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Petrol fuel quality and its effects on the vehicle technology and the environment

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Summary

This study has been done on request of the Dutch Human Environment and Transport Inspectorate, ILT. The objective is to evaluate petrol fuel quality and its effects on the vehicle technology and the environment.

Over the past five decades, the petrol fuel quality has been improved step by step in order to reduce the polluting vehicle emissions and also as precondition for vehicles to comply with increasingly stringent emission legislation (e.g. Euro 1 through Euro 6 in Europe). In general the current petrol fuel quality in Europe, and other main regions, is fully compatible to older vehicles. One exception is the compatibility with ethanol blends containing 5 and 10 volume percent ethanol (E5 and E10). Therefore, E5 or ethanol free petrol should remain available for a number of vehicle types built before 2010.

The evaluation has shown that a good fuel quality is of key importance to protect the health of people and the environment, independent of the age of the vehicle, the technology used or even the maintenance of the vehicle. The most relevant fuel specifications include Fuel Sulphur Content (FSC), benzene- and metals content (particularly manganese) and vapor pressure. Fuels customary in Europe since 2009 contain sulphur level <10ppm, benzene < 1% and no addition of metals (WWFC petrol category 4 requirements). An increase in sulphur level up to 30 or 50 ppm could be acceptable for common, yet older petrol cars (WWFC petrol category 3 requirements).

The adverse health effects of high benzene content and high vapor pressure are even higher for older technology or poorly maintained vehicles, since there is a less effective aftertreatment or even no emission aftertreatment and no carbon canister on the fuel tank to mitigate the adverse health effects and environmental impact. Hence, it can be concluded that limitation of these components in petrol fuel is even more important for older vehicles than for younger vehicles.

On top of the direct effect of sulphur and metal components in petrol on health and the environment, these components will seriously compromise the efficiency of the emission control systems of petrol engines, leading to a steep increase of other tailpipe emissions like NO_x, CO, PM and unburned hydrocarbons. For example, 500 ppm sulphur can already lead to severe increase in emission after 15000 km. It is likely that after a prolonged poisoning period using high sulphur fuel, the NO_x, CO and HC emissions of Euro-3 and Euro-4 vehicles increase tenfold or more to the level of a vehicle without three-way catalyst.

Contents

List of Abbreviations

CO – carbon monoxide
CO_2 – carbon dioxide
CONCAWE - CONservation of Clean Air and Water in Europe
E5 - 5 volume percent ethanol in petrol
E10 - 10 volume percent ethanol in petrol
EC – European Commission
EEC - European Economic Community
EPA - Environmental Protection Agency
Euro - Euro emission level (Europe)
GHG - Greenhouse gas
HC - hydro carbons
IARC - International Agency for Research on Cancer
ILT - Dutch Human Environment and Transport Inspectorate
LEV - Low Emissions Vehicle (USA)
m/m - mass/mass
MMT - Methylcyclopentadienyl Manganese Tricarbonyl
NH_3 - ammonia
NO_x – Nitrogen Oxides
PAH – Polycyclic Aromatic Hydrocarbons
PM – Particulate matter
PN – Particle Number
ppm – parts per million
S - Sulphur
SO_2 – Sulphur dioxide
SO_x – Sulphur oxides
THC - Total hydro carbons
Tier - Tier emission level (USA)
ULEV - Ultra Low Emissions Vehicle (USA)
UNECE - United Nations Economic Commission for Europe
v/v - volume/volume
VOC - Volatile Organic Components
WHO - World Health Organisation
WWFC - World Wide Fuel Charter

1 Introduction

The Dutch Human Environment and Transport Inspectorate, ILT, has requested TNO to provide background on the environmentally related specifications of petrol fuel in relation to the technology development of vehicles in the European fleet. The technical specifications and regulations for petrol fuel have changed extensively in Europe over the last fifty years. The changes were mainly initiated by environmental regulations and air quality standards to protect the general wellbeing of people and to ensure that vehicle technology, responsible for reducing harmful tailpipe emissions, is functioning well over the lifetime of a vehicle. The proper functioning of vehicle technology is an important aspect in reducing vehicle emissions and the environmental impact of vehicles. The fuel specifications have been developed in the context of ensuring a single European fuel market.

The objective of this report is to evaluate petrol fuel quality and its effects on the vehicle technology and the environment. In this study a wide scope of vehicle technology and fuel composition is taken into account.

This report evaluates the reasons for changes in petrol fuel specifications in the last fifty years. With the introduction of new and more efficient emission reduction technologies, as well as growing environmental concerns, newer and more stringent fuel specifications were needed and adopted over time. Central to the report is a timeline of the last decades, of fuel specifications and the reasons certain fuel compositions were no longer appropriate. If vehicles are older, or have older technology, they may fit with fuels with less stringent specifications. Newer vehicles require fuels within strict specifications. To put this in short, the fuel specifications have to match the vehicle emission reduction technology to function properly to minimize the environmental impact. The most relevant fuel specification in this respect include Fuel Sulphur Content (FSC), benzene- and metals content (particularly manganese) and the vapor pressure. The most relevant vehicle emissions include SO_x, NO_x, unburned hydrocarbons including benzene, and CO.

The report is build up as follows. Chapter 2 describes the development of EU fuel quality standards since the 1970’s along with the impact on the total emissions of air pollutants of traffic in Europe. Also an overview of Dutch statistics on fuel quality is given. Chapter 3 analyses the technological aspects of the main fuel impurities on the emissions and durability of vehicles. In Chapter 4, the technological aspects and the impact on environment and health are summarised. Finally, a compact set of conclusions is given in Chapter 5.

2 Petrol fuel quality standards 1970-2019

In this section the development of the EU fuel quality standard since the seventies until 2019 is described in paragraph 2.1. Along with the development of fuel quality standards embodied by the Fuel Quality Directive also came the responsibility of Member States to monitor the fuel quality which is highlighted in Section 2.2. An overview of the monitoring results of The Netherlands since 1980 is provided as well. In Section 2.3 an illustration of the impact of the Fuel Quality Directive on the total emissions of air pollutants of traffic in Europe is given.

2.1 Development of fuel quality standards

The introduction of fuel quality standards in Europe started in the early seventies. The primary objectives were to limit air pollutant emissions, to protect the engine technology and also to support the function of an EU internal market for fuels. After 2000, reduction of GHG (Green House Gas) emissions was added to the fuel quality standards.

For the development of a fuel quality standard it is important to understand the relation between the components in petrol fuel, how they behave in an internal combustion engine and emissions control system.

The following mechanism for petrol fuel components can be distinguished:

- Components which do not combust and flow through a petrol combustion engine such as lead, manganese, or evaporates from the fuel tank such as Volatile Organic Components (VOC) and benzene.
- Components which combust incompletely: benzene, PAH, VOC
- Components which combusts but are (very) polluting: sulphur forms SO_x and PM.
- Components which poison the emission control systems such as catalysts and sensors, like sulphur and metals like lead, manganese and others. This is an indirect effect and will lead to much higher NO_x, HC and CO emissions over time.

To reduce pollutants by means of changing the fuel quality standard, the focus during 1970 – 2010 was on reduction of the following components (historically in this sequence):

- Lead
- Benzene
- Sulphur (leading to SO_x)
- Polyaromatic Hydrocarbons: PAH (referred to as "aromatics" in EN 228)
- Manganese
- Volatile Organic Components: VOC (via vapor pressure)

Important fuel quality related directives to regulate components are:

- 75/716/EC First restrictions on sulphur content (not yet for petrol)
- 78/611/EC Lead content of petrol
- 85/210/EC Lead & benzene (<5% in 1989)
- 85/536/EC Crude oil savings with substitutes → max O_2 content
- 91/441/EC Sulphur petrol reference fuel (<400 ppm)
- 93/12/EC Sulphur in petrol
- 98/70/EC Sulphur + vapor pressure + fuel quality monitoring
- 1999/32/EC Sulphur of diesel and marine gas oil
- 2003/17/EC Sulphur
- 2009/30/EC Manganese (MMT) + GHG + fuel quality monitoring

The concentration limits for the indicated components in petrol are summarized in Table 1. Especially until about 2000, there was often a transition period indicated by two years. The first date indicated when the fuel needed to be available (especially for new vehicles equipped with catalysts that required the higher fuel quality) and the second date when the old specification could not be sold any more. The limitation of sulphur in specifically diesel was the start of environmental fuel regulation in Europe. Traditionally, petrol had much lower sulphur levels compared to diesel. The limitations of sulphur were restricted to diesel until 2000 after which the limit also applied for petrol.

As reference, the average sulphur content in USA regular gasoline was already 900 ppm in 1951. Hence, it seems that despite limited regulation of the sulphur content in petrol, the actual levels have been low compared to diesel and heavy gas oil, which were easily a few thousand ppm, prior to regulation.

Table 1: Summary of limitations of polluting components in petrol according to EU directives for fuel quality: year of entry into force and maximum level.

Directive	**Lead**	**Benzene**	**Sulphur**	**PAH**	**Manganese**	**Vapor pressure**
75/716/EC			2000 – 3000 ppm diesel*			
78/611/EC	1981: 0,4 (0,15) g/L					
85/210/EC	1989: Unleaded required (0,013g/L) Leaded voluntary max 0,4	1989: 5% v/v for all petrol or earlier for unleaded				
EN 228			1993: 1000 ppm 1995: 500 ppm			1993: 80 kPa
93/12/EC			1995: 500 ppm (diesel)			
98/70/EC	2000: 0,005 g/L	2000: 1%	2000: 150ppm 2005: 50ppm	2000: 42% 2005: 35%		2000: 60 kPa
2003/17/EC			2005-2009: 50ppm 2009: 10ppm			
2009/30/EC					2009: 6mg/L 2014: 2mg/L	

* Natural sulphur content in petrol is estimated between 240 – 900ppm. These numbers refer to respectively content in Europe and USA prior to sulphur regulation. As reference, the average sulphur content in USA regular gasoline was already 900 ppm in 1951.

From Table 1, it can be concluded that the phasing out of sulphur, lead and benzene started in the seventies and eighties, and was almost completed in the nineties. In the year 2000, 20 years ago, the sulphur and benzene limits were reduced to respectively 150 ppm and 1%, a factor of ten or more lower than in the early seventies. In Section 2.2, statistics of fuel supplied show that sulphur was already almost eliminated from petrol at the start of the eighties. The average content was 240 ppm in the eighties.

The reduction of vapor pressure started in the nineties, with a limit value of 80 kPa, in 2000 further reduced to 60 kPa. The reduction was considered necessary both for the proper functioning of cars with 3-way catalysts, as well as for the direct emission into the air, either from the fuel tank ventilation or from the tailpipe. Manganese was always low, but it was added as an option to increase the octane number of the fuel. Limit values were introduced in 2009 and further reduced in 2014 due to its adverse effect on emission control devices.

In line with the requirements of the EU fuel quality directives, the EN228 petrol specification standard was updated. The European standard EN228 limit values for the most important components, as summarized in Table 2.

Table 2: European standard EN228 petrol specifications over time with the maximal values for Sulphur, Benzene, and vapour pressure.

Year		1993	1995	2000	2005	2009	2014
Sulphur	ppm (mass)	1000	500	150	50	10	
Benzene	% (volume)	5		1			
Manganese	mg/litre					6	2
Vapour pressure	kPa (summer)	80		60			

2.2 Market petrol quality monitoring 1980 - 2019

2.2.1 Fuel Quality Directive (FQD) monitoring

On the basis of Directive 98/70/EC amended by Directive 2009/30/EC, European Member States have to monitor their market fuel quality. From 2000 onwards, in view of the relevance for environmental issues and climate change, different fuel properties have been monitored. Prior to 2000 the European Commission and the environmental research centre CONCAWE of the European Petroleum Refiners Association monitored fuel quality across Europe. The properties in the FQD (Fuel Quality Directive 2009/30/EC) include, for petrol, RON (Research Octane Number), MON (Motor Octane Number), and distillation fractions relevant for engine operation, benzene, sulphur, lead, and vapour pressure for environmental impact, and oxygen and oxygenates for bio-admixture. Manganese is not part of this directive.

In the Netherlands the ILT is responsible for monitoring the fuel quality. The ILT takes around hundred fuel samples, petrol and diesel, per year. The results are part of the annual FQD reports.

2.2.2 Netherlands Statistics fuel composition

Trends of fuel compositions were recovered from the first general tables of the Traffic and Transport Taskforce of 2012 as part of the emission inventory and shown in Table 4. Metals in petrol are well below the 1 mg/litre requirement of the automotive industry, with Copper concentration the highest at 0.032 mg/kg fuel. The time series of lead and sulphur of petrol and sulphur content of diesel show that the typical fuel composition has been ahead and below of the successive limits set in European directives and EN 228 standards.

The results of Statistics Netherlands are similar compared to other Member States across Europe. For example, AEA (now part of Ricardo research company) reported in 2006, that of all petrol sold across Europe, 58% was low sulphur (<50 ppm) and 42% sulphur ‘free’ (<10 ppm). Sulphur levels below 10 ppm is close to the measurement accuracy. The averages, with the required availability of low-sulphur, and sulphur-free fuel, were met two to three years ahead of the set dates.

Table 3: Table of Statistics Netherlands from 2012 of average fuels, based on the measurements and reporting of fuel additives and composition in market fuels.
Some numbers are estimates (est.).

	Petrol		**Diesel**
	Lead	**Sulphur**	**Sulphur**
Year	**g/litre**	**ppm**	**ppm**
1980	0.36	*240 (est.)*	3300
1985	0.36	*240 (est.)*	2000
1990	**0.071**	**240**	**1780**
1991	0.057	*213 (est.)*	1800
1992	0.042	*185 (est.)*	1800
1993	0.036	*157 (est.)*	1800
1994	0.027	*130 (est.)*	1750
1995	0.021	*102 (est.)*	1600
1996	**0.011**	**74**	**1189**
1997	0.0004	74	500
1998	0.00001	74	500
1999	0.00001	74	500
2000	0.00001	74	290
2001	0.00001	51	42
2002	0.00001	60	34
2003	0.00001	26	31
2004	0.00001	29	34
2005	0.00001	19	8
2006	0.00001	22	11
>2006	0.00001	22	10-11

2.3 Impact Fuel Quality Directive on emissions

The impact on emissions of the Fuel Quality Directive was evaluated in 2017 (EC, 2017). In this evaluation, several graphs were produced regarding the development of the fuel quality standards and the reduction of polluting components. Several of these graphs are presented in this section.
Figure 2 shows the average fuel sulphur content for petrol and diesel from 2001 to 2011 and the SO_x emission for the period 1995 to 2013. Figure 3 shows respectively the lead and NO_x emissions of the EU transport sector.

The two figures show the large impact of the fuel quality, restriction on polluting and toxic components in fuels on the emissions of air polluting components.
It shows a tenfold reduction despite the growth in fuel sales.

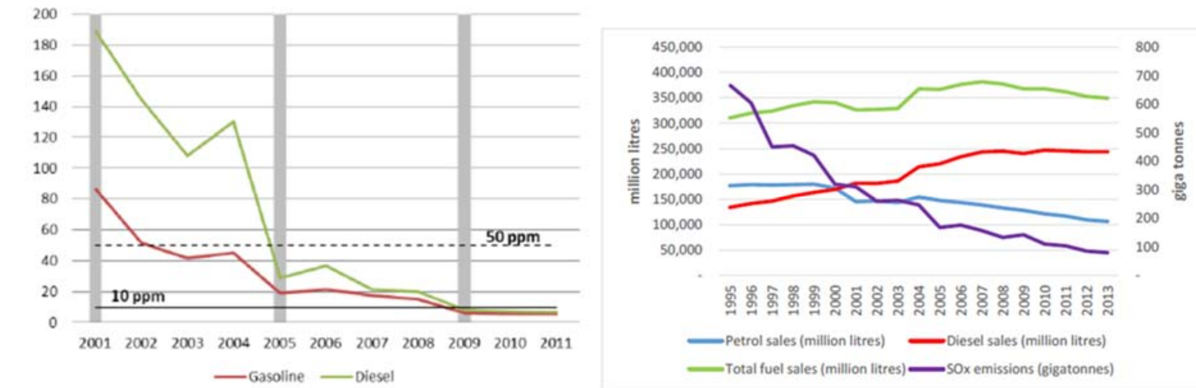

Figure 1: Average fuel sulphur content (left) of road transport fuel in Europe (in ppm). SOx emissions (right) from road transport in Europe from 1995 to 2013. (Source EC, 2017).

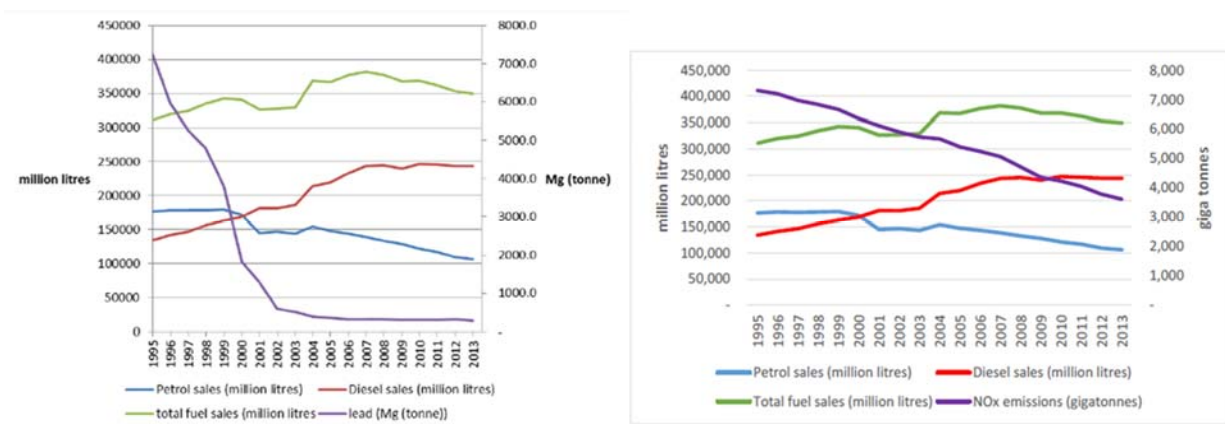

Figure 2: Lead (left) and NO_x (right) emissions from the EU transport sector compared to the fuel sales in the period 1995 to 2013. (Source EC, 2017).

3 Development of fuel quality in relation to vehicle technology

This chapter aims to put fuel quality development on a timeline, linking them to vehicle technology. The link between the development of fuel quality and vehicle technology is described in the first section. In the following sections the effects from sulphur, benzene, manganese and vapour pressure on vehicle technology is described in more detail.

3.1 WorldWide Fuel Charter, WWFC

The WorldWide Fuel Charter (WWFC) provides recommendations and guidelines with respect to the fuel quality by associated car and truck manufacturers worldwide (WWFC, 2019). Participating manufacturers organisations include organisations from Europe, Japan and USA, namely ACEA, Auto Alliance, JAMA and EMA. The recommendations and guidelines are primarily focussed on preserving the durability and the emissions compliance of the vehicles.

The WWFC of automotive manufacturers distinguishes six categories of petrol fuel quality. Each of the categories is intended for vehicle technologies necessary to comply with the emissions legislation. An overview of the petrol categories, along with the most relevant requirements and the corresponding vehicle types in Europe and USA, is given in Table 4. The main requirements for the categories 4, 5 and 6 are the same. Categories 5 and 6 are intended for the reduction of GHG emissions, increased fuel efficiency and reduction of Real Driving Emissions (RDE). One of the differences is that they allow a higher oxygen content (3.7% instead of 2.7%) such that more ethanol can be blended.

Petrol category 1 was necessary for the first vehicle categories with three-way catalyst, initially in the 1980s but standard with Euro-1 in 1992 in Europe and Tier 0 in the USA. The main difference with earlier petrol was that no lead was used to increase the octane number and to reduce wear of certain engine components. It should be noted that in Europe also USA Tier 0 type approved vehicles were sold up to 1992. Category 2 has the more stringent fuel quality limits to ensure proper functioning of three-way catalysts on petrol engines, introduced with Tier 1 in 1994-1997 and Euro-2 in 1996. With the categories 3 and 4, the max sulphur content was gradually further reduced to respectively 30ppm and 10ppm. This is to ensure emissions and durability compliance with Euro 4, 5 and 6. Category 3 was intended for LEV (Low Emission Vehicle) and ULEV (Ultra-Low Emission Vehicle) requirements in USA and California and also for Euro 4. Category 4 was intended for US Tier 2 and 3 and for Euro 4 through 6b.

Basically, a vehicle in certain WWFC technology category requires a fuel of minimally the same category to function properly. In many cases older vehicles are perfectly able to run on the newer fuels, with a few exceptions that have been regulated separately. For example, leaded fuels have been kept for some time after the phase-out around 2000, to prevent higher maintenance costs. Unleaded fuel lead to high valve wear in certain older (pre-catalyst) vehicles.

Also, ethanol addition to petrol, in higher fractions like E10, has been related to problems in Euro-4 and older vehicles that were sold till 2009.

Table 4: Vehicle emission technology classes and year of introduction, provided by the European automotive industry (ACEA) within the WWFC.

<table>
<tr><th>Petrol category</th><th>Main petrol requirements</th><th>Corresponding vehicle emission class</th><th>Year first introduction</th></tr>
<tr><td>1</td><td>S < 1000 ppm m/m
Benzene < 5% v/v
Metals < 1 ppm m/m or non-detectable</td><td>US Tier 0
Pre-Euro with 3-way catalyst
Euro 1</td><td>1985
1985
1992</td></tr>
<tr><td>2</td><td>S < 150 ppm m/m
Benzene < 2.5% v/v
No addition of metals, chlorine and organic contaminants</td><td>US Tier 1
Euro 2
Euro 3</td><td>1994
1996
2000</td></tr>
<tr><td>3</td><td>S < 30 ppm m/m
Benzene < 1% v/v
No addition of metals, chlorine and organic contaminants</td><td>US LEV
California LEV & ULEV
Euro 4 (except lean burn)</td><td>2003
2004-2010
2005</td></tr>
<tr><td>4</td><td rowspan="3">S < 10 ppm m/m
Benzene < 1% v/v
No addition of metals, chlorine and organic contaminants</td><td>Euro 4
US Tier 2
US Tier 3
Euro 5
Euro 6 / Euro 6b</td><td>2005
2004-2009
2017
2009
2014</td></tr>
<tr><td>5</td><td>Euro 6c
Euro 6dTEMP
Euro 6d</td><td>
2017
2020</td></tr>
<tr><td>6</td><td>Euro 6dTEMP
Euro 6d</td><td>2017
2020</td></tr>
</table>

3.2 Sulphur content in petrol

The natural sulphur content in petrol is estimated to be between 240 – 900ppm. These numbers are based on the sulphur content in petrol before legislative requirements. In Europe the sulphur content in the 1980s was around 240 ppm. In the USA the sulphur content in the 1950s was about 900 ppm. In diesel fuel, the sulphur quantities were higher. In the 1970's, the limit was initially set at 2000-3000 ppm (directive 75/716/EC). With the introduction of the three-way catalyst, there was a need to reduce sulphur content in petrol, because sulphur had a detrimental effect on the functioning and lifetime of the catalyst. Vehicles were to be tested with less than 400 ppm sulphur in the reference fuel (see Directive 91/441/EEC). At the time of the introduction of the three-way catalyst for petrol vehicles around 1990, the average sulphur content of market fuels was reduced to 240 ppm. Around the same time, petrol specifications were set in a European standard, EN 228, from 1993, which limited the sulphur to 1000 ppm maximum. This corresponds to the category 1 petrol requirements.

Soon after, in 1995, this limit was lowered to 500 ppm, to ensure proper operation of Category 2 vehicle technology. The EN 228 is an internal standard, not necessary fully implemented by all European countries.

The WWFC (2019) gives an overview of a number of studies worldwide, which show the influence of sulphur level NO_x, HC and CO emissions. It shows for example that when the Fuel Sulphur Content (FSC) is reduced from 200 – 600ppm down to 20-50 ppm, the NO_x is reduced on average by 41%. Similar reductions apply to CO and HC. Particularly important is the poisoning effect of the SO_x in the catalysts. Some examples given in the WWFC are shown in the figures below. Both figures show the increasingly adverse effect on NO_x emissions proportional to the FSC.

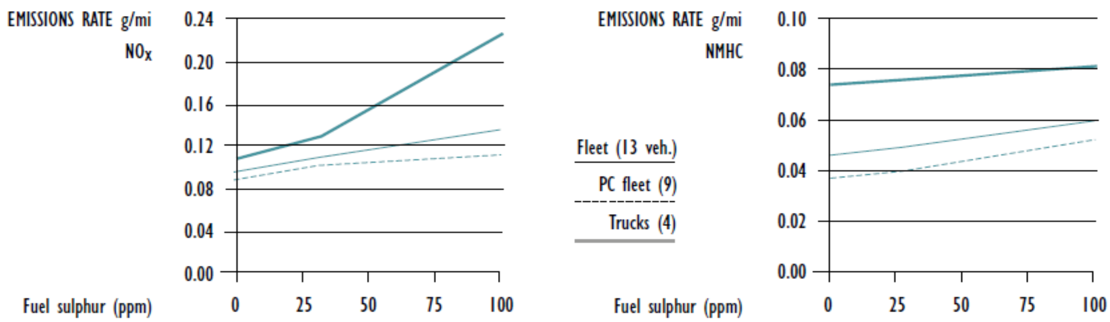

Figure 3: Effect of fuel sulphur level on NO_x and NMHC emissions, based on a fleet of 13 vehicles. (Source Auto Alliance AIAM low sulphur study, 2001).

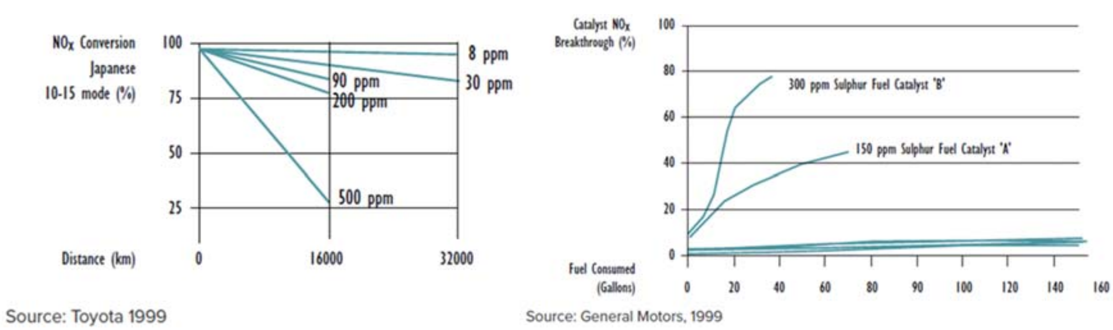

Figure 4: Examples of effect of fuel sulphur content on catalyst NO_x emissions due to catalyst aging (poisoning). From (WWFC, 2019).

It is generally known, that the FSC has a direct linear impact on the particulate matter (PM) emissions, because a small percentage of the sulphur is oxidised to sulphate (SO_4^{2-}). Sulphate and adsorbed water attach themselves to the PM and thus increase the total mass. The first fuel quality Directive EC/98/70, and the later extension with greenhouse gases, monitoring and the full fuel spectrum in Directive EC/2009/30 provide the general framework for minimal requirements of fuels in Europe.

Successive directives lowered the maximal sulphur content in petrol:

Directive 98/70/EC:
- Sulphur below 150 mg/kg from 1-1-2000 to 1-1-1-2003.
- Sulphur below 50 mg/kg from 1-1-2005.

Directive 2003/17/EC:
- Sulphur below 50 mg/km from 1-1-2005 to 1-1-2009.
- Sulphur below 10 mg/kg, from 1-1-2009.

The range in dates indicate the availability of the fuel with lower sulphur content till the end date of availability of fuels with higher sulphur content. The European limits in the directives were reflected in the changes in the EN 228 specifications, which followed the last dates of the directives.

From 1993 till 2009 the maximum sulphur content in petrol went from 1000 ppm to 10 ppm; a factor of hundred. This transition was deemed necessary to secure durability and emission limits for category 4 petrol vehicle. Vehicles which are less than 25 years old today are not intended to run on petrol with more than 500 ppm sulphur. Since 25 years is beyond the typical lifetime of vehicles, it is safe to say that petrol vehicles in general are not suitable for petrol with more than 500 ppm sulphur. Considering an average life time of 25 years, and equal vehicle production over the years, this would mean that more than two thirds of the vehicles world-wide is built after 2000. From 2000 a sulphur content of less than 150 ppm was required for category 2 vehicles until another drop was made around 2003-2004 towards 30 ppm of sulphur for category 3 vehicles. A large portion of petrol vehicles produced after 2000, are produced in Europe, America, Japan, and Korea, and do already fall in the category 4 standards, which require a sulphur content of less than 10 ppm.

Europe was not an exception; in the USA and Japan, which are major automotive markets, low sulphur petrol fuel was also introduced in the period from the late 1980s to 2009 with the worldwide 10 ppm limit on sulphur for petrol (EU, USA, Japan, Korea). Many countries implemented a 10 ppm sulphur limit (‘sulphur-free’) years ahead of the worldwide 2009 date.

3.3 Benzene as toxic component

Benzene (C_6H_6) is carcinogenic. Benzene in the fuel is one major source of benzene in the exhaust gas. Other polyaromatic compounds also produce benzene under partial combustion conditions. There is a limit to the volume fraction of polyaromatics and, separately, a limit to the volume fraction of benzene. Many polyaromatics are toxic as well, but benzene has a separate issue of being volatile and evaporating into the air during fuelling and from the fuel tank. There are no real technical reasons to reduce benzene in petrol fuel. The benzene limit in fuel is arranged for environmental reasons and to limit human exposure to benzene. In 1989 (85/210/EC) the limit was 5% and from 2000 onwards the limit has been 1%.

Benzene and polyaromatic hydrocarbons (PAH) have a relatively high carbon content and low heating value per kilogram. The variation of the fractions of these components in petrol lead to fuel-related variations in energy efficiency and CO_2 emissions of a few percent. Consequently, higher levels of these toxic components are also related to lower quality petrol fuels.

3.4 Metals like manganese

The automotive industry is against adding metal additives to petrol fuels. These should not be intentionally added according to the WWFC[1]. Metals are known to cause damage to the engine. With the ban of lead in petrol as an anti-knocking agent, introduced in 2000, MMT (Methylcyclopentadienyl Manganese Tricarbonyl) containing manganese, became popular replacement as fuel additive and anti-knocking agent. MMT was subsequently linked to reduced performance of catalysts, and oxidized deposits on spark plugs and sensors, and malfunctions (see also Figure 5).

With surmounting evidence, from 2004 onwards, a limit on MMT in the form of a limit on manganese, was introduced. In Directive 2009/30/EC manganese was limited to 6 mg/litre initially, with a 2014 limit of 2 mg/litre. In order to avoid such problems in the future, and to address the concerns of the automotive industry, a general compulsory labelling of all metallic additives in fuel was introduced. Hence, although there was no limit on manganese before 2009, it can be concluded that manganese is detrimental to both the performance of the engine as well as the catalyst. In addition to manganese, the automotive manufacturers list also mentions copper, iron, sodium, lead, phosphor, silicon, zinc, and chlorine as unwanted components in fuel additives. They can cause damage to the engine, but also deteriorate the functioning of the catalyst.

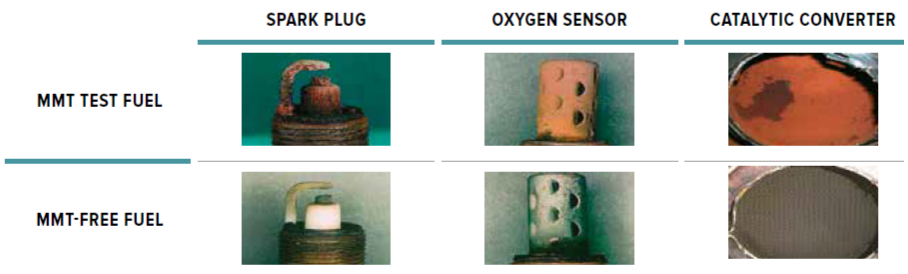

Figure 5: Impact of manganese based additive (MMT) on Tier 1/LEV emission control components. (Source Alliance, AIAM and CVMA, 2002)

3.5 Vapour pressure

Volatile components and poorly dissolving components in petrol fuels will both raise the vapour pressure and generate fumes. For the presence of ethanol in petrol some allowances are made for the vapour pressure in Directive 2011/63/EU, but generally vapour pressure must be kept in bounds, initially at 80 kPa in 1993 reduced to 60 kPa in 2000 (at 37.8^{o} C) for summer fuels, sold between 1st of May and 30th of September. High vapour pressure will result in higher evaporation of volatile organic compounds like benzene but also, e.g., butane. The volatile organic compounds are partly toxic, but also a contributor to ozone formation and smog.

Vehicles from petrol category 2 onwards (Directive 98/69/EC), will have a carbon canister in the fuelling system that collects volatile organic components during vehicle standstill and overnight parking. The canister is purged during vehicle operation. With Regulation EC/715/2007 the level was set at 2 g/test, where the test

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[1] Or for category 1 petrol: below 1 ppm, or the detection limit.

is a diurnal soak, i.e., leaving the vehicle a full day after refuelling. Details of the test procedure, i.e., Type IV test, are part of UNECE Regulation 83, adopted by the European Union. As early as in 1970, with Council Directive 70/220/EEC in place, evaporative emissions already had the attention, although limited to crankcase emissions at the time. Smog, carbon monoxide and acidification were the major concerns at that time. These problems were caused by high SO_x (sulphur oxides), NO_x (Nitrogen oxides), CO (Carbon monoxide), and HC (hydrocarbons) emissions of transport and industry.

Generally, countries with a hotter climate have more concerns with evaporative emissions, and a stricter control on vapour pressure. In the 1970s Japan already had an evaporation limit set at 5 g/day, and the USA in 1971 had a standard of 6 g/test, lowered to 2 g/test in 1972 and 4 g/day.
The recommended petrol vapour pressure in 1972 was 10 psi (69 kPa). In the 1970s evaporative losses, without such canister systems, were as high as 50 grams per test.

For Euro 1 and 2 vehicles, compulsory for all registrations from 1993 and 1996 respectively, the canister technology is strongly linked with the petrol fuel quality and the evaporation test prescription. The canister size is dimensioned to the vapour pressure and the period of parking. Hotter weather, longer parking, older canisters, non-functional and removed canisters and higher vapour pressures all lead to a manifold increase in evaporative emissions.

Actual evaporative emissions depend on many circumstances. But the emission reduction technology introduced from the 1970s, will function only if vapour pressure is below 50 to 80 kPa. Fuels with higher vapour pressures are therefore expected to result in substantial increases in evaporation emissions, as the system will fail.

3.6 Conclusions

It can be concluded that fuel quality and vehicle emissions reduction technology and performance go hand in hand. The gradual improvement in fuel quality from 1985 to 2020 was an enabler for the introduction of more stringent emission limits. The six WWFC petrol fuel quality categories have been described in relation to the vehicle technology.

- All six petrol categories have a very low metals, chlorine and organic contaminates content in common (no intentional addition allowed or < 1ppm). Significant metal content is basically not allowed for vehicles with catalysts (starting as early as 1985 US Tier 0, and in 1992 with Euro 1).
- In category 1 - 4, the sulphur content was gradually decreased from 1000 ppm to 10 ppm. 10 ppm sulphur content is recommended for vehicles manufactured since 2005.
- All vehicles from Euro 1 / US Tier 0 thru Euro 6 / US Tier 3 can perfectly use category 4 petrol fuel (backward compatible; new fuel can be used with older vehicle technologies).
- Category 5 and 6 only deviates from category 4 in terms of oxygen content, allowing up to 10% ethanol (E10). For E10 there can be restrictions for Euro 4 and older vehicles, mainly due to the corrosive nature and problems with deterioration of gaskets.

4 Impact of petrol vehicles on environment and health

Sections 4.1 and 4.2 will summarize the impact of petrol fuel quality on technological, environmental and health aspects.

The considered authoritative organisations and sources in this section are:

- World Wide Fuel Charter;
- World Health Organisation, including the IARC;
- USA Environmental Protection Agency;
- European Environmental Agency;
- UNECE Convention on Long-range Transboundary Air Pollution WGE.

Both the pollutant formation and the health and environmental effects are often disputed. Great care must be taken to consult other sources and research results, as many contradicting conclusions can be found. The organisations above ensure an internal review of existing and published research, and strive for transparency.

In Section 4.3 the impact on the emissions and emission reduction technology degradation is indicated when a lower quality fuel is used in newer vehicles.

4.1 Petrol vehicle emissions

4.1.1 Direct emissions of sulphur oxides and benzene

Sulphur in the petrol will lead to sulphur oxides in the exhaust gas. Benzene in fuel is the major source of benzene in the exhaust gas. Moreover, benzene is highly volatile and may escape from the tank or the crankcase.

4.1.2 Catalyst poisoning by sulphur or metals

The sulphur and many metals will poison the three-way catalysts. The reduced functionality of the three-way catalyst will lead to higher pollutant emissions of NO_x, hydrocarbons and carbon monoxide. This poisoning will partly be reversed if sulphur-free and metal-free petrol is used. Nevertheless, it is expected that the original functionality of the catalyst is not fully restored.

4.1.3 Volatile organics tank emissions with high vapour pressures

High vapour pressure in the fuel tank will lead to high emissions of volatile organic compounds during vehicle standstill. Once the canister is full, there is no further buffer to limit evaporative emissions.

4.1.4 Formation of particulate matter

Sulphur, organic compounds, and nitrogen oxides are all factors in the formation of particulate matter. In part this formation takes places before the exhaust gas leaves the tailpipe, but they also partly contribute to the formation of particles in the ambient air, either via the direct route such as Sulphates (as part of particulate matter) or as agents into the formation of particles.

4.2 Impact on the environment and the health

4.2.1 Acidification (acid rain)
Sulphur dioxide and nitrogen oxide will produce acid with the water in the atmosphere. The acid will precipitate in rain. Acidity sensitive plants and animals, corrosive and calcium-based building materials are all affected by the acid rain.

4.2.2 Eutrophication (nitrogen deposition)

Nitrogen deposition from Nitrogen oxides (NO_x) and Ammoniac (NH_3) in the air will increase the plant nutrients in the soil, and the change in vegetation and, eventually, insects and animals.

4.2.3 Summer smog (photochemical)
Smog is a general term of states of high and visible air pollution. Photochemical reactions of volatile organic compounds and nitrogen oxides with the air produce ozone and other radical elements that are reactive and cause irritation of air ways.

4.2.4 Winter smog (weather)
In the winter stable conditions and low temperatures will not disperse air pollutants and will facilitate the formation of aerosols, i.e., small particles. The increase in household heating aggravates the problem of winter smog.

4.2.5 Cancer
Diesel exhaust gas is directly linked to cancer (IARC). The underlying actor is assumed to be particulate matter, consisting of small particles around 100 nm size. Such particles are also produced in petrol cars, albeit to a lesser extent, but high sulphur content is a major factor in the amount of particles produced.

Other sources of cancer are benzene and other aromatics. The combination of volatile components in particle emissions have been suggested to be the worst of both worlds. However, metals in particles will also aggravate health effects, but the problem is less common now with fuel regulation, and the effects are not studied extensively.

4.2.6 Chronic obstructive pulmonary disease (COPD), pneumonia, and acute lower respiratory infections in children
The presence of air pollutants will increase the rate of hospitalization associated with the respiratory system. Some of these will result in premature death, but also the quality of life is lower under poor air quality conditions.

4.2.7 Foetal growth retardation, ischaemic heart disease, and stroke
Smoking is bad for the health. It causes cancer and many other diseases.
The effects for smoking can be translated partially to air pollution as well. It has also been shown that there is no lower threshold for negative effects of exposure (WHO). In particular, systemic effects, such as affecting the vascular system, have a correlation with air pollution and lower quality of life.

4.3 Increase in emissions due to low quality fuel

Considering older yet common petrol vehicles, Euro-3 (registrations: 2000-2005) and Euro-4 (registrations: 2005-2010), the emission levels are low compared to older technologies and diesel vehicles. Some deterioration may have taken place, leading to increases in the emissions. However, sulphur poisoning has an enormous effect on the emissions. In (WWFC, 2019) a number of examples are shown demonstrating this deterioration, including the speed of deterioration. Some examples of the latter are shown in Figure 5 (Section 3.2).

This shows a:

- loss of catalyst NO_x conversion from over 95% to 26% in 16000 km with 500 ppm sulphur fuel.
- loss of catalyst NO_x conversion from about 95% to 60% with NO_x adsorption catalysts[2] after 50 gallons of fuel consumption with 150 ppm sulphur. Further reduction to 20% after about 40 gallons with 300 ppm sulphur.

It seems that adsorption catalysts deteriorate faster than three-way catalysts: severe deterioration in about 1000 km, versus about 15000 km. There are no signs of levelling off of these deteriorations.

It can be assumed that after a prolonged poisoning period, the emissions of a Euro-3 or Euro-4 vehicle will deteriorate to emission levels of a Euro 0 vehicle (the generation without three-way catalysts). The emission factors for Euro-0, Euro-3 and Euro-4 vehicles are shown in Table 4-1 below. As shown in the right part of the table, the gaseous emission components are expected to increase tenfold or more.

Table 4-1: Dutch emission factors for Euro-3, and Euro-4 as a basis of the emission levels, and the levels for 1992 (Euro-0) vehicles as the end-point for deterioration effects.

		Emission factors				**Maximal emission increases to Euro-0**			
	g/km	NO_x	THC	PM*	CO	NO_x	THC	PM*	CO
Euro-3	Urban	0.145	0.437	0.002	6.647	1119%	563%	1199%	104%
	Rural	0.058	0.215	0.001	3.291	3010%	381%	1434%	56%
	Motorway	0.032	0.022	0.002	1.885	13623%	7033%	846%	256%
Euro-4	Urban	0.053	0.420	0.002	5.615	3240%	591%	1199%	142%
	Rural	0.024	0.212	0.001	2.873	7454%	389%	1434%	79%
	Motorway	0.014	0.019	0.002	1.652	31331%	8059%	846%	306%
Euro-0	Urban	1.767	2.900	0.030	13.592				
	Rural	1.799	1.036	0.018	5.137				
	Motorway	4.339	1.540	0.024	6.704				

* The PM emission factors for Euro-0 were derived based on measurements with sulphur levels that were common for that period (pre-WWFC petrol category 1). The PM levels are an indication as the exact PM value with other fuel specifications are unsure. Sulphur is known as contributor to the formation of PM.

[2] A NOx adsorption catalyst is a NOx reduction catalyst suitable for lean-burn petrol engines and for diesel engines

If high-sulphur petrol is replaced with a lower sulphur level petrol, some functionality will return. However, the restoration of functionality will depend both on the sulphur levels and on time. The higher the retained sulphur levels, the harder it is to restore the functionality of the three-way catalyst of Euro-3 and Euro-4 vehicles.

For benzene, SO_x and manganese, the levels in the fuel translated directly into the levels in exhaust gas. For benzene, the same proportionality is true for evaporative and fuelling emissions. Since benzene is incorporated in the vapour pressure, there is no substantial additional effect expected from benzene content in evaporation emissions with benzene levels of 2%-5%.

The use of manganese in petrol have also shown to lead to a moderate increase in emissions: an increase of gaseous emission between 15% and 30% after 100,000 miles for example (WWFC, 2009). In worse cases, it leads to complete failures such as blockage or holes in the catalyst, which may lead to a tenfold increase or more.

4.4 Conclusions

It can be concluded that petrol impurities like sulphur and metals lead to higher emission of a range of species including SO_x, particulates, NO_x, CO and hydrocarbons. These in turn lead to secondary particle formation, acidification, eutrophication and smog. They also lead to adverse health effects like cancer, (COPD), pneumonia, acute lower respiratory infections, Foetal growth retardation and ischaemic heart disease. The use of high sulphur fuel, for example with 500 ppm, already leads to a severe increase of emissions after some 15000 km, or even much faster for NO_x adsorption catalysts. It is likely that after a prolonged poisoning period using high sulphur fuel, the NO_x, CO and HC emissions of Euro-3 and Euro-4 vehicles increase tenfold or more to the level of a vehicle without three-way catalyst.

5 Conclusions

Historically, the petrol fuel quality has been improved step by step over the past five decades in order to reduce the polluting vehicle emissions and also as precondition for vehicles to comply with the increasingly more stringent emission legislation (e.g. Euro 1 through Euro 6 in Europe). In general the current petrol fuel quality in Europe and other main regions, is fully compatible to older vehicles. One exception is the compatibility with ethanol blends containing 5 and 10 volume percent ethanol (E5 and E10). Therefore, E5 or ethanol free petrol should remain available for a number of vehicle types built before 2010.

The evaluation has shown that a good fuel quality is of key importance to protect the health of people and the environment, regardless of the age of the vehicle, the technology used or even the maintenance of the vehicle. The most relevant fuel specifications include Fuel Sulphur Content (FSC), benzene- and metals content (particularly manganese) and the vapor pressure. Fuels customary in Europe since 2009 contain sulphur level <10ppm, benzene < 1% and no addition of metals (WWFC petrol category 4 requirements). An increase in sulphur level up to 30 or 50 ppm could be acceptable for common, yet older petrol cars (WWFC petrol category 3 requirements).

The adverse health effect of high benzene content and high vapor pressure are even higher for older technology or poorly maintained vehicles, since the aftertreatment is less effective or lacking and there is no carbon canister on the fuel tank to mitigate the adverse health effects and environmental impact. So it can be concluded that limitation of these components in petrol fuel is even more important for older vehicles than for younger vehicles.

On top of the direct effect of sulphur and metal components in petrol on health and the environment, these components will seriously compromise the efficiency of the emission control systems of petrol engines, leading to a steep increase of other tailpipe emissions like NO_x, CO, PM and unburned hydrocarbons. For example, 500 ppm sulphur can already lead to a severe increase in emission after 15000 km. It is likely that, after a prolonged poisoning period using high sulphur fuel, the NO_x, CO and HC emissions of Euro-3 and Euro-4 vehicles increase tenfold or more to the level of a vehicle without three-way catalyst.

6 Literature

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7 Signature

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