CRC Report No. E-114-2

Effect of Metallic Additives in Market Gasoline and Diesel

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COORDINATING RESEARCH COUNCIL, INC.

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Final Report for

CRC Project No. E-114-2

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Contents

List of Acronyms

AAM	Alliance of Automobile Manufacturers
ASTM	American Society for Testing and Materials
ATC	Technical Committee of Petroleum Additive Manufacturers in Europe
AVSR	Anti-valve seat recession
CARB	California Air Resources Board
CFR	Code of Federal Regulations
CRC	Coordinating Research Council
CVMA	Canadian Vehicle Manufacturers Association
DCA	Deposit control additive
DOC	Diesel oxidation catalyst
DOE	Department of Energy
DPF	Diesel particulate filter
EGR	Exhaust Gas Recirculation
EPA	Environmental Protection Agency
FAME	Fatty Acid Methyl Esters
FBC	Fuel borne catalyst
GRPE	Working Party on Pollution and Energy
HEI	Health Effects Institute
HPCR	High pressure common rail
ICP	Inductively coupled plasma
JRC	Joint Research Council
LEV	Low emission vehicle
LNT	Lean NO_x Traps
LRP	Lead replacement petrol
MECA	Manufacturers of Emission Controls Association
MFA	Metallic fuel additive
MMT	Methylcyclopentadienyl manganese tricarbonyl
NCWM	National Council on Weights and Measures
NEDC	New European Drive Cycle
NLEV	National Low Emission Vehicle
NM	Not measured
OEM	Original Equipment Manufacturer
ON	Octane number
PEA	Polyether amines
PIBA	Poly isobutyl amines
PIBSI	Poly isobutylene succinimide
PM	Particulate matter
PN	Particle number
SAE	Society of Automotive Engineers
SCR	Selective catalytic reduction
SI	Spark ignition
TEL	Tetraethyl lead

UNECE	United Nations Economic Commission for Europe
UNEP	United Nations Environment Program
VERT	Verification of Emissions Reductions Technologies
WOS	Web of Science
WWFC	World Wide Fuel Charter

Executive Summary

Recently, a joint task force was formed between ASTM and the National Conference on Weights and Measures (NCWM) to evaluate the effects of organometallic components on gasoline vehicles. A previous CRC project (CRC-E-114) was conducted to provide information to the ASTM group on the use of MMT and its effects on engines, emissions, and emissions control systems from modern, Tier 2 vehicles. This information was used in consideration of revisions to ASTM D4814, "Standard Specifications for Automotive Spark-Ignition Engine Fuel."

Within this follow-on project, additional information on the use of other metallic fuel additives and their effects on vehicle performance and exhaust systems was investigated to provide useful guidance to ASTM during the consideration of future fuel specifications. The objectives of this project were to obtain, organize, summarize, and synthesize relevant information regarding the use of metallic fuel additives (MFAs) in market gasoline and diesel fuel, and the effects of such usage on vehicle engines and exhaust aftertreatment systems. The focus of literature searches on these effects was on modern vehicles (post-2000), which are equipped with on-board diagnostic (OBD) systems and advanced emission control systems. For gasoline, this includes vehicles categorized as National Low Emission Vehicles (NLEV) and Tier 2 or beyond in the U.S., and Euro-3 through Euro-6 in the EU. For diesel, this includes engines/vehicles with OEM-equipped oxidation catalysts and diesel particulate filters. Other historical information was also included where relevant.

This search returned over 100 items that were relevant to the use of organometallic fuel additives. The information found in these respective items was used to compile a database on the use and purpose of specific metallic additives in the compendium, which includes 88 items (although some are repeated). The literature includes only publically available literature, which was supported through direct personal communication where necessary. Additionally, it should be noted that evidence of use of these additives was only obtained from literature and web searching, and supported with personal communication from a variety of sources, including the EPA and several commercial additive providers. However, we expect that much more literature and evaluations on various products may exist, but are retained as proprietary.

This literature search does not provide significant evidence of wide spread use of organo-metallic additives in either gasoline or diesel fuels. There is some indication that metals are occasionally incorporated into additive packages, however, the highly proprietary nature of the additive industry makes it challenging to determine the extent to which they are used, particularly at the refinery level. Recent fuel survey information was obtained to confirm levels of organometallics in gasoline fuels. As of 2015, the most widely used organometallic additive was manganese, which was found in fuel samples from 48 countries. While most instances of its use were within specified limits for the country, in some cases it was detected as high as 66 mg Mn/L. Iron was detected less frequently and in much smaller quantities worldwide. However, it was found at elevated concentrations ranging from 5 to 25 mg Fe/L in 5 countries. Other metals were detected in relatively few instances, with the exception of Silicon, which is a contaminant that can result in significant engine damage. Silicon was found in 111 samples from 35

countries. Generally, the fuel survey information supported the conclusion that organometallic additives are not widely used.

A summary of known organometallic additives and their function in gasoline and diesel is outlined in Table 1. Many of these additives have been used in the past but are no longer acceptable for use with modern emission controls systems. The use of these additives is recommended against by particular organizations such as the World Wide Fuel Charter or United Nations Economic Commission. The range of use of these metallic additives found in gasoline from the SGS fuel survey is also shown in Table 1, along with a count of the number of samples worldwide in which the metal was detected (out of 1579 fuel samples collected over summer and winter seasons). Manganese and ferrocene are found the most frequently, and in the highest quantities. Copper was seen occasionally, but in relatively low concentrations. Silicon and zinc were also frequently seen in small quantities, but are not used as additive packages in gasoline, so are not found in the table.

Table 1: Use of organometallic additives in gasoline and diesel. (NM= not measured)

	GASOLINE					DIESEL		
				Fuel Survey				
	Anti-knock	AVSR	Other	Sample Count	Range of Use (min, mean, max) (mg/kg)	Soot Suppressant	FBC for DPF	Other
Al				0	--			Lubricant/ Catalyst
B				6	0.1, 0.1, 0.2			Lubricant
Ba				0	--	X		
Ce				-	NM	X	X	Antioxidant
Cr			Antistatic	0	--			
Cu				26	0.1, 0.5, 2.8		X	
Fe	X	X		75	0.1, 3.3, 25	X	X	Demulsifer, Corrosion Inhibitor
K		X	Fuel Stabilizer	4	0.4, 3.7, 8.2			Stabilizer
Mg		X		6	0.1, 0.2, 0.4			Lubricant
Mn	X			267	0.1, 11, 91		X	Lubricant
Na		X		8	0.1, 0.9, 1.3			
Pb	X	X	Lubricant	-	NM			
Pd				-	NM			Antifoam
Zr				-	NM			Lubricant

Iron as ferrocene has been used in both gasoline and diesel. However, its use can lead to iron oxide deposits, which have been shown to build up in the combustion chamber and on emission control system components. In SI engines, these deposits can result in increased electrical conductivity and abnormal spark as they build up on spark plugs and can also contribute to plugged catalysts. However, in diesel engines, the use of ferrocene in additive packages has been shown to reduce the occurrence of injector plugging or fouling. The World Wide Fuel Charter recommends against the use of ferrocene and Mn (as MMT) in both gasoline and diesel applications. Fuel survey information indicates that with the exception of a handful of countries, iron is rarely added to gasoline fuels.

Barium, cerium, copper, iron, potassium, manganese and magnesium were all found to be used in various diesel fuel additives, with other metals used primarily in catalysts, but not as fuel additives. The most frequently applied organometallics in diesel additives were cerium, iron as ferrocene, manganese and barium, used as either fuel borne catalysts (FBCs) or soot suppressants. However, none of these additives appear to be widely used, with the exception of FBCs for diesel particulate filter (DPF) regeneration. Targeted searches for other additives did not reveal any commercially available products for diesel fuels. Most of the recent literature on organometallic additives involved investigations of their use as FBCs to aid in regeneration of diesel particulate filters. Iron as ferrocene and cerium MFAs have been used for this purpose in commercially available products. However, their market is limited, and they are available primarily as aftermarket packages to be used with specific vehicle technologies as recommended by vehicle manufacturers, and are not available in fuel pools. Other MFAs have been evaluated as FBCs in the literature but do not appear in commercial products.

MFAs have primarily been used in gasoline as antiknock or anti valve seat recession (AVSR) additives. However, their use is no longer recommended. Lead has been phased out and is currently only allowed in three countries (Algeria, Iraq and Yemen). It is still permissible in gasoline up to 13 mg/kg, however, the effects of these low levels on engine and exhaust components have not been studied or reported in recent literature. Older literature has clearly documented the adverse effects of lead contamination on three way catalytic converters. Iron as ferrocene is marketed as an antiknock by some additive producers in China and Canada. However, there does not appear to be evidence of broad use of ferrocene in the gasoline pool. Potassium has been used in lead-replacement gasoline, and can act to protect valve seats. Its use is still recommended as an AVSR by the World Wide Fuel Charter. The problems with valve seat recession were found mainly in older cars that were designed to use leaded fuels, and generally do not occur in modern vehicles with hardened valves. Therefore, nearly all AVSR additives, including potassium, are sold as aftermarket products.

1 Introduction and Background

There is a long history of using metallic additives in market fuels to promote various beneficial performance attributes. In most cases (but not all) these metals are included as organometallic compounds. The best known and most widely used metallic fuel additive (MFA) is tetraethyl lead (TEL), which has been used world-wide as an anti-knock additive in gasoline. Manganese-based additives, particularly methylcyclopentadienyl manganese tricarbonyl (MMT), have also been widely used in gasoline as anti-knock agents. In diesel fuel, barium-containing additives have been used for soot suppression [1] and cerium-based additives have been used to reduce emissions of ultrafine particulate matter (PM). [2] In more recent years, a variety of MFAs have been evaluated in diesel engines to serve as fuel-borne catalysts for diesel particulate filter regeneration, and numerous other MFAs have been used in gasoline and diesel fuel for a variety of other purposes. [3,4,5]

Recently, a joint task force was formed between ASTM and the National Conference on Weights and Measures (NCWM) to evaluate the effects of organometallic components on gasoline vehicles. A previous CRC project (CRC-E-114) was conducted to provide information to the ASTM group on the use of MMT and its effects on engines, emissions, and emissions control systems from modern, Tier 2 vehicles. [6] This information was used in consideration of revisions to ASTM D4814, "Standard Specifications for Automotive Spark-Ignition Engine Fuel."

Within this follow-on work, additional information on the use of other metallic fuel additives and their effects on vehicle performance and exhaust systems was investigated to provide useful guidance to ASTM during the consideration of future fuel specifications. The objectives of this project were to obtain, organize, summarize, and synthesize relevant information regarding the use of metallic fuel additives (MFAs) in market gasoline and diesel fuel, and the effects of such usage on vehicle engines and exhaust aftertreatment systems. The focus of literature searches on these effects was on modern vehicles (post-2000), which are equipped with on-board diagnostic (OBD) systems and advanced emission control systems. For gasoline, this includes vehicles categorized as National Low Emission Vehicles (NLEV) and Tier 2 or beyond in the U.S., and Euro-3 through Euro-6 in the EU. For diesel, this includes engines/vehicles with OEM-equipped oxidation catalysts and diesel particulate filters. Some supporting historical literature and field experiences prior to 2000 were also include when relevant.

This information obtained through the published literature and additional web searching was used to develop a compendium of MFAs and their known effects on vehicle performance. The compendium of information is assembled into an accompanying Excel table which lists information on MFAs found in literature or in the marketplace within recent years (post-2000). Information regarding each additives' use, its effects on engine and exhaust aftertreatment systems, its producer, location of use, and recommended range of use is listed or summarized in the table. A description of the compendium is provided in Appendix A.

1.1 Approach

To develop the compendium of metallic additives, we began with information found in a recent (2013) Bio Intelligence Service report to the European Commission, which included an extensive literature review on metallic additives to provide information for a health and environmental risk assessment. [5] Metallic additives identified in this report included aluminum powder, boron nanoparticles, cerium oxide, iron fuel additives, chromium, copper compounds, lead based fuel additives, magnesium oxide, MMT, perovskite compounds, potassium compounds, platinum, rhodium, palladium, and zirconium salts, each of which was added to the compendium. We further investigated specific additives through a literature review and a web/ on-line search, focusing on publications with information relevant to vehicle transportation. In particular, our search excluded items that focused on health effects, exposure assessments, and measurement/ characterization methodologies. With these exclusions, our literature search returned information of fewer metallic additives than those listed in the Bio Service Intelligence report.

The literature review was conducted using the following computer-based search tools and approaches:

1. Web of Science (WOS) - Web of Science enables key word searches of over 5,300 technical/scientific journals, as well as some patents and conference proceedings. Key word search terms such as “organometallic” and “additives” returned fewer than 30 published papers. Additional specific key word searches included various combinations of “organometallic”, “fuel additive”, “metallic,” “ferrocene”, “barium”, “fuel borne catalyst”, “cerium”, “diesel”, “gasoline”, etc., and returned around 60 abstracts when limiting the timespan to anything after the year 2000. These abstracts were further reviewed, reducing the number of relevant items to fewer than 20 journal articles.
2. SAE literature search engine- The SAE literature search tool has much less flexibility than the WOS search, but returned around 80 items of interest from as early as 1945, which were all included into the reference list with a notation regarding its relevance.
3. DOE citation database—This literature search returned numerous reports, yet very few had any relevancy to the use of MFAs in market fuels.
4. Trade literature, patents, conference proceedings, and other on-line sources

Screening of abstracts and articles was done by selecting material relevant to vehicle transportation, focusing on gasoline and diesel additives, but excluding jet fuel or marine application additives. The additives of interest include those containing metals that are deliberately introduced into market fuels. While specific searches were not conducted for aftermarket additives, any that were returned are included in the list. In addition, although many metallic additives used for diesel particulate filter (DPF) regeneration are considered aftermarket additives, they were included as relevant search items. Metallic materials arising from lubricant additive packages or trace fuel contaminants were not considered, nor were literature items that focused on health effects, exposure assessments, and measurement/characterization methodologies.

While the literature search returned numerous items regarding scientific research of several additives, reports on the marketplace usage of MFAs were generally not found in this body of literature. We suspect that much of the relevant information regarding MFAs exists in company reports and other grey literature. However, very little of this type of literature was found in on-line and web searching, likely due to the highly proprietary nature of fuel additives or the lack of use of such additives.

Therefore, to get a better idea of the use of MFA's in market gasoline, recent fuel survey information from Summer of 2015 and Winter of 2015/2016 was purchased from SGS. [7,8] Summer 2015 data included 784 gasoline samples, while the Winter 2015/16 dataset included 794 gasoline fuel samples, both collected worldwide from 139 countries. Only the ICP analysis of metals was included in the purchased dataset, which measured 19 different metals, including Al, B, Ba, Ca, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Si, Sn, Ti, V, and Zn. Equivalent information regarding metals in diesel fuels was not obtained.

The remainder of this report includes a brief synopsis of uses and categories of MFAs, and any known effects and engine and exhaust treatment systems, and a review of their current use as illustrated by the fuel survey information.

2 Fuel Specifications and Regulations

Standard gasoline fuel specifications within the US are defined in ASTM D4814, which is followed in many places around the world. ASTM specifications are driven by performance, and include requirements on vapor pressure and distillation, vapor lock protection, volatility, and octane number. ASTM D4814 also places maximum limits on lead, phosphorous and sulfur content at 0.013 g/L, 0.013 g/L, and .0080 mass %, respectively in unleaded gasoline, with no intentional addition of lead or phosphorous allowed. [9] Diesel standards are specified in ASTM D975. [10] Specific metals are not limited in the ASTM standard, however, ash content is specified not to exceed 0.01% m/m to avoid injector, fuel pump, piston and ring wear and engine deposits from abrasive solids. The standards also outline testing methodologies for fuel contaminants.

The World Wide Fuel Charter (WWFC) provides worldwide recommendations and specifications of fuels for different market categories, and outlines testing methodologies for each property. These recommendations tend to be slightly more stringent than ASTM specifications. The most recent WWFC is the 5th edition, published in 2013. [11] Within this version, testing methodology was added to measure trace metals in gasoline and diesel, and a 5th category for markets with highly advanced requirements for emission control and fuel efficiency was added. [11] Category 4 market specifications include requirements for emission controls such as US Tier 2 and Tier 3, US 2007/ 2010 Heavy Duty On-Highway, California LEV II, Euro 4/IV, Euro 5/V, EURO 6/VI, and JP 2009 or equivalent emission standards. Category 4 fuels enable sophisticated NOx and PM after-treatment technologies, while the new 5th Category includes US 2017, California LEV III or equivalent emission control and fuel efficiency standards, in addition to Category 4.

Within gasoline fuels, the WWFC recommends that ash-forming additives such as organo-metallic additives be avoided. While the use of lead has already been phased out, the WWFC also recommends limiting the use of MMT (citing results from a 2008 report by Sierra Research [12]), and ferrocene in gasoline, stating that ferrocene causes iron oxide deposits to form on spark plugs, catalysts and other exhaust system componenets, which results in premature failure of spark plugs (no citation for this work is provided).

The WWFC also recommends that phosphorous, silicon and chlorine should not be added to gasoline, nor used as a component of an additive package, as they have been found to act as contaminants to engine or exhaust systems components. Phosphorous, occasionally used as a valve seat recession additive, can foul spark plugs and deactivate catalytic converters. Contamination of silicon can cause failure of the O_2 sensors and high levels of deposits in the engine and catalytic converters, leading to catastrophic engine failures. Chlorine can form highly corrosive acid during combustion and reduce the durability of the engine, fuel system or emission control system.

The gasoline and diesel fuel recommendations and testing procedures specified within the WWFC are given in Appendix B. The only specifications related to metal content of the fuels pertain to trace metals in both gasoline and diesel. In each case, trace metals, including Cu, Fe, Mn, Na, P, Pb, Si, Zn and Cl are not to exceed 1 mg/kg, and the intentional addition of metal-based additives in not allowed. The ash content of diesel fuels is also specified not to exceed 0.001 %m/m (10 ppm), with additional considerations under review for DPF related issues. Testing related to metals in gasoline include methodologies for potassium, phosphorous, silicon, chlorine, lead and other trace metals listed above. Within diesel, testing methodologies include trace metal testing and ash content.

2.1 European Regulations

The EU Fuel Quality Directive 98/70/EC sets legal parameters in petrol and diesel that have an effect on the environment and health, and specifies greenhouse gas reduction targets. To help monitor fuel quality, the EU monitors a limited number of parameters including FAME content, Within the European Union, metallic additives may be approved for use following the evaluations of short term and long term vehicle effects. [13]

The United Nations Economic Commission for Europe (UNECE) promotes the development of international transport through harmonization of rules and requirements of transport within its Working Party on Road Transport (SC.1) and Working Forum for Harmonization of Vehicle Regulations (WP.29). [14] A subsidiary of this group, the Working Party on Pollution and Energy (GRPE) prepares regulatory proposals to develop emissions and energy requirements for vehicles. This group provided a market fuel quality guideline to recommend minimum fuel quality of gasoline and diesel in a 2014 meeting. [15] The recommendations applied to fuel quality parameters that directly affect the performance and durability of engine and exhaust emissions control equipment, and recommended “no intentional addition” of lead and no permitted additions of other metallic additives including manganese, iron and phosphorous for gasoline. In addition, sulfur limits are recommended, and decrease for each emission standard, beginning at a limit of 500 ppm for Euro 2, and decreasing to 150 ppm and 50 ppm for Euro 3 and Euro 4 gasoline. Similarly, sulfur content of diesel fuels decreases from 500 ppm for Euro II, 350 for Euro III ppm and 50 ppm for Euro IV. Other metals contents are not specified for diesel fuels, although ash is recommended to be less than 0.01% m/m with total particulate contamination less than 24 mg/kg.

These recommendations are based on evidence that organo-metallic components create ash that adversely affect operating systems and increase emissions, providing examples of effects of MMT and ferrocene. The effects of MMT were cited primarily from a 2008 report by Sierra Research. [12] The report also described negative effects of iron as Ferrocene, which included deposition of iron oxide onto spark plugs, catalysts and other exhaust system parts, resulting in premature spark plug failure and 90% reduction in spark plug life. [15] In addition, iron oxide was reported to act as a physical barrier between the catalyst/ oxygen sensor and exhaust gases and led to erosion and plugging of the catalyst, resulting in poor functioning of the catalyst.

Although these parties recommend against the use of metallic additives, a 2008 fuel survey showed the presence of metals in fuel pools. As part of a study to evaluate emission factors of heavy metals from on-road vehicles, 65 petrol samples and 110 diesel fuel samples were collected from service stations in nine EU countries by CONCAWE in early 2008. [16] Concentrations of metals (As, Cd, Cr, Cu, Hg, Ni, Pb, Se and Zn) showed high variability among the samples. Cadmium, selenium, arsenic and nickel were not detected or were minimally detected in diesel fuel. Relative to the other metals, high concentrations of Zinc were seen in both gasoline and diesel. As, Hg, and Se exhaust emissions were dominated by fuel combustion, while Cd, Cr, Cu, Ni, Pb and Zn exhaust emissions were dominated by lubricant oil combustion. From this study, emission factors of heavy metals from on-road European vehicles were generated, which were much lower than those reported previously. More recent SGS fuel survey information of gasoline indicates a small fraction of Si, Zn, and Cu content in several samples of fuel. Fe, Mn, K and Ca were detected in only 1 or 2 of the fuel samples collected throughout the EU. None of the other metals measured through ICP analysis were reported in concentrations exceeding 0.1 mg/kg. [7,8]

2.2 U.S. Regulations

Within the US, the EPA manages and monitors fuels and fuel additives as defined in CFR part 80. While the regulations define sulfur limits, which are planned to be reduced to 10 ppm in 2017, other metallic components are not individually defined. The EPA requires that all fuel additives be registered, and the list of 10,020 registered fuel additives is available to the public. [17] However, details about specific inclusion of each additive are unavailable through this website as the information is proprietary to individual companies. [18] Gasoline and diesel fuel additives are allowed waivers based on “substantially similar” interpretations.

Substantially similar was first termed in Section 211(f) of the Clean Air Act. James W. Caldwell was Chief, Fuels Section, Field Operations and Support Division at that time. His department made these “substantially similar” interpretations to make it easier for manufacturers and EPA to process waivers. Section 211(f) of the Clean Air Act prohibits any fuel or fuel additive to be manufactured that is not substantially similar to any fuel or fuel additive utilized in the certification of vehicles or engines under Section 206. [18,19] However, a compromise on the definition of “substantially similar” was made between ASTM and additive manufacturers, allowing metallic fuel additives on the market today. Several of these additives have received waivers from the EPA for their use, for example, MMT was allowed a waiver in 1995. However, recent fuel survey information indicates that metallic additives are not used in gasoline fuels in the US.

3 Current Use of Metallic Additives in Gasoline

The usage of metallic fuel additives in marketplace fuels is difficult to garner from literature sources, so fuel survey data from Summer of 2015 and Winter 2015/2016 was acquired from SGS Fuel Survey. [7,8] Within these surveys, 784 gasoline samples were collected during Summer 2015 and 794 gasoline samples were collected during Winter 2015/16 from 139 countries worldwide. A complete set of analyses was conducted on each of the samples, however, only the ICP analysis of the metals was purchased for this work. ICP detects 19 different metals, including Al, B, Ba, Ca, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Si, Sn, Ti, V, and Zn. The presence of the metals is reported in mg metal / kg of fuel sample for all metals, and anything that is below detection limits is presented as <0.1 mg/kg. Selected metals (Cu, P, Fe, and Mn) are also reported in mg/ L. [1]

Of the 19 metals measured, eight of them (Al, Ba, Cr, Mo, Ni, Sn, Ti, and V) were not detected in amounts greater than 0.1mg/kg in any of the fuel samples collected. In addition, Mg, B, and Ca were detected in less than 1% of the samples in quantities under 1 mg/kg. The range of concentrations of the remaining elements found in the samples are shown in Table 2. The three most frequently detected include iron (Fe), manganese (Mn), and Silicon (Si), all of which are highlighted in the Table. Zinc (Zn) is also seen relatively frequently, albeit in very small quantities. No metals were detected in any samples collected from the United States or Canada.

Table 2: Summary of metals content from SGS Fuel Survey.

	Summer 2015					Winter 2015/2016				
Element	Min (mg/kg)	Max (mg/kg)	Mean (mg/kg)	Count	Country Count	Min (mg/kg)	Max (mg/kg)	Mean (mg/kg)	Count	Country Count
Cu	0.1	2.8	0.5	15	10	0.1	0.8	0.4	11	9
Fe	0.1	25	3.3	55	25	0.1	16	3.2	20	12
K	0.4	5.5	2.2	3	3	8.2	8.2	8.2	1	1
Mn	0.1	72	11.7	129	31	0.1	91	9.8	138	31
Na	0.1	0.6	0.4	2	2	0.9	1.3	1.1	6	1
P	1.1	1.1	1.1	1	1	0.5	1.1	0.8	2	1
Si	0.1	58.5	2.8	41	20	0.1	12	1.2	70	27
Zn	0.2	1.7	0.4	47	21	0.2	2.2	0.6	24	15

Manganese (Mn) is detected more frequently and in higher concentrations than any other element in both summer and winter, reaching as high as 91 mg/kg (66 mg/L) in the winter season, although the average dosing is much lower. In total, Mn was seen in 267 fuel samples collected from 48 different countries, with some seasonal variation for certain locations. Regional summary of manganese content, reported as mg/L, is shown in Figure 1, with the bars representing the average of all measurements above detection limits, and the error bars representing the minimum and maximum concentrations within a country. In 113 cases (42%), the concentrations measured were less than 2 mg/L, the maximum

[1] The fuel densities were measured in the survey, but not reported in the data we reviewed. Due to differences in fuel density throughout the samples, the data are reported as provided, without further calculations or conversions.

specification in locations such as China and the EU. Another 72 (27%) of the samples had concentrations less than 8.3 mg/L (corresponding to 1/32 g Mn/gal, the most recently revised ASTM specification). In 9 instances, however, the concentration exceeded 33 mg Mn/L. These samples were collected in the countries of Mauritania, Pakistan, Algeria, Senegal and Tanzania. In general, the locations of Mn use was primarily in Latin American, African, Middle Eastern, and Asian countries. No Mn was detected in any samples collected in Canada or the U.S.

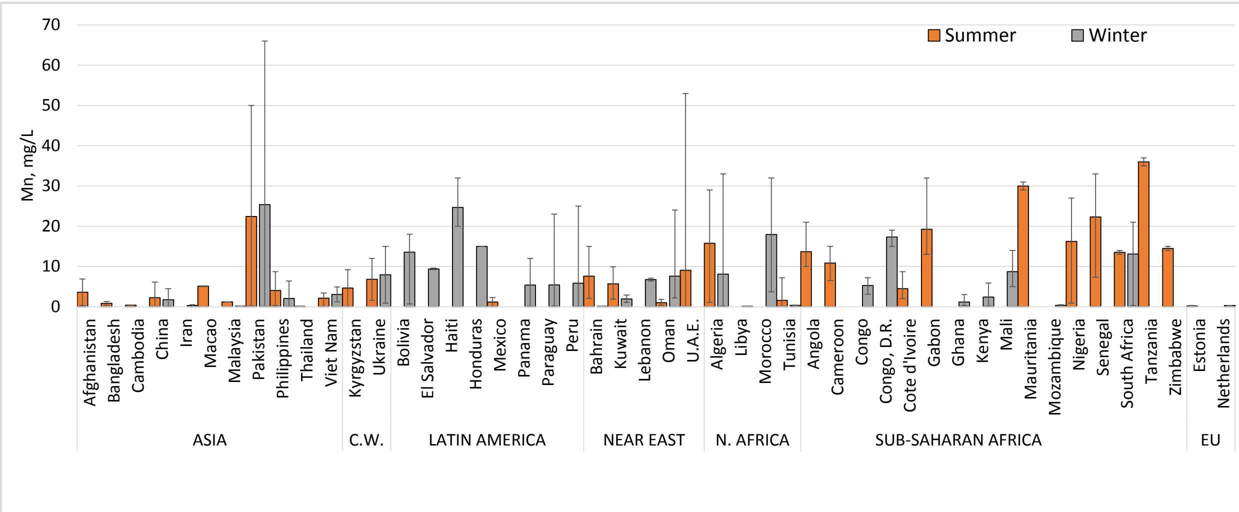

Figure 1: Manganese content (in mg Mn/L) from fuel samples collected in Summer 2015 and Winter 2015/2016. The colored bars represent the average of all samples, with the error bars representing the maximum and minimum concentration seen in fuel samples from the specified country. Source: SGS Fuel Survey

Iron is detected relatively frequently, and was measured in 75 samples collected from 32 countries. When identified, however, it is most frequently measured in low concentrations: 44 of the total 75 samples with measured concentrations of Fe were below 1 mg/kg (~0.73 mg/L), the recommended limit by the WWFC, while another 13 samples were below 5 mg/kg (3.6 mg/L). The remaining 18 samples had concentrations ranging from 5.0 to 25 mg/kg and were found in multiple fuel samples from Myanmar, Cameroon, Kenya, Mauritania, and Tanzania. A regional summary of iron content, reported as mg/L, is shown in Figure 2, with the bars representing the average of all non-zero recordings, and the error bars representing the minimum and maximum concentrations within a country.

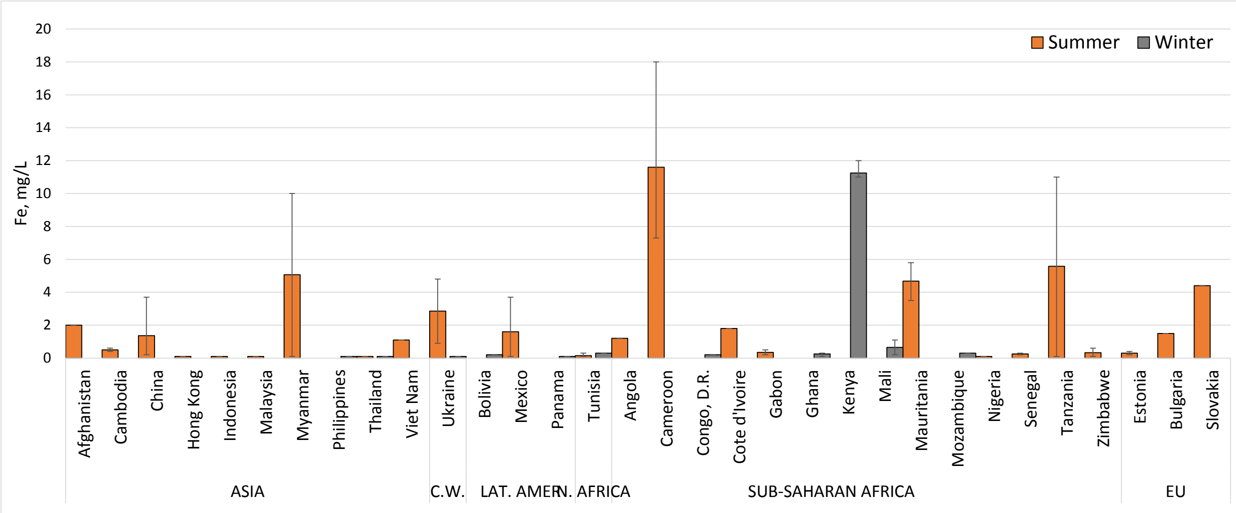

Figure 2: Iron content (in mg Fe/L) from fuel samples collected in Summer 2015 and Winter 2015/2016. The colored bars represent the average of all samples, with the error bars representing the maximum and minimum concentration seen in fuel samples from the specified country. Source: SGS Fuel Survey

Silicon is a contaminant that was detected in a relatively large number of fuel samples from around the world: it was found in 111 fuels samples collected from 35 countries. The highest frequency of detection was in samples collected from China, with 29 of the samples collected showing some level of Si contamination, and one sample reaching 59 mg/kg. The Russian Federation, Panama, and Paraguay also had multiple instances of Si in fuel samples, as shown in Figure 3. In 22 countries, Si was detected in only one or two fuel samples in relatively low concentrations.

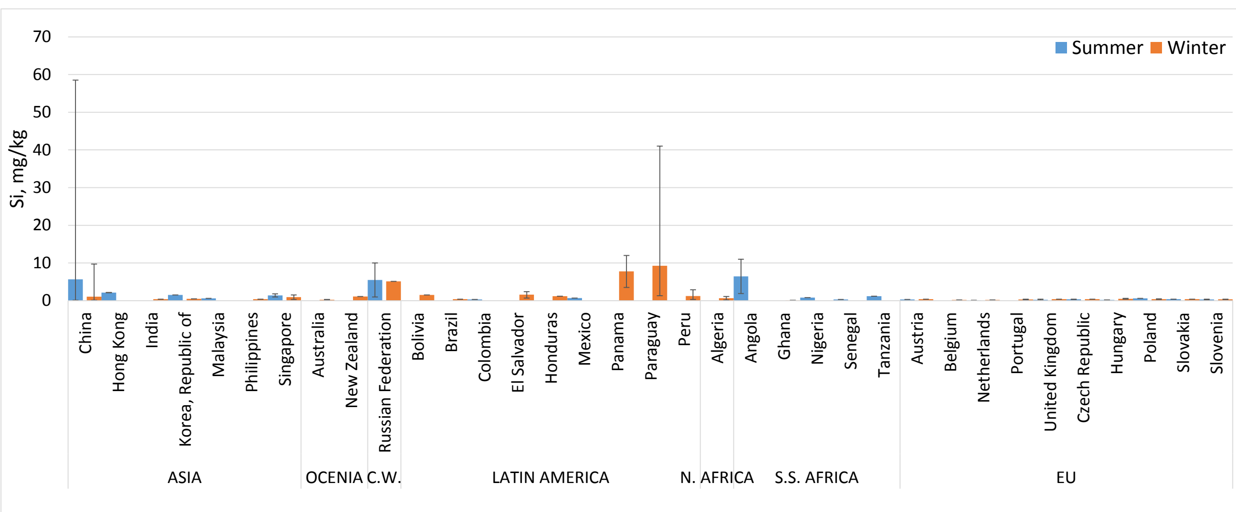

Figure 3. Silicon (in mg Si/kg fuel) from fuel samples collected in Summer 2015 and Winter 2015/2016. The colored bars represent the seasonal average of all samples, with the error bars representing the maximum and minimum concentration seen in fuel samples from the specified country. Source: SGS Fuel Survey

Traces of other metals are seen occasionally. Phosphorous (P), potassium (K) and sodium (Na) are rarely detected in any fuel samples. K has been seen in relatively high concentrations in South Africa, where it has been used as an anti-valve seat recession additive.[20] Copper is seen in a relatively high number of fuels from the European Union. Zinc (Zn) is also seen frequently, but at very low concentrations. Summaries of the combined seasonal results are shown in Figure 4.

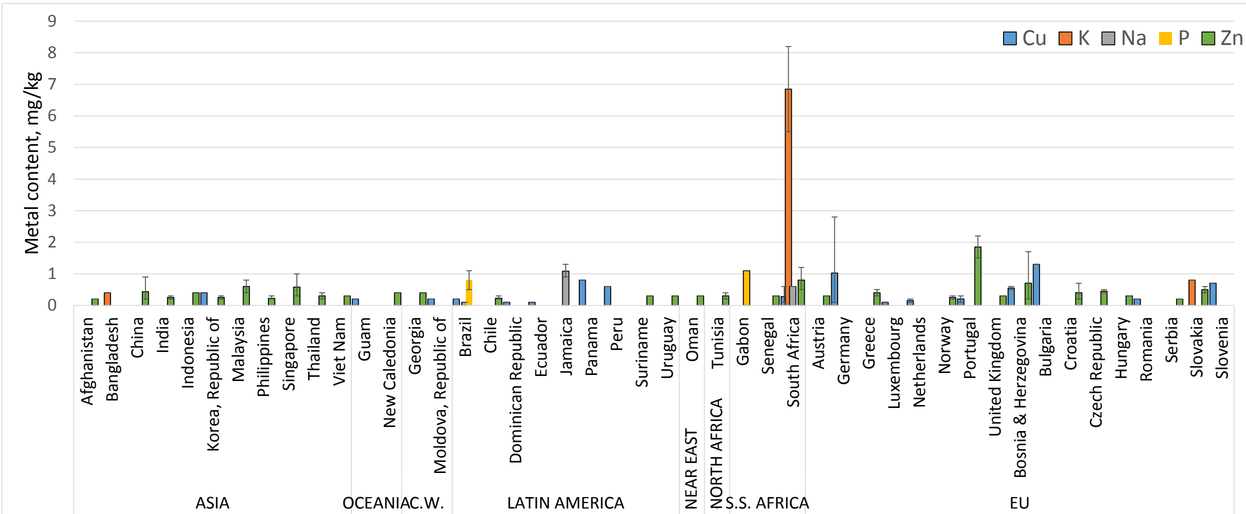

Figure 4: Copper, Potassium, sodium, Phosphorous, and Zince (in mg metal/ kg fuel) from fuel samples collected in Summer 2015 and Winter 2015/2016. The colored bars represent the average of all samples, with the error bars representing the maximum and minimum concentration seen in fuel samples from the specified country. Source: SGS Fuel Survey

4 Additives in Gasoline

There is a long history of additive use in gasoline, beginning with the use of anti-knock additives. [21] More recently, the focus of additive usage has been on maintaining clean and functioning engine and exhaust system components. In addition, increased use of biofuels and ethanol have increased the risk of deposit formation, requiring higher levels of additives to be used. [22] The world wide additive market continues to grow, despite reductions in fuel demand. [23] The primary gasoline additives include deposit control additives (DCA) or detergent additives which prevent the formation of deposits. These are usually composed of polyether amines (PEA) or polyisobutyl amines (PIBA), and do not include organometallics. Other non-metallic additves include fluidizers, friction modifiers, antioxidants, demulsifiers, and corrosion inhibitors. [22] Additives that sometimes include organometallic materials include anti-knocks or octane boosters, anti-valve seat recession (AVSR) additives, and conductivity improvers. Each of these is described further below.

4.1 Anti-knock Additives/ Octane Boosters

Traditionally, one of the primary uses of organometallic additives in fuels has been to provide octane enhancement. Such octane boosters, or antiknock additives, are blended at the refinery to meet fuel octane requirements. Organometallic additives functioning as octane boosters typically include tetraethyl lead (TEL), ferrocene, or methylcyclopentadienyl manganese tricarbonyl (MMT). [24] Iron pentacarbonyl was investigated as a lead replacement antiknock agent in ethanol as early as 1945. [25]

However, engine studies conducted at that time found that iron oxides readily formed and while iron was an effective antiknock agent, the deposits could seriously interfere with engine operation.

Lead, primarily in the composition of TEL, was widely used as an antiknock prior to its phase out after the U.S. Clean Air Act of 1970. Since then, it has been eliminated from gasoline in most countries worldwide. According to the United Nations Environment Program (UNEP), as of January, 2016, only three countries still allowed the use of TEL- Algeria, Iraq, and Yemen. [26] Innospec Ltd, a UK-based company claims to be the only producer of TEL in the world [27], yet faces scrutiny for doing so. [28] TDS Chem, a company in China, also claims to manufacture and sell TEL additives. [29]

In the US, after the phase-out of lead, alcohols and ethers were the primary additives used in gasoline to increase octane levels. [30] Organometallics have been used in fewer circumstances, due to other concerns of health effects and vehicle impacts, although manganese and ferrocene have been used in some instances, and patents on such additives have been filed. [31,32]

Several companies produce additives containing manganese, ferrocene or lead that are marketed for blending with fuel prior to dispensing. Cestoil, Innospec, Afton Chemical, and TDS, are several chemical producers throughout the world that market antiknock additives containing metallic additives.

Manganese as MMT has been widely used, and a large body of literature exists on its effects on engine and exhaust components. This literature was previously summarized in the CRC-E-114 report and in an SAE publication. [6,33] Along with Afton Chemical, which produces MMT under the trade name Hi-Tec 3000™, MMT is included in products from Innospec under the trade name Octaburn™, Cestoil under the trade name CESTOBURN 8000™ series, and TDS Chemical. Recommendations for use include dosing rates ranging from 8 to 36 mg/L, although the WWFC and UNECE recommend against the use of MMT, and ASTM is undergoing a revision process for ASTM D4814 with respect to manganese content. [11,14,9]

Ferrocene has also been used as an octane number (ON) booster in gasoline, with other benefits such as anti-valve seat recession. [34] However, literature searches for the use of ferrocene in gasoline returned a very limited number of items. An investigation conducted in the early 1990's of the effects of ferrocene dosed at 15 ppm into gasoline found that lower pollutant emissions and improved fuel economy resulted from the additive. [35,36] More literature about ferrocene involves its use as a diesel fuel additive, particularly for DPF regeneration (See Section 5.1). One recent evaluation of MMT and Ferrocene on gasoline properties has shown that the additives have little effect on early regions (0 to 50% distillate volume fraction) of the fuel distillation curves. [37]

Ferrocene is offered for sale by some fuel additive producers, and can be found in products listed by Innospec (PLUTOcen G®), Cestoil (CESTOBURN 9000) and TDS Chem. As of 2001, it was used as an anti-knock in Russia, [38] and has been evaluated in Bulgaria. [39] (Note that recent fuel survey information indicates that there is very little iron in fuels in either of these locations, See Section 3.) Some after-market additives may exist, however, one such product, Ferox Fuel Tabs was produced by Parish chemicals, which is no longer in business. The former manufacturing location is currently an EPA superfund clean-up site.

An evaluation of the effects of ferrocene on engine and vehicle performance has shown that gasoline containing ferrocene results in iron oxide (Fe_3O_4) deposits that adhere to the combustion chamber, spark plugs, and exhaust pipe. [40] Iron oxide deposits on the spark plugs resulted in abnormal electrical discharge as Fe_3O_4, which appeared black in color. These deposits were changed to Fe_2O_3, which appeared reddish-brown, under high temperatures, increasing conductivity. The high conductivity of the deposits results in current leakage that was observed as thin spider-web like lines across reddish-brown deposits over the insulator. In addition, reddish-brown deposits were observed over the inlet of the catalytic converter, and an increase in fuel consumption, exhaust temperatures, and exhaust emissions were seen in engine testing as a result of ferrocene use. [40] Iron oxide has also been found to act as a physical barrier between the catalyst/ oxygen sensor and exhaust gases and leads to erosion and plugging of the catalyst, resulting in poor functioning of the catalyst. [11]

The effects of lead on engine and vehicle performance were well studied prior to its phase out. Since then, few evaluations have been conducted to identify lead in gasoline fuels, or evaluate its effects at the low levels currently allowed in fuels (0.013 g /L in the U.S.) Our literature search on lead returned no results related to low level impacts on vehicle components. Some chemical producers claim to produce and sell TEL (Innospec [27] and TDS [29]), although there are only three countries that currently allow lead in gasoline. There are also several aftermarket lead additives available, primarily marketed to high performance specialty vehicles, race vehicles, or classic cars. Octane 130 is one such example in the US [41] and Tetraboost is a similar product available in the UK. [42]

4.2 Conductivity Improvers

Static electricity can accumulate during fuel pumping operations at refineries, terminals, or filling stations, which presents an obvious fire or explosion hazard. Additives are often used to enhance conductivity of blended fuel and prevent static discharge. Fuel-soluble chromium materials or other non-metallic additives are used for this purpose, with typical treat rates ranging from 1-40 mg/kg. [22] The use of chromium has been seen through fuel surveys. [16] However, our literature search returned items on the use of chromium in fuel oil and with gas turbine engines, but not in gasoline.

4.3 Anti-Valve Seat Recession (AVSR) Additives

Exhaust valve seat recession occurs during prolonged high temperature or high speed operation during which the like-metal components of the valve seat and valve are repeatedly welded together and torn apart. This process can generate hard wear particles that grind or abrade valve seats during repeated opening and closing contact exposures to the hot exhaust valves. This valve seat erosion can result in loss of compression, which leads to power loss, rough engine operation and increased emissions, and may eventually lead to engine failure. [22]

Engines that were designed for use with leaded fuels had relatively soft valve seats that were more susceptible to recession. However, lead in the fuel formed lead oxide during combustion, which formed a protective layer on valves and seat surfaces to prevent metal-to-metal contact and the formation of hard particles. The lower limit of lead's effectiveness as an AVSR is 0.026g Pb/L [43], so its phase out caused the onset of valve seat recession problems in existing vehicles at that time, and necessitated the use of other AVSR additives. [44]

The combustion of phosphorous, potassium, sodium and manganese organometallics also produces ash that deposits a similar protective layer on valve seats. Typical treat rates range from below 50mg/kg to 200 mg/kg of the active element. [22] However, there is no standard test methodology applied to evaluate the effectives of AVSR additives, so it is up to the additive supplier to recommend a dose rate that does not lead to harmful side effects. [43]

Problems related to VSR were significantly reduced after the early 1970's, when induction hardened exhaust valve seats were implemented. [45] A report on valve seat recession issued by the United Nations Environment Programme (UNEP) Partnership for Clean Fuels and Vehicles in 2004 reported that no significant issues of valve seat recession had been experienced in up to 13 countries that had phased out lead. [46] At that time, France was the only country reporting the use of an AVSR additive (potassium), but had plans to phase it out. The report noted that some countries in Europe that had used lead replacement additives had not observed valve wear problems, but reported other engine problems such as destructive corrosion of turbo-chargers, valve sticking and valve burnout.

Other metallic additives have been evaluated for their effectiveness as an AVSR agent. Hutcheson et al. performed evaluations of different metallic additives, including phosphorous, manganese, potassium and sodium, to determine the additive level under which full protection would be delivered. They determined that a treat rate of 8mg/L of different additives provided sufficient protection for the majority of service conditions, and 36 mg/L offered complete protection under all possible in-service conditions. [43] However, they also found other engine durability issues associated with the use of these additives. The use of sodium was correlated with hot salt corrosion of turbochargers, while alkali metals were prone to promoting valve sticking.

The Associated Octel Co. investigated the use of ferrocene as an AVSR additive, and found that while it was useful as an ON boost, a treat rate of 25 mg Fe/kg offered very little AVSR protection. [34] On the other hand, when combining ferrocene with phosphorous, a high level of AVSR protection was seen as well as an ON boost. In 2006, the Associated Octel company became Innospec, Inc., which currently markets ON boosting additives using the organometallics MMT and ferrocene, although no products are marketed specifically as AVSR additives.

Potassium was frequently used in lead replacement petrol (LRP) in European markets and other countries, including South Africa. [43,20]. However, the use of LRP was also phased out beginning in the early 2000's in Europe and other locations such as New Zealand. Little information is available on the on-going use of AVSR additives at the refinery level in other markets. This is due to decreasing problems with valve seat recession, as modern vehicles are no longer susceptible to the problem as hardened valve seats have replaced the soft valve seats that existed in pre-1986 vehicles. Therefore, AVSR additives are not frequently blended into fuels prior to fuel dispensing in most markets, although some markets that have a large fleet of older vehicles may still use AVSR additives.

A targeted search of AVSR additives in fuels did not result in any products (see Compendium). However, other after-market products containing metallic additives are still available at auto parts shops in select markets. (e.g. Penrite Valveshield)

4.4 Effects of Metallic Additives on Engine and Exhaust Components

Within the body of literature reviewed, very few reports investigated the durability or emissions effects of specific metallic fuel additives. Much of the literature on this topic is related to the use of MMT, which was summarized and reported in a previous CRC review project. [6] The effects of lead have also been studied on older vehicles, but no literature on its effects in MY 2000 and newer vehicles was found, even at low levels of use.

Other works, however, reported on the effects of oil additives and contaminants. While these topics were not specifically included in the literature search, any information that surfaced in related searches is summarized here. However, we should note that a targeted search was not performed for other contaminants or oil additives, so this information is incomplete.

In one such study, engine oil additives containing calcium (as calcium salicylate), zinc (as zinc dithiophosphate) or molybdenum (as molybdenum dithiocarbamate) were diluted directly into combustion fuels. [47] Calcium and zinc were found to increase deposit formation in the combustion chamber and facilitate auto-ignition and knock intensity. Molybdenum compounds showed no significant effects.

An evaluation of various combustion chamber and valve deposits showed that calcium, phosphorous, sulfur, zinc and molybdenum represent the most significant inorganic fraction of combustion chamber deposits, likely from the engine oil package or contamination. These same elements contribute to valve deposit formation. [48] In addition to these, valve deposit formation has been attributed to silicon, iron, and chromium. [49,50] Another investigation of valve deposits showed that an additive containing calcium phenate resulted in higher inlet valve deposit formation than other metallic detergent additives studied, which included calcium sulfonate (CaSu), calcium phenate (CaPh), magnesium sulfate (MgSu), or neutralized calcium sulfonate (Neut. CaSu.) [51]

A summary of pre MY 2000 vehicle effects can be found in a recent review of abnormal ignition by fuel and lubricant derivatives. [52] Phosphorous and Boron as deposit control additives (DCA) have been shown to suppress abnormal ignition. However, these metals have been removed from DCAs as they act as catalyst poisons.[2] The use of phosphorous, barium, calcium and zinc as engine oil additives has also been shown to reduce surface ignition, although there are some contraindications of these effects. [52]

Ferrocene has been shown to improve exhaust emissions and increase fuel economy. [35] However, some field problems have been experienced with ferrocene. In April 2003, members of the Canadian Vehicle Manufacturers Association (CMA) became aware of a ferrocene additive field trial that was

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[2] EPA implemented 40 CFR 80.161 – the Detergent Additive Program, in 1997, which mandates that additives must be certified for use. To become certified, the program requires a fuel injector deposit control test and an intake valve deposit control test. A list of EPA-certified additives can be found on their website. However, supporting information is not available on the website and is maintained as confidential. Personal contact with an EPA representative has told us that metallic additives are not allowed in certified additives.

publically launched in 2002 in Vancouver Island BC by two major oil companies. [53] In this trial, the gasoline supplied to Vancouver Island was treated with sufficient ferrocene to provide approximately a one number boost in AKI (approximately 7 mg/L Fe). [54] (At this time, MMT was widely used as an additive in Canada, typically at about 10 mg Mn/L.) Within a few months of the field trial, complaints of spark plug fouling manifesting as poor driveability and mis-firing were reported by dealers when customers used gasoline containing both ferrocene and MMT. Total failures were found in the range of a few hundred vehicles and affected a variety of late model common vehicles, although reports of MIL illumination were very low or zero. Replacing the spark plugs alleviated the complaint. [54]

Two redacted reports on the analyses of returned parts during this time frame were blindly submitted for this report. One of the reports, dated May 28, 2003, details the analyses of two spark plugs that were returned due to misfiring issues after running approximately 30,000 miles in a 2001 MY vehicle in Western Canada. [55] The spark plugs both had reddish brown deposits and black glazed areas on the insulator core noses. The glazed areas exhibited spider-web-like tracking marks where the spark energy traveled across the deposits rather than firing the gap. XRF analyses showed the deposits were comprised mainly of manganese, iron, and phosphorous. The manganese was attributed to the use of MMT, the iron was a result of another fuel additive, and the phosophorous was a result of oil. It was concluded that the spark plugs misfired due to the conductive manganese and iron deposits left on the insulator core noses from fuel additives. A second report focused on a single core nose, and found similar visual and analytical results. [56]

Other literature supports that iron oxide particle deposits in the combustion chamber and on spark plugs result in abnormal function of the spark plugs and spark plug failure. [40,15] Iron oxide deposits that appear black or reddish-brown increase conductivity on the surface, and result in spark plug current leakage. In addition, reddish-brown deposits have been observed over the inlet of the catalytic converter, accompanied with an increase in fuel consumption, exhaust temperatures, and exhaust emissions as a result of ferrocene use. [40] Iron oxide has also been found to act as a physical barrier between the catalyst and oxygen sensor and exhaust gases, which leads to poor functioning of the catalyst. [11]

Catalytic converter performance is typically reduced from thermal degradation or chemical poisoning. Phosphourous, zinc, sulfur and lead are known contaminants of catalytic converters. [57] Other contaminants include calcium, copper and iron. These contaminants irreversibly deposit onto the catalyst washcoat and reduce the catalyst surface area. Degradation of catalysts and other exhaust system components has been shown to occur due to deposit formation on catalyst surfaces, which results in plugging. Plugging can cause reduced conversion efficiencies as well as increased back pressure. Thermal degradation over time also causes reduced catalytic converter performance.

Contamination of silicon into fuels has also been found to have harmful effects on catalysts and oxygen sensors. Experimental tests of fuel containing only 20 ppm of Si resulted in significantly decreased efficiencies of three-way catalysts after only 1500 miles of use, with continual decline to less than 40% efficiency after 15,000 simulated miles. [58] Deterioration of the exhaust gas oxygen sensors also results. In 2007, widespread reports of vehicle damage in the UK were linked to traces of silicon found in batches of suspect fuel. [59] As many as 4,000 motorists complained of juddering, misfiring, and loss of power.

In 2001, a survey of early to mid 1990's MY catalytic converters was performed to evaluate catalytic degradation over various mileage intervals. [60] Low levels of contamination by Zn, Ca, K, Cu, Na, Fe, Mg and Ba were found on the catalysts. Low amounts of Pb contamination were found in catalysts taken from low odometer vehicles, but high contamination from the high odometer vehicle group. The greatest contamination was found from Phosphorous (P). However, thermal deterioration of the catalyst was found to have the strongest influence on loss of catalytic performance, not the presence of metallic contaminants. Other effects of contamination and plugging from use of MMT have been observed. [61,62,33]

5 Additives in Diesel

Diesel fuel additives are used for a variety of purposes, including engine and fuel delivery system performance, fuel handling, fuel stability, and contaminant control. However, it appears that very few if any of these additives that are blended at the refinery level contain organometallics. Some organometallics have seen limited use as smoke suppressants around the world. In addition, advanced diesel technologies such as common rail injection systems are particularly prone to problems from deposit formation, so deposit control additives are typically used. While organometallics are not typically used in these DCAs, they have been evaluated in this area. The bulk of recent literature regarding the use of organometallic fuel additives included their use in conjunction with diesel particulate filters for reduction of PM emissions, an emerging technology for stricter emission controls. Emissions control devices in diesel vehicles consist of multiple components as no single device can simultaneously reduce NO_x, PM, HC and other emissions. Advanced diesel emissions control technologies include De-NO_x systems, such as lean NO_x traps (LNT), Selective Catalytic Reduction (SCR) to remove NO_x, diesel particulate filters (DPF) to reduce PM emissions in combinations with diesel oxidations catalysts (DOC) to reduce HC and CO, and exhaust gas recirculation (EGR). The use of organometallic additives to aid in DPF regeneration has been a focus of recent evaluation. This, along with other uses of organometallic additives in diesel fuel are described further.

5.1 Fuel Borne Catalysts for DPF Regeneration

One method to reduce PM emissions to meet progressively stricter emission standards is the use of a diesel particulate filter (DPF), which functions by trapping soot and particulates from exhaust. A DPF typically consists of a filter material that is designed to collect solid and liquid particulate emissions while allowing exhaust gases to pass through. A variety of filter materials and designs have been evaluated with PM collection efficiencies varying from 50%-90%, including ceramic monoliths, woven silica fiber coils, ceramic foam, wire mesh, and sintered metal filters. [63] The trapped particulate matter builds up over time, however, and must be removed periodically for continued operation. Apart from removing the filter frequently for manual cleaning, there are several methods of DPF regeneration, during which the collected PM is oxidized or combusted into CO_2. In order for auto-ignition of the collected particulate matter to occur, temperatures of 600-650°C must be achieved. Normal engine exhaust temperatures are typically not sufficient, ranging between 200°C to 500°C, so either exhaust temperatures must be raised to achieve auto-ignition, or the oxidation temperature of the particulates must be lowered through the use of a catalysts.

There are several methods to achieve regeneration, which can occur either continuously or periodically. Two continuous approaches include the continuously regenerating DPF (CR-DPF) or the catalyzed DPF (CDPF). The CR-DPF utilizes a diesel oxidation catalyst (DOC), typically containing platinum, upstream of the DPF to generate NO_2, which functions as an effective low-temperature oxidizing agent for PM. [64] The CDPF regenerates via a catalyst coating on the DPF to promote oxidation.

A third method of periodic regeneration occurs through the use of a fuel borne catalyst (FBC). Catalytic materials such as transition metals including cerium, iron, copper, manganese, sodium, strontium or calcium act at a late stage of the soot formation process and help to catalyze the burning of soot in a DPF. These FBCs can reduce the temperature of activation to 300-350°C, which reduces the interval between regeneration events. [63,65,66,67] Regeneration events occur as particulate is collected on the filter causing back pressure to increase and temperatures to rise. During regeneration, the organic fraction of the additive is combusted with the PM, leaving the inorganic metal or oxide catalyst finely distributed within the soot particle and other combustion products, while some of it remains as inorganic ash along with other products of lubricant combustion and normal engine wear. This ash accumulates within the filter, which periodically must be physically removed and cleaned as part of a filter maintenance program to prevent excessive increase in back pressure across the filter. These filter maintenance events for ash removal depend on engine oil consumption characteristics, total ash content of engine lubricant formulations, vehicle duty cycles, filter designs, and dosing of the FBC.

Wide introduction of DPFs on passenger cars was initially limited by difficulties including safe, reliable regeneration under all driving conditions, a fuel penalty with their use, and the development of a low cost system. [68] In Europe, DPFs have been in commercial use in light-duty vehicles since 2000, [69,70] and have been in increasing use in the U.S. since 2006. [71] A survey by the Manufacturers of Emission Controls Association (MECA) in 2014 reported a 65% increase in DPFs sold in California in the first six months of 2014 compared to the same period in 2013, including both OEM and retrofit devices. MECA and the California Air Resources Board (CARB) each maintain a list of manufacturers and verified providers of retrofit devices. [70,72][3] However, DPF with FBC technologies do not appear to be as widely adopted as other methods of continuous regeneration. [71] The majority of heavy duty diesel manufacturers have selected DPF in combination with a selective catalytic reduction (SCR) system and EGR to meet emissions standards. [74]

5.1.1 FBC Additives

Fuel borne catalysts (FBC) for DPF regeneration can be mixed directly into the fuel tank or prepared via an on-board dosing system. Typical dosing levels are in the range of a few ppm. [75] FBCs are not added to a fuel at the refinery level as their use may result in an increase in emissions in vehicles that

[3] A global market survey of DPF filters is available for licensing. [73]

are not equipped with DPF technologies. However, since they are required for use in specific systems, they are considered as a metallic fuel additive for this study.

Various metallic additives that could be of use for DPF regenerations have been evaluated since at least the early 1980s. [76,77] The effects of metals including zinc, calcium, iron, cerium, copper, barium and manganese have been evaluated by universities, car companies, and additive producers. [78,79,80]

One of the first commercial introductions of an active DPF system with an FBC was in the Peugeot Citroen in Europe. This vehicle used a common rail direct injection engine with an on-board dosing system of Rhodia's Eolys Cerium FBC. Cerium oxide has been shown to reduce soot and lower oxidation temperatures of regeneration. [81] However, early introduction of this technology resulted in a 5% increase in fuel consumption, and a 2% reduction in maximum engine output, but with complete suppression of black smoke and a reduction of PM by three to four orders of magnitude. [68] Other evaluations of Rhodia's cerium-based additives in conjunction with various DPF filter systems confirm high reductions in PM and minor reductions in HC emissions that are typically accompanied by an increase in NO_x and a fuel penalty. [82,83] Many of these studies also focused on the effects on particle size and concentrations, showing that the reduction of particle number is relatively insensitive to dosing level. [84,85] An evaluation of cerium by the Health Effects Institute (HEI) showed that a DPF used in conjunction with Eolys decreased particle mass by greater than 90% and particle number by as much as 99% in diesel exhaust. [86] A small fraction of cerium was found in the particle emissions, totaling 3-18% of the total mass of the emitted particle.

CARB and the Joint Research Council (JRC) conducted a joint study to evaluate PM emissions during DPF regeneration events using a cerium-based FBC. Testing was completed during 5 unique regeneration events. Significant increases in PM mass emissions were observed during each regeneration event although PM emissions remained below relevant standards during these events. [75]

Other metallic additives have been evaluated for their low temperature oxidation behavior in conjunction with a DPF. In addition to cerium, iron, zinc, strontium, potassium, and cobalt have been evaluated. Iron in the form of Ferrocene has demonstrated effective DPF regeneration, sometimes in combination with other metals. Several publications describe development and testing of various metallic FBC additives for DPF regeneration.

The Associated Octel Co. has investigated the effects of a variety of different additives on DPF regeneration. In early work, they investigated a fuel-soluble combination of sodium-based FBC with traces of strontium at 20 ppm with a ceramic DPF filter, which showed effective regeneration characteristics and no adverse effects on the engine or on size distribution of particulate matter. [87] Due to issues with the presence of sodium leading to high temperature degradation of the ceramic filter, however, they soon turned their focus to combinations of iron and strontium that showed improved performance. [88] The group continued to investigate these iron-based additives in comparison to cerium in support of their product Octimax 4804, which contained iron and strontium in a 4:1 ratio. [89] These studies indicated that iron-based additives perform better than cerium-based additives at the same dosing rate (by weight), achieving lower temperature regeneration, as indicated by lower back pressure increases. [90,69] Dosage rates as low as 10 ppm of iron-based additives (including iron/strontium blends) were found to achieve similar regeneration temperatures as 30 ppm cerium-based additives, while the iron-strontium blends were found to achieve lower temperature oxidation than iron alone. Lower dosing rates can reduce the ash accumulation and extend service intervals. "No harm" emissions testing of the same additive showed no adverse effects on the number of fine particles. [91] An independent evaluation of Octimax showed it resulted in high reduction of soot emissions at low load, when FBC-doped soot is more likely to be enriched by metal oxide on the outer periphery of the particle, thereby increasing oxidative reactivity compared to high load conditions. [92]

The Associated Octel Co. also performed durability testing of Octimax 4804 over 80,000 km on the road and on a dynamometer. No drivability issues were noticed despite significant backpressure increases before regeneration and no signs of clogging or failure were observed. [93] Fuel consumption increased by 5.5% and an increase in CO emissions accompanied the significant reduction in PM emissions.

In 2006, The Associated Octel Co. was rebranded into Innospec, Inc. Octimax 4804 no longer appears as a product on the Innospec web page. Currently, their list of fuel borne catalysts includes a product line called Satacen®, a ferrocene-based product that does not appear to include strontium. [94] Satacen® is listed as the tradename of the product sold in Germany, Switzerland and Austria. In the rest of the world, the product is called Octel Octimax, although it doesn't appear on the Innospec web page. [95]

Other evaluations of ferrocene have been published, indicating that it behaves as an effective oxidation catalyst in conjunction with a DPF. Retrofits of a DPF using ferrocene as an FBC has been shown to reduce unregulated emissions, including a 16% reduction in carbonyl compounds, an 80% reduction of formaldehyde and acetaldehyde, a 66% reduction of total PAH, and 91% and 88% reductions in fluoranthene and pyrene, respectively. However, Benzo[a]pyrene equivalent increased from 0.016 to 0.030 mg/kWh, and brake specific NO_x increased 4.3%. [96] Evaluation of a range of ferrocene dosage rates (0 to 200 ppm) indicated that higher dosage rates decreased particle mass, total particle volume, and black carbon emissions, but increased particle number concentrations. In addition, the Fe concentrations in the particles increased from 0.1% to 7.5% with higher dosage rates. [97]

The US Bureau of Mines evaluated the effect of ferrocene on fuel consumption in the early 1990's, finding that its use in diesel fuel contributed to an increase in CO_2 and NO_x emissions, indicating an increase in fuel consumption. A layer of ferric oxide was found on the combustion chamber components after 250 hours of operation. [98]

Several publications include investigations into a variety of FBC additives to determine which perform the best. The Oil and Gas Institute in Poland recently evaluated a range of FBC additives containing iron, cerium zinc, potassium, or cobalt to determine the most effective additive for DPF regeneration. In total, seven different additives with different blends of metals were synthesized and bench tested, along with two other commercially available Fe-based additives. Based on the test results, the two most effective additive were manufactured, one of which contained Fe in the amount of 12.14 %m/m and the other containing Fe and K in the amount of 7.20 and 1.80 %m/m, respectively, although the results of the tests were blinded in the report. [65]

An evaluation of MMT on the performance of a DPF found significant beneficial impact on the rate of soot accumulation within the DPF and on the DPF balance point temperature, indicating that MMT behaves as a soot suppressant. [99]

Infineum UK also evaluated various metallic additives with respect to regeneration performance. [100] Initially, 15 different additives were screened containing various combinations of metals (including calcium, sodium, and iron) in various amounts to determine regeneration capabilities. An iron-based additive was selected for further testing, which included evaluating various treat rates in combination with other ashless components and in comparison to a commercially available cerium additive. It was concluded that the novel iron-based additive had superior performance at a dosage of 3 ppm metal in the fuel in comparison to the commercially available cerium additive. VERT (Verification of Emissions Reduction Technologies) testing also confirmed that the additive had no impact on unregulated emissions when used in combination with a DPF up to a treat rate of 25 ppm.

Several investigations, including reports under the VERT program, have indicated that high metallic additive dosage rates in conjunction with a DPF filter may lead to reductions in particulate emissions, but tend to increase the number of ultra-fine particle engine-out emissions. [100,101,102] In addition, it has been noted that increased dosage rates beyond the onset of particle formation provide no additional decrease in soot emissions, but contribute to an increase in both large and small particle emissions. [101] However, since particles are effectively trapped by the DPF, it is recommended that metallic additives should only be used in conjunction with a DPF. [100] One study found that an unexpectedly high proportion of the additive was trapped in the engine and exhaust components, and only 10% reached the particle trap. [102] Another study showed that ultra low dose rates of 4-8 ppm on a bimetallic Pt/Ce FBC did not increase ultra-fine PM emissions but provided several benefits, including reducing PM, HC, and CO emissions while increasing fuel economy. [103] The study also found that 94% of the additive is retained in the engine and exhaust components.

An evaluation of particulates was conducted by the European Commission to investigate the trade-offs and relationships between PM and PN during DPF regeneration, showing the PN emissions during regeneration were two orders of magnitude higher than those from non-regenerating NEDC cycles. [104] Gaseous and PM emissions during non-regenerating cycles were compliant with Euro 4 regulations, however, higher gaseous emissions were observed during regeneration events, with NO_x emissions exceeding Euro 4 limits by 100%.

5.1.2 FBC effects on engine and exhaust components

Results of durability using FBCs or metallic additives and their effects on engine and other exhaust components have not been widely published in recent literature, although some information exists. Early investigations by Volkswagen of manganese FBC with both prototype exhaust treatment filters and on road testing showed that the particulate filter with the Mn-FBC had the potential to reduce PM emissions with no significant effect on gaseous emissions, fuel economy, or exhaust gas treatment systems. [105,106]

Iron oxides have been shown to build up in the combustion chamber over time, and have also been shown to deposit onto spark plugs in gasoline engines. [98,11] One investigation by Solvay Rare Earth Systems on the effects of an Fe FBC used for DPF regeneration on engine deposits was performed, showing that an advanced FBC using nano-particles of Fe, formulated with a deposit control additive at typical treat rates (4-7 ppm) could prevent nozzle coking deposits in indirect injection engines, and also showed no increased internal engine deposits following continuous testing. [107] In addition, the advanced Fe-FBC[4] was reported to be more stable than a conventional FBC in conventional fuels or 10% biofuel blends. Other investigations of an iron-based additive, ferrous picrate, without a DPF have shown that fuel economy and NO_x emissions are decreased, but HC and CO emissions may increase. [109]

Some metallic additives have been shown to contribute to fuel injector fouling. Trace amounts of zinc can contribute significantly, while lead contributes to a lesser extent. [110] Other metals, such as calcium, copper, sodium and iron were not found to contribute significantly to injector deposit formation.

Much of the literature evaluating various DPF-FBC combinations has focused on reductions in PM emissions, with some reporting on the effects on other pollutants or fuel consumption. Emissions have been shown to increase during regeneration events of fully loaded traps, particularly at high space velocities, although they remain below standards. [102] HEI reported that only a small fraction of cerium-based FBC was found in the particle emissions, totaling 3-18% of the total mass of the emitted particle, indicating that the rest must remain behind on the filter itself or throughout the engine and exhaust components. [86] One study found that an unexpectedly high proportion of the additive was trapped in the engine and exhaust components, and only 10% reached the particle trap. [102] In addition, the use of metallic FBCs without a DPF have also been shown to increase particle emissions of metals. [97,111].

5.2 Smoke/ Soot Suppressant

A literature search for additives used in diesel for the purpose of soot suppression returned a limited number of recent items. Metals such barium, calcium, iron, magnesium, manganese and nickel have been evaluated for soot suppression for similar reasons as their use in DPF regeneration, namely, their ability to reduce soot oxidation temperature and enhance soot oxidation rates during combustion. [112,113,114] Additives such as ferrocene, cerium, manganese and barium have seen further use as a soot suppressant. [115] However, these additives do not appear to be widely available. Several products, including Lubrizol 565 [116] containing barium and cerium-based additives by the OMG Group were found in literature or on websites to be marketed as soot suppressants.[5]

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[4] The advanced Fe-FBC in the article was referenced as Eolys Powerflex, a Rhodia product. Solvay Rare Earth Systems, the primary author's affiliation, purchased Rhodia in 2011. [108]

[5] During initial investigations, information about OMG Group was found at the webpage omgi.com. During subsequent investigations, that webpage was found to no longer exist and now re-directs to www.vectraco.com. The cerium based additive, referred to as Cerium Hex Cem or Cerium Cem-All is no longer referenced.

The recent research and literature on these additives are primarily focused on the relationship between NO_x and soot formation for the purpose of investigating the "biodiesel NO_x penalty."[116,117,118] It has been theorized that higher PM concentrations reduce combustion chamber temperatures due to radiative heat transfer, thus reducing the formation of thermal NO_x. [119] Accordingly, it has been argued that the use of biodiesel or soot suppressant additives, both of which reduce PM, may result in an increase in NO_x. Soot suppressants such as barium and ferrocene have been used in an attempt to demonstrate this relationship, but with no clear effects on NO_x formation. [116,117,118,115] One use of ferric chloride with biodiesel showed a decrease in NO_x emissions accompanied by an increase in brake specific fuel consumption and CO_2. [120]

Smoke suppressant additives do not appear to be widely available, as alternative technologies such as DPF filters and similar devices are applied. [121]

5.3 Effects of Additives in Diesel Systems

Literature on durability testing and specific effects of particular additives on engine or exhaust components was limited. One study evaluating durability testing of Octimax 4808, the Strontium and Ferrocene blend, reported no negative effects on vehicle components although an increase in fuel consumption over the life of the vehicle was measured. [93]

Other general problems that metallic fuel additives may contribute to were investigated. One common problem with operability of diesel engines arises from the development of injector deposits. In particular, diesel common rail fuel injectors are prone to coking or fouling, which can have a negative impact on engine performance, emissions and fuel consumption. Today's modern HPCR (high pressure common rail) fuel injection systems have very tight clearances and can't tolerate even trace amounts of dirt, particulate or corrosion related particles. [122] Sophisticated injector designs and technologies and growing levels of biodiesel blending can increase the coking severity. Deposits on diesel fuel injectors have been found to be caused by a variety of components, including sodium carboxylic salts, likely a result of poly isobutylene succinimide (PIBSI) detergent additives or pipeline corrosion inhibitors. [123,124,125] Some metallic additives have been shown to contribute to injector fouling. Trace amounts of zinc can contribute significantly to the formation of deposits, which have a tendency to accumulate in spray-holes and contribute to nozzle coking. [110] Other metals, calcium, copper, sodium and iron do not contribute significantly to deposit formation. [110] The WWFC reports that fuel and lubricant- derived ash can contribute to coking on injector nozzles and may reduce the life of diesel particulate filters. This ash can be present as suspended solids and organometallic compounds, as metallic soaps, as soluble metals in biodiesel, and as metals that originate in water entrained in the fuel. [126] To address these problems, industry standards have been recommended to limit ash content in diesel fuel to less than 0.001%

In 2008, the CEC approved a new test procedure based on the Peugot DW10B engine, which has a high pressure common rail (P=1600 bar) and 6-hole piezoelectric prototype Siemens injectors of 110 microns. [107,127] During the CEC-98-08 DW10B test, a trace amount of zinc salt (1 mg/kg zinc as zinc neodecanoate) is added to the test fuel to simulate high-fouling fuels, and engine power is measured over a sixty hour test cycle to determine the level of injector fouling. The test is widely accepted as a measure of base fuel and additive performance in modern direct injection common rail equipped vehicles.

Some fuel-additive producers have evaluated their products using this test cycle. Evaluations of an advanced Fe-based diesel FBC for DPF regeneration with a proprietary deposit control additive (DCA) was evaluated by Solvay Rare Earth Systems and Lubrizol to show that the additive (likely Lubrizol 9040 ZerO™) did not contribute to injector fouling, and could even prevent nozzle coking deposits in direct injection common rail engines. [107] Other analysis of failed fuel injectors by Lubrizol showed that calcium and/or sodium were always present in failed or sticking injectors, along with high levels of sulfur or chlorine in some cases. [128]

The effects of ferrocene on heat release rates, NO_x emissions, and PM emissions have been conducted in single-cylinder test engines with different configurations. [129] Testing incorporated a run-in period with a high additive treat rate of 250 ppm, followed by testing at 25 ppm treat rate. While changes in heat release patterns, NO_x and PM emissions were observed, they were inconsistent between tests and instruments, and in some cases, too close to the detection limits to make strong conclusions.

The use of biodiesel has also been shown to increase the propensity for injector fouling, due primarily to contaminants and salts that remain from biodiesel production. [130] Use of sodium hydroxide or potassium hydroxide as a catalyst in the transesterification process to produce biodiesel can result in residual amounts of sodium or potassium in the finished biodiesel fuel. [131] In addition, calcium and magnesium may be used in the fuel purification process. These metallic fuel contaminants are converted to oxides, sulfates, hydroxides or carbonates in the combustion process to form inorganic ash that can be deposited onto the exhaust and emission control devices. These alkali and alkali earth metals have been shown to penetrate into heavy-duty diesel DOC and SCR catalysts. Effects of this include reduced NO_x conversion and degraded catalytic activity of the DOC for HC and NO oxidation after 150,000 miles, as well as decreased thermal shock resistance of cordierite DPF. [132]

Sodium contamination can also occur from diesel tank water bottoms, with levels exceeding 0.1%. [122] Other fuel contamination can occur during handling and storage of diesel fuels. Contamination by sodium, calcium and other metal cations can occur from sources such as sea water, refinery caustic neutralization, insufficient catalyst removal during biodiesel production, use of alkali metals for hydrogen removal during desulfurization, sodium based corrosion inhibitors for pipeline protection, de-icing compounds such as sodium chloride and calcium chloride, used lubricating oils, or engine oil lubricated fuel pumps. [122]

Fuel degradation during storage is promoted by the presence of certain metals such as copper and zinc, which can lead to additional problems during use. Many of the main fuel system contaminants such as phosphorous, calcium, and zinc can be found in lubricating oils. [133] Other metals can also lead to problems. For example, Lead is attacked by fuel acids and forms soap precipitates. Copper may catalytically accelerate fuel oxidation and promote deposition of solids. Non-ferrous metals should be excluded from use in fuel pipes and storage tanks and in the entire vehicle fuel system. [122]

6 Summary and Conclusions

Within this project, we have searched for literature regarding the use and effects of organometallic additives in transportation fuels with the objectives to identify the uses of specific metallic additives, determine if and where these additives are marketed, and investigate their effects on modern engine system and exhaust components. Through literature and web searches, a compendium of known metallic additives was developed. A review of the scientific literature was supported through Fuel Survey information purchased from SGS of gasoline samples collected worldwide. This report summarizes information included in that compendium, as well as provides a synthesis of retrieved information and state of knowledge regarding the use of organometallic additives in gasoline and diesel fuel.

The literature search returned over 100 items that were relevant to the use of organometallic fuel additives (excluding items related to health effects). The information found in these respective items was used to compile a database on the use and purpose of specific metallic additives in the compendium, which includes 88 items (although some are repeated). Conclusions from this body of information are as follows.

- Metallic additives do not appear to be widely used in gasoline or diesel fuels. The scientific literature does not give a good indication regarding their level of use in the marketplace. Web searches of specific additives indicate that organometallic additives are available in some locations. However, it is not clear if they are marketed on a large scale to commercial providers or refiners, or as aftermarket packages. However, gasoline fuel survey information indicates that several metals are found in fuel samples around the world.
- None of the gasoline fuel samples collected from the U.S. and Canada contained measurable amounts of metals.
- In gasoline fuels, metallic additives have included lead, iron and manganese, all of which were primarily used as antiknock agents or octane enhancers. Other metallic compounds may be present, but originate from lube oil packages or are trace contaminants.
- Manganese has been the most broadly used metallic additive in both gasoline and diesel. Recent fuel survey data supports that manganese is still used in gasoline around the world, and is the most common metallic additive seen in gasoline fuels. It is primarily seen in Latin America, African, Middle Eastern and Asian countries, and is most frequently used in allowable quantities. In a few instances, its use exceeds the maximum recommended dose of 33 mg Mn/L.
- The effects of manganese as MMT on vehicle systems and exhaust emissions are somewhat controversial, and have recently been thoroughly investigated and summarized. Mn in gasoline has been shown to deposit onto catalysts, reducing their exhaust conversion efficiencies and contributing to driveability problems.
- Iron as Ferrocene has been applied broadly, in gasoline as an antiknock, and in diesel as a fuel borne catalyst and/or soot suppressant. Its use can lead to iron oxide deposits, which have been shown to build up in the combustion chamber and on emission control system

components, and have also resulted in field problems, particularly when combined with manganese. In SI engines, these deposits can result in increased electrical conductivity and abnormal spark discharge as they build up on spark plugs and can also contribute to catalyst plugging. However, in diesel engines, the use of ferrocene in additive packages has been shown to reduce the occurrence of injector plugging or fouling. Fuel survey information does not indicate widespread use of iron in large quantities. Although its presence was detected in 75 gasoline samples collected within 32 countries, it was most frequently seen in low concentrations (<1mg/kg). Fuel samples that had iron content exceeding this limit were collected in 10 countries, however, and were measured as high as 25 mg/kg.

- Lead in gasoline has been phased out around much of the world, although it is still permissible in gasoline up to 13 mg/kg. The effects of these low levels on engine and exhaust components have not been reported in recent literature, as searches for low-level use of lead did not return any results. However, older literature has clearly documented the adverse effects of lead contamination on three way catalytic converters. Several additive producers list products containing TEL, and it is available as an aftermarket additive in some areas for specialty vehicles and racing applications.
- Potassium has been used in lead-replacement gasoline, and can act to protect valve seats. Its use is still recommended as an AVSR by the World Wide Fuel Charter. However, the problems with valve seat recession are found in mainly older cars that were designed to use leaded fuels, and generally do not occur on modern vehicles with hardened valves. Therefore, nearly all AVSR additives, including potassium, are marketed as aftermarket products. A fuel survey returned only 4 gasoline samples worldwide that contained any measurable amount of potassium, although it was seen in fairly high quantities in several samples collected from South Africa, where it is used as an AVSR additive.
- Most of the literature regarding organometallic additives was found on the topic of fuel borne catalysts (FBC) for DPF regeneration. These additives are primarily considered aftermarket additives, as their use on a wider scale without DPF technologies could result in increased emissions.
- These FBCs primarily include cerium and iron, although others have been evaluated. Several commercial products exist. However, other methods of DPF regeneration now appear to dominate, and the use of FBCs is not widely adopted.
- Barium, cerium, copper, iron, potassium, manganese and magnesium were all found to be used in various diesel fuel additives. Scientific literature indicated the use of cerium, manganese and iron as FBCs and the use of cerium, iron, and barium as soot suppressants. However, none of these additives appear to be widely used, with the exception of cerium and ferrocene FBC additives, which are used for specific technologies as an aftermarket additive. Targeted searches for other additives did not reveal any commercially available products for diesel fuels, and fuel survey data on diesel fuels were not acquired.
- Cerium has been used primarily in diesel fuel for DPF regeneration or as a soot suppressant. It has been included as a component of various commercial products, although these appear to be available only in Europe, and are marketed as aftermarket additives for specific diesel

vehicles equipped with DPF technologies. While several studies have shown that much of the cerium is retained within the engine and exhaust system (ranging from 82 to 94%), negative effects of its use on engine system and exhaust components have not been reported in literature, although it has been shown to increase fuel consumption.

- Fuel survey data provides evidence of contamination of Silicon and small amounts of Zn in a significant fraction of the fuel samples.
- The World Wide Fuel Charter recommends against the use of any ash-forming additives, including MMT and ferrocene.

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Appendix A: Description of Accompanying Metallic Fuel Additive Compendium

The accompanying compendium of MFAs is assembled into an Excel table, and includes entries for each item listed below. It is arranged so that it can be sorted or searched based on primary topics of interest, including by metal, by fuel type, by function of the additive, etc. To do this, is it set up so that each field of these primary interests for sorting has a single entry. Therefore, there may be multiple entries for a single additive type. For example, since ferrocene can be used as an antiknock and as an anti-valve seat recession (AVSR) additive in gasoline, but can also be used as a soot suppressant or as a fuel borne catalyst in diesel, it has four separate entries, one for each use. In addition, one entry is included for each specific product name found, and for each of that particular product's uses, if more than one exists. The primary, single entry fields are highlighted in the list below.

1. "**Additive"** : Provides the chemical name of the additive
2. "**Metal**": Provides the primary metal used in the additive. Metals found that are included in the database include Al, B, Ba, Ce, Cr, Cu, Fe, Fe &Sr, K, Li, Mg, Mn, Na, Ni &Al, Pb, Pd, Pt, Rh, Ti and Zr.
3. "**Formul**a": Provides the chemical formula of the structure of the metal used in the additive, when given.
4. "**Chemical Names**": Provides other common chemical names for the additive
5. "**Product Names**": Provides specific commercial product names for the additive, listed as one name per entry, if given.
6. "**Producer**": provides the producer or commercial supplier of the specific product, if given.
7. "**CAS Number**": provides the CAS number of the additive, if available.
8. "**Fuel Type**": specifies if the additive is used in either gasoline or diesel. If it is used in both, a separate entry was made for each fuel.
9. "**Function**": defines the specific function claimed for the additive. If it can be used for more than one purpose, a separate entry was made, with "other uses" listed in the next column. The function of additives includes use for "air breathing propulsion systems", antistatic, antifoam, antiknock, antioxidant, AVSR, catalyst, cetane improver, color stabilizer, corrosion inhibitor, DCA, demulsifier, detergent, FBC, freeze protection, fuel stabilizer, lubricity improver, lubricant, NOx reducer, oxygenate, and soot suppressant.
10. "**Other uses**" lists other functions of the additive so that when sorting by function, its other uses are also visible.
11. "**Physical and Chemical Structure based grouping**" describes the physical or chemical structure of the additive, and includes such description as nanoparticles, iron-based additives, rare earth metal oxides, transition metal, metal carbonyl, etc.
12. "**Concentration of Metals in Additive**" provides information about the dosing or amount of metal in each commercial additive, when available. This field is blank for many entries, for

example, when no commercial product was found, of if the information was not found for a commercial product.

13. “**Range of Use**” provides either the recommended dosing or range of use of the commerical product, or the dosing rate applied if the additive was used in a particular study.
14. “**Market, Company Location**” provides information on the region or country where the product may be used. This information is based on either the product company location or on where the product is sold, if available.
15. “**Allowable limits**” specifies the limits of the metal in the identified geographic region, if available.
16. “**Fuel Impacts**” provides specifics of research or marketing claims about the product’s use. Primarily claims include octane number (ON) boost for various gasoline additives. Many of these fields are blank.
17. “**Vehicle Impacts**” describes specific impacts of the additive found on vehicles or exhaust systems. This information was reported in only a few cases, and primarily in literature. Any effects, when found, are also summarized in this report.
18. “**Emissions Impacts**” describes any reported findings on the additive’s impacts on emissions including PN, PM, CO,HC, NO_x, and SO_x. Many of these results were found in literature, and are also summarized in this report.
19. “**Additive Timing**” lists when the additive might be additized to the fuel.
20. “**Note**” includes any additional notes or items of relevance.
21. “**Reference**” lists any reference from which information on the product was found. This includes reports, publications, and/ or websites.

The primary focus of this search was to identify market additives, or those that are blended at the refinery or fuel terminal in order to meet fuel specifications or performance requirements. However, other additives that are blended at the pump or fuel terminal (usually in order to meet marketing claims), and some after-market additives that are sold directly to the consumer were also included, when relevant. Primarily, the expansion of the search to include aftermarket additives was for the purpose of including metallic additives used for diesel particulate filter (DPF) regeneration. These additives are not typically blended directly into a fuel, but are required for use in vehicles with specific DPF technologies.

While the compendium can be used to search specific additives, it also includes a list of reference items investigated for this work. Where returned references did not have specific information pertaining to the use of metallic additives, the reference is included, but listed as non-relevant. Other articles that contained relevant information have a detailed summary included in the excel table. This information from relevant or supporting literature items is summarized in the remainder of this report.

Appendix B: Tables from World Wide Fuel Charter

Table 3: Recommended fuel World Wide Fuel Charter specifications for Category 4 Gasoline Fuels, From [11]

PROPERTIES		UNITS	LIMIT	
			Min.	Max.
'91 RON' (1)	Research Octane Number		91.0	
	Motor Octane Number		82.5	
'95 RON' (1)	Research Octane Number		95.0	
	Motor Octane Number		85.0	
'98 RON' (1)	Research Octane Number		98.0	
	Motor Octane Number		88.0	
Oxidation stability		minutes	480	
Sulphur		mg/kg (2)		10
Trace metal (3)		mg/kg		1 or non-detectable, whichever is lower
Oxygen (4)		% m/m		2.7 (5)
Olefins		% v/v		10.0
Aromatics		% v/v		35.0
Benzene		% v/v		1.0
Volatility			See Tables, page 8	
Sediment (total particulate)		mg/l		1
Unwashed gums (6)		mg/100 ml		30
Washed gums		mg/100 ml		5
Density		kg/m3	715	770
Copper corrosion	rating			Class 1
Silver corrosion	rating			Class 1
Appearance			Clear and bright; no free water or particulates	
Fuel injector cleanliness, Method 1, or		% flow loss		5
Fuel injector cleanliness, Method 2		% flow loss		10
Particulate contamination, size distribution		Code rating		18/16/13 per ISO 4406
Intake-valve sticking		pass/fail	Pass	
Intake valve cleanliness II				
Method 1 (CEC F-05-A-93), or		avg. mg/valve		30
Method 2 (ASTM D5500), or		avg. mg/valve		50
Method 3 (ASTM D6201)		avg. mg/valve		50
Combustion chamber deposits (6)				
Method 1 (ASTM D6201), or		% of base fuel		140
Method 2 (CEC-F-20-A-98), or		mg/engine		2500
Method 3 (TGA FLTM BZ154-01)		% mass @ 450°C		20

Footnotes:

(1) Three octane grades are defined for maximum market flexibility; availability of all three is not needed.

(2) The unit mg/kg is often expressed as ppm.

(3) Examples of trace metals include, but are not limited to, Cu, Fe, Mn, Na, P, Pb, Si and Zn. Another undesirable element is Cl. No trace metal should exceed 1 mg/kg. No intentional addition of metal-based additives is allowed.

(4) Where oxygenates are used, ethers are preferred. Methanol is not permitted.

(5) By exception, up to 10% by volume ethanol is allowed if permitted by existing regulation. Blendstock ethanol should meet the E100 Guidelines published by the WWFC Committee. Fuel pump labelling is recommended for gasoline-ethanol blends to enable customers to determine if their vehicles can use the fuel.

(6): To provide flexibility (for example, to enable the use of detergency additives that increase unwashed gum levels), the fuel may comply with either the Unwashed Gum limit or the Combustion Chamber Deposits limit.

Table 4: Gasoline Test Methods, Specified in the 5th Ed. of the World Wide Fuel Charter[11]

PROPERTIES	UNITS	ISO	ASTM	JIS	OTHER
Research Octane Number		EN 5164	D2699	K 2280	
Motor Octane Number		EN 5163	D2700	K 2280-96	
Oxidation stability [1]	minutes	7536	D525	K 2287	
Sulphur content	mg/kg		D2622	K 2541	
		20846	D5453		
		20884			
Lead content	mg/l		D3237	K 2255	EN 237
Potassium (K) content	mg/l				NF M 07065 EN 14538
Trace metal content	mg/kg				ICP; ASTM D7111 modified
Phosphorus content	mg/l		D 3231		
Silicon content	mg/kg				ICP-AES (Reference in-house methods with detection limit = 1 mg/kg)
Chlorine content	mg/kg		D7359 or D7536		
Oxygen content	% m/m		D4815	K 2536	EN 13132
Olefin content [2]	% v/v	3837	D1319	K 2536	
Aromatic content [2]	% v/v	3837	D1319	K 2536	EN 14517
Benzene content	% v/v		D5580	K 2536	EN 238
			D3606		EN 14517
Vapour Pressure	kPa		D5191	K 2258	EN 13016/1 DVPE
Distillation: T10/T50/T90, E70/E100/E180, End Point, residue		3405	D86	K 2254	
Vapour/liquid ratio (V/L)	°C		D5188		
Sediment (total particulate)	mg/l		D5452		
Unwashed gums	mg/100 ml	6246	D381	K 2261	May be replaced with CCD test
Washed gums	mg/100 ml	6246	D381	K 2261	
Density	kg/m3	3675	D4052	K 2249	
		12185			
Copper corrosion	rating	2160	D130	K 2513	
Silver corrosion	rating		D7671		
Appearance			D4176		Visual inspection
Carburettor cleanliness	merit				CEC F-03-T
Fuel injector cleanliness, Method 1	% flow loss		D5598		
Fuel injector cleanliness, Method 2	% flow loss		D6421		
Particulate contamination, size	code rating	4406			
distribution	no. of particles/ml	4407 & 11500			
Intake-valve sticking	pass/fail				CEC F-16-T
Intake valve cleanliness I	merit				CEC F-04-A
Intake valve cleanliness II	avg. mg/valve				
Method 1, 4 valve avg.					CEC F-05-A
Method 2, BMW test			D5500		
Method 3, Ford 2.3L			D6201		
Combustion chamber deposits					
Method 1	% of base fuel		D6201		
Method 2	mg/engine				CEC F-20-A
Method 3	% mass @ 450°C				FLTM-BZ154 [3]

[1] Updated procedures are needed to better measure oxygenated blends.

[2] Some methods for olefin and aromatic content are used in legal documents; more precise methods are available and may be used.

[3] This method is available at http://global.ihs.com.

Table 5: Recommended fuel World Wide Fuel Charter specifications for Category 4 Diesel Fuels, From [11]

PROPERTIES	UNITS	LIMIT Min.	LIMIT Max.
Cetane Number		55.0	
Cetane Index (1)		55.0 (52.0) (1)	
Density @ 15°C	kg/m3	820 (2)	840
Viscosity @ 40°C	mm2/s	2.0 (3)	4.0
Sulphur	mg/kg (4)		10
Trace metal (5)	mg/kg		1 or non-detectable, whichever is lower
Total aromatics	% m/m		15
PAH (di+, tri+)	% m/m		2.0
T90 (6)	°C		320
T95 (6)	°C		340
Final Boiling Point	°C		350
Flash point	°C	55	--
Carbon residue	% m/m		0.20
CFPP or LTFT or CP (7)	°C		Equal to or lower than the lowest expected ambient temperature
Water	mg/kg		200
Oxidation Stability			
Method 1	g/m3		25
Method 2a (Rancimat, modified) (8), or	hours	35	
Method 2b (Delta TAN) (8), or	mg KOH/g		0.12
Method 2c (PetroOxy) (8)	minutes	65	
Foam volume	ml		100
Foam vanishing time	sec.		15
Biological growth (9)		no growth	
FAME (10)	% v/v		5 (10)
Other biofuels (11)	% v/v		(11)
Ethanol/Methanol	% v/v	Non-detectable (12)	
Total acid number	mg KOH/g		0.08
Ferrous corrosion			Light rusting
Copper corrosion	rating		Class 1
Ash	% m/m		0.001 (13)
Particulate contamination, total	see test method		10
Particulate contamination, size distribution	code rating		18/16/13 per ISO 4406
Appearance		Clear and bright; no free water or particulates	
Injector cleanliness (Method 1)	% air flow loss		85
Injector cleanliness (Method 2)	% power loss		2
Lubricity (HFRR wear scar dia. @ 60°C)	micron		400

Footnotes:

(1) Cetane Index is acceptable instead of Cetane Number if a standardized engine to determine the Cetane Number is unavailable and Cetane improvers are not used. When Cetane improvers are used, the estimated Cetane Number must be greater than or equal to the specified value and the Cetane Index must be greater than or equal to the number in parenthesis.

(2) May relax the minimum limit to 800 kg/m3 when ambient temperatures are below -30°C. For environmental purposes, a minimum of 815 kg/m3 can be adopted.

(3) May relax the minimum limit to 1.5 mm2/s when ambient temperatures are below -30°C or to 1.3 mm2/s when ambient temperatures are below -40°C.

(4) The unit mg/kg is often expressed as ppm.

(5) Examples of trace metals include, but are not limited to, Cu, Fe, Mn, Na, P, Pb, Si and Zn. Another undesirable element is Cl. No trace metal should exceed 1 mg/kg. No intentional addition of metal-based additives is allowed.

(6) Compliance with either T90 or T95 is required.

(7) If compliance is demonstrated by meeting CFPP, then it must be no more than 10°C less than cloud point.

(8) Methods 2a and 2b must be used with fuels containing FAME. Method 2c correlation data are based on fuels containing FAME.

(9) Alternative test methods, with appropriate limits for "no biological growth," can be used.

(10) For FAME, both EN14214 and ASTM D6751, or equivalent standards, should be considered. Where FAME is used, the blendstock should meet the B100 Guidelines published by the WWFC Committee, and fuel pumps should be labelled accordingly.

(11) Other biofuels include HVO and BTL. Blending level must allow the finished fuel to meet all the required specifications.

(12) At or below detection limit of the test method used.

(13) Limit and test method are under review to assure DPF endurance.

Table 6: Diesel Test Methods, Specified in the 5th Ed. of the World Wide Fuel Charter[11]

PROPERTIES	UNITS	ISO	ASTM	JIS	OTHER
Cetane Number		5165	D613	K 2280	D6890, D7170 [1]
Cetane Index		4264	D4737	K 2280	
Density @ 15°C	kg/m3	3675 12185	D4052	K 2249	
Viscosity @ 40°C	mm2/s	3104	D445	K 2283	
Sulphur content	mg/kg	20846	D5453	K 2541	
		20884	D2622		
Total aromatic content	% m/m		D5186		EN 12916
PAH content (di+, tri+)	% m/m		D5186		EN 12916, D2425
T90, T95, FBP	°C	3405, 3924	D86	K 2254	D2887
Flash point	°C	2719	D93	K 2265	D56
Carbon residue	% m/m	10370	D4530	K 2270	
Cold Filter Plugging Point (CFPP)	°C		D6371	K 2288	EN 116, IP 309
Low Temperature Flow Test (LTFT)	°C		D4539		
Cloud Point (CP)	°C	3015	D2500	K 2269	D5771, D5772, D5773
Water content	mg/kg	12937	D6304	K 2275	
Oxidation stability					
Method 1	g/m3	12205	D2274		
Method 2a (Rancimat, modified)	induction time (hours)				EN 15751
Method 2b (Delta TAN) [2]	mg KOH/g		D664 & D2274 (modified)		
Method 2c (PetroOxy)	minutes				EN 16091
Foam volume	ml				NF M 07-075
Foam vanishing time	sec.				NF M 07-075
Biological growth					NF M 07-070, IP385
FAME content	% v/v		D7371		EN 14078
Ethanol/Methanol content	% v/v		D4815 (modified)		
Total acid number (TAN)	mg KOH/g	6618	D664		
Ferrous corrosion			D665 [3]		
Copper corrosion	merit	2160	D130	K 2513	
Appearance			D4176		Visual inspection
Ash content	% m/m	6245	D482 [4]	K 2272	
Particulate contamination, total	see test method		D6217 FAME-free (mg/l) D7321 with FAME (mg/l)		EN 12662 (mg/kg)
Particulate contamination, size distribution	code rating no. of particles/ml	4406 4407 & 11500	D7619		
Injector cleanliness, Method 1	% air flow loss				CEC (PF-023) TBA
Injector cleanliness, Method 2	% power loss				CEC-F-098 [5]
Lubricity (HFRR wear scar diameter @ 60°C)	micron	12156-1.3	D6079		CEC F-06-A, D7688
Trace metal content					ICP, D7111 modified

[1] ASTM D6890 and D7170 measure Derived Cetane Number (DCN) and are being widely used as alternatives to D613.

[2] Measure Acid Number using D664 before and after aging fuel per D2274 (modified – 115°C).

[3] Procedure A.

[4] Minimum 100 g sample size.

[5] CEC has initiated test development for Internal Diesel Injector Deposits (IDID).