

MMT Effects on Gasoline Vehicles: A Literature Review

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ABSTRACT

Methylcyclopentadienyl manganese tricarbonyl (MMT) is an octane-boosting gasoline additive that has been used for over 50 years. This usage has been controversial; particularly in modern gasoline vehicles equipped with advanced emissions control systems. There is concern that extended use of MMT will lead to build-up of Mn-containing deposits on engine and emissions system components, thereby adversely affecting vehicle emissions performance and durability. This paper provides a comprehensive review of the literature regarding the effects of MMT on gasoline vehicles, with an emphasis on modern, Tier 2 vehicles.

Numerous test programs have been conducted - including wide ranges of vehicle model years, technology types, and testing conditions. The reported MMT effects over this body of literature are not consistent. In general, studies by automakers have concluded that under certain test conditions, use of MMT is detrimental; contributing to catalyst plugging, deteriorated performance, and increased emissions. In contrast, most studies by Ethyl/Afton have concluded that under typical operating conditions, use of MMT does not cause harm, and does not contribute to exceedances of vehicle emissions standards. These opposing conclusions can be attributed largely to two factors: (1) differences in test cycles/conditions and (2) the basis for emissions comparisons.

To achieve compliance with stringent Tier 2 emissions standards, automakers have adopted more active catalysts having 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, promoting more rapid initial heating and higher overall catalyst temperatures. These technology enhancements have increased concerns about the use of MMT. There is credible evidence that under certain in-use operating conditions, MMT has contributed to catalyst plugging in Tier 2 vehicles. Similar concerns are expected to apply to future Tier 3 technology vehicles.

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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 (4.7×10^{-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].

The use of MMT as a gasoline octane enhancer has been controversial for many years. In particular, the potential impacts of extended MMT use upon vehicle emissions and emissions control systems have been of concern. This literature review effort was conducted under the auspices of the Coordinating Research Council (CRC) to compile, review, and summarize available information

regarding the effects of MMT upon gasoline vehicles, with an emphasis on model year 2000 and newer vehicles. The review focuses 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. A more detailed version of this review is available in CRC Report E-114 [4].

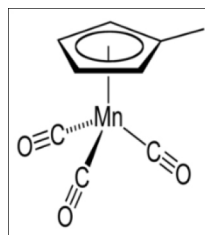


Figure 1. Chemical structure of MMT



BACKGROUND

Before reviewing the literature regarding MMT usage and its effects in gasoline vehicles, it is useful to provide some background information. In this section, we briefly describe the history of MMT, combustion products and ambient Mn levels resulting from its usage, vehicle emissions standards, and the evolution of emissions control technologies to meet these standards.

History of MMT Use

MMT was first marketed by Ethyl Corporation in 1959, as a supplement or replacement for tetraethyl lead (TEL) [5]. 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 [6]. The MMT-based anti-knock package marketed by Ethyl was known as *HiTEC 3000*TM (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. [6,7]. 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](#) for common dosage levels.

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 [8, 9, 10, 11, 12, 13]. 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.¹ (There is an extensive body of literature regarding the health effects of MMT. Much of this is summarized in papers by EPA [9,14]). 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, 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 [15].

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 [15,16]. This Act prohibited the importation of MMT into Canada, and the trade of MMT 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

¹Around this 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 µg Mn/M³ established in 1984 was reduced to 0.4 µg/m³ in 1990, and further reduced to 0.1 µg/m³ in 1993. EPA's derivation of this inhalation RfC for Mn is described in the literature. [Davis (1998) and Davis et al. (1998).]

Canadian-specific Tier 2 exhaust standards in 2004, all major Canadian refiners voluntarily eliminated MMT from their gasoline supply [17]. 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) [12] and the European Automobile Manufacturers' Association [18]. This information about allowable MMT levels, combined with more recent updates from the International Fuel Quality Center, is summarized below in Table 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 [19,20]. Yet, there are concerns about airborne Mn, as the impacts of exposure through inhalation are quite different from the impacts through ingestion [15,21,22]. Mn is somewhat unusual with respect to toxicity in that it is relatively non-toxic to humans, except for its effect on the brain [23]. 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 [15,24,25].

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

Combustion of gasoline containing MMT produces emissions of manganese oxides, including MnO, MnO₂, and Mn₃O₄, manganese phosphates and manganese sulfates [26,27]. 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]. More recent work has shown 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) [28,29]. While Mn₃O₄ 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 [26,28,30,31].

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 [15,29,32, 33, 34]. Numerous studies have found that between 5 and 45% of the manganese in MMT-containing fuel is exhausted as particulate [35, 36, 37]. 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 [36,38,39]. 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 [28].

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 [40, 41, 42], while other studies show mixed results [43,44]. 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 [8]. 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/m³, respectively. (For comparison, the RfC level is 50 ng/m³.) These researchers also concluded that crustal contributions to ambient Mn concentrations are approximately 1-2 ng/m³ 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 [45]. 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 [46, 47, 48, 49]. It has also been shown that ambient Mn

levels in Montreal declined once MMT was removed from gasoline [50]. A similar decrease in ambient fine particle Mn was noted in Australia following a decline in MMT usage [51].

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 [47], Toronto [34,52, 53, 54], Indianapolis [55], Sydney [56], and elsewhere. Most studies show very low exposure levels, typically in the range of 0.01-0.02 $\mu\text{g}/\text{m}^3$, 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" [57]. 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" [14].

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. Because these deposits build up over time, there is 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 (g/mi)

Bin	Emission Limits at 50,000 miles					Emission Limits at 120,000 miles				
	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	0.10	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 1), so too have components that control and reduce emissions of the exhaust gases: CO, NO_x, and hydrocarbons (HC). Achieving 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 [58]. 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

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 catalysts, 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 typically contain highly dispersed precious metals (Pt, Pd, or Rh), along with promoters and stabilizers, on aluminum oxide particles that are coated onto the monolith (washcoat) to store and release oxygen for oxidation of CO and HC.

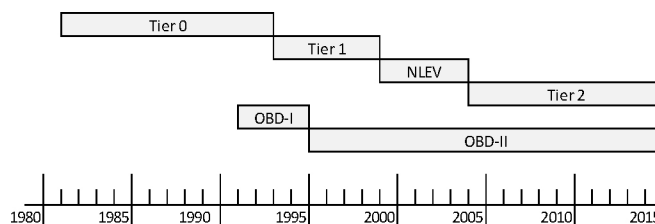


Figure 1. Approximate timeline of U.S. Federal light-duty vehicle emissions standards. (Stated dates vary due to phase-in schedule, exemptions, and other factors.)

In Tier 1 vehicle applications, monoliths typically had channel sizes that equate to 400 cells per square inch (cps). However, to improve conversion efficiencies, HCD substrates have been developed, which provide more flow area, higher surface area, and reduced thermal mass to enable more rapid catalyst heat-up - a key to achieving low tailpipe emissions during cold-starts. Cell densities have increased to 600 - 900 cps, which provides large benefits in emissions performance [58]. 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 [59])

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

A vehicle's OBD system is responsible for monitoring the emission control system components to ensure that emissions do not exceed 1.5 times the emissions standard. This is done through continuous monitoring of oxygen storage capacity of the catalyst using 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.

LITERATURE SOURCES

Numerous sources of literature were accessed and reviewed during the course of this project. The starting point for this review was a database being maintained by the National Conference on Weights and Measures (NCWM). At the time this review project began, the NCWM database contained about 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 this database, a systematic search was performed using two other sources: (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, approximately 70 additional relevant, publicly-available documents were uncovered, creating a total database of about 145 items.

The identified literature items were examined to determine which ones focused on the following main items of interest for this review:

- Effects of MMT on emissions of criteria pollutants
- Effects of MMT on engine hardware
- Effect of MMT on emissions control systems

This subset of the literature was further reduced by focusing on items determined to have “high” or “medium” relevance. “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 referred 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.

Most of the medium and high relevancy literature reports were published by a small handful of organizations that included various automakers and Ethyl Corporation (later reorganized as Afton Corporation). Figure 2 shows a histogram of these publications apportioned by the groups/sponsors responsible for the studies. These 68 critical literature references are identified in Appendix Table A-1.

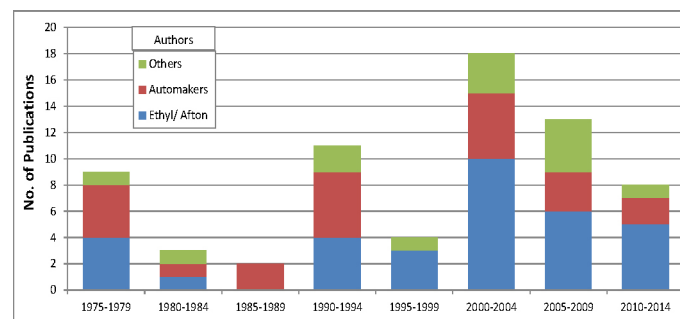


Figure 2. Number of medium and high relevancy publications about MMT's effects on gasoline vehicles.

In the sections that follow, this literature is summarized and discussed. First, the effects of MMT on pre-Tier 2 vehicles are briefly presented; then the effects on Tier 2 vehicles are presented in greater detail. Additional information about MMT's effects on both sets of vehicle technology is provided in the CRC E-114 report [4].

SUMMARY OF PRE-TIER 2 EFFECTS

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 [60]. In addition, several related publications and reviews were

provided by EPA. Following limitations imposed in the 1977 amendments to the Clean Air Act, much of the literature focused on efforts related to Ethyl's waiver applications to the EPA [35,61, 62, 63]. Concerns about the use of MMT were related to its interaction and effects on new oxidation and three way catalysts, 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 groups) 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 [64].
- In some tests, MMT-fueled vehicles showed increases in catalyst performance, due to scavenging of catalyst poisons, such as phosphorus and zinc [65]. However, some studies by the automakers showed that catalyst efficiency decreased as exposure to Mn increased [66, 67, 68].
- 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 [60,69], while Ethyl concluded that MMT-fueled vehicles would still meet all applicable emissions standards [70].
- 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 [71].
- Catalyst placement and exhaust temperatures were shown to have strong influences on how rapidly plugging occurs [72]. 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 [72].

Tier 1 Vehicle Effects (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. Also during this time, concerns about MMT's effect on OBD systems were growing. 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. [73]. Fuel effects and emissions varied across all vehicle models such that there was no consistent effect on any single emission category. However, from statistical analysis of the fleet it was 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 50k miles."

Part 2 was conducted to address concerns regarding effects seen in the LEV vehicles during Part 1 [74,75]. 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 NO_x. Post-mortem laboratory analysis performed on one set of vehicles showed that manganese deposits on the valves and catalyst pores contributed to increased emissions [76].

Ethyl took issue with various aspects of the AAM study and presented their own evaluation of the data [77, 78, 79, 80]. 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 analysis of different vehicle categories showed that fleet average compliance margins were not statistically different between MMT-treated and clear² 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.

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 HCD catalysts in a close-coupled configuration (HCD-CC or HDCC). Technologies have increased cell densities from the historically typical 400 cells per square inch (cps) to 600-900 cps. 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, which has been shown to increase the rate of plugging [81].

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 catalyst temperature from 705°C to 843°C [72]. Therefore, close coupled catalysts with higher temperatures may be more susceptible to plugging.

²The term "clear" gasoline is typically used to indicate unleaded, non-MMT gasoline.

Two different conditions are referred to as catalyst plugging: (1) channel obstruction and (2) pore-mouth blockage [82]. 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 increase in pressure drop across the catalyst. Channel obstruction can affect drivability of the vehicle, presumably due to higher backpressure. Pore-mouth blockage is caused by inhibition of mass transfer between the gas phase pollutants and the solid catalyst, resulting in blockage of catalyst active sites, which reduces 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 failures of catalysts when using MMT in Tier 2 and similar vehicles [83,84]. In-use surveys conducted by Afton have not supported this observation [85,86]. 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 [87]. 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 further summarized below.

It should be noted that reports of several studies described herein were obtained from the NCWM database. While some of this literature is published elsewhere in peer-reviewed journals, or is available through web searches, other studies are documented in technical reports or white papers that are not publicly available or easily 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 always 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®.

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 methodologies for evaluating effects of metallic fuel additives on emissions performance of LD vehicles, with the aim of generating data on regulated emissions, as well as speciation of emitted metals [88]. 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.

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 engine test benches to compare the use of MMT at 15 mg Mn/L to Super Plus gasoline in the European market [89]. The emissions control system in each setup consisted of two 400 cpsi metal substrate catalysts for each of the two cylinder banks in the engine, arranged with a short distance between the two catalysts. 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/km) 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 3, were found to be responsible for the increased exhaust-gas backpressure and resulting torque and power losses. Deposits also resulted in a 25°C increase in light-off temperature of