Vehicle Pollutant Formation & Adverse Health Implications

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Vehicle Pollutant Formation & Adverse Health Implications

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1 Introduction to Combustion

As a means to explain the formation of pollutants within an internal combustion engine, the following sections outline the operation of internal combustion engines, as used in surface vehicles, and briefly describes the salient points of combustion chemistry. In this current work, an assessment of engine-out emissions is given, that is without any form of after treatment. After treatments will be discussed at a later date.

1.1 The Internal Combustion Engine

Most people will be familiar with the concept of an internal combustion engine. For surface vehicles, two principal types exist, namely the positive or spark ignition engine and the compression ignition. The physical design of these engine types is governed by the fuel type used, either petrol or diesel respectively, and the method of initiating combustion \cite{4, 10, 12, 20}.

By way of introduction to pollutant formation within an internal combustion engine, it is useful to consider the combustion process within the cylinders of the engine. For most automotive applications, a reciprocating engine is employed. The combustion chamber is formed using a piston moving within a cylinder and a cylinder head. The reciprocating movement of the piston is converted to rotational motion via the connecting rod and crank shaft.

Four processes are involved in the production of a net power output from the engine, hence the term four-stroke engine, namely induction, compression, expansion and exhaust.

1.1.1 Spark Ignition Operation

In spark ignition (SI) operation, a mixture of fuel and air are induced into the engine cylinder \cite{12}. For many years, the correct mixture of fuel and air was controlled almost exclusively by a carburettor. This system worked on the very simple principle of a pressure difference, allowing for flow of fuel into the intake air stream. It was hoped that a homogeneous air-fuel mixture would be created. Very often, such mixtures were stoichiometric or slightly rich, depending on the required power output.

In more recent years, the not so accurate fuel metering system of the carburettor has been replaced by electronic fuel metering systems \cite{20}. For the most part, only smaller spark ignition engines, such as those used in lawnmowers or small electrical generators still use a carburetted system. Within the more modern systems, fuel is usually injected through individual injectors located close to the inlet port of the cylinder. Alternatively, fuel may be introduced through a single injector located close to the throt-
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Figure 2: Sequence of events in four-stroke spark-ignition engine operating cycles. Each of cylinder pressure \( p \), cylinder volume \( V_{\text{max}} \) and mass fraction burned \( x_b \) are plotted against crank angle \( ^\circ \text{CA} \). Taken from Heywood [12].

The events that occur in the cylinder of a spark ignition engine may be illustrated as shown in Figure 2. Here, several variables – such as pressure, cylinder volume and mass fraction burned – are plotted against crank angle. Crank angle tends to be a useful independent variable to consider since many of the processes within the cylinder will occupy a constant crank angle interval which is almost independent of engine speed [12].

Consider valve timing for a typical automotive engine. In order to ensure high mixture flow rates, even at high engine speed – which in turn ensures high power outputs – the inlet valve will open before the cylinder reaches top dead centre (TDC) and will close some time after bottom dead centre (BDC). Within the cylinder, the new induced fuel and air will mix with the residual gas from the previous combustion process. After the inlet valve has closed, the contents of the cylinder are compressed to above atmospheric pressure and temperature. During this process a small amount of heat is transferred to the piston, the cylinder head and the cylinder walls but the overall effect on the unburned mixture is negligible [12].

Between 10°CA and 40°CA before TDC, an electrical discharge across the spark plug initiates the combustion process. A turbulent flame develops from this point and propagates across the mixture of compressed fuel, air and residual gas until it is extinguished at cylinder wall [12]. While the length of time for this process to occur will vary with engine speed, it is typically of the order of between 40°CA and 60°CA. During this combustion process, the pressure and temperature of the gases in the cylinder rise dramatically [12]. It is this rise in pressure and temperature that causes work to be done on the piston.

For a given mass of fuel and air within the cylinder, there is an optimal spark timing that results in a maximum torque output. By advancing or retarding the spark timing, the power output can be considerably lower. This so-called maximum brake torque (MBT) timing is an empirically determined compromise between starting combustion too early in the compression stroke – when work transfer is to the gases – and completing combustion too late in the expansion stroke – thus lowering the peak pressures achieved during expansion [12].

From Figure 2, it can be seen that the exhaust valve begins to open approximately two thirds of the way through the expansion stroke. Since the pressure in the cylinder is higher than that of the exhaust manifold, a blow down process occurs [12]. The burned gases flow through the valve and into the exhaust manifold until the cylinder and manifold pressures are equal. Clearly, the duration of such a process will depend on the relative difference between cylinder pressure and exhaust manifold pressure. The subsequent movement of the piston toward TDC then displaces the majority of the remaining gases. The exhaust valve opens before the end of the exhaust stroke to ensure that the blow down process does not last too long in the exhaust stroke. Again, the timing is a compromise which balances reduced work transfer to the piston before BDC against reduced work transfer to the cylinder after BDC [12].

The exhaust valve will remain open until just after the piston reaches TDC and the intake valve will open just before TDC, as described in Figure 2. In order to avoid excessive noise or wear, the valves are opened and closed slowly. In order to ensure that the valves are fully open when piston velocities are at their highest – at high engine speeds – the valve periods often overlap.

1.1.2 Compression Ignition Operation

Unlike the spark ignition system, in the compression ignition or diesel engine, air alone is taken into the cylinder during the intake stroke. The fuel is then injected directly into the cylinder, just before the combustion process is required to take place. Load is controlled by varying the volume of fuel injected into the cylinder for each cycle. Thus, air flow at a
given engine speed remains largely unchanged [12].

There is a wide variety of compression ignition engines, ranging from small automotive types to very large marine or power production engines. Depending on the application, it may be advantageous to use either a naturally aspirated system, whereby atmospheric air is induced, or, for higher power applications, to use turbo- or super-charging. In the turbocharged arrangement, air is compressed by a turbine-compressor arrangement which is powered by flow of hot exhaust gases. In the supercharged system, the air is compressed by means of a mechanically operated pump or blower [12]. In each case, power output is increased over the naturally aspirated system by increasing the mass flow per unit displaced volume. This in turn allows for a greater flow of fuel into the cylinder [12]. Although such systems were usually employed in larger engines, so that the size and weight of the engine can be reduced while still achieving the power output of a larger engine, it has become normal for smaller automotive engines to be turbo- or super-charged.

As before, it is possible to describe the operation of a diesel engine by examining a variety of parameters plotted against crank angle. For the most part, the process is very similar to that of spark ignition. Air at close to atmospheric pressure is inducted into the cylinder during the intake stroke. The air is then compressed to about 4 MPa and reaches a temperature of about 800 K. At approximately 20° before TDC, fuel is injected into the cylinder.

The liquid fuel is injected at high pressure through a series of small orifices in the injector tip, thus atomising the fuel into droplets that disperse throughout the cylinder and entrain the air. Evaporation of the liquid fuel drops means that fuel vapour mixes with the air to form a combustible mixture. The high pressure and temperature of the air are above the fuel’s ignition point so after a short delay period, parts of the non-uniform fuel and air mixture spontaneously ignite. This autoignition causes the combustion of most of the remaining material and the cylinder pressure rises above that of a non-firing engine [12]. The flame spreads rapidly through the portion of the charge that is sufficiently mixed for combustion to take place. At the same time, the rapid increase in temperature causes further evaporation of the still liquid fuel and so shortens the time taken for the fuel to evaporate. The processes of atomisation, vaporisation, mixing of fuel and air and combustion continue throughout the combustion and expansion processes. As described previously, the exhaust valve will open to allow for escape of the burned gas due to the pressure differential. The remaining gas is forced out by the piston, with some small amount of gas remaining in the cylinder. The process can now begin again.

This very brief summary should indicate that the process of diesel combustion is quite complex. Successful combustion will depend on the characteristics of the fuel, the design of the combustion chamber and the fuel injection system. Since the fuel is sprayed into the cylinder containing high pressure air, it is necessary for the injection system to exert high pressures on the fuel itself. The diesel fuel injection system consists of a number of parts, including an injection pump, delivery pipes and fuel injector nozzles. The method of fuel delivery will vary depending on the application and the size of the engine [12].

A number of important consequences of the combustion process on engine operation should be highlighted [12]:

1. There is no knock limit in a compression ignition engine as there is in a spark ignition engine, since the fuel is injected just before the combustion process is to begin and the combustion process depends on the autoignition of the fuel. Thus, compression ratios can be significantly higher in compression ignition engines, usually in the range of 12 to 24. This results in better fuel conversion rates over spark ignition engines.

2. The injection timing of the fuel is used to control the combustion timing. As a result, the delay period – the time between injection of the fuel and combustion initiation – must be kept short and reproducible. A short delay is also needed to ensure that the maximum cylinder gas pressure remains below the maximum pressure that the cylinder can tolerate. The spontaneous ignition characteristics of the fuel must therefore be controlled and held within a specified range. This tendency to autoignite is measured by the cetane number of the fuel.

3. The torque output of the engine is controlled by varying the amount of fuel injected into the cylinder each cycle. Thus the amount of air induced each cycle is essentially unchanged and there is no need for throttling of the air intake. Since there are therefore reduced pumping losses, the part load efficiency of a compression ignition engine, relative to a spark ignition engine, is improved.

4. As the quantity of fuel injected per cycle increases, there can be problems with air utilisation, resulting in the formation of excessive...
amounts of soot. The soot or black smoke in the exhaust constrains the fuel:air ratio at maximum power to values 20% or more lean of stoichiometric. As a result, the indicated mean effective pressure of a naturally aspirated diesel engine will be lower than the values obtained for a corresponding spark ignition engine.

5. Compression ignition engines always operate with lean fuel:air ratios, which may be very lean at part load. This means that the effective value for $\gamma$ – the ratio of the specific heat at constant pressure to the specific heat at constant volume ($\gamma = \frac{C_p}{C_v}$) – is higher over the expansion process than for a spark ignition engine. As a consequence, the compression ignition engine offers higher fuel conversion efficiency rates than spark ignition engines for a given expansion ratio.

The principal problem in diesel combustion chamber design is ensuring that there is sufficiently rapid mixing of the injected fuel and the air in the cylinder in order to have complete combustion within a relatively short crank angle interval. The mixing rates will in fact control the burning rate [12]. Commercial diesel engines are available in a variety of sizes with cylinder bore varying from 70 mm to approximately 900 mm [12]. The mean piston speed at maximum rated power is approximately constant over this size range. So, since

$$\bar{S}_p = 2LN \quad (1)$$

where $\bar{S}_p$ is the mean piston speed, $L$ is the stroke and $N$ is the engine rotational speed, it follows that maximum rated engine speed will be inversely proportional to the stroke:

$$N = \frac{\bar{S}_p}{2L} \quad (2)$$

$$N \propto \frac{1}{L} \quad (3)$$

So, for a fixed crank angle interval for combustion – which is typically in the range 40°CA to 50°CA to maintain high fuel conversion efficiency rates – the time which is available for combustion will scale with the stroke. Therefore, for smaller sized engines, the mixing of the fuel and air must take place on a time scale some ten times shorter than larger sized ones [12]. In order to achieve this more rapid mixing, considerable work has been done in the areas of cylinder design, port positioning and design and fuel injection system development to ensure that the required motion of fuel and air exists so that the desired mixing is achieved. As the engine size decreases, more vigorous mixing is required while jet penetration is not such a big issue. Consequently, significant variations in engine design exist over the range of engine types employed.

1.2 Combustion Chemistry

The formation of pollutants is not a simple process. Fuel composition, engine operation and engine design all play a major part in determining what species are formed. Thus, it should be clear from this brief outline of the principal combustion systems that both diesel and petrol engines will exhibit different pollutant species. This idea is further strengthened on examination of the chemistry of combustion.

*Combustion* of a hydrocarbon fuel is a chemical process whereby the carbon and hydrogen in the fuel are oxidised, resulting in the formation of certain chemical products and heat [26]. This heat is then used as the means to achieve the increase in temperature and pressure required for a net work output from the engine.

Consider a general combustion equation of the form, where the fuel, $C_aH_b$ is oxidised using pure oxygen, $O_2$ under stoichiometric conditions:

$$C_aH_b + (a + \frac{b}{4})O_2 \rightarrow aCO_2 + (\frac{b}{2})H_2O \quad (4)$$

From the above equation, it should be noted that both carbon dioxide ($CO_2$) and water ($H_2O$) are the products of combustion and will occur as a result of every combustion process involving the oxidation of a hydrocarbon fuel.

However, combustion in an engine uses air rather than pure oxygen. There are many reasons for this. It is often difficult and costly to produce large quantities of oxygen and storage is extremely problematic due to the highly oxidising nature of oxygen. Since air is composed of 21% oxygen, with approximately 78% nitrogen and 1% other gases, this provides a ready source of oxygen; but use of air as an oxidising agent also introduces complications. The extra nitrogen must also be accounted for in the combustion equation. Thus, Equation 4 must be rewritten to include the nitrogen

$$C_aH_b + (a + \frac{b}{4})\left(O_2 + \frac{78}{21}N_2\right) \rightarrow aCO_2 + (\frac{b}{2})H_2O + \frac{78}{21}N_2 \quad (5)$$

As with Equation 4, Equation 5 describes the stoichiometric case. Thus, for each unit of fuel, the
precise number of units of air are present. However, as described above, each of petrol and diesel vehicles operate at different equivalence ratios. The equivalence ratio is a ratio of the actual ratio of fuel and air used in a combustion process to the stoichiometric fuel-air ratio. Mathematically:

$$\phi = \lambda^{-1} = \frac{F_{\text{actual}}}{F_{\text{stoichiometric}}}$$  

(6)

From this it should be clear that for $\phi = \lambda^{-1} = 1$, the combustion will be stoichiometric. For higher values of $\phi$, and consequently lower values of $\lambda$, the mixture will be rich, since there is a larger amount of air than is required for complete combustion. In the converse case, the mixture will be lean, since there is excess fuel.

For different values of the equivalence ratio, or indeed the relative air fuel ratio, $\lambda$, different pollutant species are formed. This concept is discussed more fully in later Sections. Thus, the chemical composition of the emissions from each vehicle type will differ.

For petrol vehicles, the equivalence ratio is close to 1, such that combustion is close to stoichiometric. This ensures that the three-way catalytic converter can operate at its maximum possible efficiency. If extra power is required, extra fuel may be injected into the cylinders, resulting in local rich pockets. In such areas, there is insufficient oxygen, either in molecular ($O_2$) or radical ($O^*$) form, to fully oxidise the carbon. This leads to the formation of carbon monoxide (CO). In the converse case, that is in lean, or fuel restricted cases, there is always sufficient oxygen for oxidation to occur. It also results in oxygen being found in the exhaust stream.

While the above discussion is valid for ideal conditions, there will always be some degree of variation in the chemical constituents of the exhaust stream. Thus, even if the vehicle engine is operating at lean conditions, trace amounts of carbon monoxide will be present. Similarly, oxygen may be present even if a rich mixture is being used. Also, despite the fact that nitrogen is an inert gas, the high temperature and pressures found in the cylinder can cause dissociation and allow the formation of other nitrous compounds. For diesel engines, the formation of particulate matter is also an issue due to the combustion process. Further details of emission production are covered in more detail in the following Sections.

Perhaps a generalised combustion equation of the form

$$\text{CH} + \text{O}_2 + \text{N}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{O}_2 + \text{N}_2 + \text{CO} + \text{NO}_x + \text{PM} + \text{HC}$$  

(7)

is a more accurate representation of combustion.

## 2 Pollutant Formation

In this Section, an examination of the principal formation paths of the by-products of combustion is presented. Although many thousands of species can be produced, four principal components are examined, namely carbon monoxide, oxides of nitrogen, unburned hydrocarbons and particulate matter.

### 2.1 Carbon Monoxide

Emissions of carbon monoxide (CO) are primarily governed by the relative air fuel ratio ($\lambda$) [12]. For rich mixtures, CO emissions rise with increasing equivalence ratio, whereas for lean mixtures, emissions show only a slight variation with equivalence ratio. Such variations are invariably very small, of the order of as little as $10^{-3}$ mole fraction [12].

Traditionally, or in the case of smaller engines, engine operation tended to be rich, due to the excess power that could be generated [12]. Today, there is a variety of reasons for engines to operate close to stoichiometric, mostly on account of emissions legislation and the need to operate the engine in such a way as the catalytic converter will operate satisfactorily. Hence, CO emissions can be an issue for petrol driven engines [12]. In the case of compression ignition systems, since combustion is always in the lean region, CO emissions tend to be low, as shown in Table 1, and are generally not considered to be terribly important in terms of overall ambient CO concentrations [12].

Carbon monoxide levels in a real exhaust stream tend to be lower than those levels measured within the combustion chamber. However, these levels are still considerably higher than equilibrium conditions would predict. This leads to the conclusion

### Table 1: Typical petrol and diesel exhaust gas composition for regulated harmful compounds. From Neeft et al. [18]

<table>
<thead>
<tr>
<th>Compound</th>
<th>Diesel (%)</th>
<th>Petrol (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO (%-vol)</td>
<td>0.01 – 0.1</td>
<td>0.1 - 6</td>
</tr>
<tr>
<td>HC (%-vol)</td>
<td>0.005 – 0.05</td>
<td>0.5 - 1</td>
</tr>
<tr>
<td>NOx (%-vol)</td>
<td>0.003 – 0.06</td>
<td>0.04 - 0.4</td>
</tr>
<tr>
<td>PM (mg m$^{-3}$)</td>
<td>20 – 200</td>
<td>1 - 10</td>
</tr>
</tbody>
</table>
that CO levels within the exhaust are governed by kinetics \[12\].

The formation of CO is one of the principal reactions in the combustion of a hydrocarbon fuel. This reaction process may be described by:

\[
RH \rightarrow R \rightarrow RO_2 \rightarrow RCHO \rightarrow RCO \rightarrow CO \tag{8}
\]

where R is a hydrocarbon radical. The CO produced in this manner is oxidised to carbon dioxide (CO\(_2\)) at a slower rate. This process may be given as an equilibrium equation:

\[
CO + OH \rightleftharpoons CO_2 + H \tag{9}
\]

It is widely assumed that for a spark ignition engine, the post-flame combustion products, composed of a carbon-oxygen-hydrogen complex, are in equilibrium at the prevailing peak conditions, typically in the region of 2,800 K, with pressures between 15 and 40 atmospheres \[12\]. As a result, it can be assumed that within the immediate post-flame burned gases, the CO concentrations are close to equilibrium. However, as the gases cool during the expansion and exhaust processes, or if quenching to below 1,700 K occurs \[11\], the chemical equilibrium described in Equation 9 no longer holds true. Thus, the forward reaction will not take place, resulting in local increases in CO concentration.

Alternatively, it is possible to produce carbon monoxide through quenching of:

\[
CO + H_2O \rightarrow CO_2 + H_2 \tag{10}
\]
at temperatures of about 1,700 K or less \[10\].

Under ideal lean conditions, as has been outlined above, carbon monoxide emissions should be nil \[10\] since there should be sufficient oxygen to allow for complete oxidation of the carbon to carbon dioxide. However, there are still traces of CO even under these conditions, of the order of 1,000 ppm to 3,000 ppm \[10\]. This is due to a number of secondary effects. Firstly, there can be a non-homogeneous mixture of fuel and air within the cylinder or even between cylinders \[10\] resulting in rich pockets being formed, causing CO formation. Additionally, there can be partial oxidation of hydrocarbons within the exhaust stream. As a result of this, it is interesting to point out that spark ignition engines, operating at stoichiometric and burning conventional petrol, can have much higher carbon monoxide emissions than diesel ones, even after catalytic conversion \[10\].

Despite the volume of work being carried out on pollutant emissions, there are still very many questions that remain about the exact mechanisms of CO formation and oxidation. Even with this ambiguity, it seems reasonable to suggest that for practical purposes, CO emissions may be regulated by modifications to the air-fuel ratio \[12\]. The level of carbon monoxide emissions is also dependent on the carbon content of the fuel itself \[10\]. Table 2 shows the carbon monoxide levels that may be expected from various fuels, based on their carbon content. It is possible to reduce the carbon monoxide emissions by use of oxygenated fuels such as alcohols. While this may have a beneficial result in terms of reducing emissions due to lower equivalence rations, it increases the likelihood of carbonyl group emissions.

**Table 2:** The effect of fuel composition on CO levels in the exhaust gas at \(\phi = 1.1\) at thermodynamic equilibrium and with quenching at 1,700 K. Taken from Guibet \[10\].

<table>
<thead>
<tr>
<th>Type of Fuel</th>
<th>Carbon Content (%)</th>
<th>Exhaust CO Content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_4)</td>
<td>75</td>
<td>2.2</td>
</tr>
<tr>
<td>(CH(_2))(_n)</td>
<td>83</td>
<td>2.7</td>
</tr>
<tr>
<td>C(<em>8)H(</em>{16})</td>
<td>84.2</td>
<td>2.8</td>
</tr>
<tr>
<td>(CH(_2))(_n)</td>
<td>85.7</td>
<td>2.9</td>
</tr>
<tr>
<td>(CH(_3))(_n)</td>
<td>87.3</td>
<td>3.0</td>
</tr>
<tr>
<td>(CH(_3)OH)(_n)</td>
<td>88.2</td>
<td>3.1</td>
</tr>
<tr>
<td>C(_6)H(_6)</td>
<td>92.3</td>
<td>3.5</td>
</tr>
</tbody>
</table>

Advances in engine technology, many being spurred on by ever more stringent emissions legislation, allow for greater control of fuel and air mixing, ensuring an homogeneous mixture entering the cylinders. This is an issue in multi-cylinder engines, which ac-
counts for the vast majority of motor vehicles on our roads, since variations in the fuel-air ratio in one cylinder compared to another can cause excessive CO emissions. Cold start is of major concern, since richer mixtures are used to ensure combustion and to promote heating of the engine and its ancillary components [12]. Similarly, transient engine operation, such as hard acceleration and deceleration, are known to adversely affect fuel consumption and lead to higher emissions, including CO, due to the over-rich mixtures employed to cope with the surge in power demanded. Modern engine management systems are being improved all the time to cope with these concerns.

2.2 Oxides of Nitrogen

Although multiple oxides of nitrogen exist, nitrogen monoxide (NO) is the principal nitrogen compound formed within the cylinder. This is then further oxidised to nitrogen dioxide (NO₂) both in the exhaust system and in the atmosphere. Chemical equilibrium is reached when the concentration ratio of nitrogen dioxide to nitrogen monoxide reaches a value of approximately 0.1 or 0.2 [10]. A third species, nitrous oxide (N₂O) can also be formed through the catalytic treatment of the exhaust gas.

It is the oxygen and nitrogen in the air that are the principal contributors to nitrogen monoxide formation. Under normal conditions, nitrogen is an inert gas, but the high temperatures within the combustion zone can cause it to react chemically. Figure 4 shows the NO formation rate as a function of gas temperature and fuel-air equivalence ratio in the postflame gases within the cylinder. It is clear that both the high temperatures and the presence of excess oxygen are contributing factors to NO formation.

The reactions involved can occur at both a molecular and an atomic level. The Zeldovich mechanism is often used to describe NO formation [10, 12]:

\[
\begin{align*}
N₂ + O & \rightleftharpoons N + NO \quad (11) \\
N + O₂ & \rightleftharpoons NO + O \quad (12) \\
N + OH & \rightleftharpoons NO + H \quad (13)
\end{align*}
\]

This is described as the extended Zeldovich mechanism, since the first two steps were proposed by Zeldovich and the last step was proposed by Lavoie et al. [12]. It has been found to be a significant contributor to NO formation.

Nitrogen sources within the fuel are also known to contribute to the formation of NO but the mechanisms are still not fully understood [12]. In distillate fuels, the nitrogen can exist as amines and ring compounds such as pyridine, quinoline and carbazoles. During the combustion process, it is possible for these compounds to undergo thermal decomposition before reaching the combustion zone. Thus, the precursors to NO formation will be low molecular weight nitrogen compounds such as NH₃, HCN and CN. The detailed kinetics for these compounds are limited [12].

While chemical equilibrium considerations would indicate that the concentration ratio of nitrogen dioxide to nitrogen monoxide should be negligibly small, this tends to occur only for spark ignition engine [12]. Diesel engines, on the other hand, can exhibit NO₂ concentrations corresponding to as much as 10% to 30% of the total exhaust emissions of NOₓ.

A plausible mechanism to account for this level of NO₂ is the following. NO is formed in the flame zone and can be rapidly converted to NO₂ by mechanisms such as

\[
\text{NO} + \text{HO}_₂ \rightleftharpoons \text{NO}_₂ + \text{OH} \quad (14)
\]

this NO₂ is then converted to NO via

\[
\text{NO}_₂ + O \rightleftharpoons \text{NO} + O₂ \quad (15)
\]

unless the NO₂ formed is quenched by the cooler fluid. Such an explanation is consistent with the highest [NO₂]:[NO] ratio occurring at light load in diesels, where quenching of the conversion back to NO is widespread. For petrol engines, it has been found that the maximum value for [NO₂]:[NO] is 2% at an equivalence ratio of 0.85. For diesel engines,
this ratio is much higher and is highest at light load. It is also heavily dependent on engine speed [12].

2.3 Unburned Hydrocarbons

The emission of unburned hydrocarbons is caused by the incomplete combustion of a hydrocarbon fuel in the cylinder of an engine. However, the term unburned hydrocarbon is often used to describe any form of hydrocarbon emission. The actual emissions are normally composed of hydrocarbon by-products, produced through the combustion process, or fuel compounds that have not undergone any reaction [10]. The level of unburned hydrocarbon material in the exhaust stream is usually specified in terms of the total hydrocarbon emissions and is expressed in parts per million (ppm) carbon atoms (Cₙ). Engine exhaust gases tend to contain a wide variety of hydrocarbon compounds. The relative importance of the hydrocarbon species as a pollutant emission is normally determined by means of its reactivity. Certain hydrocarbons are unreactive and do not contribute in any major way to atmospheric chemical reactions. This is not to say, of course, that they are not harmful – but this will be discussed in greater detail later. There are also a wide variety of reactive species which actively take part in atmospheric reactions and can cause such phenomena as photochemical smog.

The composition of the fuel used in the combustion process will have a significant influence on the composition and relative magnitudes of the organic emissions from an engine. High levels of aromatic compounds or olefins will produce more reactive hydrocarbon emissions. Also, the processes of pyrolysis and further synthesis will allow for the inclusion of chemicals not initially in the fuel to be present in the exhaust gas sample.

Oxygenates are found in the exhaust stream and are known to contribute to the generation of photochemical smog [12]. They are also irritants and odourants. Oxygenates are usually categorised as carboxyls, phenols and noncarbonyls. The carboxyls of particular interest are aromatic ketones and low molecular weight aldehydes. These aldehydes are irritants to the eyes and the respiratory tract. Formaldehyde makes up approximately 20% of the total carbonyl concentration of the exhaust. This is of course dependent on the composition of the use being used. Carbonyls are emitted prominently from compression ignition engines, with approximately 10% of the total exhaust being carbonyl based. Emissions from spark ignition engines tend to be lower, of the order of just a few percent [12]. The phenols emitted are also odourants and irritants. The noncarbonyl fraction of the emissions from engines include such compounds as methanol, ethanol, nitromethane and methyl formate. As one would expect, oxygenate emissions will increase with increased alcohol blending [12]. This becomes an issue in terms of modern attempts to augment fuel reserves through alcohol blending or by using alcohol as a primary fuel.

Typical concentrations of unburned hydrocarbons from spark ignition engines tend to be in the region of 1000 ppm and 3000 ppm C₁. This corresponds to roughly 1% to 2 1/2% of the fuel flow into the cylinders. The emission of hydrocarbons rises rapidly as the mixture becomes too rich (φ < 1), since not all of the material can be consumed in the combustion process. At the same time, very lean mixtures φ > 1 also lead to hydrocarbon emissions, since there is insufficient fuel to allow combustion, resulting in incomplete combustion or misfire, and so the unreacted fuel is passed straight through to the atmosphere.

Four possible mechanisms exist that contribute to the formation of hydrocarbon emissions from spark ignition engines [10, 12].

To begin with (i) the flame may be quenched at the cylinder wall, leaving behind it a layer of unburned fuel adjacent to the wall. Also (ii) crevices may be filled with unburned air-fuel mixture, since quenching can also occur at the entrance to a crevice, such as at the joint between the cylinder and the cylinder head or between the piston and the cylinder wall. It is also possible for (iii) fuel vapour to be absorbed into the layer of oil on the cylinder during the intake and compression phases of the cycle and then for that same vapour to be desorbed during expansion and subsequent exhaust. Finally, (iv) the incomplete combustion of the fuel in a fraction of the engine’s operating cycles can contribute greatly to hydrocarbon emissions. This usually occurs when the quality of combustion is poor, due to engine transients, where air-fuel ratios, exhaust gas recirculation or spark timing may not be adequately controlled [12].

The overall composition of unburned hydrocarbons in diesel exhaust gas is significantly more complex than those found in petrol engines. A number of reasons exists for this. Fuel composition is different, with the hydrocarbons in diesel fuel showing higher molecular weights and boiling points. Also, significant pyrolysis of the fuel occurs within the fuel spray during combustion.

Figure 6 helps to illustrate how unburned hydro-
carbons may be produced via incomplete combustion. Two principal paths exist by which fuel can escape the normal combustion process and be released to the atmosphere. Fuel injected during the injection delay may mix with the air and produce local mixtures with a wide range of equivalence ratios. Certain pockets will have mixed rapidly to equivalence ratios lower than the lean limit of combustion, known as over leaning, and so autoignition will not occur. Alternatively, other pockets will be overly rich due to slower mixing of the fuel and air, causing under mixing, and so will not support combustion.

A third option, which also applies to spark ignition engines, is quenching and misfire. Hydrocarbon emissions of diesel engines have been shown to be sensitive to both oil and coolant temperatures. With the increase of these temperatures from 40°C to 90°C in direct injection diesel engines, hydrocarbon emissions were decreased by 30% [12]. With a constant ignition delay, the overmixing phenomena should remain approximately consistent. So, wall quenching of the propagating flame may also be a significant source of hydrocarbon emissions from diesel engines. This, of course, would depend on the degree to which the fuel spray impinged on the combustion chamber walls.

Cycle-to-cycle combustion variations tend to be lower in diesel than spark ignition engines. That said, under adverse conditions, such as low compression temperatures and pressures and retarded injection timings, substantial variations are thought to occur. If misfire occurs in a small number of operating cycles, the hydrocarbon emissions rise. In general, complete misfire in a well-designed and adequately controlled engine is unlikely to occur during normal operation [12].

Another serious problem is that of the evolution of polycyclic aromatic hydrocarbons. These are aromatic compounds that include between two and six benzene rings. Benzene has been found by the State of California to have carcinogenic properties [25]. Such chemicals are found in the exhaust stream of both petrol and diesel vehicles and, indeed, in similar quantities [10]. Depending on the molecular weight, different PAHs are found in different parts of the exhaust steam. Lighter ones, containing two or three rings, are found as gaseous by-products, where higher weight compounds, with between four and six rings are found in agglomerations of soot, as described in Section 2.4. As a result of this, many of the problems associated with PAHs can also be associated with diesel particulate matter, due to the inclusion of PAHs within the agglomerations. For diesel engines, the PAHs formed tend to be of the higher orders.

PAHs are formed through a dehydrogenation process, whereby vinyl radicals are converted to acetylene (C₂H₂). Acetylene is also an important factor in the formation of soot and particulate matter. This process may be described as:

$$\text{CH}_2 = \text{CH}^* \rightarrow \text{CH} \equiv \text{CH} + \text{H}^* \quad (16)$$

Further reactions between the acetylene and the CH≡C⁺ radical result in formation of aromatic precursors, such as

$$\text{CH} \equiv \text{C}^* + \text{CH} \equiv \text{CH} \rightarrow \text{CH} \equiv \text{C} - \text{CH} = \text{CH}^*$$

$$\rightarrow \text{CH} \equiv \text{C} - \text{CH} = \text{CH} - \text{CH} = \text{CH}^* \quad (17)$$

This ultimately leads to the formation of the phenyl radical following cyclisation.
2.4 Particulate Matter

Particulate matter is fast becoming one of the largest health concerns with regard to vehicular emissions. Particulates are primarily composed of combustion generated carbonaceous material, onto which organic compounds are adsorbed [12]. Respirable particulate matter is usually described as material with an aerodynamic diameter below about 10 µm, normally designated as PM$_{10}$ [8]. Smaller particulate matter also exists, and is usually categorised by aerodynamic diameters of less than 2.5 µm (PM$_{2.5}$) or smaller, normally referred to as ultrafine particles (PM$_{0.1}$ or UF).

Particulate matter is primarily produced through the incomplete combustion of a hydrocarbon fuel but lubricants can also be contributors to particulate emissions [10, 12]. Indeed, new research, using a hydrogen fuelled engine, suggests that at high loads and engine speeds, lubricants can be caused to form particulate matter in a fashion similar to the formations of ‘normal’ particulate matter [17]. Using the hydrogen fuelled engine, it was possible to suppose that no particulate matter was being produced through the direct combustion process but rather through some other means. Such emissions will vary greatly depending on the engine size and operating conditions. Similarly, the emission of such matter to the atmosphere will be greatly influenced by the exhaust and the presence or absence of particulate collection devices, such as filters or traps.

The physical morphology of the particulates is heavily influenced by the temperature. For temperatures above approximately 500 °C, the particles are composed mainly of clusters of many small carbon spherules with small associated hydrogen concentrations. Such spherules are of the order of between 10 nm and 80 nm but usually have an average diameter of 15 nm to 30 nm. For temperatures below 500 °C, the particles normally become coated with adsorbed or condensed hydrocarbon compounds of high molecular weight. Such compounds are normally oxygenated hydrocarbons and include, among other compounds, ketones, esters, ethers and organic acids. Certain inorganic compounds are also present, such as sulphur dioxide (SO$_2$), nitrogen dioxide (NO$_2$) and sulphuric acid (H$_2$SO$_4$). These primary spherules are then agglomerated into aggregates, or particles [18].

The following paragraphs will discuss, in more detail, the creation of particulate matter from the combustion process. Since the relative contribution of petrol engines to the overall concentrations of particulate matter is actually quite small, this present discussion will focus primarily on particulate matter emitted from diesel sources.

Soot particles are primarily formed from the carbon present in diesel fuels and formation of soot begins.
Table 3: Major polycyclic aromatic hydrocarbons present in engine exhaust streams. Adapted from Chen et al. [5] and Guibet [10]

<table>
<thead>
<tr>
<th>Product</th>
<th>Rings</th>
<th>Molecular weight (g mol$^{-1}$)</th>
<th>Relative Proportion</th>
<th>Carcinogen</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Minimal</td>
<td>Significant (3)</td>
</tr>
<tr>
<td>Naphtalene</td>
<td>2</td>
<td>128</td>
<td></td>
<td>*</td>
</tr>
<tr>
<td>Acenaphthylene</td>
<td>3</td>
<td>152</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>Flourene</td>
<td>3</td>
<td>165</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>3</td>
<td>178</td>
<td></td>
<td>*</td>
</tr>
<tr>
<td>Anthracene</td>
<td>3</td>
<td>178</td>
<td></td>
<td>*</td>
</tr>
<tr>
<td>Flouanthene</td>
<td>4</td>
<td>202</td>
<td></td>
<td>*</td>
</tr>
<tr>
<td>Pyrene</td>
<td>4</td>
<td>202</td>
<td></td>
<td>*</td>
</tr>
<tr>
<td>Benzo[a]anthracene</td>
<td>4</td>
<td>228</td>
<td></td>
<td>*</td>
</tr>
<tr>
<td>Chrysene</td>
<td>4</td>
<td>228</td>
<td></td>
<td>*</td>
</tr>
<tr>
<td>Benzo[b]fluoranthene</td>
<td>5</td>
<td>252</td>
<td></td>
<td>*</td>
</tr>
<tr>
<td>Benzo[k]fluoranthene</td>
<td>5</td>
<td>252</td>
<td></td>
<td>*</td>
</tr>
<tr>
<td>Benzo[e]pyrene</td>
<td>5</td>
<td>252</td>
<td></td>
<td>*</td>
</tr>
<tr>
<td>Benzo[a]pyrene</td>
<td>5</td>
<td>252</td>
<td></td>
<td>*</td>
</tr>
<tr>
<td>Indeno[1,2,3-cd]pyrene</td>
<td>5</td>
<td>276</td>
<td></td>
<td>*</td>
</tr>
<tr>
<td>Dibenzo[a, h]anthracene</td>
<td>5</td>
<td>278</td>
<td></td>
<td>*</td>
</tr>
<tr>
<td>Benzo[g, h, i]pyrene</td>
<td>6</td>
<td>276</td>
<td></td>
<td>*</td>
</tr>
<tr>
<td>Coronene</td>
<td>7</td>
<td>300</td>
<td></td>
<td>*</td>
</tr>
</tbody>
</table>

with carbon chains of between 12 and 22 atoms in length. High temperatures, combined with fuel rich reaction zones, ensure that particles develop around individual unburned fuel drops. Within the soot particle, the ratio of hydrogen to carbon is approximately 2. The final product of the soot formation process is a particle with a typical aerodynamic diameter of about $10^2$ nm. While much work has been done on examining the formation of soot in simple premixed and diffusion flames [12], the complex nature of diesel combustion makes it difficult to interpret how these simple rules apply to the high temperature, high pressure, turbulent, unsteady nature of combustion in a diesel cylinder.

Soot formation occurs at temperatures of between 1000 K and 2800 K and at pressures of approximately 50 atmospheres to 100 atmospheres. The principal cause is a local lack of oxygen to allow the carbon to fully oxidise. The resulting aerosol is usually described in terms of the total amount of the condensed phase present, denoted as the soot volume fraction, $F_v$, the number of soot particles per unit volume, $N$, and the particle size, described using an aerodynamic diameter, $d$.

Although all of the above parameters are mutually dependent, for simplicity, it is often easiest to consider the soot volume fraction and the number of soot particles, since each of these parameters relate to almost independent phases of soot and particulate formation.

During the formation stage, the first condensed phase material arises through either the oxidation or pyrolysis of the fuel [12]. This is a process in which gas-phase molecules form soot precursors molecules through free radical mechanisms. Two types of pyrolysis exist, one in an oxygen-free zone and the other in an oxygen rich zone [18]. Despite the different pyrolysis mechanisms, both processes result in the formation of aliphatic and aromatic fuel molecules to form acetylene and its analogues ($C_2H_2$) or polycyclic aromatic hydrocarbons (PAHs). Acetylene is considered to be a major soot precursor. Such initial particles tend to be small, generally less than 2 nm in diameter, and so the soot loading of the formation area is negligible from a soot volume fraction point of view.

In the nucleation stage, the soot precursors grow into small soot nuclei. This is perhaps a misleading term since the soot nuclei can already be considered to be large PAH molecules. To this end, inception would be a more appropriate name for the process [18]. During this stage, oxidation of the pyrolysed material takes place at high temperature at high concentrations of reactive compounds, such as $O^*$ and $•OH$. Under these conditions, the decomposition rate of the soot nuclei is lower than the reaction rate with other unsaturated, charged or radical hydrocarbon species. Thus the nuclei begin to ‘grow’ [18]. At this point the soot nuclei tend to be very small, of the order of 2 nm in aerodynamic diameter, and the formation of large numbers does little to increase the soot loading levels in the regions of formation [12].
During the surface growth stage, the precursor molecules grow from this small size to diameters of between 10 nm and 20 nm. At this point, the most important reaction is thought to be the fast addition of acetylene and poly-acetylene molecules by mechanisms similar to nucleation. The H:C ratio of the soot decreases due to the addition of these compounds. The rate of soot formation is seemingly dependent only on the number of nuclei present. It is surface growth that accounts for the majority of the mass of soot formed. The process occurs a few microseconds to about 0.05 milliseconds after the formation of the nuclei.

Simultaneously with surface growth, coagulation occurs. During this stage, the soot particles collide and coalesce and create larger and more-or-less spherical particles. This is easy to visualise in hydrocarbon pyrolysis where the beginnings of a soot particle may have the viscosity of a tarry liquid [12]. Also, the individual particles tend to be small and rapid surface growth will restore the spherical shape quickly. While this contributes to particle growth, surface growth is still the dominant growth mechanism. The process will occur up to diameters of approximately 10 nm.

Aggregation begins at approximately 0.02 ms to 0.07 ms after nucleation begins [18]. By this stage, the spherules have normally solidified before the collision of two or more particles and the surface growth rates will have begun to decline [12]. It is this process that causes the well-known fractal chain structure of soot, characterised by chain-like structures of discrete spherules. The spherules are normally of the order of 20 nm in diameter and the final chain structure tends to be of the order of hundreds of nanometres.

Oxidation of the soot particles tends to occur, thus lowering the tailpipe emissions of soot. In general, oxidation does not seem to play a role during the surface growth and coagulation phases of particulate formation. The principal oxidation species are radicals, such as *OH and O*, and oxygen (O₃), although both carbon monoxide and water are thought to cause oxidation to some extend [12, 18]. Since the amount of soot that is oxidised appears to depend on temperature, time and the concentration of oxidising species, it seems reasonable to suspect that oxidation takes place both inside and outside the cylinder [18]. Several works, reported in [18], suggest that as much as between 60% and 95% of all soot formed is subsequently oxidised.

Within the tailpipe, exhaust gases cool down. Low vapour pressure hydrocarbons, sulphates and sulphuric acid present in the exhaust stream, plus the condensed water, all condense on the soot particles. The resulting conglomerates are known as particulates.

### 3 An Introduction to Human Respiration

The hazard posed by a given particle will depend on both the chemical composition of the particle and the location within the respiratory system that it is deposited [13]. As a result, an evaluation of the hazards associated with an aerosol needs to know how and where the particles are deposited.

The human body includes many defence mechanisms to prevent particle access to the lungs. The methods of particle removal are close to those of filtration. A difficulty arises due to the complexity of air flow within the lungs – flow is unsteady and the system geometry is changing constantly. As a result, basic theory of aerosol induction and deposition are not sufficient and empirical relationships must instead be described [13].

#### 3.1 The Human Respiration System

Figure 9 shows a schematic of the human respiratory system. Broadly it can be divided into three regions, with each region being characterized by different airflow patterns, function and sensitivity to deposition. The head region [13] or nasopharynx region [16] comprises the nose, mouth, larynx and pharynx. The region that stretches from the larynx to the bronchioles is known as the tracheobronchial region. The final region encompasses the tiny air sacs or alveoli and is called the pulmonary region.

A normal healthy adult will process between 10 m³ and 20 m³ of air per day, or in mass terms 12 kg to 24 kg [13]. The gas exchange within the lung takes place at the alveoli, with a total surface area of approximately 30 m². The alveoli are perfused with over 2,000 capillaries. With each breath, approximately 700 ml of fluid is inhaled and exhaled. At any given time, approximately 1,100 ml is held in reserve [13].

Inhaled air will pass through an average of 23 branchings on its way from the trachea to the alveolar sacs. The relative length of time that the material is retained by the lung will depend on a number of factors, namely the chemical properties of the particle, the location within the lung and the clearance mechanism prevalent in that region of the lung. Both the head and the tracheobronchial regions are
Figure 9: Schematic of the human respiration system, showing the principal air passages and the alveolar sacs, where gaseous exchange occurs.

covered in a mucous layer. This layer can vary in thickness from 8.3 µm in the trachea to just 1.8 µm in the smaller bronchioles [2]. The mucous is pushed through ciliary action to the pharynx where it is then swallowed sub-consciously to the gastrointestinal tract. Removal of deposited material through this process can take a matter of hours.

Since the pulmonary region is responsible for gas-exchange, there is no mucous layer and so clearance of particles is more difficult [13]. For insoluble particles, the clearance time frame can be of the order of months. Soluble particles can often pass through the alveolar membrane and enter the bloodstream, which can often cause other undesirable effects. Solid particles can eventually be dissolved or encapsulated by phagocytic cells. These can then be transported to the mucociliary escalator. Fibrogenic materials, such as silica dust or asbestos fibres, can interfere with the removal process, causing gradual scarring or fibrosis of the alveolar region.

3.2 Particle Deposition in the Respiratory System

Inhaled particles are deposited within the respiratory system by the complex interaction of the five deposition mechanisms [13]. Of these five, the most important mechanisms are impaction, sedimentation and diffusion, although interception and electrostatics are also involved.

As described above, full characterisation of aerosol deposition within the respiratory system is not possible due to the dynamic nature of breathing in humans. Such characterisation would involve the solution of a constantly changing hydrodynamic flow field, upon which is superimposed the aerosol particle motion. Instead, an insight into factors involved may be gained by examining the mechanisms by which particles are deposited at various points within the system [13].

Consider a healthy adult. Inhalation through the nose and mouth results in the induced air having to pass through a large number of direction changes down through the branching system in the lungs. Suspended particles will often continue for a short distance before changing direction. Thus, deposition of particles close to the airway wall can take place through inertial impaction. This results in large particles being retained by the mucous coating on the airway. A consequence of retaining the largest particles, this deposition mechanism is also responsible for the removal of the largest mass of material. Most impaction occurs at the carina, that is the first bifurcation at the end of the trachea, with lesser quantities being deposited at other branching points, since the streamlines are most sharply bent at such points.

Smaller airways, particularly in the alveolar region, are more susceptible to sedimentation. The maximum removal effect is found to occur in those airways oriented horizontally, with the majority of material being deposited at the distal end of the airway. Hygroscopic particles will increase in size as they pass through the water-saturated airways, thus favouring deposition by both sedimentation and inertial impaction.

The Brownian motion of sub-micrometre particles leads to an increase in the likelihood that they will be deposited on the walls of the airway. Deposition by diffusion is the predominant mechanism for deposition of particles of 0.5 µm or less and is governed by geometric rather than aerodynamic size. In general, the flow conditions that favour sedimentation will also favour diffusion.

Interception is the process whereby a particle comes in contact with the airway wall on account of its physical size. At no time does the particle deviate from its gas streamline. The likelihood of interception is quite low even within the narrowest of airways. One exception is the case of long fibres, such as asbestos. Despite the length of the particle, its aerodynamic diameter is very small. As a result, it is possible for the fibre to follow convoluted paths
and become lodged deep within the lung. It is also possible for highly charged particles to become attracted to the airway surface due to electrostatic deposition. An electrostatic image charge is induced on the airway surface by the particle itself. Mutual repulsion within highly charged aerosol samples can also drive particles towards the wall.

3.3 Deposition & Retention of Aerosol

The total deposition of particulate materials is measured by means of examining the total concentration of both inhaled and exhaled mono-disperse test aerosols under controlled conditions [13]. As stated previously, in order to fully understand the hazard posed by particulate matter, both the chemical composition and the deposition site must be known. General trends have remained constant over many years but minor variations in measurement sensitivity can shed new light on the dangers of particle size and relative retention [10, 13, 25].

When one considers the total deposition of material in the lungs, it is interesting to point out that nearly 100% of all material of aerodynamic diameter of 10 µm (PM\textsubscript{10}) or larger is temporarily retained by the body [13]. Later studies [25] have reduced this number to just over 80% but have included a greater range of particle sizes to account for newer interest in ultrafine particles [6]. A minimum occurs for particles of between 0.15 µm and 1.20 µm. While Hinds [13] reports a minimum deposition in this range of about 20% deposition efficiency, the World Health Organisation [25] give a higher value of 30%. These values most likely reflect the advances in measurement techniques in the period 1982 to 2004.

![Figure 10: Deposition and retention rates for particulate matter as a function of aerodynamic diameter. After WHO Europe [25]](image)

Many studies have focused only on total deposition [13] but knowledge of regional or site specific deposition is also important for hazard assessment. By examining the methods of removing deposited material, it should be clear that he majority of the material deposited within the nasopharynxal and tracheobronchial regions is removed by ciliary action. The material deposited in the alveoli is more difficult to remove. The upper regions of the respiratory system tend to filter out the particles that would be most irritating or harmful to the alveolar region [13].

Head deposition is highly variable and will depend on the flow rate, the particle size and whether the air was inhaled through the nose or the mouth. For nasal inhalation, air is warmed and humidified as it passes around the turbinates at the back of the nasal cavity. The largest particles are removed through sedimentation and nasal hair impaction as well as inertial impaction at the bends and bifurcations within the upper respiratory tract.

Within the tracheobronchial region, impaction is the dominant removal process for particles of aerodynamic diameter greater than 3µm. If the flow rate is below 20 L min\textsuperscript{-1} or the particle size is less than 3µm, sedimentation is the dominant mechanism. Particles in the 5 µm to 10 µm range are removed with a 50% to 90% efficiency. Ultrafine particles (UF or PM\textsubscript{0.1}) have enhanced deposition due to Brownian motion in this region.

Particles of aerodynamic diameter of 10 µm tend not to penetrate the alveolar region and particles in the range 2 µm to 10 µm appear in greatly attenuated numbers [13]. Hinds reports that alveolar deposition for the range 0.1 µm to 1 µm is about 20% and is largely independent of particle size. This trend is in close agreement with later works [10].
although here a deposition efficiency of just 15% is noted. However, Guibet [10] also indicated that it is this range of particle size that most likely emitted from diesel exhausts.

The effect of mouth or nasal breathing also has an effect on the deposition of particles in the deeper regions of the lungs. Both Hinds [13] and Guibet [10] report on these trends. The earlier work [13] indicates that the maximum deposition efficiency occurs for particles of 3 µm (ηd = 50%) for mouth inhalation while nasal inhalation shows a smaller particle size (2.5 µm) and a lower efficiency of deposition (ηd = 50%). While these values are mirrored by Guibet [10], this later work expands the study. Advance measurement techniques allow for analysis of ultrafine particulate matter, which Engleff points out has been of increasing concern over the last decade or so [6]. These data show a sharp increase in deposition efficiency, reaching nearly 50%, for particles in the 0.01 µm to 0.1 µm range. This is again evident in the World Health Organisation report [25]. This report also goes on to even smaller particle sizes (0.001 µm), which are retained most effectively by the bronchi and head. For particles of 0.001 µm, almost 100% deposition efficiency is noted [25].

4 Adverse Health Effect of Pollutant Species

Although in this Paper certain divisions are made between the adverse health effects of various pollutant species, in reality, it is very difficult to deal with any one species in isolation. In many respects, the concept of the sum of the parts being greater than the whole is important when discussing pollutant emissions. The interactions between emissions species, to form new species or to create a ‘toxic cocktail’ is becoming increasingly important to understand but also increasing difficult to quantify. As much as possible the following discussion aims to describe the salient points about the health concerns associated with combustion based pollutant emissions.

4.1 Carbon Monoxide & Human Health

With an increased number of vehicles on the world’s roads, the health implications of pollutants such as carbon monoxide has become more of an issue. Carbon monoxide is a colourless, odourless and tasteless gas that does not exhibit any irritating properties [21]. Carbon monoxide is easily absorbed through the lungs and into the blood stream where it bonds with haemoglobin to form carboxyhaemoglobin (COHb). While the formation of COHb is a reversible process, such reversal can take some time due to the very high affinity of carbon monoxide for the haemoglobin. It can take anywhere from two to six and a half hours to remove half the carbon monoxide inhaled, depending on the initial levels of exposure. As a direct result of this, accumulation of carbon monoxide in the system is an issue [21].

The key human health effects which can be clearly associated with exposure to carbon monoxide are listed in Table 5. Very high doses of carbon monoxide are known to be lethal [21], while effects caused by prolonged exposure to carbon monoxide at lower concentrations is much more subtle and indeed less threatening [21]. In general, levels of COHb in the blood are taken as the best indicator of a potential health risk.

It is interesting to point out that exercise performance can be significantly affected in athletes with COHb concentrations above about 4.3%. However, for most people, there would be little or no effect on performance with COHb levels as high as 15% or 20%. The level of COHb in the blood will be influenced by both the exposure duration and the level of activity during exposure, as indicated in Figure 11. As would be expected, people who already have a serious ailment are more likely to be affected by COHb levels in the blood. For people suffering from coronary artery disease (CAD), the length of time taken for the onset of angina during exercise is significantly reduced by as little as 3% to 6% COHb. Significant numbers of tests carried out around the world, reported in Raub [21], suggest that exposure to CO, either prolonged or acute over a short period, increase the risk of hospitalisation or death in patients with severe heart disease.

Other portions of the body are also adversely affected by higher than normal levels of COHb in the blood. Tests suggest that at levels above 5% COHb, hand-eye coordination, attention and vigilance are

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Units</th>
<th>Dublin Mean</th>
<th>Annual Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>mg m(^{-3})</td>
<td>5 – 6</td>
<td>10</td>
</tr>
<tr>
<td>NO(_2)</td>
<td>µg m(^{-3})</td>
<td>22 – 35</td>
<td>40</td>
</tr>
<tr>
<td>PM(_{10})</td>
<td>µg m(^{-3})</td>
<td>17 – 21</td>
<td>40</td>
</tr>
<tr>
<td>C(_6)H(_6)</td>
<td>µg m(^{-3})</td>
<td>2.5</td>
<td>5</td>
</tr>
</tbody>
</table>

Note that CO are averaged over an 8 hour period. Adapted from O’Leary [19].
Table 5: Key health effects of exposure to carbon monoxide. Adapted from Raub [21]

<table>
<thead>
<tr>
<th>Target Organ</th>
<th>Health Effects</th>
<th>Tested Population</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lungs</td>
<td>Reduced maximal exercise duration with 1 hour peak CO exposure resulting in more than 2.3% COHb</td>
<td>Healthy individuals</td>
</tr>
<tr>
<td>Heart</td>
<td>Reduced exercise duration because of increased chest pain (angina) with peak CO exposure resulting in more than 2.3% COHb</td>
<td>Individuals with CAD</td>
</tr>
<tr>
<td>Heart</td>
<td>Increased number and complexity of arrhythmia with peak CO exposure resulting in more than 2.3% COHb</td>
<td>Individuals with CAD</td>
</tr>
<tr>
<td>Heart</td>
<td>Increased hospital admissions with increased ambient pollutant exposure with CAD resulting in more than 2.3% COHb</td>
<td>Individuals over 65</td>
</tr>
<tr>
<td>Brain</td>
<td>Central nervous system effects, such as reduced hand–eye coordination and decrements in attention and vigilance with peak 1 hour exposure leading to 5-20% COHb</td>
<td>Healthy individuals</td>
</tr>
</tbody>
</table>

4.2 Oxides of Nitrogen & Health Implications

Since vehicle exhaust systems are found at very low elevations, that is, close to the ground, traffic contributes more to ambient levels of NO\textsubscript{x} than would be initially expected from the actual percentage contribution to annual NO\textsubscript{x} emissions. Ambient NO\textsubscript{x} content will depend on the surrounding effects such as the canyon effect in urban areas. Thus it is not surprising that high levels of NO\textsubscript{x} exist along roadways within urban centres.

NO\textsubscript{x} is of particular concern for a number of reasons. Firstly, NO\textsubscript{2} is a strong respiratory irritant and can reach deep into the respiratory tract to affect both the bronchial and the alveolar regions of the lungs. NO\textsubscript{2} also has a pungent odour which can be stifling and have significant effects on olfactory sensitivity [14]. Apart from these unpleasant effects from a comfort point of view, studies in rats have shown that short term exposure to concentrations of more than 200 mg m\textsuperscript{-3} can cause death in rodents. The death is normally as a result of retarded lung oedema some time after exposure. Fluid at the entry to the lungs and other symptoms of oedema are noticeable after doses of the order of 10 ppm. At lower concentrations, unwanted effects of NO\textsubscript{2} exposure include increased respiratory resistance,
changes in pulmonary function, decreased infection defence and so on. Morphological damage has also been observed and fibrotic changes and emphasyne have also been reported [14].

Nitrogen dioxide (NO\textsubscript{2}) is almost entirely absorbed in the respiratory tract. Less than 40% is absorbed in the nasal passage while 60% or more of the dose is absorbed in the deeper regions of the lungs. An increase in respiratory frequency enhances the general absorption but retention by the nasopharyngeal tract is reduced [14], probably due to increased fluid velocity and fluid mechanics effects. Absorption of the gas by the body is regulated by the reactions between the NO\textsubscript{2} and components of the epithelial lining fluid. A description of these processes is presented in Kraft et al. but is beyond the scope of this document.

Many studies exist that try to correlate the levels of ambient NO\textsubscript{2} with negative human health effects. One of the easiest ways to do this is to examine hospital admissions. In London, for example, an estimate was made of the increased number of hospital visits as a function of increases in NO\textsubscript{2} levels. It was found that for a daily mean increase of 67 \(\mu\)g m\(^{-3}\), the number of hospital emergency admissions rose by 1.6%, while for those over 64 year of age, the percentage rise was 2.5%. Consultations due to respiratory diseases rose by 1% to 2% and by 4% for those under 64 years and those over 64 years of age respectively [14]. This report also describes how children were more sensitive to the effects of increased NO\textsubscript{2} than adults in the case of asthma specifically, Sun et al. [22] This is most likely due to the fact that children have a larger lung surface area per unit mass than adults and the epithelial layer is more permeable [24].

In certain cases, a direct correlation has been drawn between excessive NO\textsubscript{2} levels in the atmosphere and increase with mortality rates. European studies show that for an increase in NO\textsubscript{2} concentrations of 100 \(\mu\)g m\(^{-3}\), the number of deaths increased by between 2% and 7.6% [14]. It should be noted that these tended not to be violent deaths. In the case of cardiovascular death, a meta-analysis using European data shows a 1% estimated increase in cardiovascular related deaths with as little as a 50 \(\mu\)g m\(^{-3}\) increase in NO\textsubscript{2} concentrations.

### 4.3 The Implications of Hydrocarbon Emissions for Human Health

The prevalence of vehicles in the modern world, particularly in the urban environment, has led doctors to study the possible effect of PAHs on humans. Exposure to PAHs has been linked with a number of diseases such as skin cancer, lung cancer and bladder cancer [3]. Certain specific PAHs, such as benzo[a]pyrene, chrysene, indenopyrene and benzo[k]fluoranthene have produced carcinogenic, mutagenic and genotoxic effects in animal tests [5]. In the case of humans, PAHs have recently been associated with elevated levels of DNA adducts [5]. This is particularly true of people who have been exposed to smoke inhalation or who inhale PAHs in the workplace. Human reproduction is also reported to be effected, with results published in 2002 indicating that the DNA adducts described above are found in newborns whose mothers were exposed to PAHs [5, 8]. Preterm births and intrauterine growth restrictions were also reported [5, 8]. Results from Poland [8] expand the number of possible adverse effects of PAH exposure to include chromosome aberrations (CA), sister chromatide exchanges (SCE) and ras oncogene, all of which are markers for genotoxicity. Although the principal method of PAH exposure is through inhalation, it has also been found that dermal contact is becoming increasingly important.

Clearly the risk to humans from PAHs will be highest in cities, due to the large number of vehicles but also due to the large population densities. Within the confines of the city, aerosol dispersal rates can often be low due to the effect of the street canyon, resulting in higher residence times of certain chemicals. Recent work carried out in Taiwan, reported in Chen et al. [5], shows that PAH levels in cities and industrial areas are significantly higher than in rural areas. It is also interesting to note that the concentration range band is significantly larger in urban areas.

Due to these factors, and the serious mutagenic and carcinogenic risks posed by PAHs, it would seem prudent to set regulated limits on PAH exposure and emissions levels. This, however, is quite difficult due to the limited data available and the difficulties with interpreting experimental and epidemiological results.

<table>
<thead>
<tr>
<th>Area</th>
<th>Concentration (ng m(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Industrial</td>
<td>1,232 – 1,650</td>
</tr>
<tr>
<td>Urban</td>
<td>700 – 1740</td>
</tr>
<tr>
<td>Rural</td>
<td>610 – 831</td>
</tr>
</tbody>
</table>

Table 6: Polycyclic aromatic hydrocarbon concentrations in Taiwan. From Chen et al. [5]
4.4 Particulate Matter & Human Health

Due to the small size of particulate matter, it is clear that serious respiratory problems, such as decreased pulmonary function and increased risk of cardiovascular disease [9], will be associated with inhalation of respirable particles. The complex mixture of the chemicals found in particulate matter, many of which are toxic, have been linked to increased mortality and morbidity from respiratory and cardiovascular diseases [8]. The complexity of the situation is further enhanced by the fact that local climatic conditions can have a significant effect on the formation of particulate matter [23]. Tests carried out in Ghent and Barcelona, two cities which must conform to the same European Legislation on particulate exposure [7], the mass concentration of both PM$_{10}$ and PM$_{2.5}$ were found to be different in each location and a difference was clearly discernible between winter and summer conditions. Examination of the mass concentrations of particulate size were carried out, as was analysis of the chemical composition of the material [23]. Similar tests carried out in Japan showed the same general trends, in terms of seasonal variation in concentrations [15]. Thus, questions are raised about the suitability of generalised legislation for particulate control. It also serves to show that, although different locations may experience the same general trends, in terms of hospital admissions and mortality, the specific cases can vary hugely.

High exposures to PM are associated with increased cancer risk and toxicological studies have also pointed to primary combustion-derived particles as having a higher toxic potential than non-combustion based particulate [25]. However, the specific mechanism by which harm to humans is caused is still not fully understood [9]. It is quite clear that the adherence of PAHs onto particulate matter, and in particular the presence of carcinogenic PAHs or c-PAHS, will cause higher levels of mutations in human cells. Again, this helps to highlight that no one pollutant species can be considered in isolation.

In children, increased levels of PM$_{10}$ have been associated with increased Accident and Emergency Department admissions [22]. This article also reports that similar trends have been observed at numerous other locations. In the Utah valley, for example, hospital admission rates for asthma cases increased when the local steel mill was operating. In 2001, the destruction of the World Trade Centre caused huge cloud of dust to be dispersed. The continuing fires also contributed to the release of particulate matter. Indeed, despite the warnings of paediatricians, new cases of asthma and exacerbation of existing cases rose dramatically in the aftermath of 11 September 2001. This event helps to highlight the vulnerability of children to excessive levels of outdoor pollution.

One long term study has provided significant evidence of the damage caused by prolonged exposure to particulate matter. In the study, which involved around 500,000 people between 1982 and 1998, it was found that for every 10 µg m$^{-3}$ increase in PM$_{2.5}$, an associated risk increase of 6% was found for all deaths, a 9% increase for cardiopulmonary mortality and a 14% increase in the rate of death caused by lung cancer [1]. There are also short term concerns about exposure of both adults and children to particulate matter.

5 Conclusions

Vehicular pollutant emissions are a complex mixture of gaseous and particulate species. The particular species that are formed will depend on a variety of parameters, such as the combustion system employed, pressures, temperatures, the fuel used, geographic location and climatic conditions. It is not possible to separate any one element and examine it in isolation. In many respects, it is this problem that makes the control of pollutant species so difficult. Clearly, work must be done to reduce pollutant emissions in the future. The idea of test cycles and emissions control will be discussed further at a later date.

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References


