



## **POLYCYCLIC AROMATIC HYDROCARBONS AND DIESEL PARTICULATES**

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### **1. ABSTRACT**

This work is concerned with the identification of the organic compounds emitted by diesel engines. The majority of these compounds are components of the fuel that have survived combustion. Accompanying this unburnt fuel in the exhaust are other components, some new compounds produced as a result of chemical reactions in the engine and others, identical in structure to the fuel species, but which have also been produced pyrosynthetically. In a previous study (Bachmann, Gong et al. 2002) some of us reported analytical studies on the polycyclic aromatic hydrocarbons (PAH's) bound to diesel engine particulates. PAH's are important environmental contaminants because of their suspected carcinogenic properties. Fourteen of the sixteen PAHs in the priority pollutant list of the US EPA were identified in samples of the particulates. In this work we have extended the analysis to include some of the other major components of the exhaust. Gas and silica gel chromatography were used to separate the components and mass spectrometry was used to identify them. Two vehicles, a well maintained (1999) Mitsubishi Pajero, 2.4L turbo and a 1987 Nissan Bluebird, 2L, which was untuned, were used in the experiments. The engines of these vehicles were operated under a number of different load and speed conditions. We have found that the concentration and relative proportions of the PAH's emitted by the engine are affected by the engine operating conditions and the results of those studies are presented.

### **2. INTRODUCTION**

There is growing concern internationally with the long-term effects of air pollution on human health. Associations have been found between particulate air pollution and increased risk of adverse health effects. An ongoing prospective mortality study of ~1.2 million adults by the American Cancer Society has shown that each 10 $\mu\text{g}/\text{m}^3$  elevation in fine particulate air pollution is associated with approximately a 4%, 6%, and 8% increased risk of all-cause, cardiopulmonary, and lung cancer mortality, respectively (Pope III, Burnett et al. 2002). Measures of the coarse particle fraction and total suspended particles were not consistently associated with mortality. The elderly, infants, and persons with chronic cardiopulmonary disease are particularly at risk (Schwela, 2000).

Particulate matter is experimentally classified into two fractions PM<sub>10</sub> ( $\leq 10 \mu\text{m}$  in aerodynamic diameter) and PM<sub>2.5</sub> ( $\leq 2.5 \mu\text{m}$  in diameter). Of particular concern are the smaller particles because when inhaled these particles are trapped in the small airways and alveolar regions of the lung where they are retained because of their low solubility (Anderson, 2000). A study conducted in Grenoble, France has shown

that between 20% and 45% of the exposure to  $PM_{2.5}$  in the non-smoking adult population can be attributed to traffic emissions and in high exposure situations this proportion can reach 75% (Boudet, Zmirou et al. 2000). In Christchurch, New Zealand road traffic accounts for less than 10% of the particulate emissions but in other New Zealand cities the proportion is probably higher (Town 2001). The lungs of never-smoking female residents of Mexico City, a region with high ambient particle levels (3-year mean  $PM_{10} = 66 \mu\text{g}/\text{m}^3$ ), have been compared with controls from Vancouver, British Columbia, Canada, a region with relatively low particulate levels (3-year mean  $PM_{10} = 14 \mu\text{g}/\text{m}^3$ ). Total particle concentrations in the Mexico City lungs were significantly higher ( $2,055 \times 10^6$  particles/g dry lung vs.  $279 \times 10^6$  particles/g dry lung) (Brauer, Avila-Casado et al. 2001). Road transport is not necessarily the most hazardous means of transport in this context. The measured exposure levels for surface transport, bicycle, car and bus, in central London were similar to each other, but the mean exposure levels on the London Underground rail system were 3-8 times higher than the surface transport modes (Georgiadis, Stoikidou et al. 2001). What is not clear from the studies reported to date is whether the adverse health effects attributed to the particles are due to the particles themselves or to the chemical compounds absorbed on the surface of these particles. There is evidence to suggest that the adverse health effects are much greater with  $PM_{2.5}$  particles than with  $PM_{10}$  particles (Churg and Brauer 2000).

Since the use of diesel engines in motor vehicles is increasing and the emissions from diesel engines are more visible than emissions from petrol engines, these emissions are of particular concern. Particles emitted by diesel engines are mainly elemental carbon together with some inorganic materials, principally sulfates and phosphates. Organic compounds that are adsorbed onto the particles are readily extracted into an organic solvent such as dichloromethane.  $PM_{2.5}$  particles constitute almost all of the mass of the particles emitted by diesel engines. The soluble organic compounds bound to the particulate emissions from a diesel engine constitute 70-75% of the total hydrocarbon emissions of such engines (Andrews, Iheozor-Ejiiofar et al. 1983). The extractable component can be up to 80% of the total mass of the particles and it contains hundreds if not thousands of different compounds (Levsen, 1988; Zinbo, Hunter et al. 1989). These compounds are either components of the fuel that have survived combustion or are compounds produced as a result of the combustion process. The chemical composition of these emissions is thus strongly dependent on the composition of the fuel. Some of the synthesized components are identical to compounds present in the fuel. Using radioactive tracer methods have shown that 0.48% of the naphthalene in a diesel fuel survived combustion and this unburnt component represented 24% of the total naphthalene emissions (Rhead, and Pemberton 1996). The remaining naphthalene emitted was derived largely from methyl-naphthalenes present in the fuel.

Overseas studies of these emissions have confirmed the presence on the emitted particles of more than forty substances that are listed by the United States Environmental Protection Agency (U.S. EPA) as hazardous air pollutants. The US EPA has identified sixteen PAH's as priority pollutants cf. Figure 1. The International Agency for Research on Cancer lists fifteen of these compounds as, probable, possible or known human carcinogens. PAHs are organic compounds that typically contain from two to eight aromatic rings. They are formed during the incomplete

combustion of organic compounds and are released and dispersed whenever natural biomass is burned. These natural processes result in a general background level of PAHs in the environment. The main anthropogenic sources of these compounds are vehicle emissions ( ~35% of the total PAH's emitted annually in the US) (Harvey, 1997), fuel used for heating purposes, industrial processes and power generation. Diesel engines are a major source of the lighter PAHs and petrol engines are the major source of the higher molecular weight PAHs (Edwards, 1983). Also of concern is the finding that despite recent advances in engine technology and emission control devices that have reduced the weight of emitted particles, the number of emitted particles in some types of engines has actually increased. This means that the modern diesel engine is emitting many more particles with a much greater surface area per gram of particulate matter and so the particles have a much greater ability to absorb the organic components of the exhaust.

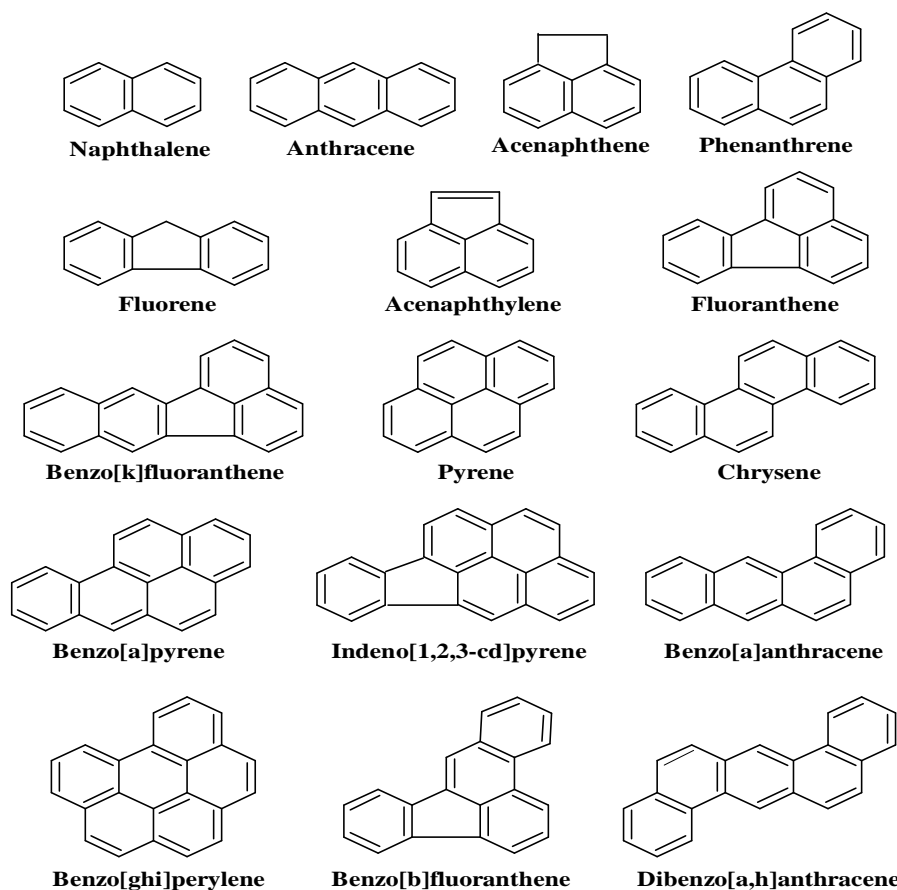


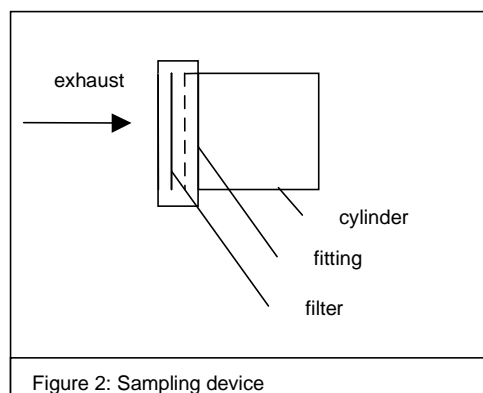
Figure 1 Structures of the polycyclic aromatic hydrocarbons identified by the U. S. EPA as priority pollutants

Several PAHs have been identified as cancer causing agents. Many carcinogens, including PAHs, are inactive *per se* but are metabolically altered by enzymes to new compounds that have mutagenic, genotoxic, and carcinogenic properties (Cerniglia, 1984). In mammals, PAHs are activated by the enzyme cytochrome P450 dependent monooxygenase, to form dihydrodiol epoxides. These epoxides are capable of forming

adducts with DNA, and these adducts lead to the induction of tumours. Known cancer causing PAHs include pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[a]pyrene, benzo[ghi]perylene, indeno[1,2,3-cd]pyrene and dibenzo[a,h]anthracene (Zhang and Harvey, 1999).

In this study we have determined the composition and concentration of some of the EPA priority pollutants and other compounds bound to the particulate emissions from diesel engines, run under a variety of operating conditions, using New Zealand diesel fuel. The chemical composition of diesel fuels is variable, being dependent on the regulatory requirements of each country and the actual refining conditions. For this reason similar studies performed in one country will not necessarily give the same results in a different part of the world.

### 3. EXPERIMENTAL



Samples were taken from three engines, under a variety of different operating conditions. Examples of the operating conditions used are shown in Table 1. The particles were collected, the organic component was isolated by soxhlet extraction and column chromatography and finally analysed with GC/MS.

#### 3.1 Sampling device

A relatively simple device (Figure 2) was constructed to collect the samples, without focusing on the volume of the exhaust going through the device. Glass microfibre filter paper (Whatman International, England) was pressed between two stainless steel grids to prevent fluttering in the exhaust stream. Initially samples were collected from a four-cylinder VM 292 diesel engine with varying numbers of revolutions/minute and collection times. Varying the load on this engine was not possible. The engine speed was varied between 1000 and 2900 rpm. The second set of samples was taken from two different cars, kindly made available by International Dynamometers Ltd. The first vehicle was a 1999 Mitsubishi Pajero, with a 2.4L direct injection turbo engine, the second vehicle was an untuned 1987 Nissan Bluebird, with a 2L engine fitted with a pre-combustion chamber. Samples were collected in duplicate. The test vehicles were operated on a portable dynamometer facility.

VM 292 Diesel Engine Sampling regime	Nissan Bluebird Sampling regime	Load in Nm	Mitsubishi Pajero Sampling regime	Load in Nm
Revolutions per minute	Revolutions per minute		Revolutions per minute	
Cold start	1000	599 (half load)	1000	480
1000	1000	599 (full load)	1000	680
1000	2000	440	2000	400
2000	2000	645	2000	1000
2000	3000	450	3000	480
2500	3000	670	3000	900
2500	4000	235	4000	350
2900	4000	620 (full load)		

Table 1: First (VM 292 diesel engine) and second series (Nissan Bluebird, Mitsubishi Pajero) sampling regimes

All samples were stored in the dark below 0°C until preparation. Additionally, diesel samples were taken from all engines and oil samples were taken from the VM 292 engine.

### 3.2 Sample Preparation

The method of sample preparation basically followed the U.S. EPA methods 3630C and 3540C.

### 3.3 Soxhlet extraction

The glass microfibre filters were extracted for 24 h in a cellulose extraction thimble with 200 ml of dichloromethane. After adding 10 ml of cyclohexane, the extract was evaporated down to 2 ml and made up to 5 ml using cyclohexane in order to exchange the solvent.

### 3.4 Silica gel cleanup

A column of 33 cm height and 1.0 cm diameter with silica gel of size 0.05-0.1 mm was used. Before use, the silica gel was washed with acetone and chloroform and dried for at least one day in a glass tray. A column height of between 15 – 23 cm was used. The column was pre-eluted with a ca. 30 ml of a dichloromethane/ cyclohexane mixture, and then 2 ml of the soxhlet extraction sample were poured onto the column and eluted with 20 ml of cyclohexane. This procedure separates the PAHs from lower molecular weight aliphatic compounds. Then the column was eluted with 20 ml of a 1:3 mixture of dichloromethane/cyclohexane. Finally the PAHs were eluted from the column using 20ml dichloromethane. The flow rate was kept below 2 ml/min. The eluates were concentrated on the rotary evaporator to a final volume of 5 ml. The third elution was assumed to contain the largest proportion of polycyclic aromatic hydrocarbons. Nevertheless it is believed, that some compounds may have been retained on the silica column and therefore the soxhlet extract was also analyzed.

### **3.5 Sample Analysis**

The gas chromatograph, a Fisons Trio 100 GC/MS was run in the splitless mode, initial temperature 30°C, hold 3 min., the temperature was then increased at 5°C min<sup>-1</sup> to a final temperature of 320°C. The temperature was held at this point for 10 min.; the injector temperature was 300°C, column head pressure 135 kPa, interface temperature 250°C. The column used was a HP 5 MS crosslinked 5.5% Phenyl Methyl Siloxane 30m x 0.25 mm x 0.25 µm. Because the splitless mode can lead to early contamination, four different compounds (benzidine, pentachlorophenol, DFTTP, 4,4-DDT), described in a method AN 9157 of Thermo Finnigan, have been used to observe the status of the column. No significant changes were observed. In addition, a regular sensitivity test secured the ability of the mass spectrometer to detect trace compounds.

The samples (1 µl) were injected with the internal standards acenaphthene D<sub>10</sub> and p-terphenyl D<sub>14</sub>. A standard solution containing all 16 U.S. EPA priority PAHs and 14 different alkanes obtained from Chromspec Distributors Ltd was used for calibration (Table 2, appendix). With the help of these internal and external standards, it was possible to identify and to quantify the PAHs. Because other compounds were of interest, we endeavored to identify as many of the compounds present in the sample as possible. The NIST library of compounds associated with the mass spectrometer suggested the most likely compounds on the basis of the observed mass spectrum. These results could then be compared with the known or expected retention time of the compound in question and with the probability of these compounds being present in the sample. Not all of the peaks could be identified reliably and therefore only the most likely results are presented.

## **4. RESULTS**

Figure 3 shows a gas chromatogram of a sample before column chromatography was used to separate these compounds. The vertical scale is detector response and the horizontal scale is time in seconds. The largest peak corresponds to the internal standard.

The column chromatography that the sample is subjected to separates the compounds on the basis of their chemical properties. Highly polar compounds and PAH's are strongly attached to the silica gel whereas alkanes and alkenes are not strongly bound. Consequently the alkanes and alkenes are eluted from the column with the cyclohexane elution, more polar compounds are eluted during the second elution and the more strongly attached compounds are eluted with the methylene chloride. There are probably compounds still attached to the column after the methylene chloride elution but these have been ignored in this analysis. Addition of the deuterated internal standard to the sample after the soxhlet extraction procedure showed that 97% was recovered in the first elute, 1.5% was recovered in the second elute and finally  $2.3 \cdot 10^{-2}$  % was present in the third eluate.

Diesel fuel is an extremely complex mixture of organic compounds most of which contain between 10 and 25 carbon atoms (Andrews, Li et al. 2001). Many previous studies have shown that different PAHs are present, both in the diesel fuel and on the particulates emitted by the engines (Dorie, Bagley et al. 1987; Pointet, Milliet et al. 1997). A major source of organic compounds on the particulates is the unburnt diesel fuel. Thus it is important to identify the PAHs present in the fuel. The following

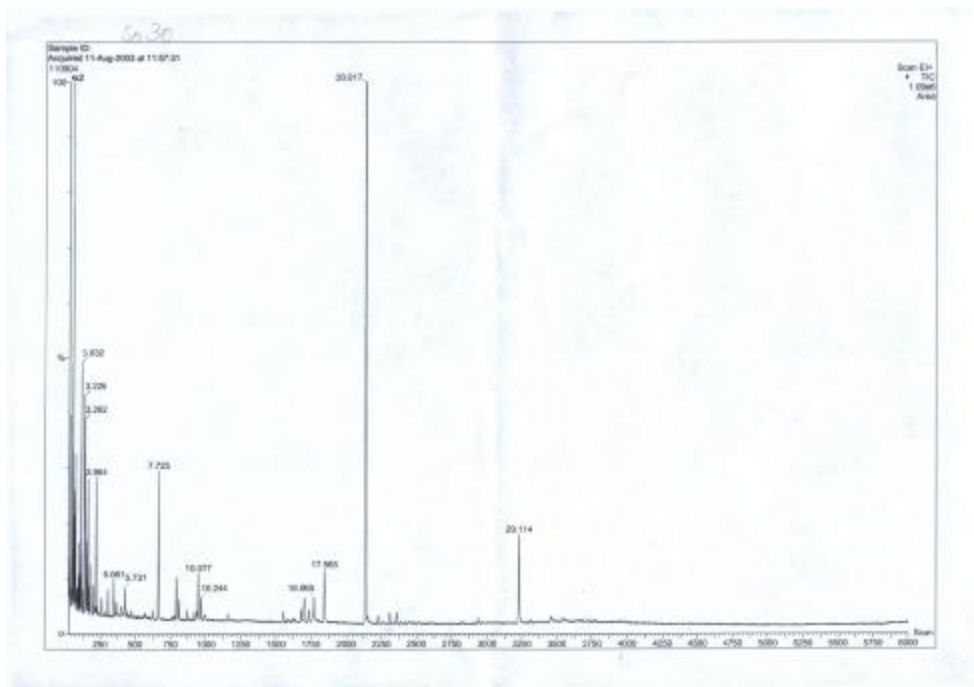


Figure 3: Gas chromatogram of a diesel exhaust sample immediately following Soxhlet extraction. The large peak at 20.0 minutes represents the internal standard.

PAHs were detected in the fuel used in these experiments: naphthalene (at very low concentrations), a number of different methylnaphthalenes and dimethylnaphthalenes, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, and chrysene. There are probably other PAHs present in the fuel, e.g. methylphenanthrenes but these have not been specifically identified nor quantified in the fuel samples. Because of their long retention times under the conditions of the experiment, benzo[ghi]perylene and indeno[1,2,3-cd]pyrene were not detected. The PAH components of the diesel found in this study are very similar to the average composition of five diesel fuel samples collected in 1997 in California with the exception that benzo[ghi]perylene was also detected in Californian diesel (Marr, Kirchstetter et al. 1999).

The compounds identified were somewhat dependent on the engine operating conditions. A selected list of the compounds found in the samples is given in Table 3 (Appendix). With the VM 292 engine idling, examination of the solution following the soxhlet extraction showed that the PAHs fluoranthene, fluorene, anthracene and chrysene were present. The concentrations in the extract were 12.7 µg/ml for phenanthrene, 27.2 µg/ml for fluorene, 32.5 µg/ml for fluoranthene and 30.5 µg/ml for acenaphthylene. Instrumental difficulties have not yet allowed analysis of the Nissan and Mitsubishi diesel exhausts for PAHs using the mass spectrometer. Nevertheless chromatograms of these samples have indicated that PAHs are present in significant amounts.

The following compounds were found in the extracts of all engine exhausts under all conditions: alkanes with carbon number up to C<sub>24</sub>, cyclohexane, methylbenzene, p-xylene, thiophenes, benzoic acid and phthalate esters whereas benzaldehyde and benzenemethanol occurred only with the VM 292 exhaust (Table 3). Between 1000 and 2000 rpm phenols and esters of phthalic acid were observed for the VM292 engine. Large amounts of alkanes and cyclohexanes were found in the exhaust at engine start-up. 3-amino-1,4-dimethyl-5H-pyrido[4,3-b]indole was present in samples from the run at 1500 rpm. This compound is a known carcinogen and has previously been identified in diesel exhausts (Manabe, Izumikawa et al. 1991). At 2500 rpm a compound, N-cyclohexyl-3,3,5-trimethyl-cyclohexylamine, which is used as a fuel additive, was identified. With this engine it was possible to analyse the oil vapour and the compounds 2-ethylpiperidine, 4,7-dimethyl-3-(2H)benzofuranone, acenaphthene, benzaldehyde, 1,6-, 2,3- and 1,8-dimethylnaphthalenes, 2-methylnaphthalene, tetrachloroethylene and phenanthrene were detected.

Toluene and dimethylbenzenes were not found at 1000 rpm in both Nissan and Mitsubishi engine exhausts; 5-hexenyloxirane was found in the Nissan exhaust at 1000 and 3000 rpm both at half load. Low molecular weight aromatic compounds were found in the exhaust from the Mitsubishi engine at 3000 rpm. The Nissan engine also formed these aromatic compounds at 1000 rpm but at 3000 and 4000 rpm this engine formed aromatic compounds with high molecular weights. Alkyls and (saturated carbonyls) appear more intensively with higher speed.

## **5. DISCUSSION**

There are four possible explanations for the presence of a particular compound in diesel exhaust. 1. The compound was present in the diesel fuel and survived the combustion process. 2. The compound is formed by partial combustion of the fuel followed by pyrosynthetic reactions in the combustion chamber. 3. The compound was present in the lubricating oil and is volatilised in the exhaust gas stream. 4. The compound originates from engine or exhaust system deposits. All four explanations have received experimental support (Scheepers and Bos 1992). It has been suggested that the consumption of engine oil is a significant factor governing PAH emissions from cars in ordinary city service (Handa, Yamamura et al. 1979; Zinbo, Hunter et al. 1989). Using a radioactive tracer technique, Mayer et al. determined that 1.5-25% of the particulate matter in diesel exhaust (depending on speed and load) was derived from engine oil (Mayer, Lechman et al. 1980).

In a previous study we found that the PAHs included in the US EPA's list of priority pollutants were present on the particles emitted by diesel engines and that the amounts of these compounds were dependent on the engine operating conditions (Bachmann, Gong et al. 2002). We have expanded that study in order to identify other compounds that are present on the particles. In particular we were interested in identifying any oxygenated compounds and nitro-substituted compounds as these could have increased carcinogenic and mutagenic properties. The oxygenated compounds may include carboxylate, hydroxy, dihydroxy, aldehyde, carboxaldehyde, ketone, and acetoxy functional groups. These compounds if not present in the fuel would arise from the partial oxidation of components in the fuel. The nitro-substituted derivatives could arise from the reaction of the organic compound with either HNO<sub>3</sub> (nitric acid), NO or NO<sub>2</sub>.



Some compounds in the exhaust extracts, such as N-cyclohexyl-3,3,5-trimethylcyclohexylamine and chloroacetophenone are used as fuel additives. These compounds have not been identified in the fuel used, but we consider that they are likely to be present. Oxygenated compounds on the emitted particles contain carboxylate, hydroxy, ester, aldehyde, and ketone functional groups. These would most likely be formed in the combustion process. Compounds containing nitro-functional groups have not yet been identified. Besides the PAHs, other carcinogenic substances and substances that act as irritants (alkanes) and inducing or exacerbating agents of asthma (e.g. oxirane), have been identified. A nitrogen containing carcinogenic compound with a surprisingly elaborate structure, 3-amino-1,4-dimethyl-5H-pyrido[4,3-b]indole, was identified. This compound has previously been reported to be a component of diesel exhausts.(Manabe, Izumikawa et al. 1991). Since New Zealand diesel has a high sulfur content, we looked for sulfur containing compounds. Thiophene and probably some substituted thiophenes have been identified as being present in the Nissan and Mitsubishi exhausts.

One surprising observation of this study was that naphthalene was not present in large amounts in neither the diesel nor the exhaust. Large amounts of methyl derivatives of naphthalene were found in the diesel, and were found in the exhaust, and these are known to break down to naphthalene during combustion. We suspect that naphthalene was not trapped in the filter because the temperature of the filter during collection resulted in the volatilisation of this and other low boiling-point compounds. Another surprising observation was the presence of tetrachloroethylene on the diesel exhaust particles. We have not observed this compound in the diesel and therefore assume that it is formed during the combustion process. Some chlorinated compounds are used as fuel additives but sea salt in the air is the probable source of most of the chlorine found. Chlorinated hydrocarbons are known to be resistant to combustion so that once formed this compound would be resistant to chemical change in the engine.

Most of the compounds we have identified from the extracted particles can be regarded as toxic. The actual toxicity of many of these compounds in humans is not known but the chemical nature of the molecules suggests that they will be harmful. The concentration of the compounds on the particles is very low but they could still be toxic at these levels. Carcinogenic compounds such as chrysene, anthracene, pyrene and 3-amino-1,4-dimethyl-5H-pyrido[4,3-b]indole are of particular concern and there may not be a concentration level below which they are not harmful. Mixtures of these compounds as found on the particles may be more harmful than the individual compounds.

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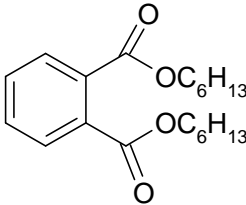
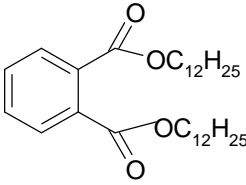
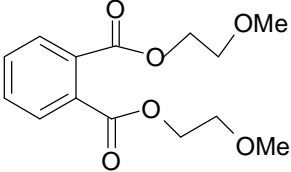
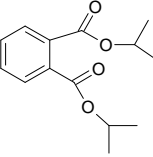
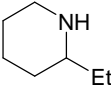
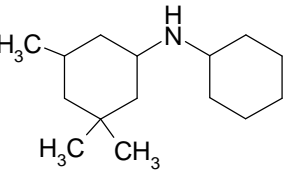
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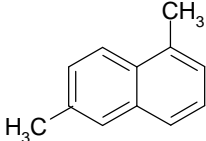
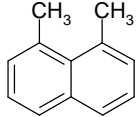
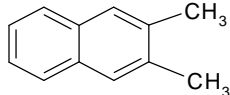
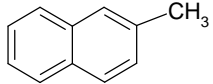
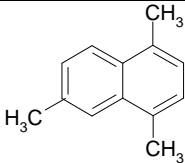
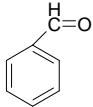
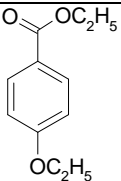
## APPENDIX

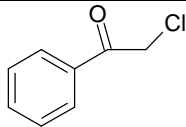
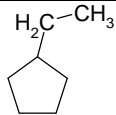
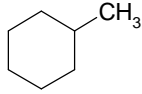
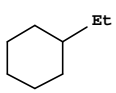
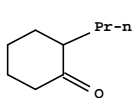
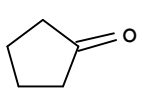
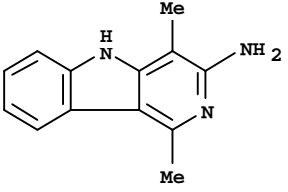
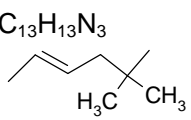
Table 2 List of standards used

Polycyclic Aromatic Hydrocarbons	Formula	n-Alkanes	Formula
Acenaphthene	C <sub>12</sub> H <sub>10</sub>	Decane	C <sub>10</sub> H <sub>22</sub>
Acenaphthylene	C <sub>12</sub> H <sub>8</sub>	Docosane	C <sub>22</sub> H <sub>46</sub>
Anthracene	C <sub>14</sub> H <sub>10</sub>	Dodecane	C <sub>12</sub> H <sub>26</sub>
Benzo[a]anthracene	C <sub>18</sub> H <sub>12</sub>	Eicosane	C <sub>20</sub> H <sub>42</sub>
Benzo[a]pyrene	C <sub>20</sub> H <sub>12</sub>	Hexacosane	C <sub>26</sub> H <sub>54</sub>
Benzo[b]fluoranthene	C <sub>20</sub> H <sub>12</sub>	Hexadecane	C <sub>16</sub> H <sub>34</sub>
Benzo[g,h,i]perylene	C <sub>20</sub> H <sub>12</sub>	Hexatriacontane	C <sub>36</sub> H <sub>74</sub>
Benzo[k]fluoranthene	C <sub>20</sub> H <sub>12</sub>	Nonane	C <sub>9</sub> H <sub>20</sub>
Chrysene	C <sub>18</sub> H <sub>12</sub>	Nonadecane	C <sub>19</sub> H <sub>40</sub>
Dibenzo[a,h]anthracene	C <sub>22</sub> H <sub>14</sub>	Octacosane	C <sub>28</sub> H <sub>58</sub>
Fluoranthene	C <sub>16</sub> H <sub>10</sub>	Octadecane	C <sub>18</sub> H <sub>38</sub>
Fluorene	C <sub>13</sub> H <sub>10</sub>	Tetracosane	C <sub>24</sub> H <sub>50</sub>
Indeno[1,2,3-D]pyrene	C <sub>22</sub> H <sub>12</sub>	Tetradecane	C <sub>14</sub> H <sub>30</sub>
2-Methylnaphthalene	C <sub>11</sub> H <sub>10</sub>	Triacontane	C <sub>30</sub> H <sub>62</sub>
Napthalene	C <sub>10</sub> H <sub>8</sub>		
Phenanthrene	C <sub>14</sub> H <sub>10</sub>		
Pyrene	C <sub>16</sub> H <sub>10</sub>		

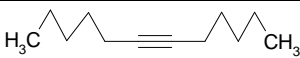
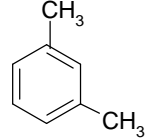

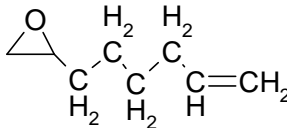

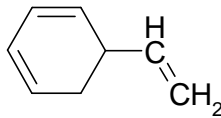
**Table 3**  
**Compounds identified as being present in diesel exhausts**  
**and/or oil vapour**


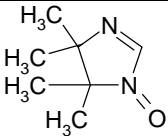
Compound	Formula &/or Structure	Occurrence	Comments
dihexylphthalate		VMDE NDE, MDE	Used as an engine lubricant. Phthalate esters are toxic.
didoceylphthalate		VMDE, NDE, MDE	
bis-(2-methoxyethyl) phthalate		VMDE, OV, NDE	
Bis(2-methylethyl)phthalate		MDE	
butyl-(2-methylpropyl) phthalate	C <sub>16</sub> H <sub>22</sub> O <sub>4</sub>	VMDE	
1-dotriacontanol	C <sub>32</sub> H <sub>66</sub> O	VMDE, O	
2-ethylpiperidine		OV, NDE, MDE	
N-cyclohexyl-3,5,5-trimethylcyclohexylamine		VMDE,	Cyclohexamines are used as fuel additives for preventing deterioration of fuel oils during storage, or cold flow improvers for crude oils

acenaphthene	$C_{12}H_{10}$	OV	May be harmful, irritant, toxicology not fully investigated
acenaphthylene	$C_{12}H_8$	VMDE	
anthracene	$C_{14}H_{10}$	VMDE	Possible tumor promotor, irritant
chrysene	$C_{18}H_{12}$	VMDE	Possibly carcinogenic
fluoranthene	$C_{16}H_{10}$	VMDE	carcinogenic in experimental animals
fluorene	$C_{13}H_{10}$	VMDE	
1,6-dimethylnaphthalene		D	
1,8-dimethylnaphthalene		OV, D	
2,3-dimethylnaphthalene		OV, D	
2-methylnaphthalene		OV, D	
phenanthrene	$C_{14}H_{10}$	VMDE,OV	
pyrene	$C_{16}H_{10}$	VMDE	
1,4,6-trimethylnaphthalene		D	
benzaldehyde		VMDE, OV	
benzene methanol	$HO-CH_2-Ph$	VMDE	Diesel fuel and oil additive
ethyl p-ethoxybenzoate		VMDE,OV, NDE, MDE	toxic

chloroacetophenone		VMDE	used as a stabilizer in diesel
ethylcyclopentane		NDE	
methylcyclohexane		MDE	
ethylcyclohexane		VMDE	
2-propyl-cyclohexanone		VMDE	2-cyclohexyl-oxetane fuel additive (Patino, Mendez et al. 2002)
cyclopentanone		VMDE	Lubricating oil additive (Oppenlaender, Mohr et al. 1995)
3-amino-1,4-dimethyl - 5H-pyrido[4,3-b]indole		VMDE	Carcinogenic (Manabe, Izumikawa et al. 1991)
4,4-dimethylpent-2-ene	$C_{13}H_{13}N_3$ 	MDE, NDE	
nonane	$C_9H_{20}$	VMDE,OV, MDE, NDE	
decane	$C_{10}H_{22}$	VMDE,OV, MDE, NDE	
undecane	$C_{11}H_{24}$	VMDE, OV, MDE, NDE	
dodecane	$C_{12}H_{26}$	VMDE, OV, MDE, NDE	
tetradecane	$C_{14}H_{30}$	VMDE,OV, MDE, NDE	
hexadecane	$C_{16}H_{34}$	VMDE,OV, MDE, NDE	
octadecane	$C_{18}H_{38}$	VMDE,OV, MDE, NDE, O	



nonadecane	$C_{19}H_{40}$	VMDE,OV, MDE, NDE	
eicosane	$C_{20}H_{42}$	VMDE,OV, MDE, NDE	
docosane	$C_{22}H_{46}$	VMDE,OV, MDE, NDE	
tetracosane	$C_{24}H_{50}$	VMDE,OV	
tetracontane	$C_{40}H_{82}$	VMDE,OV	
6-dodecyne		OV, NDE	
pentene	$C_5H_{10}$	OV	
1,3-dimethylbenzene		VMDE, NDE, MDE	toxic
Oxirane	 $C_2H_4O$	OV	Induces or exacerbates asthma, air pollutant (Leikauf 2002; Tanaka, 2002)
5-hexenyloxirane		NDE	
p-xylene		VMDE, NDE, MDE	Has been reported to occur in diesel exhaust (Westerholm, Almen et al. 1991), toxic
Styrene		VMDE	Has been reported to occur in diesel exhaust (Nelson 1989)
Tetrachlorethylene	$Cl_2C=CCl_2$	OV, NDE, MDE	Causes asthma

Toluene	C <sub>7</sub> H <sub>8</sub>	NDE, MDE D,	
Thiophene		NDE, MDE	changes the function of liver, nervous system, and cardiovascular system
tetramethylimidazoline 3-oxide		NDE, MDE	

VMDE: identified in the four-cylinder VM 292 diesel engine exhaust

NDE: identified in the Nissan diesel exhaust

MDE: identified in the Mitsubishi diesel exhaust

D: identified in Diesel

OV: identified in Oil vapour from VM 292 diesel engine

O: identified in engine Oil