-feng, Shuai Shi-Jin and Xiao Tian-hua. Report from State Key Laboratory of Automotive Safety and Energy, Tsinghua University. Presented at the 3rd Conference of the Oil and Products and Clean Fuels (OPCF) Branch of the Chinese Society for Internal Combustion Engines. Beijing, China. May 21-22, 2011.

In this work interactions of combustion products from MMT at 18 mg Mn/L were investigated at different temperatures on 600 cpsi catalysts using an engine bench set-up for 200 hours of durability testing. Two types of driving operation were tested: 1) a steady state condition in which air-fuel ratio, catalyst inlet temperature, engine speed and other operating conditions were held constant for the duration of the test, and 2) a fuel-cut in which 5 minutes of steady state operation was followed by a 5-second fuel cut to simulate closed throttle deceleration. Inlet catalyst temperatures of 760°C and 820°C were evaluated with and without MMT. The paper concluded that the only significant increase in back pressure was observed for the high temperature catalyst operating with MMT fuel when no fuel cut was used. Less significant back pressure increases were observed for cases with MMT and with no-MMT (although it is difficult to determine the magnitude of the differences since legends in the figures and graphs are in Chinese). They also observed that higher catalyst operating temperatures and fuel-cut operating modes increased the aging of the catalyst. In addition, reddish-brown manganese deposits were observed on the faces of all catalysts operating with MMT, while none was observed on the non-MMT catalysts, as shown in the figure below.

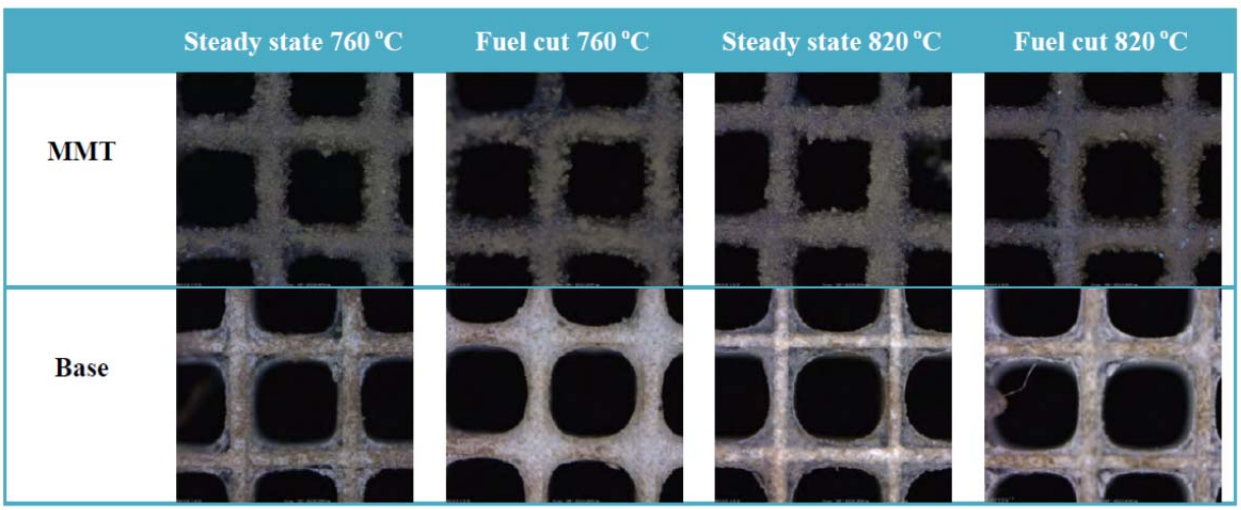


Figure 2.6.1-2: Deposits observed on catalysts from Tsinghua University study.

Appendix 6 of the "Global Solutions Document" includes Afton's supporting materials and response to the Sierra 2008 report. This is summarized separately in Section 3.3.

2.6.2 Ref. 138. Appendix 3, Attachment 4. "Emissions Effects of MMT for Light-Duty Vehicles." Research of Environmental Sciences Vol. 19 No. 5, 2006. Zhang Yan, Cui Ping, Ding Yan, Shang Qi, Xiong Chun-hua, Zhang Hai-yan, Zhang Dan, Tang Da-gang.

Note that this article appears as a translation from a Chinese journal (which is not searchable from US libraries and databases) and does not include any Figures, Tables, Data, or references. A Chinese version of the paper was supplied by Afton, with an English translation of the abstract only. The abstract in the published version is very different than the draft translation. All figures and data were presented in Chinese and were interpreted by DRI.

In this study by the Chinese State Environmental Protection Agency (SEPA) six light-duty GM Opel-Agila that reach Euro 4 standards with 600 cpsi close-coupled TWC were tested to 80,000 km (50,000 miles). Half of the fleet was tested at an MMT treat rate of 18 mg Mn/L. Durability testing was completed using 28 driving modes to represent urban and highway driving. The testing cycles was reported as “serious”, with 81.5% of the driving occurring above 80 kph (50 mph). This resulted in a calculated MMT consumption of 96.8 grams of Mn per vehicle. The report concludes that HC and CO emissions deteriorate with mileage for both groups, but the average of each during testing met Euro 4 emissions. Figures show that emissions from MMT vehicles are slightly higher than no-MMT vehicles. Likewise, NO_x emissions are reported to deteriorate with mileage for both vehicle groups, and it was reported that both vehicle groups exceeded the Euro 4 NO_x standard (0.08 gm/km).

2.6.3 Ref. No. 139: Afton, 2014. Evaluation of the Impact of Gasoline Containing MMT® Fuel Additive on Particulate Matter Emissions in Vehicles Designed to Meet Euro 5 Standards and Implications for the New U.S. Tier 3 PM Emissions Standards

Sponsor/ Author Affiliation	Afton Chemical	
Study Type	Europe 2012 (Primary)	Europe 2013 (primary)
Vehicle Test Fleet Description	8 gasoline passenger cars purchased second hand from hire fleets	14 gasoline passenger cars purchased second hand from hire fleets.

Information for Vehicles Tested

Test Programme	Make	Model	Year	Test Vehicle ID	Emission Standard	Displacement (cm^3)	Power (HP)	Injection Type	Turbo
Europe 2012	BMW	318i	2011	BMW	EURO 5	1995	140	DIG	No
Europe 2012	Ford	Focus	2011	Focus-1	EURO 5	1596	104	PFI	No
Europe 2012	Ford	Focus	2011	Focus-2	EURO 5	1596	104	PFI	No
Europe 2012	Nissan	Micra	2011	MIC	EURO 5	1198	79	DIG	Super
Europe 2012	Renault	Megane	2011	MEG	EURO 5	1598	99	PFI	No
Europe 2012	Vauxhall	Meriva	2011	MER	EURO 5	1364	138	DIG	Yes
Europe 2012	Volkswagen	Golf	2011	Golf 1	EURO 5	1390	104	DIG	Yes
Europe 2012	Volkswagen	Golf	2011	Golf-2	EURO 5	1390	104	DIG	Yes
Europe 2013	BMW	1 series	2009	VU59FHM	EURO 5	1995	120	DIG	No
Europe 2013	BMW	1 series	2009	YG09XGC	EURO 5	1995	120	DIG	No
Europe 2013	BMW	Mini	2010	EJ10WUM	EURO 5	1598	118	PFI	No
Europe 2013	BMW	Mini	2009	BK59XUN	EURO 5	1598	118	PFI	No
Europe 2013	Fiat	500	2011	SK11 LPL	EURO 5	900	85	PFI	Yes
Europe 2013	Fiat	500	2011	VK11 UKL	EURO 5	900	86	PFI	Yes
Europe 2013	Ford	Focus	2012	EA12XVG	EURO 5	1596	104	PFI	No
Europe 2013	Ford	Focus	2012	BN12YBL	EURO 5	1596	104	PFI	No
Europe 2013	Nissan	Micra	2012	FL12NWW	EURO 5	1198	79	DIG	Super
Europe 2013	Nissan	Micra	2012	V012 UYV	EURO 5	1198	79	DIG	Super
Europe 2013	Vauxhall	Meriva	2011	DS61 LVG	EURO 5	1364	138	DIG	Yes
Europe 2013	Vauxhall	Meriva	2011	DN61KWL	EURO 5	1364	138	DIG	Yes
Europe 2013	Volkswagen	Golf	2012	FT12AUK	EURO 5	1390	104	DIG	Yes
Europe 2013	Volkswagen	Golf	2012	FV12 ZKG	EURO 5	1390	104	DIG	Yes

Mn Concentration	0 , 6, and 18 mg Mn/L	0 and 18 mg Mn/L
Baseline Fuel	Ultra low sulfur gasoline (26 ppmS)	RF-02/08/E5
Test Protocol		Two matched vehicles from 7 models tested, incl. 3 PFI and 4 DIG models, all turbocharged
Mileage Accumulation		
Emission Test Protocol	NEDC and CADC cycles at Ricardo	NEDC and CADC cycles at Ricardo,

	and Mahle	Mahle, or MIRA
Catalyst Technology		

Summary: Afton conducted this two part study in Europe, using the EC protocol for evaluating the risks to human health and the environment from metallic fuel additives. The work focused on PM measurements from vehicles complying with Euro 5 emission standards. Vehicles were purchased second hand from for-hire fleets with the criteria that they each have “sufficient service.” Emissions testing was conducted on each vehicle at one of several different testing centers, with and without MMT. PM testing showed that all test vehicles met the Euro 5 “type approval” emission standard, though emission performance varied considerably between vehicle make and model. The study concluded that the presence of MMT during testing did not alter the emission performance of any of the 22 vehicles. [Note: our own interpretation of figures and data showed that PM emissions from MMT-fueled vehicles exceeded MMT-free vehicles in 15 out of 22 vehicles.]

2.6.4 Ref. No. 131: Arcadis, 2013: Assessment of the Impacts of MMT (Hi-TEC 3000) Additive on the Emissions Performance of Vehicles. Appendix A of Unknown Report

Sponsor/ Author Affiliation	Afton Chemical Corporation
Study Type	Secondary Analysis of Other Studies
Vehicle Test Fleet Description	54 Vehicles representative of European Market (from 3 other surveys)
Mn Concentration	18 mg Mn/L
Baseline Fuel	
Test Protocol	Following EU protocol
Mileage Accumulation	
Emission Test Protocol	
Catalyst Technology	

Summary: This report is provided as an Appendix to an Unknown report. In this appendix, Arcadis provides an evaluation of data from other fleet studies following recommended EU protocols. The analysis was conducted in two parts that coincide with the EU protocol: in the first part, an instantaneous comparison of emissions is made from emissions testing completed on vehicles using MMT and MMT-free fuels. In the Second phase, analysis of durability testing is performed.

Phase I: Instantaneous Emissions. In Phase I, statistical analysis of results from 54 vehicles evaluated in 5 different programs was completed. The programs include:

1. AVL 1997 – unknown test program, not included in literature
2. U.S. 2013 – unknown test program, not included in literature
3. Europe 2012 (Ref. No 139, Afton 2014)
4. Europe 2013 (Ref. No 139, Afton 2014)
5. EPA 1998 - unknown test program, likely includes waiver application data

The statistical analysis on all Tier 1 vehicles (excluding Program 5 above) showed that vehicle type and drive cycle had significant impacts on the regulated emissions, while the level of Mn content (0, 8.3 or 18 mg Mn/L) did not have any impact. Further breakdown of the data by fuel injection technology again showed that drive cycle had the most dramatic impact, regardless of injection type or amount of MMT used. When breaking down the analysis into smaller subsets of data, there were findings of statistically significant differences between MMT and MMT-free fuels. For example, Euro 5 vehicles on the NEDC cycle had higher instantaneous HC and PM emissions than non-MMT fuels. However, this was not true for the same vehicle types on the CADC cycle. In general, the report concludes that MMT caused no adverse instantaneous effects of any significance to regulated tailpipe emissions as measured by the EU protocol. However, some vehicles with some technologies on some drive cycles did exhibit different behavior for MMT vs. MMT-free fuels. Also, the composition of manganese particulate does not depend upon the vehicle type or cycle driven, and is in the form of phosphates, sulfates and oxides.

Phase 2: Durability Testing. The analysis of durability testing results included 37 vehicles from 3 separate evaluation programs:

1. AAM Part 2
2. Europe Euro 4 (Ref. #105, Cunningham, SAE 2005-01-3840)
3. U.S Tier 2 – 13 cars (Ref. #138, Appendix 3, Attachment 1)

For each program and test cycle, compliance margins were calculated as the average integrated emissions over the lifetime of the vehicle below the applicable emissions standard. The vehicles were also segregated into mileage bins of <80K km and >80K km. 14 of the 15 different cases investigated showed no statistically significant differences in compliance margins. Only in one case (HC emissions in the Euro 4 test program) was the difference in compliance margins between MMT and MMT-free fuels significant. However, emission levels from both sets of vehicles fell well below the applicable standard. Nonetheless, in 11 out of 15 cases, compliance margins for the MMT-fueled fleet were lower than for the MMT-free fleet.

Integrated emissions from the combined MMT and MMT-free fleets were also compared. The combined integrated NOx emissions were 11% higher in the MMT-free case, while HC emissions were 16% higher with MMT. An analysis of OBD MIL illumination of the 3 evaluation program fleets was also performed, showing that 11 MIL illuminations were recorded over nearly 3 million kilometers of vehicle operation. Of those, only two base vehicles displayed codes for O_2 sensor deterioration, and none were registered for catalysts.

The authors claim this work confirms that use of MMT at the treat rates evaluated has no impact on the deterioration of vehicle emission control systems, and does not cause material differences in vehicle emission levels, nor does it impact the vehicles' ability to meet emission standards. It was concluded that use of MMT is "without appreciable risk of adverse impacts on the environment or public health from regulated vehicle emissions compared to the non-use of MMT."

[In the final section, speciation results from various programs are reviewed and synthesized to conclude that manganese in the exhaust is primarily in the form of manganese phosphate (approximately 60% of the manganese in the exhaust) with the remainder being a mix of manganese sulfate (~30% of the Mn) and manganese oxide (the remaining ~10%). These compounds are thermodynamically stable and the mixture is not affected by vehicle type, engine type, operating conditions or mileage, but is dependent on the amount of phosphorous or sulfur in the lubricants and fuels. However, the percentage of manganese in the fuel that is emitted as particulate varies by driving cycle.]

3 OTHER LITERATURE REVIEWS AND REPORTS

3.1 Canadian Reports

3.1.1 Ref. No: 16: CGSB Working Group, 1986. An Assessment of the Effect of MMT on Light-Duty Vehicle Exhaust Emissions in the Canadian Environment

Sponsor/ Author Affiliation	CGSB
Study Type	Review
Vehicle Test Fleet Description	
Mn Concentration	1/16 g Mn/gal (16.5 mg Mn/L) – Canadian standard
Baseline Fuel	
Test Protocol	
Mileage Accumulation	
Emission Test Protocol	
Catalyst Technology	

Summary: The working group performed a literature review, primarily focusing on two studies: (1) CRC Field Test Program in 1979 and (2) Environment Canada In-Use Study in 1984. The objectives were to evaluate and assess the impacts of MMT on emissions, and forecast those impacts on air quality in 1988-2000. The CRC study results are summarized in Ref. No 9 (See Section 1.2). By summarizing these two studies, the Working Group concluded that HC emissions may increase by 0.03 to 0.11 g/mi, depending upon emission control technology, but CO and NOx differences were not found to be statistically significant. This evaluation was performed at a time when the HC emission standard in Canada was being reduced from 2.0 to 0.41 g/mi for light duty vehicles (and 0.8 g/mi for light duty trucks), so it was concluded that the increase in HC emissions relative to the new standard would still be a reduction from 74 to 78% (relative to the old standard). Therefore, the group concluded that MMT should be retained at the current levels as an octane enhancer in unleaded gasoline in Canada.

3.2 ICCT Reports

3.2.1 Ref No. 96: Blumberg, K. and Walsh, M.P., 2004. Status Report Concerning the Use of MMT in Gasoline (ICCT Status Report)

Summary: The International Council of Clean Transportation (ICCT) prepared this report in 2004 based on summaries of existing literature and vehicle studies regarding the use of MMT. They focused primarily on results from the 2002 Alliance/ AAM study (along with subsequent reports and Ethyl's responses), as well as a health review from the Health Effects Institute (HEI). The report highlights negative impacts of MMT on both human health and vehicles/emissions. ICCT recommended that the use of MMT be delayed because they were "unable to conclude that the use of MMT will not result in direct adverse health impacts, nor that emissions of CO, HC, and NOx from catalyst equipped cars will not increase." (p4) They applied the "precautionary principle" to recommend that the use of MMT be discontinued or banned since it cannot be proven that no harmful effects exist. (A summary of the AAM study can be reviewed in Section 1.7 of this report to CRC.)

3.2.2 Ref. No: 97: Afton Response to ICCT 2004 Report

Summary: Afton prepared this report in response to the 2004 Report by ICCT that concluded MMT should be discontinued based on the "precautionary principle." Afton disagreed with ICCT's conclusions, explaining that few studies or results were considered regarding both health impacts and vehicle emission impacts. They also claim that the precautionary principle was applied incorrectly since uncertainties will always exist, but the best available science (including many studies not considered in the ICCT report) shows that the use of MMT has no negative effects.

Afton criticized the authors of the ICCT report for focusing primarily on the 2002 AAM study (and its related literature) to assess vehicle and emissions impacts. Afton pointed out the inconsistencies in the AAM report, which are already summarized in their response to the AAM report –in sections 1.7.5 and 1.7.6. It was stated that the AAM study results actually showed MMT to cause little or no harm. Additionally, Afton pointed out that the post-mortem analysis was conducted on the Ford Escorts used in the AAM study (See Section 1.7.7.), which were the worst performing pair of vehicles and had questionable maintenance records.

3.2.3 Ref. No. 124: ICCT Report, 2009. Methylcyclopentadienyl Manganese Tricarbonyl (MMT): A Science and Policy Review

Summary of vehicle effects: The ICCT prepared an updated report in 2009, reiterating concerns about the health and vehicle effects of MMT. Again, much of the focus of vehicle effects was from a review of the AAM study, and the follow-on post-mortem analysis, which had not been finalized at the time of ICCT's 2004 Report. (Ford's Post Mortem Analysis is described here in Summaries 1.7.7 and 1.7.8). It was again concluded that "without a high degree of confidence that adverse impacts will not occur, the ICCT recommends that countries avoid use of manganese-based fuel additives like MMT in gasoline."

3.2.4 Ref. No 126: Afton Chemical Corporation, 2010. MMT® and the Precautionary Principle: Insights to a Recent ICCT Paper on MMT. A Response to the International Council on Clean Transportation's (ICCT) Report Entitled "Methylcyclopentadienyl Manganese Tricarbonyl (MMT): A Science and Policy Review"

Summary: Afton again responded that the precautionary principle used by the ICCT was misapplied, and even ICCT stated that substantial uncertainty exists about the use of MMT. It was pointed out that the ICCT report has not addressed the entire body of research, citing only the AAM study, while ignoring numerous other bodies of research providing evidence that MMT does not cause harm. Additionally, Afton stated that if the precautionary principle were applied to gasoline, this fuel would not be in use.

3.3 Sierra Research Review Reports

3.3.1 Ref. No. 84: Lyons, J., 2002. Impacts Associated with the Use of MMT as an Octane Enhancing Additive in Unleaded Gasoline: A Critical Review

Summary: Sierra Research reviewed information and technical literature regarding the impact of the use of MMT on vehicle technology and performance, focusing on peer-reviewed technical literature (not on regulatory proceedings). The review concluded that manganese deposits build up in the combustion chamber, on spark plugs, and in the exhaust system. This leads to negative effects of increased HC emissions, changes in oxygen storage properties of the catalyst that could lead to failures of OBD monitoring systems, and increased PM emissions. Positive effects included improvements in catalytic converter efficiency from decreased deposition of catalyst poisons, such as phosphorous, and reduced NOx tailpipe emissions.

3.3.2 Ref. No. 120: Lyons, J., 2008. Impacts of MMT® Use in Unleaded Gasoline on Engines, Emissions Control Systems, and Emissions.

Sierra Research prepared this report to summarize existing bodies of literature about the use of MMT and its effects on engines and emissions control systems for Canadian vehicle manufacturers. In addition, the report includes data collected in anticipation of a review of MMT by the Canadian government from 2003 to 2005. However, the review was never completed after Canadian refiners voluntarily phased out MMT.

The report gives detailed history of the use of MMT, the evolution of emissions control technologies, and emissions standards employed in the U.S., California, and Canada. It then summarizes articles related to different brackets of technology (early assessments before 1980, 1980-1990 model year vehicles, the AAM study, late model year, and in-use assessments) in terms of effects on emissions, emission control systems, and engine components. A general summary points out that studies conducted by Afton demonstrate use of MMT improves catalyst performance, reduces certain emissions, and is generally benign. However, studies performed by the auto industry have consistently shown that MMT causes increased engine-out HC emissions, sparkplug misfire, exhaust valve leakage, varying degrees of catalyst plugging, and increased tailpipe emissions. A review of literature since the AAM study in 2002 (and up to the time of the publication of this study, 2008) suggested that MMT's impacts on vehicles having more advanced emissions control systems may be more pronounced.

The data collected in anticipation of the Canadian review was also evaluated and compiled in this Sierra Research report. This included a survey of eighteen vehicle manufacturers conducted to collect real-world operational data about MMT's impacts on Canadian vehicles using advanced emission control technologies prior to MY2004. The data, provided in blinded reports, demonstrated that MMT in gasoline adversely impacted at least 19 models (out of 25 models that reported) of 1999-2003 MY vehicles produced by nine manufacturers who represented approximately 86% of the Canadian light duty vehicle sales in 2006. In these models, the primary warranty issues and problems were associated with catalyst plugging by Mn_3O_4. The conclusions from this assessment include:

- Plugging of catalysts by Mn_3O_4 is a substantial problem for different in-use Canadian vehicles and causes drivability problems due to excessive back pressure that can only be corrected by catalyst replacement. Vehicles with these problems will generally experience MIL illumination. Also, some vehicles operating in Canada have a higher ratio of catalyst warranty replacement.
- Plugging of catalysts is more frequently observed on vehicles with advanced emissions control systems that incorporate HCD-CC catalysts.
- Catalyst plugging has been demonstrated to increase tailpipe emissions of NMOG, CO and NO_x,

- The rate of catalyst warranty replacement in Canada slowed in direct response to the reduction in use of MMT.

Based on the manufacturers' data as well as the literature review, the Sierra Research report concluded that the adverse effects of MMT can be divided into two main groups: the formation of manganese oxide deposits in the combustion chamber, and those associated with formation on the faces of catalysts. The report also concluded that the use of MMT is not compatible with HCD-CC catalyst systems that are needed to achieve compliance with Tier 2 standards, and that presently there is no other method to ensure advanced emissions control systems comply with Tier 2 requirements, other than eliminating MMT.

The manufacturer data provided by the nine respondents are summarized in blinded reports in which each manufacturer was assigned a letter A-R. An overview of the effects on vehicles with Tier-2 relevant technologies reported by the manufacturers, and the related testing that was performed on those vehicles, is shown in Table 11-2 below (taken from the Sierra Report). The table represents only those vehicles with reported "advanced emission control technologies" that experienced adverse impacts from MMT in Canada until its cessation in 2004. Additional responses and data from Tier-2 relevant technologies from Manufacturers A, C, D, I, J, K, L, M and O are summarized below:

Table 3.3.2 – 1: Summary Table from Sierra Report (Table 11-2) showing condensed reporting by Manufacturer.

Table 11-2
Sources of Evidence of Adverse MMT® Impacts on Exhaust Emissions, Operation, and Performance of In-Use Canadian Vehicles with Advanced Emission Control Technologies and Systems

MFR	Warranty Claims	In-Use Vehicle Inspection	Laboratory Testing	Emissions Testing	Number of Models Impacted by MMT® Identified	Model Years
A	Yes	Yes	No	No	1	1999
C	Yes	Yes	Yes	Yes	4	2000-2002
D	Yes	Yes	Yes	Yes	2	2003
I	No	Yes	No	No	1	2002
J	Yes	Yes	Yes	Yes	7	2002-2003
K	Yes	Yes	Yes	Yes	1	2003
L	No	Yes	Yes	Yes	3	2001
M	Yes	Yes	Yes	Yes	5	2001-2003
O	No	No	Yes	No	1	2001

Note that in the summary table from the Sierra report, 25 vehicle models are reported to have shown adverse impacts from the use of MMT. It is not clear which of those experienced high warranty claims, or which were identified to have MMT impacts though other means of testing. Through our own analysis and summarization of the blinded reports (summaries provided below), we have identified 11 models that were reported to have experienced warranty claims. Our summary of the information provided in the blinded manufacturer reports is included in Table 3.3.2-2, below. In this table, cases in which warranty claims were reported are highlighted in yellow. To protect the identity of the manufacturers, the number of warranty claims were not provided, however, in some cases, the relative amount of claims in Canada as compared to the US was given, and is noted in Table 3.3.2-2. In one case in which reports were quantified (Manufacturer A), only three warranty claims were reported. The remaining cases that were reported to experience adverse impacts (in Table 3.3.2-1 above) are highlighted in blue. These models were reported to have seen adverse effects measured through other means of durability testing or inspection. In these cases, the number of vehicles evaluated in the study is shown in the table. The remaining models which reported no known issues with MMT are left white. It should also be noted that several manufacturers reported on additional vehicles that were not assigned numbers. In addition to the 31 models that were assigned numbers shown in Table 3.3.2-2, Manufacturer D reported on 5 models, Manufacturer K reported on 4 models, and Manufacturer O reported on 6 models that had Tier 2-relevant technologies but had not experienced any known issues from the use of MMT.

Model	MY	Certification	Catalyst Description	Warranty Claims[1]	No. of vehicles[2]	Visual Inspection	Other Testing
A-1	1999	Tier 1	400 cpsi, not HDCC	Yes	3	Yes*	None
A-2	2000	NLEV-ULEV	600 cpsi, HDCC	No		No	None
C-1a	2000-01	LEV I	600 cpsi, HDCC in MY 2000; add'l 400 cpsi in MY2001	Yes (20 x)	NQ	Yes **	Lab, Emissions on returned catalyst
C-1b	2002	ULEV I	900 cpsi	Yes (12x)	NQ	Yes**	None
C-2	2002	LEV 1	900 cps + 600 cpsi M configuration	Yes (6 x)	NQ	Yes **	None
C-3	2002	LEV I	2-900 cpsi with 400 cpsi downstream	Yes (12 x)	NQ	Yes **	None
D-1	2003	T2B7	HDCC with 400 cpsi	Yes	NQ	Yes **	Emissions testing, engine dyno on returned catalyst; Durability testing on new D-1
D-2	2003	T2B8	HDCC with 400 cpsi	No	NQ	No	Durability testing
I-1	2002	NLEV (LEV)	600 cpsi HDCC with 400 cpsi under floor	No	5	Yes*	None
J-1	2002-03	NLEV (LEV)	600 cpsi, mid under floor, 16 in from exhaust manifold	Yes (35x)	NQ	Yes**	See GM 360, Emissions testing on 24 returned cats
J-2	2003	LEV I	600 cpsi with add’l downstream under floor. (1 AWD, 2-2WD)	Yes (AWD- 37x)	NQ		7 in-use vehicles underwent emissions testing
J-3	2001-02	LEV I	400 cpsi, CC	N/A		Yes*	Lab analysis indicates plugging by Mn
J-4	2001-02	NLEV (LEV)	350 cpsi catalyst	No	20	Yes*	No
J-5	2001-02	NLEV (LEV)	400 cpsi warm up catalyst	No	20	Yes**	No
J-6	2001-03	Tier 1	Dual CC 400 cpsi, located 16 in downstream	No	14	Yes*	No
J-7	2001	NLEV	600 cpsi located 24 in downstream	No	16	Yes *	No
J-8	2002-03	NLEV	600 cpsi located 9 in downstream	No	2	Yes	No
K-1	2003	NLEV (LEV)	600 cpsi, 17 cm downstream, 80 mm diameter	Yes	NQ	Yes**	Lab & emissions testing on returned catalyst(s), Durability on 1 new vehicle, Engine dyno on 1 engine
K-2	2003		600 cpsi, 44 cm downstream, 103 cm diam.	No			Durability testing on one new
L-1	2001	NLEV (LEV)	600 cpsi, single CC	No	1	Yes	Durability, Emissions
L-2	2001	NLEV (LEV)	600 cpsi, two CC, either side of V	No	3	Yes	Durability, Emissions on in-use catalysts
L-3	2004	T2B5	600 cpsi	No	NA	No	Durability testing on one vehicle
M-1	2001-03	ULEV	600 cpsi, manifold mounted HDCC	Yes [3]	NQ	Yes**	Lab, Durability on two production vehicles; In use assessment on 63 vehicles/ parts
M-2	2002-03	T2B5	dual bed 600 cpsi mid-under floor, HDCC	Yes (3 x)	NQ	Yes**	Durability on two production vehicles
M-3	2002	T2B5	600 cpsi, dual brick	No		No	Durability on two production vehicles
M-4	2002	T2B5	dual brick, 900/400 cpsi with perpendicular exhaust inlet to face	No		No	Durability on two production vehicles
M-5	2003	T2B5	900/400 , mid under floor, HDCC	No		No	No
M-6	2003	T2B5	900/400 , mid under floor, HDCC	No		No	Durability on two production vehicles
M-7	2003	T2B5	900 cpsi, HDCC each exhaust bank, single 350 cpsi under floor	No		No	Durability on two production vehicles
M-8	2003	T2B5	900 cpsi, HDCC each bank w/ single 350 cpsi under floor	No		No	Durability on two production vehicles
O-1	2001	ULEV	600 cpsi	No	20		

[1] A “Yes” indicates that higher warranty claims were seen in Canada in comparison to the US. A ratio or multiplier is given with respect to US warranty claims. (e.g. 3x indicates warranty claims in Canada were three times higher than in the US)

[2] NQ= Not quantified

[3] M-1was reported to have other warranty issues, however, higher rates in Canada were attributed to the use of MMT based on visual inspection of catalysts.

* Visual inspection reported reddish-brown deposits, no obvious plugging

** visual inspection reported reddish-brown deposits AND plugging

Manufacturer A: Manufacturer A reported previous experience with plugging on a single 1999 MY vehicle certified to Tier 1 standards with a 400 cpsi catalyst (shown in Table 11-2 above). Three plugged catalysts that had been returned under warranty were visually inspected and showed reddish-brown deposits. Manufacturer A also reported that they had a 2002MY vehicle with a 600 cpsi catalyst, but did not know of any plugging with this HDCC application.

Manufacturer C: Reported four models ranging from MY 2000-2002 having technologies that were later (MY2004) certified to Tier 2 Bin 5 standards that experienced catalyst plugging under warranty claims. Warranty claims were 6 to 20 times higher for each MY vehicle in Canada in comparison to the U.S. The manufacturer also noted that warranty claims peaked during the summer of 2003, and subsequently diminished, which coincided with reductions in MMT levels in Canadian gasoline. Plugging was also reported in cases in China. Manufacture C performed laboratory and emissions testing along with visual inspection of several catalysts returned under warranty in Canada. Visual inspection of three models found plugging by hard reddish-brown deposits, which laboratory analysis showed to contain Mn_3O_4. Most catalysts replaced between 40,000 to 120,000 km were more than 50% plugged. Emission testing performed by Manufacture C on a single plugged catalyst showed that the CO conversion rate could be restored (increase from 55% to 95% conversion rate) by removing MMT deposits. FTP testing in a slave vehicle on a single catalyst that was 90% plugged (removed from a Model C-1a which had a 600 cpsi catalyst conforming to Tier 1 standards in Canada) showed that emission standards were exceeded for HC, CO and NOx, with each being roughly three times the MMT-free baseline level at comparable mileage from a vehicle acquired in the U.S.

Figure 3.3.2-1**:** Color photographs of plugging of A) 600 cpsi and B) 900 cpsi Catalysts from Manufacturer C used in Canada. Catalysts shown in C and D were those used for emission testing comparison. "C" was visually assessed to be 90% plugged. "D" is a typical USA catalyst taken from a vehicle driven in an MMT-free area.

Manufacturer D: Manufacturer D reported on two 2003 MY vehicles (out of seven that were introduced that year) with HDCC. The first model was an early introduction with an "HDCC on each bank" of the V-type engine with a 400 cpsi catalyst downstream certified to "interim" Tier 2 bin 7 standards. This model experienced higher warranty claims in Canada compared to the US (when normalized for differences in sales volumes), particularly after the 30-40k mile range. Visual examination of catalysts removed from D-1 vehicles in Canada showed reddish-brown deposits that caused some degree of plugging and were confirmed to be Mn_3O_4 by XRD analysis. The frequency of plugged catalysts increased considerably in the 30k-40k mile range for the Canadian samples while US samples did not show signs of blockage.

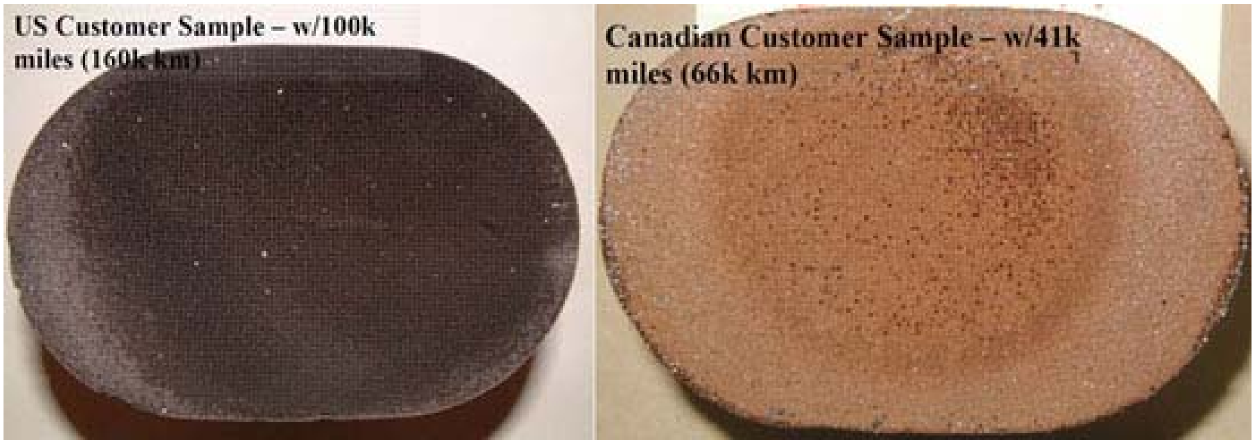


Figure 3.3.2-2: Color photographs of inlet catalyst of Model D-1 from US and Canadian customer samples.

Exhaust Emissions Testing: FTP and US06 testing was completed to compare catalysts returned under warranty in Canada (ranging from 40k-120k km and observed to 30-85% plugged) to catalysts obtained from the US customer fleet (100k-160k -km, no plugging) by testing in a US reference vehicle or a Canadian reference vehicle, both aged to 160,000 km. FTP testing of the Canadian catalysts showed an average increase of 103% NMHC, 97% CO and 17% NOx, with increases being more pronounced as catalyst plugging exceeded 50%. US06 testing showed an order of magnitude greater emissions increase, with average emissions being 10 times higher for the NMHC from the Canadian catalysts compared to US catalysts. CO and NOx were 2.1 and 3.9 times higher, respectively. This increase was thought to be due to increased space velocity in US06 testing.

Engine Dynamometer Testing: Engine dynamometer testing was performed on the D-1 engine using fuel with MMT at 18 mg Mn/L, and plugging rates in the HDCC were compared to a 400 cpsi catalyst. For catalyst inlet temperature ranging from 780°C to 850°C, the HDCC catalyst achieved 2 to 4 times the pressure drop in approximately ¼ of the time of the 400 cpsi catalyst.

Mileage accumulation testing: Manufacturer D also performed durability testing (following an EPA-approved "whole vehicle durability" protocol) of two vehicles using MMT at 18 mg Mn/L. Testing was performed on vehicles D-1 and D-2 using either an HDCC or a 400 cpsi catalyst. Model D-1 was 40% plugged through 70,000 miles and increased to 80% plugged by 90,000 miles with the HDCC catalyst, while plugging in the 400 cpsi catalyst in D-1 did not exceed 10%. The HDCC from Model D-2 plugged at a faster rate than D-1, and reached 80% plugging by 40,000 miles, while only one bank of the 400 cpsi catalyst showed plugging.

Manufacturer I: Manufacturer I reported on a single model (I-1) with low sales volume. Visual inspection of catalysts from five vehicles that were returned under warranty for reasons unrelated to MMT showed reddish brown deposits. Only one had significant plugging, although it hadn't triggered a drivability complaint.

Manufacturer J: Manufacturer J reported to have significantly higher catalyst converter warranty claims on three models (MY 2001-2003) in Canada than in the US, which was observed to begin with the deployment of Tier 2-like catalyst systems. These models experienced warranty replacement rates of

14-35 times higher than the U.S. counterparts. Examination of the Canadian catalysts showed that plugging by Mn-containing deposits was responsible for warranty issues in 94% of the cases. There are similarities between the reporting from Manufacturer J and the GM in-use report by D'Aniello (refer to section 2.4.3 for that reporting). In addition, Manufacturer J performed a qualitative analysis on five other models that revealed deposits on 4 out of 5 models, although no increase in catalyst warranty issues were noted in Canada.

Manufacturer K: Manufacturer K reported that vehicles sold after MY 2002 were not relevant because they were too new to accumulate mileage before MMT was removed from Canadian fuel. However, they reported on one MY2003 vehicle with early sales that had higher than normal warranty returns. Visual inspection was performed on all catalysts replaced under warranty, and those with plugging of at least 70% were considered to be related to MMT use. 70% plugging was observed to occur as soon as 5,000 km, but more commonly at 20,000-60,000 km. XRD analysis showed that deposits on a ~70% plugged catalysts were mainly Mn_3O_4 with some $Mn_3(PO_4)_2$.

Manufacturer K also included track testing in which one of each model (K-1 and K-2) was tested using MMT at 18 mg Mn/L, along with another FWD model with the same power train and catalyst configuration as K-2. Each vehicle was driven at a constant speed of 150 km/hr each day, stopping only for night shift and fueling stops. Model K-1 plugged at 16,000 km. K-2 and the similar vehicle were run until 100,000 km, but no plugging was observed.

Engine dynamometer testing on the K-1 engine with 600 cpsi close-coupled catalyst was performed at high, constant load using fuel with MMT concentration at 36 mg Mn/L. The catalyst plugged after 17 hours of operation. Emissions testing performed on one 90% plugged catalyst showed CO emissions to be approximately 6 times the standard. HC and NOx emissions were still within the standard.

Manufacturer K noted that plugging was more likely to occur in model K-1 rather than K-2 because of higher temperatures inherent in 4WD design and the smaller catalyst with sharper angle of incidence that was located closer to the exhaust ports.

Manufacturer L. Manufacturer L reported on two different 600 cpsi catalyst configurations sold in MY 2001, both certified to NLEV/ LEV standards. One vehicle (L-1) had a single close-couple catalyst while the second vehicle (L-2) had two close coupled catalysts on either side of the V-engine. While neither vehicle had any reported catalyst warranty claims, the manufacturer reported visual inspection of one L-1 catalyst and three L-2 catalysts from in-use Canadian operation with mileage ranging from 30k- 38k miles displayed manganese oxide coatings that were not significant enough to cause driveability issues. Emissions testing was completed on the three L-2 catalysts, which showed that performance for NMOG and CO emissions were close to certification levels while NOx emissions were significantly higher than certification levels, although still within standards.

Manufacture L completed durability testing with 17 mg Mn/L fuel on a MY 2004 vehicle with a similar catalyst layout as the L-2, but certified to Tier 2 Bin 5 standards. Driving consisted of multiple routes driven 6 days/ week. At 50,000 miles, both of the catalysts showed signs of plugging with deposits that were confirmed to be manganese oxide. Emissions testing was performed at 30k and 50 k miles during the durability test. The 50k mile testing, at which point the catalyst showed plugging, exhibited a greater increase in NMHC and CO, with less effect on NOx as compared to the in-use L-2 catalysts, which had minimal plugging.

Manufacturer M: Manufacturer M reported adverse impacts on 5 models, ranging from MY 2001-2003. Four vehicles were certified to Tier 2, Bin 5 and one was certified to ULEV standards. The manufacturer reported catalyst warranty claims in Canada for two of the vehicles.

The automatic transmission version of M-1 experienced significantly higher warranty replacement rates in Canada compared to the US, which were initiated by MIL illumination. While the warranty replacements were not entirely attributable to MMT, an inspection program of all the replaced catalysts showed that MMT-related plugging was a major contributor to the higher rates in Canada. It was observed that plugging incidents began to increase significantly around 40-60k km (25-37k mi) and peaked around 80-100k km (50-62k mi). The manufacturer noted that the manual transmission version of vehicle M-1 did not have as high a repair rate. The trend of warranty occurrences in Canada experienced by the M-1 model began to decrease as MMT was phased out of Canadian fuel. The inspection program applied to all catalysts returned under warranty and each was subjected to boroscope (visual) inspection and back pressure measurements. Because MMT use was halted, Manufacturer M believed that the warranty results seen on M-1 were likely only a small percentage of what would have been seen had the use of MMT continued.

A second major incidence of plugging was reported in model M-2, where the Canadian rate of warranty claims (triggered by MIL illumination) was about 3 times higher than the U.S rate. As with M-1, the occurrence of warranty claims with model M-2 dissipated as MMT was phased out from Canadian fuels. A similar inspection program was completed on the M-2 catalyst returns, which showed that warranty claims from plugging occurred at around 20-40k km, a lower threshold than M-1. The higher rate of plugging was attributed to higher inlet gas temperature since M-2 is a 4-wheel drive SUV which likely experiences higher loads. Additionally, it was noted that the inlet pipe to the catalyst is oriented at a slanted angle, which can accelerate MMT plugging.

Manufacturer M reported that two other models (M-3 and M-4) using a high density catalyst located at a mid-under floor position did not experience any warranty issues. This was attributed to lower operating temperatures, as well as the layout of the exhaust system which includes a near perpendicular entrance of exhaust gases to the catalyst, thereby reducing sensitivity to plugging by MMT. Models M-5 through M-8 were also introduced with HDCC designs beginning in MY 2003. None of these models experienced warranty issues, which was attributed to the low exposure rates before MMT was removed from Canadian fuel supply.

Additional durability testing was completed on M-1:

- Mileage accumulation was performed on production vehicles using a road course, with emissions testing being conducted at various mileage intervals. One vehicle was run on clear fuel and one with MMT at 8.3 mg Mn/L. Both vehicles were driven all day for seven days per week, with a rest or soak period overnight. The emissions did not change through the 30k mile test point, but NMOG and NOx increased significantly at 42k, and were 4x and 10x higher, respectively, than in the 30k test. Loss of power was experienced in the MMT vehicle at 27k miles, and an MIL illumination occurred around 40k miles, with rough running reported just before 42k miles.

- Five Canadian consumer catalysts were removed and photographed at 38k, 49k, 86k, 103k and 131k miles. All showed some degree of plugging, and analysis confirmed the material was manganese oxide.

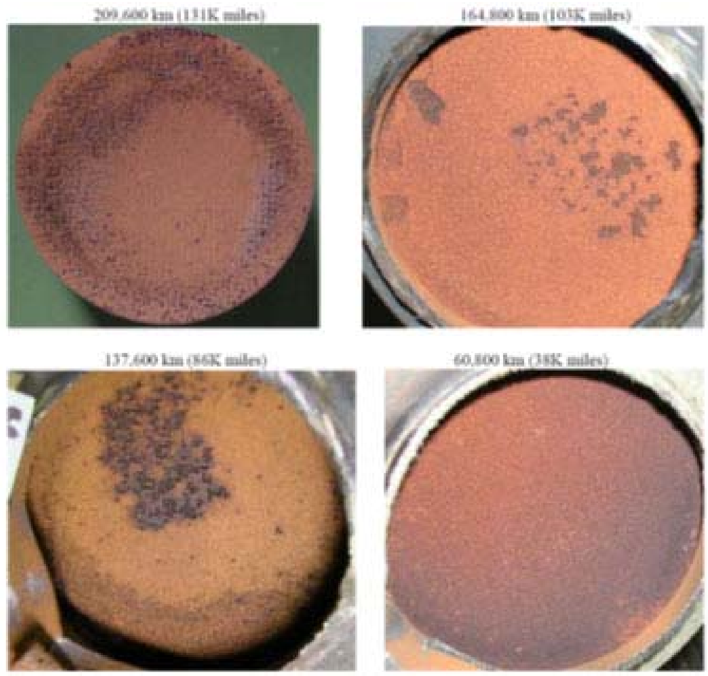
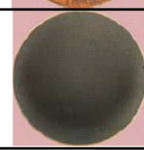
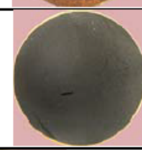
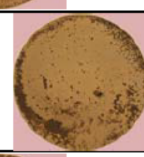
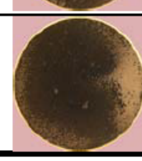


Figure 3.3.2-3: Color photographs of plugged catalysts examples.

- Six catalysts collected from MY 2001 M-1 Canadian vehicles with mileage ranging from 35k to 81k miles were tested for emissions using a single slave vehicle. Three of the six catalysts exhibited higher emissions levels than permitted by standards applicable for these vehicles. Five of the catalysts exceeded the baseline fleet by 3.5-11x for NOx, and 2-6x for THC.
- Manufacturer M conducted a “Large Canadian Survey” in which catalysts were retrieved from 63 randomly selected M-1 vehicles. Catalyst plugging on these ranged from 2 to 82% and was found to be due primarily to Mn_3O_4. Driveability issues were noted with vehicles equipped with the highly plugged catalysts. At plugging levels above 50%, THC increased to double the baseline, NO_x increased to about 4x the baseline.
- Manufacturer M reported results of its own test program on 8 vehicles. (Models M-1 through M-8 described in the table, excluding M-5). Mileage accumulation was done on each vehicle on roads and highways following two specific courses at the rate of 3630 miles per week on a city course, and 1050 miles per week on a mountain course. Eight vehicles were tested, included one matched pair of M-7 model. One M-7 was driven using “clear” fuel, while the remaining values were driven using fuel with MMT at 0.032 g Mn/gal. Emissions testing, catalyst backpressure measurements, and catalyst inspections were performed at 15k-mi intervals. All vehicles developed MMT-related deposits (shown in Figure 3.3.2-4 below). NO_x and NMHC

tailpipe emissions increased over their clear-fueled counterparts for most vehicles. Four vehicles experienced MIL illumination related to catalysts problems.

Vehicle Year & Model	Primary Catalyst	Config	MIL On?	Mn Conc	Catalyst Photos	
2001 M-1	manifold-mounted 600cpsi	A	**Yes**	.032 g/gal		@ 43,000 miles
2003 M-2	mid-underfloor 600cpsi	C	**Yes**	.032 g/gal		@ 20,000 miles
2003 M-7	manifold-mounted 900cpsi	B	**Yes**	.032 g/gal	 	@ 100,000 miles
2003 M-7	manifold-mounted 900cpsi	B	No	**No MMT**	 	@ 120,000 miles
2003 M-6	mid-underfloor 900cpsi	C	No	.032 g/gal		@ 120,000 miles
2003 M-8	manifold-mounted 900cpsi	B	**Yes**	.032 g/gal	 	@ 105,000 miles
2003 M-3	mid-underfloor 900cpsi	C	No	.032 g/gal		@ 120,000 miles
2003 M-4	mid-underfloor 900cpsi	C	No	.032 g/gal		@ 120,000 miles

Configurations

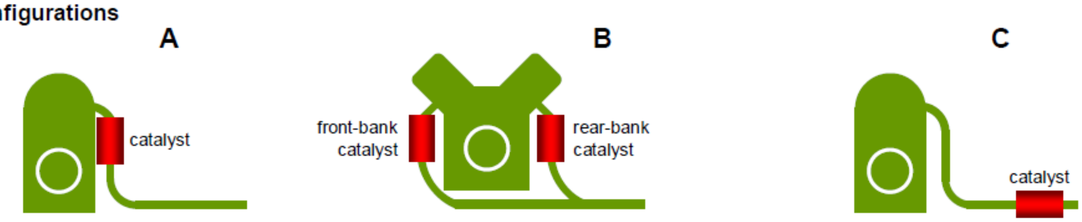


Figure 3.3.2 – 4: Summary of results from Manufacturer M including color photographs.

Manufacturer O: Manufacturer O reported that it had 6 models with HDCC systems sold prior to MY 2004. They reported no field experience in which MMT plugging was a problem, and that examination of a warranty database did not show any sign of catalyst plugging, although inspection of some catalysts showed characteristic orange coating. One MY 2001 vehicle (O-1) with a 600 cpsi catalyst that was sold in limited quantities in British Columbia was evaluated by the manufacturer in a test program that placed a single vehicle in a company fleet in which MMT was used. The vehicle was tested at 75k and 120k-km and began to show signs of catalyst plugging. Average emissions also increased over the last 70k-km of testing, with significant increases in NMOG and NO_x.

3.3.3 Ref. No: 138-c: Appendix 6: Afton, undated. A New Sierra Research Paper on mmt® Fails to Discredit the Clear Benefits of mmt and Its Compatibility with Vehicle Performance.

In this response to the Sierra Report issued in 2008, Afton disputed the conclusions made from the results presented within the manufacturer surveys, and pointed out other missed articles in Sierra's literature summary. Afton also pointed out that the Sierra report was not peer reviewed, and that the confidential nature of the individual manufacturer's reports makes them difficult to validate.

- Afton disputed the conclusion of the Sierra Report, claiming plugging of HCD (>600 cpsi) converters is highly selective and that other factors besides MMT can contribute to plugging. They included as an appendix (titled "Catalytic Converters Fail for Reasons Unrelated to mmt®") details of an investigation performed by Afton to assess converter performance in the U.S. In this program, hundreds of catalysts were collected from recyclers in TX, CA, WA and VA, many of which had obstructed pores for reasons un-related to MMT (they were all obtained from areas in which MMT was not used). Several photographs of these were provided, with examples shown below.

Figure 3.3.3- 1: Color photographs of plugged catalysts collected from catalyst recyclers in the U.S. Analysis on a 2001 Honda Civic Converter (673) showed deposits are primarily Calcium, Phosphorous and Zinc (14.4%, 12.2%, 11%, respectively). Other examples included Nissan Catalysts from California (730) and from Texas (664), and GM catalysts from Washington (504), and Texas (530). (Numbered catalysts are from right to left)

- Afton maintained that the conclusion that MMT is not compatible with HCD- close coupled catalysts is unwarranted, pointing out that 8 automakers reported they were not aware of any warranty cases due to MMT, and that of the remaining five manufacturers, 36 models out of 45 identified did not experience any warranty claims. They therefore conclude that the "majority" of 2000-2004 vehicles with advanced vehicle emission control systems did not experience problems, and those that did were at unquantified levels and could possibly have been attributed to other warranty issues. They then concluded that the Sierra report supports the demonstration that MMT is a beneficial fuel additive.

- Afton stated that since all vehicles in Canada used MMT, all vehicles should experience problems. Since the Sierra report only cited a small number of problems, Afton claimed this as an indication that the problems could be attributed to other causes.
- Afton noted that the laboratory data presented from the manufacturers on temperature profiles do not support the conclusion that temperature differences between models is a root cause of the plugging, since some of the manufacturers that reported models with no plugging also reported operating temperatures well above the "threshold" brick temperature for plugging of 800^{o}C. (E.g. 1000^{o}C brick temperature in model O-3).
- Afton also pointed out that differences in warranty programs exist between the U.S. and Canada, and therefore the rate of warranty claims are not comparable. They also refer to a letter regarding a study by Environment Canada in which Notices of Defect were correlated to the use of MMT. No such correlations were found.
- Of those manufacturers that presented vehicle and component test data, Afton noted that only a small fraction of them followed "normal" test procedures, noting that many of the cycles applied during testing were extremely severe.

In addition, Afton hypothesized that model M-1 reported by Manufacturer M was a 2001 Honda Civic. They reported that their own analysis found 2001 Honda Civic models produced for sale in Canada had a different engine calibration than those produced for sale in the U.S, and that certification data for the Canadian engine calibrations showed projected emissions to vary by 200 to 500%. In addition, they reported that the 2001 Honda Civic had other reports of widespread failure and warranty issues not associated with the use of MMT. (Note that the 2001 Civic was subject on an earlier evaluation by Afton in which failure rates were noted to be low. See Section 2.4.1).

3.4 ACEA Position

3.4.1 Ref. No: 121: ACEA, 2009. ACEA Position on Metal Based Fuel Additives

Summary: This report was prepared by the European Automobile Manufacturing Association (ACEA) to describe technical and health-related consequences from use of MMT in vehicles. The report is largely a summary of other literature and studies regarding the history and use of MMT, health impacts, and vehicle and emissions impacts.

Background on interest of MMT use in the EU: In the EU, a ban on MMT was considered in 2008 as part of the Fuels Directive (2009/30/EC), but later compromised to allow 6 mg Mn/L in fuels (with the label 'containing metallic additives'), to be modified to 2 mg Mn/L beginning Jan. 1, 2014.

The European Union has implemented Euro 5 and 6 vehicle standards, which require use of advanced emissions control technologies to achieve very low tailpipe emissions levels for periods of 160,000 km. To meet these criteria, automakers have had to increase the use of high-density close coupled catalysts, and cell densities are increasing from 300 cpsi to 800 cpsi. Studies have shown that with increasing cell density, blockage of the catalytic converter increases, and the penetration depth of manganese deposits decreases.

Health Effects summary: The human body requires manganese to function properly, and it regulates the amount that it needs. However, it is more difficult for the body to regulate airborne manganese than food-borne because it enters the lungs and is transferred directly to the bloodstream. The HEI supported a study that found manganese accumulates in the brain, because it is transported out only by the very slow process of diffusion. Two organizations (the American Academy of Pediatrics and the International Commission on Occupational Health) recommend against using MMT in the gasoline supply.

Vehicle/Emissions Effects: The report summarizes vehicle and emission impacts from other reports and references. The studies addressed include:

1. "Volkswagen" is from Schindler, 2004 (presentation given in China Summary included in Section 2.2.2);
    a. Measurable plugging of catalysts. The depth of penetration of manganese oxides in a catalytic converter depends on the cell density, as shown below. Increasing cell density increases blocking of the catalytic converter. (This figure was not included in Schindler's presentation.)

Figure 3.4.1-1: Manganese deposit depth of penetration in 350cpsi vs. 600 cpsi catalysts.

2. "Ford Characterization Results, 2008" (Note: results cannot be attributed to a particular reference; also, results from BMW testing were not referenced);
    a. Reported catalyst failures in the Chinese market where MMT was used.
3. "German car manufacturers," referenced from Richter (Porsche study in Section 2.3.1);
4. "Experience from Canada" referenced from Sierra Research, 2008 (summarized in section 3.3.1);
5. "Results of a Volkswagen field test in Argentina" cites a 2009 report "in preparation" that could not be found.
    a. Euro 4 and Euro 5 vehicles used in Argentina where average petrol contains 10 to 15 mg Mn/L. At 50,000 km, vehicle testing could not be performed because of an extreme loss in performance on three vehicles.
6. Also, notes from a rejected SAE paper by Afton were included in the ACEA discussion.

All of the automaker studies summarized in the report had negative findings for MMT, and the ACEA concluded that metallic additives are a major concern for the automotive industry due to reduced lifetime of engine components and catalysts.