Health effects of addition and combustion of fuel additives

Quick scan and deepening of a selective additive set

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Abstract

Health effects of fuel additives

The utilization and combustion of fuel additives are not expected to result in severe health effects. This is shown by a quick-scan exploring the potential health effects as described in this letter report. The outcomes of this research could be used by policymakers to frame regulations for additive use.

Fuel additives are substances added in small amounts to gasoline or diesel engine fuel. Additives are used for several reasons e.g. certain additives can result in reduced soot emission which is of interest for policymakers. Though, the decision whether or not to regulate those additives also depends on the risk for adverse health effects associated with additive use.

Conclusions quick-scan:
- Combustion of MMT results in the emission of fine manganese particulates. Chronic exposure to manganese results in the development of neuropsychological change. A potential public health risk exists if MMT is widely introduced.
- Ether fuel oxygenates like MTBE, ETBE, and GTBE have been linked to neurological symptoms. These ethers are all relatively non-toxic but MTBE and MTBE could be persistent groundwater contaminants. This adverse effect is not expected to occur with large-scale implementation of GTBE.
- Platinum group elements can enter the food chain and form harmful PGE-chloride complexes within the body.
- The toxicity of cerium oxide as a fuel additive appears to be small.

Overall, limited data complicates a good risk assessment. However, most additive concentrations are small and even prolonged exposure will not be expected to induce serious health effects.

Key words:
fuel additive, health, risk hazard, exposure, combustion products

Rapport in het kort

Gezondheidseffecten van brandstof additieven

Naar verwachting zal het toevoegen en verbranden van additieven aan brandstof, zoals benzine en diesel, niet leiden tot ernstige gezondheidseffecten. Dit blijkt uit onderzoek naar de risico´s voor de volksgezondheid verbonden aan het gebruik van brandstof additieven. De resultaten van zulk onderzoek geven handvatten voor regelgeving over het toepassen van additieven.

Brandstof additieven zijn stoffen die voor verschillende toepassingen in zeer kleine hoeveelheden aan motorbrandstof worden toegevoegd. Zo kunnen sommige additieven de uitstoot van roet reduceren wat van belang kan zijn voor het te voeren beleid.

Conclusies uit het onderzoek zijn:
- Verbranding van MMT leidt tot de uitstoot van kleine mangaan deeltjes welke bij langdurige blootstelling kunnen leiden tot neuropsychologische schade. Er zijn pas mogelijke risico´s indien MMT op grote schaal wordt toegepast.
- Zuurstofverhogende ethers zoals MTBE, ETBE en GTBE worden in verband gebracht met neurologische symptomen. Deze ethers zijn betrekkelijk onschadelijk al zijn MTBE en ETBE moeilijk afbreekbaar bij vervuiling van het grondwater. Dit nadelige effect wordt niet verwacht bij grootschalige toepassing van GTBE.
- Platina groep elementen worden toegepast in katalysatoren en er bestaat een kans dat deze stoffen in de voedselketen terecht komen. In het lichaam kunnen vervolgens schadelijke complexen met chloride gevormd worden.
- Cerium oxide lijkt als brandstof additief nauwelijks schadelijk.

Algemeen geldt dat er weinig bekend is over gezondheidseffecten van brandstof additieven. Het inschatten van risico´s voor de volksgezondheid wordt hierdoor bemoeilijkt. Naar verwachting zal zelfs langdurige blootstelling niet leiden tot ernstige gezondheidseffecten vanwege de lage additief concentraties.

Trefwoorden:
brandstof additief, gezondheid, risico, blootstelling, verbrandingsproducten

Contents

Preface

At the request of the Director-General of the Environment (DGM) of the Ministry of Housing, Spatial planning and the Environment (VROM), the National Institute for Public Health and the Environment (RIVM) has examined the health aspects of addition and burning of additives to gasoline and diesel motor vehicle fuel. These additives are for example used to replace banned substances or to improve the performance of the engine. Some of these might have a negative impact on human health. Information about these latter aspects will be useful to policy makers in the decision process of regulating (or not) these additives.

This letter report presents the results of a quick-scan in which various types of additives, their use and the potential health effects were explored. Four additives (MMT, ETBE, GTBE, and platinum) were selected to investigate the possible health effects in more detail.

1 Introduction Fuel additives

A fuel additive is a substance added in small quantities to provide improved engine performance, a desired effect or to adjust for deficiencies. By definition a substance is an "additive" in case the total amount is less than one percent (<10 g per kg) and for higher concentrations the term "blending component" is used. Usually a mix of several additives, called an "additive package", is used, rather than a single additive.

The benefits of additives as well as the reason for adding them can be diverse. The automotive industry has a major interest in additives to develop the safe, fuel efficient and environmentally acceptable vehicles needed. Their main priority is to increase the performance of the engine, decrease fuel consumption and improve emission quality. The use of state of the art engines results in improved fuel quality and the oil industry provide the quality and quantity of fuels required. The attention of the government is focussed on lowering transport emissions. This might be promoted by the use of fuel supplemented by additives. Increased environmental pollution through traffic and less back up of unrefined oil has made governments all over the world alert for sources to reduce fuel consumption and emissions. Environmental benefits will be appreciated by society as a whole. In addition, the consumer will benefit from the use of fuel additives since it has been shown that vehicles driving on fuel with additives are more reliable and fuel consumption has been reduced with an average of four percentages.

The Clean Air Act provides U.S. EPA with the authority to regulate fuels and fuel additives in order to reduce the risk to public health from exposure to their emissions. The regulations require that each manufacturer or importer of gasoline, diesel fuel, or a fuel additive, have its product registered by EPA prior to its introduction into commerce. Registration involves providing a chemical description of the product and certain technical, marketing and health-effects information. This allows EPA to identify the likely combustion and evaporative emissions. In certain cases, health-effect testing is required for a product to maintain its registration or before a new product can be registered. EPA uses this information to identify products whose emissions may pose an unreasonable risk to public health, warranting further investigation and/or regulation. According to the people responsible for registration and health effects testing in practise only the chemical data will be supplied and registered for most additives and no Material Safety Data (MSD) sheet is available. There are no regulations concerning fuel to contain additives, however, there are some regulations for fuel. On the other hand, California has some unique regulations for diesel. The aromatics content of diesel fuel is restricted to reduce emissions and this goal is reached either by the use of low aromatics diesel (LAD) with less than 10% aromatics or with an alternative low aromatics diesel (ALAD). Reduction of emission can be reached by addition of cetane improvers as used in many ALADs. Sometimes lubricity additives can be utilized in LADs.

Fuel additives can be easily subdivided into two main groups – gasoline and diesel fuel additives. Another classification in "distribution" or "vehicle" system additives can be made based on the time an additive is useful and active. Distribution system additives will usually demonstrate their benefits in the distribution system while vehicle system additives, on the other hand, only begin to provide benefits when the fuel enters the engine inlet system or combustion chamber. A third classification can be on the basis of where the additive will be put into the fuel. An example of this last classification is aftermarket fuel additives which may be added to fuel by the end-users (Additives Technical Committee (ATC) Fuel additives and the environment, 2004).

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2 Gasoline additives

The following paragraphs will give a brief description of the primary gasoline additives (ATC Fuel additives and the environment, 2004) of which an overview is given in Table 1.

Table 1 Overview of gasoline fuel additives

Additive group	Compounds
Antistatic	Chromium materials, polymeric sulphur and nitrogen compounds, quaternary ammonium materials
Metal deactivators	N,N'-disalicylidene-1,2-propanediamine
Dyes	Azo compounds, antraquinone
Demusifiers	Mixtures of non-ionic surfactants
Corrosion inhibitors	Carboxylic acids, amines, amine salts of carboxylic acids
Antioxidants	Hindered phenols, aromatic diamines, mixtures of aromatic diamines and alkyl phenols
Anti-valve seat recession	Potassium, phosphores, manganese
Deposit control	Amides, amines, amine carboxylates, polybutene succinimides, polyether amines, polyolefin amines, combinations
Oxygenates	Alcohols and aliphatic ethers

2.1 Anti-static

Static electricity can build up during pumping operations both within refineries and at filling stations, and static discharges present an obvious fire hazard. Anti-static additives can improve electrical conductivity and reduce the potential for static build-up. Examples of anti-static additives are fuel-soluble chromium materials, polymeric sulphur and nitrogen compounds, and ammonium materials. Treat levels are relatively low only 2-20 mg/kg.

2.2 Metal deactivators

Certain metals will form fuel-soluble salts that promote oxidation in the fuel and result in gum formation and deposit build-up in the fuel system. Formation of these salts can be prevented by metal deactivators. The most commonly used is N,N'-disalicylidene-1,2-propanediamine and its basic mechanism is to chelate copper. Copper can quickly catalyse the oxidation of unsaturated hydrocarbons. Again the treat levels are very small 4-10 mg/kg.

2.3 Dyes

Dyes have been added to distinguish between different commercial types of gasoline e.g. leaded/unleaded or various qualities. Coloration of gasoline is achieved by azo compounds and/or anthraquinone. Treat levels are 2-20 mg/kg and annual tonnages are estimated at 350.

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2.4 Demulsifiers

Demulsifiers are used for various purposes. They do have, however, a specific action in distribution systems where water vapour can be formed and therefore formation of an emulsion. Complex mixtures of non-ionic surfactants are used as surface active materials which modify the surface tension. Usage of 3-12 mg/kg is connected to "deposit control additives" which can stabilise the emulsion.

2.5 Corrosion inhibitors

Water contained within gasoline, or infiltrating from other sources, combines with air to attack metallic surfaces resulting in rust. Corrosion inhibitors like carboxylic acids, amines and/or amine salts of carboxylic acids can form a protective film on the metallic surface. It is estimated that around 1250 tonnes are used per annum in a concentration of 5 mg/kg.

2.6 Antioxidants

Unstable species such as olefins and dienes can polymerise to form gums. Oxidation and polymerisation of olefins takes place through a free radical mechanism. Reaction with antioxidants will disturb polymerisation and achieves both fuel storage stability and cleanliness of engine fuel systems. Normally gum formation can lead to malfunctioning and breakdown. Antioxidants comprises of hindered phenols, aromatic diamines, or mixtures of aromatic diamines and alkyl phenols. Treat levels are 8-40 mg/kg and although antioxidants are the biggest single gasoline distribution system additive the usage in Europe is still low at 2200 tonnes per annum.

2.7 Anti-valve seat recession additives

Significant wear occurs in the exhaust valve seat with unleaded gasoline. The lead additive, in addition to its primary purpose of increasing octane quality, also provides a critical wear-reducing function by depositing a thin protective layer of lead salts on valve seat surfaces. Without this protection poor valve sealing and loss of compression could occur and in turn results in loss of power, increased fuel consumption, rough engine operation, poor starting and increase in emissions, and ultimately severe engine damage. These problems can be overcome by the use of additive chemistries based on potassium, phosphorus or manganese that will prevent direct metal-to-metal contact that would otherwise cause high wear. The use of these additives at levels less than 50 mg/kg will especially keep older vehicles running.

2.8 Deposit control additives

Fuel additives are needed to reduce deposits, left over from the combustion of gasoline that builds up on engine valves. The deposits eventually affect the performance of the valves, hindering engine efficiency, driveability, cold-start efficiency, knock characteristics and emissions. The main function of the fuel-additive is the prevention of deposition on the valve by scavenging the deposit forming pre-cursors of the fuel (Sundaram et al. 2001). Deposit control additives are generally long hydrocarbon

chains attached to a polar head group. Deposit precursors are attracted to the deposit control molecule, and become bound into the dispersant miscelle.

There are several areas where deposit control additives can be effective of which the main areas are:
- ❑ Fuel injector tip – operates at about 100 degrees and deposits form especially through oxidation and polymerisation of the larger unsaturated hydrocarbons. The additives that prevent and unclog these tips are usually polybutene succinimides or polyether amines.
- ❑ Intake valves – operates at about 300 degrees, and if the valve is kept wet, deposits tend not to form, thus intermittent injectors tend to promote deposits. Additives to prevent these deposits contain a detergent and/or dispersant with carrier oil.
- ❑ Combustion chamber deposits – these deposits are the result of condensation of partially-thermally oxidized fuel, oil and additive components on the relatively cool piston and cylinder head surfaces, which then further react to form solid deposits. They are responsible for significant increases in emissions. In particular polyetheramines have the ability to reduce combustion chamber deposits but only at very high doses.

2.9   *Oxygenates*

Oxygenates have been used to increase octane number in fuel when the use of lead as an octane enhancer in petrol was banned or to meet clean fuel oxygen requirements (U.S. EPA report 1997). In the early 1990s new state and federal clean air regulations came into force in the U.S. (Shih et al., 2004), introduced in an effort to reduce vehicle carbon monoxide and ozone-forming hydrocarbon emissions. The 1990 Clean Air Act Amendments required the use of oxygenated gasoline in several areas of the country that failed to attain the National Ambient Air Quality Standard (NAAQS) for CO. One of the requirements of these regulations was that petrol had to contain at least 2%wt of oxygen to improve combustion (Noureddini, 2002). Oxygenates commonly used include various alcohols and aliphatic ethers (Ahmed, 2001).

3   Diesel additives

Diesel engines are the most efficient type of internal combustion engines. World wide, it is the engine of choice for heavy duty vehicles. In Europe diesel powered passenger vehicles account for over 50% of the new passenger vehicle market dependent on the country of choice (Kozak and Merkisz, 2007). However up until recently, diesel engines have not had to meet the stringent emission control criteria which apply to gasoline engines. Diesel engines have always been problematic with regards to exhaust emissions; diesel engine exhaust has been shown to have adverse health effects (US Environmental Protection Agency, 1993). Now a reduction in greenhouse gases and noxious exhaust emissions has become a matter of importance, European legislation has been introduced to implement increasingly stringent emission target criteria for NOx, particulate matter (PM), carbon monoxide (CO) and hydrocarbon emissions, this has been brought into effect over several years - EURO-3 in 2000, EURO-4 in 2005, and EURO-5 legislation comes into effect in 2008 (Frijters and Baert, 2006). In order to meet these criteria a multi level emission reduction approach is required.

Diesel fuel is a highly complex fuel. It changes chemical structure during the time after it leaves the refinery to the time it is pumped into holding tanks and into the fuel station to the time it gets pumped into the vehicle. Fuel molecules oxidize and change structure and the energy per unit volume of the fuel can change during this process which can negatively affect the performance of the engine. By using the proper type and ratio of fuel additives the effects of fuel degradation can be effectively combated and increase the cetane value of the fuel and allows the engine to extract more power, plus numerous other benefits. Higher cetane numbers produce improved driveability, reduced emissions and black smoke.

The following paragraphs will give a brief description of the primary diesel additives (ATC Fuel additives and the environment, 2004) of which an overview is given in Table 2.

Table 2 Overview of diesel fuel additives

Additive group	Compounds
Wax crystal modifiers/MDFI	Wax anti-setting additives, ethylene vinyl acetate copolymers
Corrosion inhibitors	Carboxylic acids, amines, amine salts of carboxylic acids
Demulsifiers	Alkoxylated polyglycols, aryl sulfonates
Antifoams	Polysilicone-based compounds
Diesel fuel stabilizers	Antioxidants (hindered phenol, phenylenediamines), dispersants (ahless succinimides, polymeric metacrylates), metal deactivators (N, N'-disalicylidene-1,2-propanediamine)
Colour stabilizers	Optically active compounds, (clay-filtering)
Detergents	Succinimides, ashless polymeric products
Cetane improvers	Alkyl nitrates, 2 ethyl hexyl nitrate
Lubricity improvers	Ashless longchain polar compounds
Multifunctional packages	Combination of the above except wax crystal modifiers plus flow improvers, reodorants, solvent for package stability
Fuel-born catalysts	Cerium, iron compounds, platina
Catalysts	Platinum group elements

3.1 Wax crystal modifiers

All crude oils contain normal paraffin in varying amounts. In some respects these paraffin's are very desirable in diesel fuel as they have a high cetane number and burn with low emissions. However, paraffin's are the least soluble components in diesel fuel and when the fuel is cooled, wax crystals form in the fuel. Uncontrolled wax crystallisation in diesel fuel can cause vehicle operability problems. Middle distillate flow improvers (MDFI) and wax anti-settling additives (WASA) can modify wax crystal size and shape so that they pass more easily through filters and lines in vehicles. MDFIs are added to the fuel at 50-1000 mg/kg while the treat rate of WASA is 100-200 mg/kg.

3.2 Corrosion inhibitors

All fuel systems are prone to corrosion with time, particularly when entrained or dissolved water is present. Corrosion inhibitors are compounds that attach to metal surfaces and form a barrier that prevents attack by corrosive agents. Typical products are carboxylic acids, amines and amine salts of carboxylic acids. Different treat levels are mentioned like 5-15 mg/kg but also 450 mg/kg.

3.3 Demulsifiers

Normally, hydrocarbons and water separate rapidly and cleanly. But if the fuel contains polar compounds that behave like surfactants and if free water is present, the fuel and water can form an emulsion. Demulsifiers are surfactants that break up emulsions and allow the fuel and water phases to separate. They are generally used in combination with diesel fuel detergents, which in wet distribution systems can cause the formation of undesirable fuel-water emulsions and hazes. Demulsifiers effectively counter these side-effects and are used at treat rates in the range of 10-20% of that of the detergent and concentrations of 5-30 mg/kg are mentioned. Typical chemistries include alkoxylated polyglycols and aryl sulfonates.

3.4 Antifoams

All diesel fuels have a natural tendency to produce foam when pumped into vehicle tanks. The foaming can interfere with filling the tank completely, or result in a spill. Most antifoam additives are organosilicone compounds and are typically used at concentrations less than 10 mg/kg as part of a multi-functional package.

3.5 Diesel fuel stabilizers

Fuel instability results in the formation of gums that can lead to injector deposits or particulates that can plug fuel filters or the fuel injection system. There are several modes of fuel instability and different additives are used to prevent this such as:

Stabilizers – interfere with acid-base reactions by reacting with weakly acidic compounds to form products that remain dissolved in the fuel, but do not react further. Stabilizers are strongly basic amines and are used in the concentration range of 50-200 mg/kg.

Antioxidants – interrupt the reactions caused by oxidation that forms sediment. Hindered phenols and certain amines, such as phenylenediamine, are the most commonly used antioxidants. They are used in the concentration range of 10-80 mg/kg.

Dispersants – the dispersant does not prevent the fuel instability reactions, but it acts to suspend any sediment particles that do form and prevent them from agglomerating and becoming a problem. Dispersants could be ashless succinimides or polymeric methacrylates and are used in concentrations of 15-100 mg/kg.

Metal deactivators – inhibit any trace amounts of dissolved metal, particularly copper, which otherwise could catalyse the instability reactions. Metal deactivators include N,N'-disalicylidene-1,2 propanediamine and are used in the concentration range of 1-15 mg/kg.

3.6 Colour stabilizers

In Japan and Taiwan it is demanded to have water-white diesel fuel and therefore colour stabilizers are added. Since tiny amounts of optically active compounds could already strongly influence the colour special techniques, like clay-filtering, are needed.

3.7 Detergents

All diesel engines use some form of fuel injection. Most small diesel engines used to use a system called indirect injection while larger engines just as most modern passenger cars today use direct injection. Clean fuel injectors are critical for efficient engine operation and therefore detergents are added to the fuel. Fuel detergents help to prevent the formation of deposits on the injector nozzle partly by providing a film on the metal surface and partly by forming a protective coating around the developing deposit precursors. Diesel fuel detergents are predominantly succinimide and other ashless polymeric products and are added in concentrations of 10-200 mg/kg.

3.8 Cetane improvers

The diesel engine is a compression-ignition engine and involves a ignition delay which is the time between injection of the fuel into the cylinder and the onset of combustion. If the delay is too long, combustion is more violent (and hence noisier) and less efficient (causing high levels of exhaust emissions and poor fuel economy). In Europe cetane quality has traditionally been good. The cetane number is defined as the ease with which a fuel ignites and cetane improvers (alkyl nitrates) are added in a concentration of 0.5-4 mg/kg to increase the ignition speed. Cetane improvers can reduce combustion noise and smoke.

3.9 Lubricity improvers

Diesel fuel injector pumps often rely on the fuel itself to lubricate their moving parts. However, introducing low sulphur diesel fuels to reduce exhaust emissions has changed this since sulphur, aromatics and other polar compounds in the fuel act as natural lubricants. Lubricity additives give a mono-molecular coating on metal surfaces and protect against scuffing wear. Treatment levels are in the range 10-1000 mg/kg.

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3.10   Multifunctional diesel additive packages

Multifunctional additive packages may contain any or all of the following: detergents, cetane improvers, fuel stabilizers, flow improvers, antifoam, reodorants, demulsifiers, corrosion inhibitors, lubricity additives, and solvents for package stability. Typical treat rates are in the range of 100-1500 mg/kg.

3.11   Fuel-borne catalysts

Current and future legislation on emissions of particulate matter has resulted in increased stimulation of particulate filters. Regeneration of these filters is essential to prevent excessive soot build up on the filter and the associated problems on filter durability. Fuel-borne catalysts, typically certain cerium and iron compounds, are an effective additive route to achieving this. A catalyst is a compound or element that facilitates a chemical reaction without its own structure being changed in the reaction process.

3.12   Catalysts

Platinum group elements (PGEs) are a group of metals highly resistant to oxidation found naturally in very low abundance in the earth's crust (Wedepohl, 1995). The chemical properties of these rare metals, namely platinum (Pt), palladium (Pd) and rhodium (Rh), make them superb catalysts. In a practical application, catalysts were developed for automotive vehicles as a means of reducing exhaust emissions of gaseous pollutants such as carbon monoxide (CO), nitrogen oxides (NOx) and hydrocarbons (HCs) by converting them into less toxic substances including CO2, water and nitrogen gas.

An automobile catalytic converter is a device fitted within a vehicle exhaust system; it generally consists of a honeycomb ceramic matrix coated with a thin layer of catalyst metal. When hot engine exhaust gases passes over the catalyst surface the gases undergo either oxidation or reduction reactions. Modern catalysts convert over 90% of these gaseous pollutants into carbon dioxide (CO_2), water and nitrogen (N_2) (Ek et al., 2004). In the mid-1970s automobile catalysts were introduced in the US, by 1989 they became mandatory in all new cars in Sweden, and from 1993 were mandatory through out the European Union (Ek et al., 2004). Prior to the mid 1990s platinum was the primary element used in catalytic converters, since then palladium has been favoured because it is considerably cheaper than platinum (Ek et al., 2004); at writing the cost of palladium was about one quarter of that of platinum (Tollefson, 2007). As well, stricter EU legislation on vehicle emission limits have contributed to the increased use of palladium because a palladium based catalyst is better able to meet these emission requirements than platinum (Ravindra et al., 2004). Another factor contributing to the move away from platinum use is that platinum is more sensitive to catalyst poisons than palladium (Ravindra et al., 2004).

4 Health aspects

This section deals with risk (= exposure x hazard) to man connected to additive use. Document 43 of the Additive Technical Committee (ATC[1]) in Europe gives a list of all possible classifications of the main categories of additive components. All of these components should be considered as relatively low hazard to both man and the environment. More than half of the main classes of petroleum additive components are not classified as dangerous: another 20% are classified as irritants only (Morris and Wallace, 1990). The ATC developed a model predicting combustion products of additives and representing them as a proportion of the total emission from gasoline and diesel fuel use. There were no significant changes in emissions and fuel additives do not appear to contribute to unregulated emissions.

To assess the human risk of fuel additives one should know the hazard and the exposure and for that at least the chemical formulation and concentration. However, manufacturers and industry are not so keen on supplying this kind of information which makes it difficult in principle to estimate the risk of fuel additives. The routes of exposure can be different: inhalation of fuel fumes or emission products, oral by exposure to components in drinking water, and man can be exposed by the dermal route during refuelling. Yet, not much is known about the emission and related to this the consumption of fuel additives. According to the ATC fuel additive ingredients are almost entirely consumed during the combustion process and mainly form CO_2 and water in the combustion process. CO and NOx are also expected, but fuel additive contributions to any unburnt hydrocarbon emissions are negligible (ATC Fuel additives and the environment, 2004). On the other hand, from the formulation of some additives it could be expected that those additives would form or release potential harmful substances after combustion. Another unknown factor in relation to hazard and exposure is the transformation of additives, which metabolites will be formed in the burning process. All these aspects make it hard to assess risks for human health and a risk assessment will therefore certainly involve high uncertainties.

The following paragraphs will address different aspects needed for risk assessment and will include several additives with a focus on MMT, ETBE, GTBE and platinum.

4.1 Metylcyclopentadienyl manganese tricarbonyl (MMT)

When lead was banned by many countries, the organic compound methylcyclopentadienyl manganese tricarbonyl (MMT) was introduced as an anti-knock additive in fuel (Tapin et al., 2006). MMT contains around 24.4 % manganese (Mn; Dorman et al., 2006), an essential element which is required for normal neural function in humans (Davis, 1998; Dobson et al., 2004; Finley, 2004).

4.1.1 Exposure

Combustion of MMT results in the emission of fine Mn particulates (0.5-1 μm) mainly in the form of manganese sulphate and manganese phosphate (Dorman et al., 2006; Tapin et al., 2006). Only 1 to 5 percent of the manganese consumed in the fuel is emitted as a respirable particulate. Typical manganese concentrations in urban air are quite low (33 ng Mn/m3; Dorman et al., 2006) and the levels of exposure remain below international guideline values (Zayed et al., 1999a). The contributions of MMT usage on urban air manganese concentrations has been studied extensively in several major

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[1] http://www.atc-europe.org/index.asp

Canadian cities were MMT was actively used in gasoline for 10 or more years. Environmental modelling approaches in the Montreal metropolitan suggest that airborne Mn levels were quite similar to those in areas where MMT was not used (Aschner, 2000). A small cohort study of personal exposures to airborne Mn in London was conducted before and after introduction of the additive to identify any major impact of the additive on exposures. Manganese exposures in this cohort did not increase as a result of introduction of the additive (Pfeifer, 1999). Furthermore, it was assumed that small amounts of manganese added to the environment by the combustion of MMT used as a fuel additive would be comparable to the normal background and should not create health problems (Cooper, 1984). Because MMT has a low vapour pressure and a short half-life in sunlight, it is unlikely that significant concentrations of MMT could occur in the environment as a result of its use as a gasoline additive (Lynam et al., 1990) but manganese particles remain and do not disappear in combination with sunlight. Yet, Zayed et al. (2003) reported that in context of a notable decrease in manganese emissions from industrial sources and that fact that atmospheric Mn pollution index seems to be stable over time, suggest that the combustion of MMT used in gasoline may be an important factor contributing to maintaining stable atmospheric Mn concentrations. The same observation was found evaluating the presence of any trend in Montreal where a correlation was observed between atmospheric manganese and traffic densities (Bankovitch et al., 2003) and manganese accumulation can occur if MMT will be widely introduced. The contribution of direct emissions from motor vehicles to the atmospheric background manganese would be around 50% at 25 meter from the source and less than 8% at 250 meter (Loranger et al., 1995). However, it is impossible to distinguish between directly emitted Mn from automobiles, Mn enriched road dust, and the naturally occurring Mn in crustal material.

The outcomes concerning effects on emissions are a bit contradictory. Geivanidis et al. (2003) reported no measurable effect on regulated emissions (CO, HC, and NOx) and on fuel consumption with MMT usage but for non-catalyst cars an increase in benzene and formaldehyde emissions was found. Another study reported that MMT usage had no effect on CO emissions, caused a slight decrease in NOx emissions, and a slight increase in HC emissions (Lynam et al., 1990). Zayed et al. (1999b) reported a small increase, although not significant, in CO and similar NOx concentrations. In addition, it was shown that MMT reduced fuel economy and increased CO_2 emissions (Benson and Dana, 2002). Manganese seems to affect catalytic converters on cars reducing catalyst function caused by potential obstruction.

4.1.2 Hazard

Inhaled manganese is absorbed directly from the respiratory tract and transported to the brain before it can be metabolized and removed in the liver (Davis, 1998; Finley, 2004). In the brain Mn is taken up specifically by dopaminergic neurons, the neurons associated with movement initiation. Since uptake is more rapid than its removal manganese can be accumulated in the neurons with chronic exposure (Yokel and Crossgrove, 2004). Chronic exposure to Mn results in the development of neuropsychological changes that resemble Parkinson's disease including tremors, difficulty walking, and facial muscle spasms (Finley, 2004; Normandin et al., 2002). This state of disease is sometimes preceded by psychiatric symptoms, such as irritability, aggressiveness, and even hallucinations (Pal et al., 1999). The oral route of exposure to manganese by drinking contaminated water is not considered as a threat due to a low rate of absorption from the gastrointestinal (GI) tract and efficient regulation by homeostatic mechanisms.

Motor performance and memory are negatively affected by long-term manganese exposure at levels too low to cause clinically evident toxicity (Davis et al., 1998; Frumkin and Solomon, 1997). Neurotoxicity

can already occur at low exposure levels (300 microgram/m^3) of Mn sulphate, one of the main combustion products of MMT (Tapin et al., 2006) and high levels of manganese exposure (especially Mn^{3+}) is well recognized as a nervous system toxin. Neurotoxicity from manganese is irreversible and is often not manifested until many years after exposure has ceased. The early signs of neurological symptoms are behavioural problems (violence) and impaired hand-eye coordination (Davis et al., 1998). Mn accumulation occurs within the striatum in the brain where it triggers neural injury and can result in decreased numbers of dopaminergic neurons (Dorman et al, 2006). Manganese is also a pulmonary toxin. Increases in respiratory symptoms, pneumonia and/or bronchitis have been reported in most cases at exposure levels well above what would be expected from MMT use in fuel (Frumkin and Solomon, 1997). There is mixed or insufficient evidence to characterize carcinogenic effects of Mn (Davis, 1998).

4.1.3 Risk

Certain subpopulations are suspected to be more prone to the effects of Mn exposure; especially iron deficient, elderly, and children. Manganese absorption from the gastrointestinal tract is complex and influenced not only by the amount of manganese but also by iron. In particular, iron deficiency, is a frequent risk factor that can result in increased manganese absorption from the GI tract and enhanced brain delivery of manganese. In particularly, neonates and women of child bearing years are at higher risk (Dorman et al., 2006). The elderly are another special population of concern since over time Mn body burdens and/or small impairments in neurobehavioral function may accumulate resulting in sooner occurrence of the Parkinsonian like symptoms in old people. Children are another group of special concern. Mn exposure during a limited period of early development might result in irreversible damage to the developing central nervous system. In addition, young children could also be at higher risk because of metabolic differences, as suggested by the fact that homeostatic mechanisms for regulating Mn absorption and elimination are not well developed in infants (Davis, 1998).

In 1994 the U.S. Environmental Protection Agency (EPA) has performed an extensive risk evaluation on the health risks related to MMT use in gasoline (EPA report no. 600/R-94/062, 1994). The outcomes of this review showed that the levels of manganese were equal or below the Mn inhalation reference concentration (RfC – 0.05 µg/m3) and it was not possible to make a statement on the risks for human health. Though, a reasonable basis exists for concern regarding potential public health risks, especially for susceptible subpopulations, if MMT were to be used widely in unleaded gasoline (Davis et al., 1998). Normandin et al (2002) have also written that in case the prospect will be worldwide MMT usage, manganese concentrations in air and water can increase and then this metal should be considered a new environmental pollutant having potentially widespread public health consequences. On the other hand, Finley (2004) has reviewed the possible health risks to healthy adults by environmental exposure to manganese. The available literature only reveals circumstantial evidence that minor environmental exposure to Mn can have deleterious effects in healthy adults. It is well accepted that inhalation of toxic amounts of Mn (e.g. >1.0 mg/d) can affect neuropsychological function, however, the Mn exposure from MMT in gasoline is so low (3 µg/d) that it is not expected to be a risk for human health. Very few inhalation toxicological studies were carried out and the possible health risk with inhalation exposure to manganese should be sorted out especially for chronic exposure. Mn toxicity may not be clinically evident until some years after exposure has occurred or terminated, which makes it difficult to detect dose-response relationships.

Until the existing research and information gaps are filled, a high degree of uncertainty will attend any judgement of the potential risks to public health associated with the use of MMT (Davis et al., 1998). Dave Kortum from U.S. EPA has let the RIVM known that the U.S. EPA is in the midst of a re-

evaluation of MMT but have not finalized anything and will probably not do for at least a year. Recently, the conclusion in an article of Walsh (2007) was to stop the sale of MMT in gasoline until and unless further data show that Mn and its combustion byproducts will not result in adverse health effects and will not damage advanced vehicle pollution control technologies. If MMT were widely used as a gasoline additive, it could take decades, as occurred with lead additives, before the full health consequences were understood and agreed upon (Walsh, 2007).

In short, a reasonable basis exists for concern regarding potential public health risks if MMT is widely introduced. However, for a more definitive estimate of risk more information should be obtained on exposure to and health effects of Mn combustion products of MMT in gasoline.

4.2 Oxygenates

Oxygenated fuels like methyl tertiary-butyl ether (MTBE), ethyl tertiary-butyl ether (ETBE), tertiary amyl-methyl ether (TAME), and 1,6-dimethoxyhexane (DMH) are chemical substances which increase the oxygen content within the combustion chamber. Oxygenates are used in fuel in concentrations >1% and are therefore no additives by definition but rather blending components. When the oxygen content is high, the fuel can be combusted more completely thereby reducing the amount of exhaust emissions from partially burned or unburned fuel, which results in the reduction of hydrocarbons and carbon monoxide. These substances are nonetheless suspected to be potentially harmful for human health since high amounts are used. Because oxygenates change the mixture of both evaporative and tail pipe emissions, they also may change the health effects of exposure to the emissions. This factor must be taken into consideration when evaluating the impact of oxygenates in fuels. Extensive testing of motor vehicle emissions with and without oxygenates demonstrates that oxygenates consistently reduce tailpipe emissions of CO by 10 to 25%.

Reducing the levels of CO is particular interest. When it enters the body, CO combines with haemoglobin in blood, which reduces the ability of the blood to deliver oxygen to the tissues. People with coronary artery disease are particularly sensitive to this effect because they have impaired ability to increase coronary blood flow. When blood flow through the heart is not sufficient to meet the oxygen demand, the heart becomes ischemic, resulting in chest pain (angina pectoris), or electrocardiographic changes, or both. Adding oxygenates also appears to cause an overall reduction in air toxics emissions, but different air toxics are affected differently; benzene emissions are reduced, formaldehyde and acetaldehyde emissions are increased in some cases, and 1,3-butadiene emissions are either reduced slightly or not changed. All four of these air toxics emitted from motor vehicles – benzene, 1,3-butadiene, formaldehyde, and acetaldehyde – are classified as either known or probable human carcinogens (HEI, 1996).

Overall, it seems that there is very little reason to expect an increase in health effects upon the use of these oxygenates. In general, however, the exposure to the compound itself may lead to adverse health effects. Below some oxygenates will be described in more detail with the exception of TAME and DMH since there is very little information on these oxygenates and the focus will be on the oxygenates with the highest potential to be used as fuel additives.

4.3 *Methyl tert-butyl ether (MTBE)*

A number of different oxygenates have been used, however the use of MTBE dominated because of its favourable coast and blending characteristics; 11%vol MTBE is required to reach the minimum 2%wt oxygen content. By around the year 2000 MTBE accounted for 85% (15 billion L/year) of all oxygenates used in the United States (Shih et al., 2004). MTBE is added to gasoline up to 15% by volume (Ahmed, 2001).

4.3.1 Exposure

In Europe MTBE is mainly used as an octane enhancer in high octane petrol (Dekant, 2001) rather than a main oxygenate. Exposure levels will therefore be considerably lower compared to the USA. MTBE has become one of the major groundwater pollutants in the US (Shih et al, 2004). The route of entry into underground aquafiers is frequently from leaking underground fuel storage facilities and from service station spills (Martin et al., 2002; Rosell et al., 2005; Shih et al., 2004). The major routes of exposure to MTBE are via drinking tainted groundwater and vapour inhalation when refuelling (McGregor, 2007; Martin et al, 2002). The impact of MTBE on vehicle emissions of volatile organic components (VOCs) was modelled and addition of MTBE to gasoline would decrease acetaldehyde, benzene, 1,3-butadiene and particulate organic matter, but increases formaldehyde tailpipe emissions. Though, the increased formaldehyde emissions were offset by the reduction of formaldehyde formation in the atmosphere from other VOCs (Ahmed, 2001).

4.3.2 Hazard

Extensive research into the toxicology of MTBE has demonstrated that it is relatively non-toxic. However, like all ethers central nervous system depression is the major toxic effect of short term exposure (Dekant et al, 2001). There appears to be a small subpopulation that reports themselves to be extremely sensitive to the effects of ether fuel oxygenates (McGregor, 2007). Ether fuel oxygenates have been linked to neurological symptoms such as headache, dizziness, nausea and mood swings (Martin et al, 2002). MTBE is an animal carcinogen, but its human carcinogenic potential remains unclear (Ahmed, 2001). No acute toxic health effects would occur during the normal use of automotive fuels (Reese and Kimborough, 1993).

4.3.3 Risk

MTBE has a number of characteristics that make it a problem, it is highly water soluble, highly mobile and slow to degrade (Squillace et al, 1997), added to this, MTBE is not readily taken up by soil particles and even at low concentrations, can taint drinking water (25-60 μg/L) (Rosell et al, 2005). Concern over ground and surface water contamination caused by persistent MTBE has lead the US EPA to propose reducing or eliminating its use as a gasoline additive (Ahmed, 2001).

MTBE is not favoured as a fuel additive. Although it is relatively non-toxic, it has been identified as potential persistent groundwater contaminant.

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4.4 Ethyl tert-butyl ether (ETBE)

In places where MTBE will be withdrawn from the market, other fuel oxygenates will be needed as a replacement. The most likely candidate is the oxygenate Ethyl Tertiary-Butyl Ether (ETBE).

4.4.1 Exposure

ETBE is another member of the ether group of fuel oxygenates, it has similar physical and chemical characteristics to MTBE, however unlike MTBE, ETBE is an ethanol based ether and comes from biological source material; MTBE is methanol based and therefore a fossil fuel derivative. ETBE has more favourable characteristics than MTBE; it is much less water soluble and hence is less mobile in groundwater (McGregor 2007) and it has a lower vapour pressure. The oxygen content however, is less than that of MTBE; therefore to give a 2%wt oxygen boost, a larger volume (12.8%vol) of ETBE is needed compared to MTBE (11%wt) (Noureddini, 2002).

Rosell and colleagues (2005) recently studied the fate of fuel oxygenates in a groundwater table near the site of a gasoline spill (from leaking service station tanks) in Germany. They were unable to detect any ETBE at any of their sampling sites. Likewise, in another study conducted around known leaking underground storage facilities in the Los Angeles metropolitan area (Shih et al, 2004), 50% of the detected maximum levels of ETBE were less than 5 μg/L. However Shih and colleagues urge caution against over-interpretation of their results since an upscale in the use of fuel oxygenates like ETBE could potentially mirror the scenario of MTBE. When MTBE was used as an octane booster at concentrations of 1-3% there were no indications of its environmental impact until its use was up scaled to that of a primary oxygenate in fuel (Shih et al, 2004).

In humans, ETBE is extensively distributed in all tissues (McGregor, 2007) however it is rapidly eliminated via either exhalation or is metabolized (tertiary-butyl alcohol (TBA) and acetaldehyde) and excreted in the urine (Johanson et al, 1995; Nihlén et al, 1998; Dekant et al, 2000). The rapid rate of elimination means that the accumulation of either ETBE or its metabolites in realistic conditions is unlikely (Dekant et al, 2000). There has been no field or epidemiological study for ETBE but since the chemical structures of ETBE and MTBE are quite similar, it might be justified to assume that these chemicals have similarities in their ability to cause potential health effects. A physiological based toxicokinetic (PBTK) model was developed for evaluation of inhalation exposure in humans to ETBE (Nihlén and Johanson, 1999). The simulations from this PBTK model suggest that TBA in urine is a suitable biomarker for exposure to ETBE and gasoline vapour.

4.4.2 Hazard

Nihlén et al. (1998b) described a single inhalation chamber study for ETBE in which healthy subjects were exposed for 2 hours to high levels of ETBE. The highest exposure level of 50 ppm ETBE are at least one order of magnitude higher than expected environmental exposure levels. Significant increased ratings of discomfort in the throat and airways were reported during and after exposure to 50 ppm ETBE. In addition, slightly impaired pulmonary function was observed at 25-50 ppm. However, the ETBE-related effects fall within the normal variations seen for healthy individuals and have no clinical relevance. In another inhalation study the ETBE biotransformation was compared in humans and rats (Amberg et al., 2000). The obtained data indicate that ETBE biotransformation and excretion are similar for rats and humans, and that ETBE and its metabolites are rapidly excreted by both species.

In animal studies ETBE has been shown to have low acute toxicity. The most typical clinical signs observed in rodents after repeated inhalation exposure were ataxia (loss of muscle coordination) and sedation. Once removed to normal air rapid recovery followed (McGregor, 2007). ETBE appears to be less of an irritant than MTBE, which has been classified in the European Union as a skin irritant, but not as an eye irritant. Based on animal studies, ETBE does not appear to have any persistent adverse neurotoxic effects, it is not suspected to be genotoxic, and evidence for carcinogenicity in rodents is unconvincing (McGregor, 2007). TBA, a metabolite of ETBE, was found to enhance nephropathy in rats (Takahashi et al., 1993). In rodents the urinary tract is the target organ for TBA toxicity, and males are more sensitive to TBA toxicity than females (Lindamood et al., 1992). This toxicity is related to a specific male rat protein, absent in humans. This species/sex specificity had many investigators question the relevance of male rat nephropathy following human exposure to ETBE (Ahmed, 2001). The outcomes of a 4-week rat inhalation study described by White et al. (1995) indicate that 500 ppm was a no observed acute effect level (NOAEL) for ETBE and in case 15% is used in fuel 30 times higher magnitudes of ETBE are used.

4.4.3   Risk

Given that the potential for exposure to the general population is high it is important to understand the potential impact of ETBE on human health. As with MTBE it is likely that a subpopulation could be particularly sensitive to ETBE however this is unlikely to be picked up in volunteer studies (McGregor, 2007). If ETBE is introduced on a similar scale as MTBE then its potential as a groundwater contaminant must be considered.

Introducing ETBE in a large scale will increase the risk of a groundwater contamination. Thus, although ETBE is relatively non-toxic and less water soluble than MTBE,it will be unlikely that it will be increasingly used for commercial purposes for similar reasons a listed for MTBE. .

4.5   *Glycero-tert-butyl-ether (GTBE)*

Glycerol-tert-butyl-ether (GTBE), a derivative of glycerol is not yet in commercial production; however it has the potential to become a solution not only to the PM emission problem, but also as a means of dealing with the growing amount of glycerin produced as a byproduct from the manufacture of biofuels. Ten percent of the product from the process of splitting plant and seed oils in the biodiesel manufacture process is glycerin (Jaecker-Voirol et al., 2005). Consider this in real terms; a directive from the European Commission requires that by 2010 5.75% of all transport fuels will be biofuels. This equates to 10 million tons of biofuel production per annum, so therefore there will be an associated production of 1 million tons of glycerin (Jaecker-Voirol et al., 2005). This glycerin production is over and above the traditional glycerin production/use of 800,000 tons per annum (Uniqema lecture, 2003); therefore in order to avoid the complete collapse of the glycerin market a large-scale use for this excess must be found.

4.5.1   Exposure

In a comprehensive experimental investigation by Jaecker-Voirol et al. (2005) a number of glycerin derived products were evaluated for use as potential diesel fuel oxygenates. The best candidates were vehicle tested, GTBE was one of these. Two vehicle types were used in the tests, one older engine technology - a vehicle equipped with a catalytic converter (Euro II vehicle); and a recent engine

technology, a vehicle equipped with a catalytic converter and common rail fuel injection equipment (Euro III vehicle). In the Euro II vehicle, fuel containing 5% GTBE resulted in a 16% reduction in PM emissions, NOx emissions did not increase significantly. PM emissions were also reduced in the Euro III vehicle (11%); NOx emissions did not increase significantly. The Euro II vehicle was more sensitive to GTBE than the Euro III vehicle. In another study (Spooner-Wyman and Appleby, 2003), a light duty diesel engine was used to re-evaluate the effects of GTBE on exhaust emissions. In this study a low-sulfur low-aromatic base fuel was blended with GTBE at two different concentrations (4% and 15%), both blends significantly reduced PM emissions by between 14-16%. There was however increase in NOx emissions, but the authors concluded that the altered engine timing setup may have created higher than normal NOx emissions. This engine was run in steady state conditions.

4.5.2   Hazard

At present virtually no toxicology data available on GTBE however from the scanty data available it appears to be relatively non toxic and it is less likely to be toxic than MTBE because of its water insolubility (Wagner et al, 1975).

4.5.3   Risk

GTBE is not expected to be a serious groundwater pollutant and as it seems relatively non toxic. Therefore, no serious risk is expected for human health.

4.6   *Overall assessment oxygenates*

The potential health effects of exposure to components of conventional gasoline (without oxygenates) include short-term and cancer effects similar to those that could result from exposure to gasoline containing oxygenates. Adding oxygenates to gasoline can reduce the emission of CO and benzene from motor vehicles, and thereby potentially lower certain risks to members of the population, At the same time, using oxygenates increases exposure to aldehydes, which are carcinogenic in animals, and to the oxygenates themselves. Adding oxygenates is unlikely to substantially increase the health risks associated with fuel used in motor vehicles; hence, the potential health risks of oxygenates are now not sufficient to warrant an immediate reduction in oxygenate use. However, a number of important questions need to be answered if these substances are to continue in widespread use over the long term (HEI, 1996).

The Oxygenates Evaluation Committee noted a general lesson to be learned from introducing oxygenates to the general public. The diverse experiences after introducing oxygenated fuels argue strongly that any future new use of a substance, like for instance GTBE, should 1) be preceded by a sufficiently comprehensive research and testing program (including mechanistic and human studies), and 2) be accompanied by rigorous exposure assessment and epidemiologic studies (HEI, 1996). The above is partly considered by the new European Community Regulation (REACH) on chemicals and their safe use.

4.7 *Platinum group elements*

Platinum group elements (PGEs) are a group of metals highly resistant to oxidation found naturally in very low abundance in the earth's crust (Wedepohl, 1995). The chemical properties of these rare metals, namely platinum (Pt), palladium (Pd) and rhodium (Rh), make them superb catalysts. A catalyst is a compound or element that facilitates a chemical reaction without its own structure being changed in the reaction process. In a practical application, catalysts were developed for automotive vehicles as a means of reducing exhaust emissions of gaseous pollutants such as carbon monoxide (CO), nitrogen oxides (NOx) and hydrocarbons (HCs) by converting them into less toxic substances including CO_2, water and nitrogen gas.

4.7.1 **Exposure**

During the life of a catalytic converter the catalyst undergoes both chemical and physical stresses caused by fast changing oxidative/reductive conditions, high temperatures and mechanical abrasion; this results in the release of minute traces of the catalyst along with the exhaust gasses into the atmosphere (Ek et al., 2004). The amount and rate of PGE emissions are affected by numerous factors including the speed of a vehicle, type of engine, age and type of the catalyst and the type of additives used in the gasoline. Emitted catalyst particles are initially airborne and most are in their metallic state (Ravindra et al., 2004).

The widespread use of catalytic converters has resulted in steadily increasing concentrations of PGEs on roadsides. One recent study showed that in the six years between 1999 and 2005, there was a 2.1 – 15 fold increase in PGE concentrations in the road dust of one German metropolitan area. Levels from 38.9 – 261 µg/kg were measured in stop start traffic (Whichmann et al., 2007). Over the next few years PGE accumulation is predicted to accelerate (Whichmann et al., 2007). Once deposited on the roadside, rain washes particles into waterways and soil (Ek et al., 2004). Over time, and with interaction with humic molecules (organic component) present in soil, a proportion of PGE particles are oxidized. It is likely that platinum, palladium and rhodium all react with different molecules (Sures and Zimmermann, 2007). Most of these oxidized PGEs precipitate but some remain soluble. Precipitated PGE oxides are less likely to be bioavailable than when they are soluble. Palladium oxides however appear to be prevented from precipitating when they are in the presence of fulvic acid, a humic component (Sures and Zimmermann, 2007); palladium is therefore more likely to remain in solution than either platinum or rhodium therefore increasing its bioavailability. There are however several factors which have been shown to increase the solubility of both platinum and rhodium; decreasing pH, smaller particle size and increased salinity (Ek et al., 2004).

When in their soluble state, PGEs are more likely to become bioavailable (i.e. can be taken up by plants, animals or humans) because they are mobile in the environment; of the three, palladium has the highest bioavailability, followed by rhodium and then platinum (Colombo et al., 2007). Platinum group element uptake has been reported in both experimental and wild animal and plant populations (Gagnon et al., 2006; Ravindra et al., 2004; Sures and Zimmermann, 2007). For humans the most likely exposure pathway is from metal contaminated soils via accidental soil ingestion, particularly by children (Colombo et al., 2007), bioaccumulation in food could be another potential source (Barefoot, 1997).

4.7.2 Hazard

In the metallic state platinum group elements are considered to be relatively inert and non-allergenic; however metallic palladium is known to cause contact dermatitis in platinum industry workers (Ravindra et al., 2004). Whether palladium has the potential to cause respiratory sensitizing is not known at the present time (Ravindra et al., 2004). With regards to potential health effects, it is what happens to platinum group elements after they are deposited on roadsides that could be of concern. When soluble, platinum group elements are able to form salts, of these salts, PGE-chloride complexes are some of the most potent allergens and sensitizers known (Ravindra et al., 2004). It is the possibility of PGE-chloride salt formation that seems to cause the greatest health and environmental concern. PGE-chloride salts can only form in the presence of chloride ions therefore one research group designed a physiological model to evaluate whether the human digestive tract provides suitable conditions for the formation of these salts. Based on their results, they concluded that the chloride ions from hydrochloric acid in conjunction with the acidic environment present in the stomach, could potentially promote the formation of PGE-chloride salts (Colombo et al., 2007). A comprehensive experimental study was performed to evaluate the uptake and toxicology and genotoxic effects of these PGE-chloride complexes in both animals (rats) and plants (Sphagnum moss) (Gagnon et al., 2006). Their results showed that PGE-chloride complexes had significant toxic and mutagenic effects in both the plant and animal models even at levels as low as 0.1 ppm. Their results suggest that PGE may interfere with phosphate metabolism of plants and perhaps in animals also. They also demonstrated that of the three platinum group elements palladium-chloride salts had the greatest toxic effect. Based on their experimental results, levels as low as 1.0 ppm were toxic to plants (Gagnon et al., 2006).

4.7.3 Risk

Given the increasing use of palladium in catalytic converters it means that in the future palladium is likely to be accumulated in the environment to a greater extent than either platinum or rhodium. Accumulation along with relatively high bioavailability means that palladium is likely to enter the food chain and, given the structure of the mammalian digestive tract has the potential to form palladium-chloride complexes. Therefore the potential health consequences of palladium need to be investigated further.

4.8 Cerium

4.8.1 Exposure

A cerium-based fuel additive in conjunction with a particulate filter is another approach to reduce emissions. The main purpose using a catalyst in combination with a particle trap is to ensure effective regeneration during normal driving conditions. However, this additive will result in emissions of cerium compounds and an increase in cerium in the ambient air and soil. A limited number of short-term diesel engine tests have shown a substantial decrease in both particle mass (>90%) and number (>99%) concentrations in the exhaust by the use of cerium (20 to 100 ppm in fuel) in combination with a particulate filter (HEI, 2001). Despite the filter's high efficiency in trapping particulate matter, however, a small amount of cerium is emitted. Cerium measured in emissions was found primarily in the oxide form and in particles less than 0.5 μm in diameter. Cerium mass relative to the total particle mass was between 3% and 18% based on two tests using two different types of filters (HEI, 2001). The main routes of exposure of the public to cerium-containing particles are inhalation and ingestion. Concerning inhalation the lungs and the lymph nodes are the most important target organs; other

organs could be affected via clearance through the blood. Cerium taken up by ingestion is excreted in the faeces after transiting in the digestive tract. Studies in rodents showed that less than 0.1% of the ingested dose is absorbed by the gastrointestinal tract and distributed to other organs. Inhalation of cerium is of more concern than ingestion because cerium is poorly absorbed by the intestine (HEI, 2001).

4.8.2   Hazard

Literature on the health effects of cerium is limited. Recently, Fall et al. (2007) reported a study in which an organotypic culture of lung slices was used to evaluate potential adverse effects from cerium oxide particles on the lung and to compare emissions from cerium oxide additized fuel to those of a reference fuel. On the basis of this study and from the prospective potential exposure to cerium oxide the authors concluded that a very low prospective risk is associated with the expected dissemination of cerium oxide in the atmosphere. The only animal inhalation study involved exposure of rats to cerium oxide particles substantially larger than those in diesel emission (HEI, 2001). Another recent publication describes an initial in vitro preliminary screening strategy to examine the potential for human health hazards following exposure to nanoparticulate cerium oxide (Park et al., 2007). The in vitro assays used in the screening strategy are all validated, internationally accepted protocols and provide a useful indication of potential toxicity of a chemical as a result of effects on various toxicological endpoints such as local site of contact (dermal) irritation, general cytotoxicity and mutagenicity. No adverse effects were found with this preliminary in vitro screening approach.

4.8.3   Risk

Based on the limited data available, toxicity of cerium oxide appears to be small, and cerium oxide might not be of concern when inhaled or ingested at the low levels that would be encountered in the environment. The absence of more complete information precludes fully assessing the possible health risk of using cerium as a fuel additive (HEI, 2001).

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5   Conclusions

The limited amount of data on both exposure and health effects make it difficult to predict the risks for human health and if risks are predicted high uncertainties remain. Overall the concentrations of fuel additives are small and therefore exposure even over a prolonged time will be low and very little adverse health effects are expected. However, the use of blending components implies an increased risk caused by higher exposure which may lead to negative health effects. These effects should be sorted out extensively for each component separately before they will be introduced as an additive.

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6 References

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