Atmospheric Pollution

Dr. Clifford Jones

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An Early 21st Century Review

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Dedicated to:

Philip Pearce MA

in gratitude for times shared with the author

in Leeds in the 1970s and in California in the 1990s.

Preface

I was delighted to respond to an invitation from Ventus Publishing to write a book on atmospheric pollution. It is a topic well enough served by books in the past, but has become increasingly important during these early years of the 21st Century. I believe therefore that there is a place for a review like this one and that notwithstanding the immense activity in the area the book will have a reasonable shelf life. This is because it continually relates the discussion to the principles of physics and chemistry, and these do not change.

To have acknowledged each and every one of the electronic sources I have drawn on would not only have lengthened the book to no real purpose but, more seriously, might even have been a distraction to a reader. I am hopeful that this acknowledgement in the preface of such sources will suffice.

I expect that students will benefit from the book as well as those already professionally involved with atmospheric pollution. I also venture to hope that it will of use to those involved in discussion of such matters in the media. I shall be delighted to hear from readers who have comments or suggestions to make.

J.C. Jones
Aberdeen, September 2008.

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1 Introduction: The gas laws

1.1 Introduction

Air is a gaseous substance, so an understanding of its behaviour requires knowledge of what are known as the gas laws. That is the purpose of this preliminary chapter.

1.2 The Ideal Gas Equation

This is:

$$PV = nRT$$

where P = pressure (N m^{-2}), V = volume (m^3), n = quantity in moles (see below), T = temperature (K), R = gas constant = 8.314 J mol^{-1}K^{-1}.

1.3 The mole concept

The following should be carefully noted.

a) Quantity in moles = quantity in grams/molar weight in grams per mole
b) molar weight in grams per mole numerically equal to the molecular weight.
c) One mole of any substance contains 6.02×10^{23} molecules. This is the Avogadro number, symbol N_o, units mol^{-1}.
d) molar weight (g mol^{-1}) = weight of one molecule (g) $\times N_o$ (mol^{-1})
e) It follows from the ideal gas equation that a cubic metre of any gas, gas mixture, vapour or gas-vapour mixture at 1 bar pressure and room temperature contains approximately 40 moles. In calculations appertaining to air quality, for temperatures in the range say 10 to 30ºC to use a value of 40 moles is acceptable. There is no need to do an ideal gas calculation to refine the value.

1.4 Sample calculations

The examples below illustrate some if these ideas.

Question:

How many moles and how many molecules are there in 35 g of nitrogen (N_2)? At 25ºC (= 298K) and 1 bar (10^5 N m^{-2}) pressure, what volume would this quantity of nitrogen occupy?

Answer:

Atomic weight of nitrogen = 14, therefore molecular weight of nitrogen gas = 28. So number of moles = 35/28 = 1.25.

$$\text{Number of molecules} = 1.25 \, N_o = 7.53 \times 10^{23}$$

Using the ideal gas equation:

$$V = nRT/P = [1.25 \times 8.314 \times 298/(1 \times 10^5)] \text{ m}^3 = \textbf{0.031 m}^3 \text{ (31 litre)}$$

$$\text{Alternatively, } 1.25 \text{ mol/40 mol m}^{-3} = \textbf{0.031 m}^3$$

1.5   The parts per million (p.p.m.) concept

Parts per million is analogous to percentage, which is of course parts per hundred, hence:

p.p.m. = (moles of gas of interest/total moles) $\times 10^6$

A related calculation follows.

Question:

At a particular place, the air standard for sulphur dioxide as an annual average is 90mg m^{-3} at 25°C. Re-express this in p.p.m. Molar mass of sulphur dioxide = 64 g.

Solution:

90mg $\equiv$ 90$10^{-6}$/64 mol in a total of 40 mol gas, therefore:

p.p.m. SO_2 = {90 $\times$ 10^{-6}/64]/40} $\times 10^6$ = 0.035 p.p.m.

1.6   Nitrogen accompanying oxygen in combustion processes

For engineering purposes air can be regarded as 79% nitrogen and 21% oxygen, the minor constituents such as the inert gases being negligible in a mass balance. This means that when something is burnt in air the accompanying nitrogen is in a quantity:

79/21 = 3.76

times that of the oxygen, molar or volume basis.

1.7   Concluding comments

Calculations like those above and variants on them abound in this book and a reader without a grasp of the contents of this part of the book is at a serious disadvantage. The calculations are in no way difficult even though, in the author's experience, students at MSc level sometimes find them so. As with any learning or skill, confidence building is essential.

2 Sulphur pollutants

2.1 Origin of sulphur pollutants

The primary origin is sulphur in fuels. When such fuels are burnt the sulphur goes to sulphur dioxide, which is harmful to humans and to vegetation as well as being a contributor to acid rain. We live in an age in which oil prices influence the world economy strongly and, at times, critically. It is because of the difficulty with sulphur that the sulphur content of a particular crude oil is a factor in its pricing, as will be explained more fully below.

2.2 Sulphur in fuels

When a crude oil is refined the sulphur within it is distributed across the fractions, tending to be more concentrated in the higher boiling fractions. In subsequent burning the sulphur will be converted to sulphur dioxide. That is why crudes are sometimes desulphurised which, of course, involves processing expenses. Benchmark crudes specify a maximum sulphur content which, if exceeded by an actual crude, will attract a reduction in price. As examples Brent crude, the North Sea benchmark, contains up to 0.37% sulphur and the West Texas Intermediate (WTI) benchmark up to 0.24%. Table 2.1 below gives some examples of sulphur contents of eleven selected crudes. In each case the sulphur content should be seen as no more than that of a representative sample having been determined by an approved standard.

Name of the field and location	Operator of the field	Sulphur content %
Alba field, North Sea, British sector	Chevron Texaco	1.24
Burgan Field, Kuwait	Kuwait Oil Company	1.6
Fateh Field, Dubai	Dubai Petroleum Company	2.0
Lufeng field, South China Sea	Statoil	0.06
Minas Field, Indonesia	Chevron	0.08
Morpeth Field, Gulf of Mexico	Eni Oil Company	1.6
Oregano Field, Gulf of Mexico	Shell	1.08
Pluntonio Field, Angola.	BP	0.39
Statfjord Field, North Sea, Norwegian sector	Statoil	0.22
Tapis Field, Malaysia	Petronas and Esso	0.1
White Rose Field, eastern Canada	Husky Energy	0.31

Average over world oil fields in operation		1.05

Table 2.1 Sulphur in selected examples of crude oil.

Considering in broad terms two of the OPEC countries, Venezuelan crudes tend to be high in sulphur and Nigerian crudes low in sulphur. Liquid fuels made from shale tend to be higher in sulphur than their counterparts from crude oil. Some examples of natural gas, as it emerges from a well, contain only traces of sulphur. There are however many examples of 'sour' natural gas, that is, natural gas containing large amounts of sulphur in the form of hydrogen sulphide H_2S.

In considering the contribution made by coal to sulphur dioxide levels in the atmosphere, a preamble on the place of coal on the current world energy scene is necessary. In many parts of the world including the UK there has been a huge reduction in coal mining over the last quarter of a century. Japan, once a major coal producer, now produces none at all and all of her mines are in a state of disuse. Major coal-producing countries include the US, Australia, India, Canada, China and Indonesia. Sulphur contents of coals across the world vary very widely from much less than one per cent to several percent.

2.3   Form of sulphur in fuels and the fate of the sulphur on combustion

Sulphur belongs to the same group in the periodic table as oxygen, hence there are sulphur analogues of many oxygenated organic compounds, e.g., the sulphur analogue of ethanol C_2H_5OH is simply C_2H_5SH. Sulphur in liquid fuels and in the organic structure of coals is bonded similarly to sulphur in simple organic sulphur compounds. Its fate on combustion is:
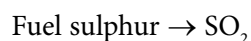
$$\text{Fuel sulphur} \rightarrow SO_2$$

and this occurs, to the exclusion of sulphur in lower oxidation states, even where conditions are fuel rich so that oxygen levels are not high.

2.4   Desulphurisation of fuels

2.4.1   Liquid petroleum fuels

The obvious strategy to make a fuel acceptable in terms of its sulphur dioxide emissions is removal of the sulphur from the fuel itself. In the case of petroleum fuels, removal might be from the crude oil initially or from fractions during processing. Technologies are many, but the basic principle is usually removal by hydrogen according to:

$$\text{Fuel S} + \text{H}_2 \rightarrow \text{H}_2\text{S}$$

Table 2.2 below gives up-to-date details of desulphurisation activity at eight major refineries in various parts of the world. In each entry the desulphurisation procedure is not necessarily the sole one at the refinery under discussion, nor of course will the desulphurisation process described be unique to that refinery. The aim of the table is give an overview of such processes whilst also introducing a reader to a number of major refineries in different parts of the world and giving him or her a feel for such details as refining capacities. The contents of the table will be supplemented by the notes following it.

Refinery details	Desulphurisation activity
Antwerp Refinery (Operator Esso. Capacity ≈ 250000 barrels per day)	Removal of sulphur from FCC gasoline by hydrogen treatment introduced in 2005.
Ruwais Refinery, UAE (Operator Abu Dhabi Oil Refining Company a.k.a. Takreer. Capacity 120000 barrels per day)	Hydrotreatment in the presence of a Co/Mo catalyst to remove sulphur from the diesel fraction.
Luena Refinery, Germany. (Operator Total. Capacity 200000 barrels per day)	Removal of sulphur from some of the incoming crude.
Port Jérome-Gravenchon Refinery, France (Operator Esso. Capacity ≈ 250000 barrels per day)	Desulphurisation unit of capacity 48000 barrels per day for transport fuels.
Szazhalombatta Refinery, Hungary (Operator Magyar Olaj- és Gázipari Nyrt, a.k.a. MOL. Capacity 161000 barrels per day)	Diesel desulphurisation using a novel catalyst.
Thessaloniki Refinery, Greece. (Operator Hellenic Petroleum. Capacity 67000 barrels per day)	A new desulphurisation facility to enter service in 2009.
Mongstad Refinery, Norway (Operator Statoil. Capacity 200,000 barrels per day)	Transport fuels with 10 p.p.m. of sulphur produced.
Edmonton Refinery, Canada (Operator Petro-Canada. Capacity 190000 barrels per day)	Upgrading of the desulphurisation plant to meet Canadian Federal requirements for sulphur content of transport fuels.

Table 2.2 Desulphurisation operations at selected refineries.

Referring to the first row, concerned with the Antwerp refinery, the term FCC denotes <u>f</u>luid <u>c</u>atalytic <u>c</u>racked gasoline. This is material initially higher boiling than gasoline, brought into the gasoline boiling range by the cracking process. Where FCC material is present in a gasoline having been blended with straight-run material it contributes by far the greater part of the total sulphur present. The method used at Antwerp is known as the Axens Prime G+ process and is also taking place in refineries in countries including Canada and the US to produce 'ultra-low sulphur' automotive fuels [1]. At the Ruwais refinery diesel having been catalytically hydrotreated as described in the table is blended with diesel not having been so treated, to give an acceptably low sulphur content of the final product. At the Leuna refinery sour crude is desulphurised, and an important product is low-sulphur distillate oil for heating. The capacity of this unit is just under a tenth that of the refinery itself. The desulphurisation plant at the Port Jérome-Gravenchon refinery is a Gofiner Unit, itself an Exxon Mobil technology. A Gofiner Unit combines desuplhurisation with other functions including cracking, enabling heavy material would otherwise have formed part of the residue to become a blendstock for distillate products.

The Szazhalombatta refinery uses a catalyst developed by Haldo Topsoe in Denmark which can be used with existing hydrotreating facilities, leading to diesel product as low as 5 p.p.m. in sulphur. The upgrade at the Thessaloniki Refinery was necessitated by Greece's entry to the EU in 2001 and the duty consequently incumbent upon her to supply fuels conforming to EU specifications. This is a fairly small refinery in terms of its capacity, and there are plans to raise this to about 90000 barrels per day. The desulphurisation plant at the Mongstad Refinery came into operation in 2003. Working for convenience in UK currency, its use added about 1.2 p to the cost of a litre of gasoline from the refinery at a time when gasoline sold in the UK for somewhat less than £1 (100p) per litre. What distinguishes the Edmonton refinery in the last row from the other seven in the table is that it receives not crude oil in the conventional sense but bitumen from tar sands.

Sulphur dioxide reduction targets began in about 1990, and by now very stringent specifications for sulphur content of motor fuels motor fuels have been set. The sulphur dioxide from transport fuels is in fact very low, in the UK less than 1% of the total.

2.4.2   Natural gas

A widely used methods of desulphurising natural gas is the Claus process, in which part of the hydrogen sulphide content of the natural gas is converted to sulphur dioxide which then reacts over a catalyst with the remaining hydrogen sulphide to form elemental sulphur. The chemical process can be summarised:

$$0.5 \ SO_2 + H_2S \rightarrow 1.5 \ S + H_2O$$
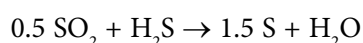
There are several hundred natural gas facilities in the world which use this method. Sulphur removal of up to 97% is achieved and there are a number of variants on and extensions to the process. An alternative favoured for natural gas with lower sulphur contents is the SulFerox process, a redox reaction of remarkable simplicity:

$$2Fe^{3+} + H_2S \rightarrow 2Fe^{2+} + 2H^+ + S$$
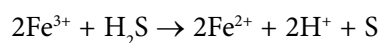
In addition to these methods which are redox reactions, there are those which simply use acid-base principles. These involve converting the hydrogen sulphide in the natural gas to sulphur dioxide and dissolving that in water to form an acid solution which can be neutralised. An amine is often used as the base, monoethanolamine being a common choice.

2.5   Sulphur credits

2.5.1   Background on emissions trading.

Such trading for sulphur dioxide emissions began in about 1990 when the matter of acid rain was addressed at international level. An organisation burning fuel (for example, a producer of electricity) is allocated a quantity of sulphur dioxide which it may release over a given period. If it exactly meets that amount well and good, but most likely it will not exactly meet it. If it emits less sulphur dioxide than it is allowed to, the balance is saleable as sulphur credits. If on the other hand the organisation exceeds the quantity of sulphur dioxide it is permitted to release it will itself have to purchase credits. Prices of credits fluctuate. An organisation with credits to sell will seek the best price for them, and one needing to buy credits will want to obtain them at the most advantageous price. In the US a sulphur dioxide credit will be well in excess of \$1000 per US ton[1] of sulphur dioxide, perhaps \$2000 or even more. Emission standards vary from place to place and from time to time. A typical standard would be 1.2 lb of sulphur dioxide per million BTU of heat[2]. In SI this converts to 1 kg of sulphur dioxide per 2 GJ of heat or equivalently 0.5 kg per GJ heat.

2.5.2   Related calculations.

Such calculations are in the shaded areas below and are interspersed with comments.

Imagine heat supplied by the combustion of heavy residual fuel oil. The calorific value of such a fuel will be $\approx$ 44 MJ kg^{-1}. A quantity of 2 GJ (2000 MJ) of heat will be produced by burning:

$$(2000/44) \text{ kg} = 45 \text{ kg}$$

Let the percentage sulphur in the fuel oil = x. If the emission standard above of 1 kg of sulphur dioxide per 2 GJ of heat is to be precisely met:

$$45 \times (x/100) \times 2 = 1$$

where the factor of 2 arises from the fact that the molecular weight of SO_2 is twice the atomic weight of sulphur

$$\Downarrow$$

$$x = 1.1\%$$

This then is the maximum sulphur content of fuel oil that could be used without exceeding the standard. The calculation continues below.

Imagine that the fuel oil previously described is used to raise steam for electricity generation at 500 MW using a turbine operating on a Rankine cycle of 35% efficiency. The quantity of sulphur dioxide from a day's operation of the turbine will be:

$$(500 \times 10^6/0.35) \text{ J s}^{-1} \times (24 \times 3600) \text{ s} \times 10^{-9} \text{ GJ J}^{-1} \times 0.5 \text{ kg GJ}^{-1} \times 10^{-3} \text{ tonne kg}^{-1}$$

$$= \textbf{62 tonne}$$

The above figure represents operation of the turbine at the very limit of its sulphur dioxide allowance. In the following we consider:

Financial penalties if a fuel oil of 20% higher sulphur content was used and

Financial benefits if a fuel oil of 20% lower sulphur content was used.

20% higher sulphur content gives 1.32% sulphur. Sulphur dioxide released in a day given by:

$$[(500 \times 10^6/0.35) \text{ J s}^{-1}/44 \times 10^6 \text{J kg}^{-1}] \times (24 \times 3600) \text{ s} \times 10^{-3} \text{ tonne kg}^{-1} \times (1.32/100) \times 2$$

= 74 tonne

20% lower sulphur content gives 0.88% sulphur. Sulphur dioxide released in a day given by:

$$[(500 \times 10^6/0.35) \text{ J s}^{-1}/44 \times 10^6 \text{J kg}^{-1}] \times (24 \times 3600) \text{ s} \times 10^{-3} \text{ tonne kg}^{-1} \times (0.88/100) \times 2$$

= 50 tonne

The fuel oil of higher sulphur content would necessitate purchase of sulphur credits of 12 tonne per day, whilst that of lower sulphur content would free up sulphur credits to the same extent. In either case, whether money was being paid or received, the sum would be something in the region of $US25000 per day.

In the following calculation a financial value is set on desulphurisation on the basis of the above figures.

Rate of burning of the fuel oil =

$$[(500 \times 10^6/0.35) \text{ J s}^{-1}/(44 \times 10^6) \text{ J kg}^{-1}] \times 3600 \times 24 \text{ s day}^{-1} \times 10^{-3} \text{ tonne kg}^{-1}$$

$$= 2805 \text{ tonne per day} \approx 3117 \text{ m}^3 \text{ per day} = 823500 \text{ US gallons per day}$$

a value of 900 kg m^{-3} having been used for the density[3]. Now at the time of going to press a gallon of heavy residual oil costs roughly $US2, so the cost of fuel for the turbine ≈ $1.6 million per day. *In this example*, a change to oil lower in sulphur content by 0.22 of one per cent results in a financial gain of $25000, about 2% of the cost of the fuel: a change to a fuel oil correspondingly higher in sulphur results in a financial penalty of the same magnitude.

It is emphasised in the calculation, and the emphasis is reiterated here, that these calculations use arbitrary though certainly sensible figures. We are however justified in arguing from the particular to the general in concluding that small changes in the sulphur composition of a fuel can have significant financial effects, and that explains the very close attention paid to sulphur content in the refining of fuels. A reader is encouraged to perform similar calculations for him/herself using different numbers. Power generation has been considered in these calculations: over 70% of the sulphur dioxide emissions in the UK are from power generation.

2.6 Methods of sulphur dioxide detection

Table 2.3 below gives details of the various methods for measuring amounts of sulphur dioxide. Some comments follow the table.

Method	Details
Detector tube	Gas drawn into a tube containing a reagent, probably in gelatinous form. Colour change signifies sulphur dioxide.
Infrared	Infrared ($\approx$ 9 mm wavelength) absorption by sulphur dioxide
Fluorescence	$SO_2^* \rightarrow SO_2 + hn$
Semiconductor	e.g., tin oxide doped with nickel
Electrochemical	$SO_3^{2-} + H_2O \rightarrow SO_4^{2-} + 2H^+ + 2e$

Table 2.3 Methods for measuring sulphur dioxide.

Detector tubes, which feature in the first row of the table, are very simple to operate and require no electrical power or other services. The basis is usually an acid-base reaction and its effect on the colour of an indicator:
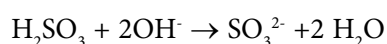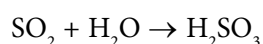
$$SO_2 + H_2O \rightarrow H_2SO_3$$

$$H_2SO_3 + 2OH^- \rightarrow SO_3^{2-} + 2\,H_2O$$

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Such methods are limited to concentrations of the order of p.p.m. or (more probably) tens of p.p.m., making them unsuitable for measurement of ambient levels of sulphur dioxide, which are of orders of magnitude lower than this. These methods therefore are restricted to such applications as flue gases where scrubbing to remove sulphur dioxide will occur before release into the atmosphere. Infrared methods are not as widely used as they once were. Currently available infrared instruments for sulphur dioxide have a resolution of the order of 1–2 p.p.m. In the fluorescence method (row 3) the emitted photon, the basis of the measurement, is of wavelength about 230 nm. Up-to-date instruments of this sort can measure down to about 0.05 p.p.m. of sulphur dioxide.

Semiconductors based on tin oxide have found very wide application in the detection of gases including carbon monoxide (see Chapter 6). Application to sulphur dioxide has been limited. Where such applications have been attempted sensitivities better than 0.01 p.p.m. have been reported. Similarly (following row) the electrochemical approach is widely used for carbon monoxide, hydrocarbons and ethanol vapour. It is in principle applicable to anything oxidisable, as sulphur dioxide is. The chemical equation given is for the conversion of sulphur IV to sulphur VI, which takes place in an electrochemical sulphur dioxide measurement device. Such an instrument constitutes a galvanic cell producing an e.m.f. which is the basis of the measurement.

2.7   Sulphur pollution levels in various countries

It has already been mentioned that coal- and oil-fired power stations account for about 70% of the sulphur dioxide emissions in the UK. It has also been described how in the UK and other developed countries including the US emission levels have been set by law, leading to sulphur dioxide credits and trading of such credits. Standards of industrial hygiene are of course higher in some countries than in others. In this section of the chapter we examine a number of countries in turn in relation to pollution by sulphur dioxide.

The world's worst emitter of sulphur dioxide is China, which released about 26 million tonne in 2005. This is sadly typical of that country, where for example standards of safety in coal mining are lamentable[4]. The country is a heavy net importer of oil in spite of heaving major reserves of her own through having allowed her oil production infrastructure to become derelict. The 2005 figure for sulphur dioxide emissions quoted represents an increase of over 25% on the 2000 figure, suggesting a situation which is out of control. The extent to which the sulphur dioxide produced in China exits its boundaries and affects other countries, including Japan, is a matter of some debate and concern. The extent of the iniquity of China in this regard is established semi-quantitatively in the shaded area below, where a comparisons with the UK and the US are made.

China

Electricity generation 2004: 2080 billion kilowatt hours

SO_2 release: 26 million tonne

SO_2 release (million tonne) per billion kWh = 0.0125

UK

Electricity generation 2004: 363 billion kilowatt hours

SO_2 release: 0.68 million tonne

SO_2 release (million tonne) per billion kWh = 0.0019

Ratio of SO_2 release per unit electrical energy, China to UK = 6.6

US

Electricity generation 2004: 3979 billion kilowatt hours

SO_2 release: 20 million tonne

SO_2 release (million tonne) per billion kWh = 0.005

Ratio of SO_2 release per unit electrical energy, China to US = 2.5

It has to be noted that the figures do not pay regard to hydroelectric power generation in the respective countries, or other means of generation which produce no sulphur dioxide including wind farms and photovoltaic cells. Moreover, in none of the countries is power generation the only source of sulphur dioxide. Even so it is clear that China is emitting sulphur dioxide in quantities well in excess of those which her extent of electricity raising could justify. It will be noted from the data in the above calculations that the UK emits less than one million tonne per annum of sulphur dioxide. India and Russia each emit about a million tonne of sulphur dioxide per year, making them roughly equal third on the world scale of emitters. The world release is of the order of 100 million tonne per year.

2.8 Sulphur dioxide emissions from shipping

2.8.1 Current standards

Where diesel is used to power vessels, severe sulphur pollution problems are not expected since (as we have seen) diesel fuels very low in sulphur are available. On the other hand, where 'bunker fuel' is used sulphur emissions can be a difficulty. Bunker fuel is residual material from refining, not a distillate. Sulphur in crude oil becomes more concentrated in the residue than in even the heaviest distillate, so the sulphur content of bunker fuel will well exceed that of the parent crude. International Maritime Organisation (IMO) have set sulphur limits on bunker fuel to apply in 'Emission Control Areas'. These are intended progressively to come down in the near future with a 1% sulphur limit applying by 2010 and a 0.1% limit by 2015. Outside an Emission Control Area a global ceiling on the sulphur content applies. Currently set at 4.5%, it is proposed that the global limit will be much lower at 0.5% by 2020.

2.8.2   Seawater scrubbing

An alternative to limiting the sulphur content of bunker fuels is the scrub the flue gas with seawater to reduce its sulphur dioxide content. Initially such scrubbing on oil tankers served two purposes: it removed sulphur dioxide and it provided an inert gas with which the payload of oil could be blanketed to prevent ignition of the vapours. A recently developed process for flue gas scrubbing on ships can achieve with bunker oil of 3.5% sulphur gaseous emissions equivalent in sulphur dioxide terms to those from fuel of 0.1% sulphur. There is a bonus by way of particulate and unburnt hydrocarbon removal.

2.9   Acid rain

2.9.1   Introduction

Sulphur dioxide as a gaseous pollutant is harmful to human beings and to other forms of life, animal and plant. Much attention has been focused on the role of sulphur dioxide in aqueous solution, that is acid rain. Rain unaffected by sulphur dioxide is naturally on the acidic side, say pH 5 to 5.5, because of the carbon dioxide in the atmosphere. The pH is pushed lower still if sulphur dioxide is dissolved, and values of around 4.5 are sufficient to have harmful effects, for example on fish life[5]. Oxides of nitrogen also contribute to the acidity of rain water, and this will be discussed more fully in the next chapter.

2.9.2 Effects on vegetation

Table 2.4 below gives details of case studies where acid rain is known to have had a harmful effect on vegetation on a large scale. They have of course been selected from a huge number of examples. Comments follow the table.

Location	Details
Shenandoah National Park, Virginia	General deterioration in the condition of the park by factors including acid rain. pH levels of precipitation in the forest around 4.6.
Krkonose National Park, Czech Republic	Damage to about a quarter of the trees through increased vulnerability, attributed to acid rain exposure, to insect attack.
Republic of India	Acid rain known to be reducing the country's agricultural output to a measurable degree.
Black Forest, Germany	Extensive damage by acid rain reported in the mid 1980s.
Southern Norway	Change in the distribution of plant species because of a decline in some as a result of acid rain.

Table 2.4 Effects of acid rain on vegetation: case studies.

Some neutralisation of acid rain can occur through the substances it contacts on the ground. At Shenandoah there is significant variation in the pH values of the streams within the park because of variations in the composition of the ground; some ground materials can act as a buffer, keeping streams which run over them at a higher pH than the rain water which enters them. The Krkonose National Park is distant from any major releaser of sulphur dioxide and yet has been severely impacted by acid rain. The sulphur dioxide had therefore originated in other parts of the Czech Republic and in bordering countries. The point made earlier that India emits about a million tonne per year of sulphur dioxide correlates with the information in row three of Table 2.4. The Black Forest, in which about half of the trees were shown to have been affected, is perhaps the most widely cited example of acid rain damage to vegetation. The flora of a particular area can change in profile because of the greater susceptibility to acid rain damage of some species than others. This has been observed in southern Norway as described in the final row of the table.

2.9.3 Effects on fish life

Here again examples will be given in tabular form and supplementary comments made.

Location	Details
Adirondack Mountains, NY	Revealed 20 years ago that most of lakes and ponds in the Adirondack Mountains had become too acidic to support fish life. Over a quarter with pH below 5.
Sweden	Total loss of fish life in 18000 lakes from acid rain.
Southern Norway	Depletion of salmon from the rivers.
Western side of the north American landmass	No effects in Alaska or western Canada. Increasing effects moving south: significant loss of fish life in Washington State and the Rocky Mountain states.
Japan	Major loss of fish life through acid rain.

Table 2.5 Effects of acid rain on fish: regional examples.

In the Adirondack Mountains the worst affected lakes were those to the west of the range, which catch acid rain from states west of NY in which power generation and other fuel-utilising activity has been taking place. Some reversal of the Swedish situation described in the second row has been brought about by raising the pH by putting lime in the lakes. This approach has been successfully taken in the UK. After an absence of over 20 years, salmon are reappearing in the River Wye after its neutralisation with lime. In Norway a brake was put on sulphur dioxide emissions in 1980 with the result that the rain acidity has been significantly reduced over the period since. No repair to the previously affected salmon rivers has as yet been observed. In some cases of fish life loss through acid rain, remedial action has produced positive results on a time scale of tens of years; there are examples of this in Scotland. Notwithstanding the absence of acid rain effects on fish life in western Canada, there are such effects on a large scale at the east side of the country because of sulphur dioxide release in the conurbations. The acid rain which has affected Japan's freshwater life might in part have originated from sulphur dioxide released in China, as noted in section 2.7.

2.9.4   Effects on buildings and structures

As shown in Table 2.6 below, the Taj Mahal is one of the structures to have been affected by acid rain.

Structure	Details
Taj Mahal, India	Loss of lustre of the surface because of exposure to acid rain.
Capitol Building, Washington DC	Observable damage by acid rain to the marble columns.
Prague, Czech Republic	Disfigurement of many historic buildings by acid rain.
Westminster Abbey, London	Accelerated erosion due to acid rain.
Statue of Liberty, New York City	Effects of acid rain observable as colour changes.

Table 2.6 Buildings and structures damaged by acid rain.

At the Capitol Building as at the Taj Mahal it was marble that fell prey to acid rain. It would be a most elementary exercise indeed in inorganic chemistry to explain this, starting with the chemical equation:

$$CaCO_3 + 2H^+ \rightarrow Ca^{2+} + CO_2 + H_2O$$

$$\Uparrow$$

calcite, the dominant constituent of marble
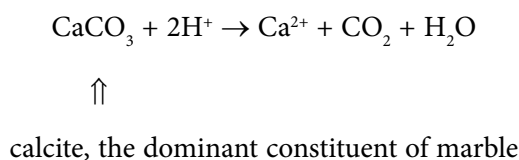
In the same city, the Lincoln Memorial is also showing symptoms of acid rain damage.

Not infrequently, rain in Prague has a pH as low as 4.0. This correlates with the entry in Table 2.4 in which damage to the Krkonose National Park, also in the Czech Republic but distant from Prague, is described. Not only is Westminster Abbey suffering from acid rain but so also is London's other famous ecclesiastical building, St. Paul's Cathedral. The latter (completed 1720) is centuries newer than the former but they both predate the industrialisation of Britain. It might be that in each case the clock started in terms of acid rain in about 1800. The only example in the table of damage to a structure through metal attack by acid rain is the Statue of Liberty, copper in the statue having been so attacked.

2.10   Acid rain in the age of greenhouse gas reductions

2.10.1   Introduction

A number of points which have exercised the mind of the author will be made here. One is that destruction of trees by acid rain has an indirect but very significant effect on carbon dioxide levels in the atmosphere. Trees provide the planet with its natural carbon sequestration capacity. (That is why the illegal stripping of forests for timber in countries including Cambodia is seen as an offence the seriousness of which enormously exceeds that of the theft alone.)

Biodiesel fuels and the like, which are being introduced in order to reduce carbon dioxide levels, have low sulphur contents. It is unlikely that this will make a measurable difference to acid rain, as so small a proportion of the sulphur dioxide in the atmosphere comes from transport fuels. In any case, conventional transport fuels extremely low in sulphur are available as described in an earlier section of this chapter.

2.10.2 Biomass fuels

A carbon dioxide reduction measure which might have a positive side-effect in reducing sulphur dioxide emissions is the use of biomass fuels such as switchgrass. This is simply because such biomass fuels have lower sulphur contents than the fossil fuels which they replace. The calculation in the shaded area below brings out these ideas.

Imagine that power is being raised at 100 MW at 33% efficiency with coal of 0.5% sulphur. The coal is replaced with a biomass fuel of 0.05% sulphur, the same efficiency being achieved. What will be the reduction in sulphur dioxide emissions over a period of one year?

First note that 0.5% is a low sulphur content for a coal and that 0.05% is a high one for a biomass fuel, so the calculation represents least favourable circumstances. We assign calorific values of 30 and 15 MJ kg^{-1} to the coal and biomass respectively.

Release rate of sulphur dioxide by the coal =
$(100/0.33) \times 10^6$ J $s^{-1}/(30 \times 10^6)$ J $kg^{-1} \times (0.5/100) \times 2 = 0.10$ kg s^{-1}
Sulphur dioxide released in a year = 3185 tonne
Release rate of sulphur dioxide by the biomass =
$(100/0.33) \times 10^6$ J $s^{-1}/(15 \times 10^6)$ J $kg^{-1} \times (0.05/100) \times 2 = 0.02$ kg s^{-1}
Sulphur dioxide released in a year = 630 tonne

It is therefore clear that when biomass fuels are used in order to meet carbon dioxide reduction targets there can be a major bonus, expressible in financial terms, by way of a reduction in sulphur dioxide emissions.

2.11 Concluding remarks

In days when air quality was not as high as it now is, a blip in the sulphur dioxide concentration of the atmosphere would be reflected by a clearly observable rise in the number of deaths due to asthma and bronchitis. That very many persons have succumbed to the effects of sulphur dioxide is clear, and its mitigation remains high on the agenda in this early 21st Century. The other heteroatom in the organic structure of fuels, namely nitrogen, also leads to atmospheric pollution on fuel combustion and this will be considered in the next chapter.

2.12 References

[1]   http://www.axens.net/press/press_releases

3   Oxides of nitrogen

3.1   Introduction

There is an important difference between the behaviour of fuel nitrogen in combustion and that of sulphur. When a fuel is burnt, its sulphur is converted quantitatively to sulphur dioxide. Its nitrogen by contrast is converted to elemental nitrogen N_2 in what, again, is likely to be approaching a quantitative yield. The small proportion that does not become elemental nitrogen becomes nitric oxide NO which is readily oxidised in the atmosphere of nitrogen dioxide NO_2. These two jointly are referred to as NO_x. There is a source of NO_x additional to that from the fuel. At combustion temperatures above about 1200°C nitrogen present in the air which is supporting the combustion can in small amounts be oxidised by elemental oxygen to form NO_x. NO_x formed in this way is referred to as thermal NO_x.

Crude oil is generally low in nitrogen. Its counterparts from shale, tar sands and bitumen can, by contrast, be as high as 2% or more in nitrogen and this necessitates nitrogen removal either from the unprocessed shale oil or from the syncrude. It is also possible, though much rarer, for coals to undergo nitrogen removal. These technologies are more fully discussed in the next section.

As noted in the previous chapter, NO_x is a contributor to acid rain. Its ability to release an oxygen atom:

$$h\nu$$
$$NO_2 \rightarrow NO + O$$
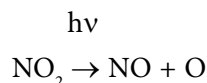
makes it a factor in the formation of photochemical smog and of ozone (see section 5.6.2). NO_2 attenuates visible light and impairs visibility. NO and NO_2 are not greenhouse gases. Nitrous oxide N_2O is a powerful greenhouse gas. This however is not formed in the atmospheric chemistry cycle of oxides of nitrogen, though it is formed naturally in forest fires and anthropogenically in certain chemical manufacturing processes.

3.2   Denitrogenation of fuels

3.2.1   Shale, tar sands, bitumen

These tend to yield final products much higher in nitrogen than those from crude oil, and analogously to hydrodesulphurisation hydrodenitrogenation of these is possible. The two can be concurrent, but under any one set of conditions there will sometimes be a preponderance of one making the extent of the other of no practical value. Although the process of removing nitrogen from such fuels is not new, R&D is ongoing in order that for particular fuels and conditions effectiveness may be enhanced. Accordingly there is much helpful information on this in investigation reports which have entered the public domain and from these can be gleaned many points of interest. Table 3.1 below summarises a number of such reports.

Atmospheric Pollution:
An Early 21st Century Review   Oxides of nitrogen

Details	Ref.
Investigation by Chevron into catalytic hydrodenitrogenation of Colorado shale oil. Nitrogen content of the oil reduced from 0.6% to 0.05%. Prior catalytic treatment of the oil with a 'guard bed catalyst' to remove arsenic and iron which would poison the hydrodenitrogenation catalyst.	[1]
Hydrotreatment of kerosene distillate from Alberta tar sands with concurrent desulpurisation and denitrogenation. Adjustment of catalyst composition to control the extent of each.	[2]
Oil obtained from bitumen sands from Whiterocks UT catalytically hydrotreated, and extents of desulphurisation and denitrogenation determined for a range of processing conditions.	[3]
Mechanistic investigation of hydrodenitrogenation of shale oil. Findings include the following: • Where nitrogen exists in an aromatic structure conversion of that to an alicyclic structure precedes C-N bond scission. • Alicyclic structures so created cause some steric hindrance to C-N bond scission.	[4]
Shale oil from Israel denitrogenated and desulphurised almost 100% by treatment with hydrogen at 350°C, 50 bar pressure with a catalyst containing nickel and molybdenum. Nitrogen in the treated product at < 5 p.p.m.	[5]

Table 3.1 Denitrogenation of fuels.

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3.2.2   Other fuels

'Flash hydropyrolysis' (FHP) of coals consists of rapid heating in a hydrogen atmosphere. This removes in part the coal sulphur and the coal nitrogen. The latter is converted to ammonia and hydrogen cyanide. There is exploratory work into the removal of nitrogen by FHP in China, where the urgent need to clean up the air means that NO_x reductions at the multitudinous coal-fired power stations in that country have to be reduced. It has been shown that extents of denitrogenation as high as 60% are achievable.

The fact that a significant percentage of the natural gas produced in the US has a high nitrogen content is a disadvantage, as obviously nitrogen as a diluent[6] reduces the calorific value. The only established way of denitrogenating natural gas is first to liquefy it and then to distil. The boiling points of methane and nitrogen are separated by 32K. There is continuing development work on the removal of nitrogen from natural gas by means of a membrane.

3.2.3   Further comment

Notwithstanding the topics in this section of the chapter and their importance, it will be appreciated that denitrogenation of fuels is much less prevalent than their desulphurisation.

3.3 NO_x mitigation during burning: the 'low NO_x burner'

Such burners first came into being in the early 1990s. The principle they work along is creation of a transition zone between the fuel-rich part of the flame and the leaner part of the flame close to the air inlet. This leads to flow conditions within the flame such that NO_x formed in the oxygen-rich part of the flame is drawn into the fuel-rich part where it is reduced to elemental nitrogen. Such burners have been used for coal and gas in the power industry. Similarly, NO_x reduction can be realised by utilising the phenomenon of swirl, whereby air entering a burner has a component to its velocity tangential to the annulus or pipe it is being conducted along. This creates recirculation patterns within a flame which can lead to reduction of the NO_x in a part of the flame where unburnt hydrocarbon is abundant. One factor in the design and adjustment of such a device is the degree of swirl. Where the fuel is natural gas the NO_x is likely to be thermal, that is, originating from nitrogen in the air.

Such facilities are by now numerous, and with coal or with natural gas as fuel a halving or better of the NO_x emission is expected from the use of low NO_x burners. NO_x emissions from power stations using such burners will typically be around 0.2 lb NO_x per million BTU of heat[7]. Notable case studies in the use of low NO_x burners are summarised in Table 3.2 below. Emission standards for flue gas from power plants are typically 30 p.p.m.

Organisation and location	Details
United Airlines, SFO Airport.	Combined Heat and Power (CHP) from boilers. Retrofitting with low NO_x burners to comply with revised emission standards set for the Bay Area.
Reliant Energy, near Houston TX.	Power generation using coal and gas, total > 4000 MW. By use of low NO_x burners, reduction of NO_x emissions at full operating load from 0.35 to 0.17 lb per million BTU.
Mirant (formerly Southern Energy California), Antioch CA.	345 MW power generation, emission levels of NO_x brought down to 30 p.p.m. by the installation of low NO_x dual fuel (oil/gas) burners with swirl. Such lowering of the NO_x levels required at the time (1996) to meet local emission standards.
ENSCO, El Dorado AR	Retrofitting of a boiler with a low NO_x burner. Emissions down to 0.066 lb per million BTU recorded.
Lingan Power Station, Nova Scotia	Installation of low NO_x burners. 40% reduction in NO_x release.

Table 3.2 Low NO_x burner case studies.

3.4   Removal of NO_x from flue gas by selective catalytic reduction

3.4.1   Introduction

Having considered pre-combustion control (denitrogenation), combustion control (low NO_x burners and swirl) for NO_x, we now turn to a method of post-combustion control. Selective catalytic reduction (SCR) of NO_x in flue gases is widely practised.

3.4.2   Principles of SCR of NO_x

A reducing agent, commonly either ammonia or urea, is added to the flue gas. In the presence of a catalyst, reduction of NO_x occurs according to:

$$NO + NO_2 + 2NH_3 \rightarrow 2N_2 + 3H_2O$$

with ammonia, and:

$$4NO + 2(NH_2)_2CO + O_2 \rightarrow 4N_2 + 4H_2O + 2CO_2$$
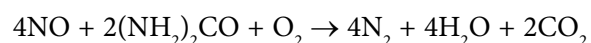
with urea. A number of catalysts are available for the process, and common ingredients of these are vanadium and tungsten.

3.4.3 Examples of usage

These are very many, the method having been in use since 1978. Any selection will therefore be arbitrary. The company E.ON are currently seeking approval for the building of a new coal-fired power station in Kent. Its specifications include NO_x removal by SCR with ammonia as reductant and with a catalyst containing vanadium and titanium. Efficiencies of 90% removal of NO_x are already being realised at other power stations using the same method. The Drax Power Station in West Yorkshire, of 4000 MW capacity, is the largest power station in Britain and the largest coal fired power station in Europe. It came into service in 1974 and does not currently use SCR to control NO_x. The role of the power station in the medium-term future has been discussed at parliamentary level [6] and it has been concluded that if the projected 2020 output is achieved selective catalytic removal of NO_x from the flue gases will be necessary by then. An advantage of coal, which in a power station is burnt in pulverised form, is that flame temperatures are only just into the temperature range where thermal NO_x forms. This and the low nitrogen content of most coals might eliminate the need for mitigation of NO_x. The situation at Drax is that that is so at present but will not be so in 2020 given the expected output by then and, quite possibly, the tightening of NO_x emission regulations.

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The Shijingshan Power Plant in Beijing has been retrofitted with SCR recently. This of course was part of the efforts to clean up Beijing by the time the Olympics were held there. In India, another country with severe pollution problems, SCR of NO_x is currently being evaluated at the Badarpur Power Station near Delhi, the nameplate capacity of which is just over 700 MW. The Dahanu Power Station near Mumbai (Bombay) is also coal fired and, with help from the US, has installed selective catalytic reduction of NO_x. It reports the NO_x concentration of the flue gases as consistently (90 ± 2) p.p.m. over a five-year period. Let it be noted that emission standards exceeding this figure apply in certain countries including Japan.

3.5 NO_x from vehicles

3.5.1   Introduction

NO_x from vehicles is thermal NO_x. Over half of the NO_x emissions in the UK are from vehicle emission. The need to control NO_x emissions from cars was first recognised in 1960s Los Angeles, where its contribution to smog had been noted. Vehicles are now classified according to emissions of unburnt hydrocarbon (a.k.a. non-methane organic gas, NMOG), carbon monoxide and NO_x. Different precise definitions of a low emission vehicle (LEV) have prevailed at different times and places. At the present time a LEV would be expected to release NO_x at a rate not exceeding 0.3 g per mile travelled, and limits for NMOG and carbon monoxide would also apply. (The limit for the former will be something like half an order of magnitude higher lower than that for NO_x and that for the latter about an order of magnitude higher.) The 'Euro V' emission limits are given in Table 3.3 below.

Type of vehicle and fuel	NO_x limit/g per km travelled (g per mile travelled)
Passenger car, diesel	0.18 (0.29)
Passenger car, gasoline	0.06 (0.10)
Light commercial, diesel	Up to 0.28 (0.45) depending on the vehicle weight.
Light commercial, gasoline	Up to 0.082 (0.13) depending on the vehicle weight.

	NO_x limit/g per kWh of energy supplied by the engine.
Heavy commercials and buses, both diesel	2

Table 3.3 Euro V emission limits.

In a diesel engine the heat of compression adds to that of combustion, resulting higher temperatures than for a gasoline engine. There is always a positive correlation between temperature and thermal NO_x formation, therefore there is a greater propensity to NO_x formation with the diesel engine than with the gasoline as the above emission standards reflect.

3.5.2 Mitigation measures

Exhaust gas recirculation (EGR) is widely used to reduce the NO_x emissions both from gasoline and from diesel engines. In EGR a proportion of the post-combustion gas is returned to the cylinder. This reduces NO_x by lowering the temperature, although there is also a more subtle effect than this obvious one. The lower temperature difference between cylinder and surroundings means less loss to the outside therefore greater conversion of heat to work. Moreover, at the reduced temperatures less if any heat will be made unavailable by dissociation of combustion products, which again enables more heat to be converted to work.

Catalytic approaches to the removal of NO_x from car exhaust gas are widely applied and there is ongoing R&D by the motor manufacturers. In 'hydrocarbon selective catalytic reduction' (HC-SCR) the NO_x is reduced to elemental nitrogen by unburnt hydrocarbon in the exhaust. The process could be summarised:

$$\text{'CH'} + 2NO + 0.25O_2 \rightarrow N_2 + CO_2 + 0.5H_2O$$
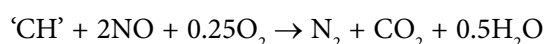
so the process has two benefits: NO is reduced and 'CH' is oxidised. Keen to meet Californian emission standards, perhaps the most exacting in the world, Nissan announced in 2007 that they had developed a catalyst in which the reaction:

$$\text{'CH'} + 0.5\ O_2 \rightarrow CO + 0.5\ H_2$$

is followed by

$$NO + CO \rightarrow 0.5N_2 + CO_2$$

$$NO + H_2 \rightarrow 0.5N_2 + H_2O$$
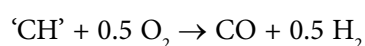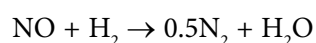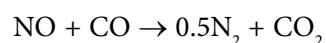
Another means of NO_x removal from vehicle exhaust gases is use of a 'storage catalyst' containing barium. The basis of this is that under lean operating conditions of the engine the NO_x is retained ('stored') by the catalyst. At periods when the engine is running more richly reduction of the stored NO_x by hydrocarbon occurs.

Car manufacturers will install NO_x emission control according to the requirements of the market, which means that for a particular model examples will differ in this regard according to where they are to be sold. In 2007 Volkswagen of America withdrew from its range certain diesel models because they did not comply with NO_x emission standards in all states.

3.6   NO$_x$ from shipping

International Maritime Organisation (IMO) have set limits on NO$_x$ release from diesel powered ships. For an engine manufactured between January 2000 and December 2010 it is 17 g per kWh of energy supplied by the engine. This will be reduced progressively to 3.4 g per kWh by 2016. Heavier fuel oils emulsified with water are sometimes used in merchant shipping. One of the benefits of these is reduced NO$_x$, a consequence of the lower combustion temperature. The total merchant shipping fleet of the world is believed to release of the order of 10 million tonne per year of NO$_x$. (See also Table 3.4)

3.7   NO$_x$ credits

3.7.1   Introduction

This is less widespread than carbon and sulphur trading but is taking place in some parts of the US. The most notable example is RECLAIM in southern California, outlined in the following section.

3.7.2   RECLAIM

The RECLAIM scheme, which covers all of Los Angeles, applies both to oxides of sulphur and of nitrogen and came into operation in 1993. Its effects have however been greater for NO_x than for sulphur dioxide. Organisations producing these pollutants in quantities greater to 4 US tons per year were allocated a number of credits on the basis of their recorded emissions from previous years. An organisation which having been allocated credits did not require all of them could sell them on, in much the same way that sulphur and carbon credits are traded.

Initially NO_x credits changed hands for about \$US1 per pound (0.454 kg) of NO_x released, but were bringing \$60 per pound in 2001. Over that period NO_x releases in the area over which the scheme applied were reduced by 25000 US tons annually. Then came legislation requiring control technology to be applied in electricity generating stations and scheduled NO_x emission reduction programmes in all industrial plant releasing 50 US ton or more per year of NO_x. Whilst some businesses affected by the legislation remained functional by complying, some closed down. The result was a hugely reduced demand for credits and a return to a price comparable to that in 2000 (see section 3.7.4).

Usually an organisation needing 'credits' in the environmental sense buys them from one with an excess and that is a one-off arrangement. In RECLAIM, NO_x credits trading can be set up as a perpetuity. In this arrangement a concern with excess credits passes an agreed number along to a concern needing credits every year at a set price. The seller has an assured market and the buyer obtains credits at a good price.

3.7.3   A further example

The engine of a diesel locomotive idles for a significant proportion of the time, and of course produces NO_x whilst doing so. It is necessary to sustain the power supply whilst a locomotive is stationary because the water and lubrication oil temperatures have to be maintained. It is however possible for an auxiliary engine to take over when the locomotive is stationary. This will sustain the operating temperatures whilst the main engine is shut off. Such an engine will of course be a much less powerful engine than that which propels the locomotive. When the locomotive is required to set off again the main engine is switched back on without having cooled during shutdown. NO_x releases during idling of over 90% have been observed, and such reductions would be saleable as credits.

3.7.4   Prices of NO_x credits

Prices of NO_x credits vary erratically. A 2006 ASME document gives a range from \$US18869 per US ton to \$US1060 per US ton. The median is \$4774 and the mean \$6700. The median value converts to \$2.39 per lb, which is reasonably consistent with the figures given in the discussion of the RECLAIM scheme in section 3.7.2.

3.7.5 Examples of NO_x release

These are given in Table 3.4. At facilities such as those referred to means of decreasing the NO_x emissions are constantly being devised. At airports, the NO_x released by aircraft on the ground is a cause for concern, accounting for around 10% of the total emissions. Fees for take-off and landing often contain a levy for NO_x: at Heathrow it is currently[8] £1.10 per kg NO_x released.

Facility	Annual NOx release/tonne
Logan Airport, Boston	≈ 1600
Edmonton waste incinerator, London (The largest such facility in the UK)	≈ 750
Texas City Refinery	≈ 825
Hong Kong harbour	≈ 16 (from vessels using the harbour)
Average size offshore oil and gas production platform in the Gulf of Mexico	≈ 50

Table 3.4 NO_x releases from selected facilities.

3.8 Means of measuring NO_x

3.8.1 Chemiluminescence

This has for a long time been the most widely used method of measuring amounts of NO_x. A 'NO$_x$ meter' using chemiluminescence requires a cylinder of oxygen. Oxygen entering the device is converted to ozone which in turn converts NO_x to nitrogen dioxide in an electronically excited state. Emission of a photon by this:

$$NO_2^* \rightarrow NO_2 + h\nu$$
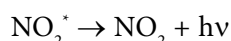
is the basis of the measurement. A modern NO_x meter working along these lines can measure NO_x in amounts of less than 1 p.p.m.

3.8.2 Superionic conductors

These are solid materials of which NASICON (sodium superionic conductor) is an important example. Its formula is $Na_3Zr_2Si_2PO_{12}$. Such substances resemble ionic solutions in that movement of ions in them produce current and are therefore sometimes referred to as 'solid electrolytes'. These can be applied to the measurement of NO_x in post-combustion gases.

When NASICON is used in a NO_x sensing device, the NO_x first encounters a noble metal surface contacting the NASICON, known as the sensing electrode. This influences current flow through the 'solid electrolyte', and this can correlated with the NO_x concentration. There are alternatives to a noble metal for the fabrication of the sensing electrode, notably certain oxides containing three metallic elements. These are sometimes loosely called 'pyrochlores'; one such having found application to NO_x sensing is an oxide of lead, ruthenium and vanadium.

3.9   Concluding numerical exercise

Ambient levels of NO_x (measured as NO_2) over a 24 hour period are typically 200 µg m^{-3}. Using principles described in Chapter 1, this will be converted to p.p.m. in the shaded area below.

$$[(200 \times 10^{-6} \text{ g m}^{-3}/ 46 \text{ g mol}^{-1})/ 40 \text{ mol m}^{-3}] \times 10^6 = 0.1 \text{ p.p.m.}$$

3.10   References

[1]   http://www.osti.gov/energycitations/product.biblio.jsp?osti_id=5387197

[2]   http://www.osti.gov/energycitations/product.biblio.jsp?osti_id=7119735

[3]   http://www.osti.gov/bridge/product.biblio.jsp?osti_id=5594465

[4]   http://stinet.dtic.mil/oai/oai?verb=getRecord&metadataPrefix=html&identifier=ADA105667

[5]   http://cat.inist.fr/?aModele=afficheN&cpsidt=2395322

[6]   http://www.publications.parliament.uk/pa/cm200506/cmselect/cmenvaud/584/584we21.htm

4   Particulate

4.1   General introduction

In almost all examples of 'applied combustion' particles are released. That is the reason why in cities and industrial areas buildings lose their original stone colour and become black, though less so now than a generation ago. In the UK in the early 70s government funds were allocated to the cleaning up of civic buildings. Particles are of course harmful to persons as well as to buildings. Such particles have become classified for pollution control purposes and this chapter will consider some such classifications in turn.

4.2 PM_{10}

4.2.1   Background on PM_{10}

Over the last decade or so particles known as PM_{10}, which by definition have a diameter of 10 μm or less, have received the most attention. This section of the chapter gives a summary of PM_{10}, its formation, effects and mitigation. In combustion, PM_{10} like other particulate is **synthesised** within a flame. Aromatic structures in the flame develop into polyaromatic hydrocarbons (PAH). PAH having exited the flame as such is itself an important pollutant as this class of organic chemicals are strong carcinogens. That which remains within the reacting zone for a sufficient period undergoes further synthesis to particles. Such particles of diameter up to 10 μm are called PM_{10}, as already discussed. Mitigation of PM_{10} formation, e.g. in vehicles, can therefore be achieved by use of a catalyst which will oxidise the unburnt fuel making it unavailable for PAH and particle synthesis.

All motor vehicles emit PM_{10}, diesel-powered ones more than gasoline-powered ones. Sources other than vehicles include heating plant, whether it uses coal or heavy fuel oil. Coal usage has diminished drastically over the period under discussion, and in the UK PM_{10} from sources other than vehicles dropped by almost an order of magnitude – from 230 kilotonnes per year to 24 kilotonnes per year – between 1970 and 2005 [1]. Of course, not all PM_{10} arises from combustion processes. Mining, quarrying and earth-moving activity are amongst the other sources. These are sometimes referred to as mechanical sources in contrast to combustion sources. In urban areas of developed countries, a PM_{10} concentration of about 50 μg m^{-3} is typical, that is, 50 micrograms of particles with diameters of 10 μm or lower in one cubic metre of air measured at 15°C, 1 bar pressure. Such a quantity of air re-expressed in weight terms is about 1.2 kg. The emphasis in the previous statement is on 'developed countries'. The concentration is in excess of three times the figure given in cities including Cairo, Delhi, Calcutta and Jakarta. In Bangkok the figure hovers around 2 to 2.5 times that for cites in 'developed countries'. Asthma amongst children there has been correlated with fluctuations in PM_{10} levels.

4.2.2   PM$_{10}$ from vehicles

In the UK at present there are $\approx$ 27 million vehicles in the 'cars and light goods' category and $\approx$ 5 million 'heavy vehicles' (trucks, buses and coaches). The annual vehicle miles travelled in the UK has been estimated as about 250 thousand million. Total release of PM$_{10}$ in the UK in 2006 was 152 kilotonne, 32 kilotonne of which was from road transport. Cars powered with unleaded gasoline emit of the order of 30 mg of PM$_{10}$ per km travelled if a suitable catalyst is fitted, twice that or more if it is not. Diesel cars emit between about 100 mg of PM$_{10}$ per km travelled at cold start down to about 30 in the same units during motorway cruising. Heavy goods vehicles using diesel can release > 100 mg of PM$_{10}$ per km travelled under motorway conditions. A reader will appreciate that each of these figures has a large plus-or-minus on it. The figures are examined and processed in the semi-quantitative calculations in the shaded area below.

Averaged emission =

32×10^6 kg $\times 10^6$ mg kg^{-1}/[250×10^9 mile $\times$ (8/5) km mile^{-1}]

= 80 mg per km

and order of magnitude agreement is clear.

Emission per vehicle per year = 32×10^6 kg/(27×10^6) vehicles

$\approx$ 1 kg per vehicle per year

which is a helpful figure for semi-quantitative work. Note that for a rough calculation like this one there is nothing to be gained from distinguishing diesel-powered vehicles from gasoline-powered ones.

In section 4.2.5 vehicular PM$_{10}$ other than that from the engine is discussed.

4.2.3   PM$_{10}$ from power generation

Coal currently accounts for a third of the UK's electricity generation and is also widely used in power generation in other countries including the USA. At a coal-fired power station PM$_{10}$ releases are expected to be up to about 10 mg m^{-3} of flue gas. In the shaded area below this figure is re-shaped to a kWh basis. Again, a reader will find necessary background in Chapter 1.

Take the coal to be ≈ 80% carbon. Any hydrogen in it will go to water which condenses at the flue gas exit temperature.

per tonne of coal 800 kg carbon burnt ≡ 66666 mol oxygen, or 80000 mol if 20% excess air is used as would be expected.

amount of excess oxygen = 13333 mol

amount of nitrogen = 300800 mol

amount of carbon dioxide = 66666 mol

_____

Total = 380799 mol ≡ 9519 m^3

1 m^3 of flue gas therefore arises from combustion of (1/9519) tonne or 0.11 kg coal

Putting the calorific value of the coal at 30 MJ kg^{-1}:

Heat released = 3.3 MJ $\Rightarrow$ ≈ 1 MJ of electricity allowing for turbine efficiency.

1 kWh ≡ 3.6 MJ

An emission of 10 mg m^{-3} of flue gas is therefore equivalent to:

36 mg per kWh

In parts of the US 'interpollutant trading' takes place, and relative figures for different pollutant are very important in such trading. Few values for this factor when PM_{10} from pollution control practice are available as credits trading between PM_{10} and sulphur dioxide is not yet widespread. The author has however seen a value of 5.3 and another of 2.0.

Solid fuels and heavy fuel oil when used to generate electrical power all give PM_{10} releases of the order of magnitude given in the calculation. That includes that dirtiest of fuels, municipal solid waste (MSW). In the UK now all MSW incineration plants are set up to generate electricity and this requires close control of conditions, including amount of excess air, to keep the PM_{10} emissions down. One expects significantly less PM_{10} from electricity generation when natural gas is used as the fuel, and typically such emissions are 0.03 g of PM_{10} per therm (10^5 BTU) of heat released on burning the gas. From a calculation similar to the one in the shaded area above, this becomes about 1 mg per kWh of electricity.

4.2.4 PM_{10} from railways and aircraft

We previously arrived at a figure for PM_{10} release from motor cars of the order of 1 kg per year. On the basis of a mileage of 12000 per year ($\approx$ 19000 km per year) with a vehicle occupied by 2.5 persons, the PM_{10} released per passenger km travelled is:

$$1 \text{ kg} \times 10^6 \text{ mg kg}^{-1}/(19000 \text{ km} \times 2.5 \text{ passengers}) = 20 \text{ mg per passenger km}$$

The company National Express have published [2] values of PM_{10} emissions from rail transport in the UK as $\approx$ 235 tonne per year. This estimate considers diesel locomotives and the generation of electricity for locomotives powered by that means. The number of passenger miles travelled by rail in the UK in a year is about 20 billion, or 32 billion passenger km. This gives for rail transport:

$$235 \text{ tonne} \times 10^9 \text{ mg tonne}^{-1}/(32 \times 10^9 \text{ passenger km})$$
$$= 7 \text{ mg per passenger km}$$

These calculations, though certainly rough, are helpful in identifying trends. It is believed that domestic air travel in the UK leads to about the same PM_{10} on a passenger km basis as rail travel.

4.2.5   Other sources of PM_{10}

These include those summarised in Table 4.1 below.

Source	Comments
Refineries	PM_{10} from the flare and from fuels used at the refinery, e.g. natural gas.
	Examples. BP refinery in Toledo OH, capacity 160000 barrels per day: annual release of PM_{10} 312 US tons
	ConocoPhillips refinery in Wood River IL, capacity 286000 barrels per day: annual release of PM_{10} 1337 US tons, expected to have decreased to 1000 US tons by 2012.
	Ineos refinery in Grangemouth, Scotland, capacity 200000 barrels per day: annual release of PM_{10} (2004 figure) 202 tonne.
Coal handling	Significant amounts of 'fugitive' particles including PM_{10} result from coal crushing and movement.
	A drop in atmospheric PM_{10} levels in the UK after the coal industry was reduced in size in the 1980s.
Forest fires	PM_{10} at 839 µg m^{-3} in Kuching following recent forest fires in Indonesia. 350 µg m^{-3} in Kuala Lumpur, distant from the fires.
Domestic wood stoves	Use of such stoves prevalent in rural areas.
	Some rural parts of New Zealand's south island have a worse PM_{10} problem than Christchurch NZ, population ≈ 0.35 million. This is attributed to the use of wood as a domestic fuel in the country areas.
Car tyres	Comparable to the PM_{10} release from the engine, but not controllable by a catalyst as the 'combustion PM_{10}' is.
	(Major release of 'mechanical PM_{10}' from aircraft tyres on landing)

Table 4.1 Sources of PM_{10}

4.2.5   Measurement of PM_{10}

PM_{10} can of course be measured by manual weighing of filters in which it has deposited. The technique is known as 'filter gravimetry'. Other methods are used including the 'oscillating microbalance', in which PM_{10}, separated from larger particles by filtration, impinges upon a vibrating surface. The vibration frequency is likely to be in the range 30 to 60 Hz. Changes in the vibration frequency as a function of mass of substance on the surface is the basis of calibration. Instruments of this sort are easily set up in the field in order to monitor PM_{10} at particular distances from a major releaser. The 'filter gravimetry' and 'oscillating microbalance' techniques can also be applied to $PM_{2.5}$ (see below).

4.3   PM$_{2.5}$

4.3.1   Background on PM$_{2.5}$

PM$_{2.5}$ is particle material below 2.5 μm diameter. All PM$_{2.5}$ is also PM$_{10}$ but vice versa is not true. It is possible for most of the mass of a sample of PM$_{10}$ to be also PM$_{2.5}$ in which case the particle size distribution will be skewed. Obviously it would be valid to regard PM$_{2.5}$ as *incipient* PM$_{10}$ having exited the synthesis zone before the particles built up to PM$_{10}$ sizes. It is often of interest to know what proportion of PM$_{10}$ at a particular site is accounted for by the PM$_{2.5}$

4.3.2   Atmospheric levels of PM$_{2.5}$

Some published figures for these are given in Table 4.2 below. Like such figures given for other pollutants, they should be seen as being representative.

Location and time	PM2.5 concentration/µg m-3	Reference
Taipei, 2002	Up to 43	[3]
London, on aboveground commuter routes. Summer 1999 Winter 2000	 34.5–39.0 33.7–38.9	[4]
London, in Underground ('tube') commuting. Summer 1999 Winter 2000	 247.2 157.3	[4]
State of Texas, May 14th 2008	In the range 2.0 ('Tyler region', inland and close to the Louisiana border) to 43.7 ('Harlingen region', southern coast).	[5]
Belgrade, former Yugoslavia, June 2002 to June 2003	Mean value over the period 61.	[6]
Singapore, 7th March 2006	21	[7]

Table 4.2 Atmospheric levels of $PM_{2.5}$.

Whereas vehicles contribute a major part of the ambient level of PM_{10} in cities, this is less so for $PM_{2.5}$. In cities most of the $PM_{2.5}$ tends to be from stationary sources and is known as the *regional* contribution, in contrast to the *vehicle* contribution.

4.4   Smaller particles than $PM_{2.5}$

This of course includes PM_1 and $PM_{0.1}$. An alternative, and widely used, way of putting that is that PM_1 and $PM_{0.1}$ are subsets of $PM_{2.5}$ (which is itself a subset of PM_{10}). $PM_{0.1}$ is sometimes called ultra-fine particles. All combustion-derived particulate carries polyaromatic hydrocarbons (PAH) on its surfaces and inhalation of particles clearly provides a route for entry of PAH, which are carcinogens, to the lungs. Table 4.3 below gives summaries of $PM_{0.1}$ and PM_1 investigations in several parts of the world.

Location	Details	Reference
Helsinki, Finland	$PM_{0.1}$ accounting for 7 to 8.5% of the $PM_{2.5}$.	[8]
San Joaquin Valley CA	$PM_{0.1}$ concentrations averaged over an 8 to 12 hour period 2.4 mg m-3. Daytime concentrations about 50% higher than night-time ones.	[9]
Selected Chinese cities of 'large and medium size'	Most of the $PM_{0.1}$ from vehicular sources.	[10]
UK, nationwide	A drop in PM_1 of 30% and of $PM_{0.1}$ also of 30% between 1990 and 1997.	[11]
Japan, Thailand and Cambodia	Concentration of PAH in the smallest particles.	[12]

Table 4.3 Examples of occurrence of particles smaller than $PM_{2.5}$.

Particles smaller PM$_{2.5}$ do seem to be mainly largely from vehicles. Of course, as with the other particle size ranges considered there are major contributions from sources other than combustion processes. The effect whereby the smaller the particle size the greater the amounts of PAH carried, noted in the final row of the table, is likely to be largely a surface area effect.

4.4 Concluding comments

A dispersion of fine particles in air is an example of an aerosol. The term applies equally to liquid droplets so dispersed. Here there is a point of contact both with the previous parts of the book on acid rain and the later part on volatile organic compounds.

4.5 References

[1] http://www.naei.org.uk/pollutantdetail.php?poll_id=24

[2] http://www.nationalexpressgroup.com/nx1/corporate/cr_reports/csr2003/csr2003ind/environment.pdf

[3] Li C-S, Lin C-H Aerosol Science and Technology, 36(4) 469–473 (2002)

[4] Adams H.S., Nieuwenhuijsen M.J., Colvile R.N., McMullen A.S., Khandelwal P. Science of the Total Environment 279 29–44 (2001)

[5] http://www.tceq.state.tx.us/cgi-bin/compliance/monops/texas_pm25.pl

[6] Tasić, M.D., Rajšić, S.F., Novaković, V.T., Mijić Z.R. and Tomašević M.N. Physica Scripta 118 29–30 (2005)

[7] http://app.mewr.gov.sg/press.asp?id=CDS3496

[8] Pakkanen T.A., Kerminen V.-M., Korhonen C.H. Hillamo R.E., Aarnio T., Koskentalo T. and Maenhaut W. Atmospheric Environment 35 (27) 4593–4607 (2001)

[9] Herner J.D., Aw J., Gao O., Chang D.P. and Kleeman M.J. Journal of the Air and Waste Management Association 55 (1) (2005)[9]

[10] http://books.nap.edu/openbook.php?record_id=10491&page=150

[11] http://lorien.ncl.ac.uk/ming/cleantech/airpollution-impact.htm

[12] http://www.aaar.org/meetings/07AnnualConf/pdfs/abstracts/07_Atmospheric_Aerosols_Urban.pdf

5 Volatile Organic Compounds (VOC) and Ozone

5.1 Introduction

VOC are released from many sources, including motor vehicles and refineries. The VOC level inside a building will exceed that of the air surrounding the building by a factor of between 2 and 5. This is because of VOC release by such 'incidental' substances as paints, polishes, office equipment and cosmetics. VOC mitigation measures are however directed chiefly at vehicles and refineries. In the UK the target for total annual VOC release by 2010 is 1200 kilotonnes. The first part of this chapter will deal with VOC with some emphasis on its role in ozone formation. Ozone *per se* will then be dealt with.

5.2   VOC from vehicles

5.2.1   Amounts released.

The table below gives details of VOC emissions from vehicles.

Vehicle type	VOC production
Volvo heavy diesel-powered truck for north American use.	An average of 8.6 pounds (4 kg) VOC per truck per year aimed for.
Gasoline-powered Ford Crown Victoria in use as a taxicab covering 100000 miles per year [1].	68.3 lb VOC (31 kg) in one year.
As above, but using natural gas as fuel [1].	12.1 lb VOC (5.5 kg) in one year.
Unspecified passenger car, diesel [2].	0.053 g VOC per km travelled.
Two-stroke motorcycle, new condition [3].	Concentrations of VOC in the exhaust up to about 500 mg m^{-3}.

Table 5.1 VOC emissions from vehicles.

The data for a diesel car in row four translate to 1 kg of VOC release for a typical annual mileage of 12000 ($\equiv$ 19200 km). This exactly matches the estimated annual PM_{10} release by a vehicle given in section 4.2.2. We can at the very least conclude that the release of each will be of the order of kilograms over a year's motoring. We also note that the vehicle under discussion in row four would release 8.5 kg of VOC over 100000 miles; this can be compared with the figures in rows two and three.

Vehicle manufacture is also a significant source of VOCs, which arise from the spray painting process. Manufacturers have implemented measures whereby such emissions are minimised. For example, Ford in the US work to a standard of 29 g of VOC per square metre of car surface painted. This is similar to the performances of other major manufacturers in this regard. (See also Table 5.2.)

5.3   VOC from refineries

A related calculation is in the shaded area below.

Annual release of VOC from refining in the UK $\approx$ 40 ktonne

Total refining capacity of the UK = 1.7 million barrels per day or:

1.7×10^6 barrel day$^{-1} \times 0.159$ m^3 barrel$^{-1} \times 900$ kg m$^{-3} \times 10^{-3}$ tonne kg$^{-1} \times 365$ days per year = 88 million tonnes per year

Proportion of the hydrocarbon inventory lost as VOC $\approx$ 1/2000th

The above result is intuitively reasonable. A follow-up calculation is below.

> The world refines 80 million barrels of oil per day (4000 million tonnes per year). If 1/2500th of this becomes VOC, the VOC entering the atmosphere in a year is 1.6 million tonnes.
>
> The mass of the atmosphere is approximately 5.1×10^{18} kg.
>
> Rise in atmospheric VOC over a year is then:
>
> $(1.6 \times 10^9 / 5.1 \times 10^{18}) \times 10^9$ parts per billion (weight basis) = 0.3 p.p.b.
>
> Chemical species comprising VOC vary in the range about C_2 (e.g., ethane molar weight 0.026 kg) to C_7 (e.g. toluene, molar weight 0.092 kg). The mean of the molar masses of those is approximately twice the molar mass of air, which is 0.0288 kg.
>
> Hence 0.3 p.p.b. weight basis becomes 0.15 p.p.b. volume basis.

The concentration of hydrocarbons other than methane in the atmosphere is expected to be in the range p.p.b. to a few tens thereof depending of course on the location and proximity to releasers. So say at 10 p.p.b background level, refining activities will bring about a 1.5% increase per annum. That this is only moderate is the result of there having been major reductions in hydrocarbon release from refineries during the opening years of the 21st Century. For example, the release of VOC by Shell summed over all of the countries in which that company has refining activity has halved since the year 2000.

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5.4 Other sources of VOC

These are given in Table 5.2 below.

Source	Comments
Electricity generation from fossil fuels.	Typically 250 mg VOC per kWh of electricity.
Crude oil terminals.	Values across the range > 0.1 to ≈ 3 kg VOC per tonne of oil transferred recorded internationally.
Adhesive usage.	Adhesives available which release 2 g VOC per litre adhesive used, or better. An adhesive chosen for a particular application needs to be evaluated for VOC emissions.
Painting of buildings.	At least a small degree of VOC release expected if the paint is oil based. With latex-based paints zero VOC emission possible[10].
Degreasing by means of solvents, e.g., in car repairs.	Amongst the 'top 10' releasers of VOC in most cities.

Table 5.2 Sources of VOC other than vehicles and refineries.

5.5 Measurement of VOC

A common method is by means of an instrument using the principle of photoionisation. A u.v. light source within the instrument ionises any VOC in gas drawn in for analysis. The electrical current so created is the basis of the signal. This sort of detector for VOC is for use at or close to a source, e.g., in a vehicle repair workshop. It cannot measure the p.p.b. background concentrations previously discussed in this chapter.

5.6 VOC and ozone formation

5.6.1 Background

The 'ozone layer' about 20 km above the earth's surface needs to be protected as it filters out parts of solar radiation which are harmful to persons. However, ozone much closer to the earth's surface is itself harmful. It is also an agent in the formation of photochemical smog, as will be explained in the following section.

5.6.2   Mechanism

This is explained in the boxed area below.

We saw in section 3.1 how NO_x reacts in sunlight to form:

$$NO_2 \xrightarrow{h\nu} NO + O$$

and that the oxygen atom so liberated can react with molecular oxygen to form ozone. The role of VOC in ozone formation is the formation of NO_2 from NO. The first step is:

$$RH + OH \rightarrow R + H_2O$$
$$\Uparrow$$
$$VOC$$

followed by:

$$R + O_2 + M \rightarrow RO_2 + M$$

where M is a third body. The peroxy intermediate so formed reacts with NO according to:

$$RO_2 + NO \rightarrow NO_2 + RO$$

making NO_2 available for ozone formation. The probable fate of the RO species is conversion to an aldehyde or a ketone.

5.7   Ozone

5.7.1   Introductory comments

Factors in the formation of ozone are NO_x and VOC. The former has a chapter of its own in this volume and the latter is covered in the first part of this chapter. A discussion of ozone itself therefore logically follows.

5.7.2   Levels of ozone in the atmosphere

Table 5.3 gives measured amounts of ozone at various places. Again, values should be taken as being representative.

Location	Ozone level/p.p.m.	Reference
California, averaged over several counties and cities.	0.07	[4]
Shanghai, China.	0.2	[5]
Delhi, India.	Up to 0.1	[6]
Rural England, averaged over several sites.	0.03	[7]
Hong Kong	Up to 0.1	[8]

Table 5.3 Levels of ozone.

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The figure given for California more than meets the 0.08 p.p.m. level of ozone set by the EPA as recently as March 2008. The figure given for Shanghai exceeds it by almost a factor of three. The figure given for Delhi is for a particularly bad day. For most of the time Delhi complies with or does not grossly exceed the WHO limit for ozone which in fact corresponds closely to the California one given at the beginning of the paragraph. Like that for Delhi, the figure for Hong Kong is a worst case: for most of the time the level there is 0.07 to 0.08 p.p.m.

5.7.3 Measurement of ozone

Ozone absorbs in the ultraviolet, so air to the extent that it contains ozone loses its transparency in this wavelength range. This is the basis of the simple 'ozone monitor'. A further consequence of this property of ozone is that it is a greenhouse gas.

5.7.4 The reaction between ozone and atmospheric hydrocarbons

Ozone is a highly powerful oxidant. Hydrocarbons in the atmosphere can be oxidised by ozone in the following way:

$$RH + O_3 \rightarrow R'CHO + O_2$$

where the alkyl group R' has one fewer carbon atoms than R. The aldehyde product reacts according to:

$$R'CHO \xrightarrow{\text{further oxidation}} R'(CO)\text{-}O\text{-}O \text{ (acylperoxy radical)}$$
$$\downarrow NO_2$$
$$R'(CO)\text{-}O\text{-}O\text{-}NO_2$$
Peroxyacyl nitrate (PAN)
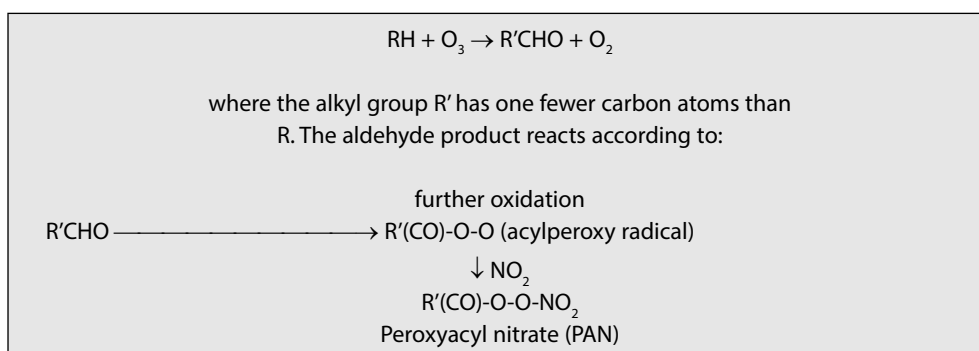
PAN's are toxic to humans and also cause damage to vegetation. The most important example of PAN is that for which $R' = CH_3$ therefore R (in the above scheme) = C_2H_5. There is concern that the rapidly increasing use of ethanol (C_2H_5OH) as a motor fuel will raise the amount of this form of PAN in the atmosphere. Sometimes the term PAN is restricted to this one form, in which case it means peroxyacetyl nitrate instead of the generic peroxyacyl nitrate*s*. PAN in the second sense, exclusively the acetyl form, is likely to be present at levels in the range 5–10 p.p.b. in a major city. This is about an order of magnitude lower than in the 1970s, an improvement attributable to increasing restrictions on NO_x, on VOC and therefore on ozone over that period.

Whereas ozone levels in the atmosphere are tens or hundreds of parts per billion, amounts of PAN as we have seen are only a few p.p.b. As with dioxins (which feature later in this book), amounts of PANs are too small to give a significant absorptivity to a sample of ambient air, and the lower limit of concentration for u.v. measurements exceeds the actual concentration. In such circumstances one has to go to mass spectrometry coupled with gas chromatography (GC-MS). There is much more to this than to a simple u.v. measurement and much scope for development and innovation. Quantities of PAN have been measured at parts per *trillion* level by GC-MS, but certainly not with the ease of a routine u.v. measurement in the field.

5.7.5   Concluding remarks

The primary subject of this chapter has been VOC, and its role in ozone formation has led to a discussion of that as well as of PAN.

5.8   References

[1]   http://www.aqmd.gov/hb/2001/011237a.html

[2]   http://www.co-operativebank.co.uk/partnership2002/pr/conversions.html

[3]   Tsai J-H, Hsu Y-C, Weng H-C, Lin W-Y and Jeng F-T Atmospheric Environment 34 (28) 4747–4754 (2003)

[4]   http://www.businessweek.com/bwdaily/dnflash/content/mar2007/db20070316_594911.htm

[5]   Zhang Y., Huang W., London S.J., Song G., Chen G., Jiang L., Zhao N., Chen B. and Kan H. Environmental Health Perspective 114 (8) 1227–1232 (2006)

[6]   http://www.cseindia.org/AboutUs/press_releases/press_20070614.htm

[7]   http://nds.coi.gov.uk/environment

[8]   http://www.hko.gov.hk/ozone/o3content.htm

6   Carbon Monoxide

6.1   Introduction

There are both natural (forest fires, volcanic activity) and anthropogenic (combustion processes) sources of carbon monoxide, and atmospheric concentrations of this highly toxic gas are considerable. However, the natural background level of carbon monoxide is considerably less than 1 p.p.m. whereas atmospheric concentrations are several p.p.m., so clearly the anthropogenic is dominating. It was mentioned in passing in Chapter 3 that carbon monoxide occurs in vehicle exhaust gases. In the first part of this chapter, control of carbon dioxide emissions from motor vehicles will be considered.

6.2   Contribution from motor vehicles

6.2.1   Amounts released

The total world release of carbon monoxide from vehicles is of the order of hundreds of megatonne (Mt). In the USA considered separately it is tens of Mt. In the shaded area below a calculation for carbon monoxide analogous to that for VOC in the previous chapter is presented.

Say 200 Mt of carbon monoxide globally from vehicles per year.

$200 \text{ Mt} \equiv 200 \times 10^9 \text{kg}$

The mass of the atmosphere is approximately 5.1×10^{18} kg.

Rise in atmospheric CO over a year is then:

$(200 \times 10^9 / 5.1 \times 10^{18}) \times 10^6$ parts per million (weight basis) = 0.4 p.p.m.

Note that because the molar masses of air and of carbon monoxide are almost the same – 0.0288 and 0.0280 kg respectively – the p.p.m. on a weight basis and that on a molar or volume basis are equal. The motor vehicles of the world therefore push up the carbon monoxide level of the atmosphere by about half a p.p.m. annually.

6.2.2   Mitigation.

Catalysts for aiding the breakdown of unburnt fuel have already been described in this volume, and such catalysts also aid the oxidation of carbon monoxide to carbon dioxide. A three-way catalyst (TWC) is a catalytic device which enables carbon monoxide and unburnt hydrcarbon to be oxidised and nitric oxide to be reduced and therefore contains an oxidation catalyst and a reduction catalyst. For them both to contain platinum is common.

6.2.3   Emission limits

In a previous chapter the Euro V emission limits for NO_x were given. Those for carbon monoxide are in the table below.

Type of vehicle and fuel	CO limit/g per km travelled (g per mile travelled)
Passenger car, diesel	0.5 (0.8)
Passenger car, gasoline	1.0 (1.6)
Light commercial, diesel	0.74 (1.2)
Light commercial, gasoline	2.25 (2.7)

	CO limit/g per kWh of energy supplied by the engine.
Heavy commercials and buses, both diesel	1.5

Table 6.1 Euro V emission limits.

Roadworthiness tests for vehicles require that carbon monoxide levels be below a certain level. These vary from place to place, but for a passenger car of recent design a typical standard would be 0.3% carbon monoxide in the exhaust gas at idling speed. A related calculation follows.

Consider all of the passenger cars of the world as a single releaser
of gas with concentration 0.3% of carbon monoxide.

In general, a gas which is a minor component of a released gas mixture is diluted
by a factor of the order of $\approx 10^3$ on dispersion into the atmosphere.

0.3% $\equiv$ 3000 p.p.m.

p.p.m. of CO in the atmosphere due to cars is therefore:

3000/1000 = 3 p.p.m.

That 3 p.p.m. of carbon monoxide in the atmosphere is due to emission from passenger cars is an altogether reasonable result. In an urban setting 10 p.p.m. would be a typical level of carbon monoxide, and a suggestion that cars have contributed 30% of this is intuitively sensible[11]. The figure would of course rise if buses and trucks were factored in.

6.3 Miscellaneous sources of carbon monoxide [1]

Mobile sources other than road vehicles, including bulldozers, mobile excavators, farm machinery and domestic lawnmowers, contribute significantly to carbon monoxide build-up, two thirds to a half the contribution from road vehicles. That from aircraft is small and that from ships and railways is even smaller. Of the non-mobile sources, by far the most important is thermal generation of electricity.

6.4 Detection and measurement of carbon monoxide

Mention was made at the end of the preceding section of the fact that power generation is a major source of carbon monoxide. At such a facility the level of carbon monoxide in the burnt gas needs to be known not only because release has to be controlled but also because carbon monoxide represents incomplete combustion and therefore fuel wastage. Effects of incomplete combustion on fuel costs are far from trivial. In an appendix to this chapter it is shown that with gas turbine fuelled by diesel generating electricity at 100 MW a reduction in the concentration of carbon monoxide in the flue gas from 0.05% to 0.02% equates to a saving in fuel costs about half a million $US per year.

Being a heteronuclear diatomic molecule, carbon monoxide is active in the infrared and this can be the basis of instrumentational measurement of amounts of the compound. In power stations it is routine for infrared devices for carbon monoxide to be fitted to ducts conveying the post-combustion gas. These measure up to about 1000 p.p.m. (0.1%). (The concentrations considered in the calculation in the appendix are in this range.)
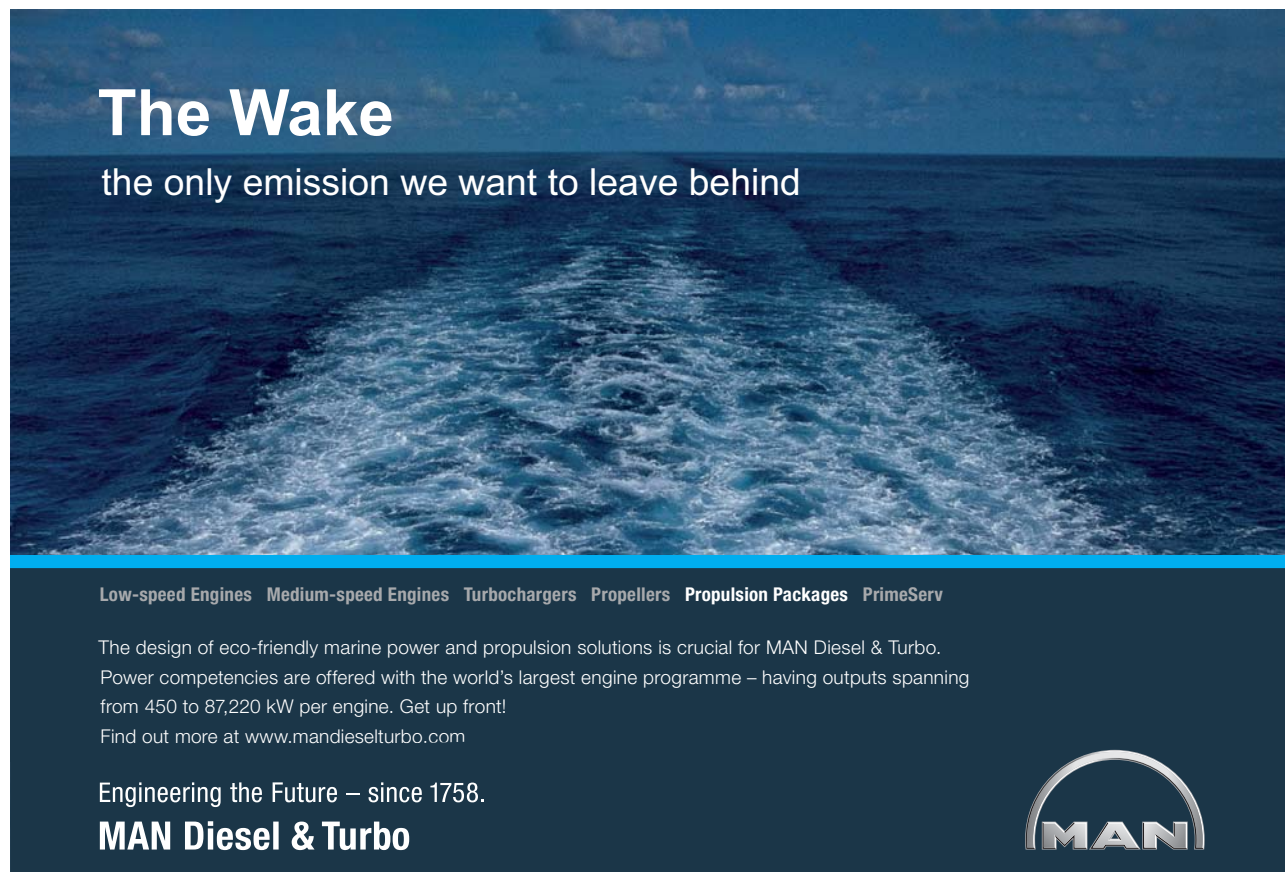
As noted in Chapter 2, carbon monoxide concentrations can be measured electrochemically. The process upon which the measurement depends is:

$$CO + H_2O \rightarrow CO_2 + 2H^+ + 2e$$
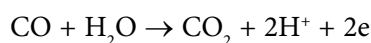
It is also noted in Chapter 2 that semiconductors can be applied to carbon monoxide measurement. With semiconductor measurement devices an important factor in development is choice of a dopant to give good selectivity in relation to the gas of interest. With a tin oxide semiconductor a cerium oxide dopant gives good carbon monoxide selectivity.

6.5   Harmful effects of carbon monoxide

Fatal poisoning with carbon monoxide, for example amongst fire fighters or where badly adjusted heating appliances are being used so that there is incomplete combustion of fuel, occurs tragically frequently. This book is more concerned with effects on health of background levels of carbon monoxide in the atmosphere. Selected epidemiological studies on the effects of carbon monoxide are summarised in Table 6.2 below.

Locality and conditions of the investigation.	Findings.	Reference.
New York City bridge and tunnel operators. Such operators exposed to CO levels above ambient when on duty.	61 of 5529 such operators employed for all or part of the period 1952 to 1981 died of heart disease. Expected number of deaths based on the NYC population statistics 45, therefore a significant excess.	[2]
Seven US cities over the period 1986 to 1989: Chicago, Detroit, Houston, Los Angeles, Milwaukee, New York and Philadelphia.	3250 hospitalisations due to 'congestive heart disease' correlated with a blip in the ambient CO. Total hospitalisations due to congestive heart disease over the seven cites for this period approx. 57000. The excess is therefore just under 6%.	[3]
Motor vehicle examiners employed as such for at least six months.	In a cohort of 1558 examiners, 124 deaths due to cardiovascular disease, representing an excess of just under 5% when compared with the expected number of such deaths.	[4]
Seoul, Korea. Birth weights correlated with ambient CO levels experienced during pregnancy.	Carbon monoxide concentrations in the atmosphere plotted as quartiles. An increased risk of 8% of a low-weight birth per unit increase in the CO so expressed.	[5]
Southern California. Frequency of preterm births correlated with CO levels experienced during preganacy.	'Women exposed to **carbon monoxide** above 0.91 p.p.m. during the last 6 weeks of pregnancy experienced increased odds of preterm birth.'	[6]

Table 6.2 Effects of carbon monoxide.

6.6   Concluding remarks: trends in carbon monoxide levels in air

Figures for the carbon monoxide levels of the atmosphere are not available for further back than the 1950s. There was a rise between then and the 1980s, when a decline began. The lifetime of a carbon monoxide molecule in the atmosphere is about two months before its oxidation to carbon dioxide occurs. This involves the hydroxyl radical OH. The decline in carbon monoxide which began in the 1980s is due to a number of factors. In some parts of the world, it is thought to have been due to an increased transparency of the atmosphere 6 to 30 miles above the earth's surface to ultraviolet radiation. Such radiation causes photolytic reactions at levels of the atmosphere closer to the earth's surface which produce OH radicals, reducing the lifetime of a carbon monoxide molecule. Additionally, there have been reductions due to restrictions on carbon monoxide release from transportation fuels and from industrial plant as discussed previously.

6.7   References

[1] http://www.teachengineering.com/collection/cub_/lessons/cub_air/cub_air_lesson03_answers.pdf

[2] Stern, F.B.W.E. Halperin, R.W. Hornung, V.L. Ringenburg, and C.S. McCammon. American Journal of Epidemiology 128 1276–1288 (1988)

[3] http://www.jstor.org/stable/3432775?seq=2

[4] Stern F.B., Lemen R.A., Curtis R.A. Archives of Environmental Health 36 59–66 (1981)

[5] Ha E-H, Hong Y-C, Lee B-E, Woo B-H, Schwartz J., Christiani D.C. Epidemiology 12 643–648 (2001)

[6] Ritz B., Wilhelm M., Hoggatt K.J., Ghosh J.K.C. American Journal of Epidemiology 166 1045–1052 (2007)

6.8 Appendix to Chapter 6

Calculation of fuel saved by reduction of CO in the flue gases from a gas turbine making electricity.

Imagine that a gas turbine using diesel as fuel is used to make electricity at 100 MW. Initially the carbon monoxide level in the hot flue gas is 0.05%. By adjustment of combustion conditions this is reduced to 0.02%. It is possible to calculate how much diesel this would save in a year's operation of the turbine in the following way.

1. Preliminaries.
100MW of power at ≈ 30% efficiency requires 333 MW of heat or:

$333/44$ kg s^{-1} of diesel = 7.5 kg s^{-1} ≡ 2.4×10^8 kg year^{-1}
(≈ a quarter of a million tonne per year)

2. Stoichiometric calculations.

A diesel with cetane number 50 would correspond in performance terms to a blend of 50% n-cetane $C_{16}H_{34}$ and 50% alpha-methyl naphthalene $C_{11}H_{10}$. It is elementary to show that such a mixture would have elemental composition 85% carbon 15% hydrogen. This corresponds to a hypothetical hydrocarbon compound of formula $C_{14}H_{21}$ of formula weight 0.189 kg. This will burn in air according to:

'$C_{14}H_{21}$' + 19.25 O_2 (+ 72.4 N_2) → 14CO_2 + 10.5 H_2O (+ 72.4 N_2)
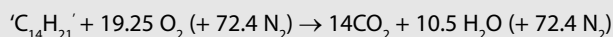
If (as would be usual) combustion was in excess air to the extent of say 20%, per kg of the hydrocarbon burnt the post-combustion gases would be:

CO_2 74 mole, H_2O (vapour) 56 mole, N_2 460 mole, O_2 20 mole. Total 610 mole from 1 kg hydrocarbon.

3. The CO reduction.
Let the flue gas be x% in CO, and let x be sufficiently small for the percentages of the other constituents of the flue gas not to be significantly changed by it. Similarly, the quantities calculated in part 1 of the calculation are not affected by the small extent of departure from the reaction as written.

Per kg of fuel burnt the amount of CO is then:

610 x/100 mol.

CO per year = (610 x/100) × 2.4×10^8 = $1.5 \times 10^9 \times$ mol.

Putting x = 0.05, CO per year = 7.5×10^7 mol

Putting x = 0.02, CO per year = 3×10^7 mol

Difference ≈ 3.5 ´ 10^7 mole. The heat of combustion of CO is approximately 280 kJ mol^{-1}, hence heat which this amount of CO can release on burning ≈ 1×10^7 MJ of heat

4. Calculation of the amount of the diesel saved and its financial value.
Quantity of diesel which would release 1×10^7 MJ of heat ≈ 225 tonne With diesel at around $US2 per kg this becomes about $US 0.5 million.

7 Metals in the Atmosphere

7.1 Lead

7.1.1 Current ambient standards

The current UK air quality standard for lead is 2.5 µg m^{-3}, equivalent to 0.3 parts per billion (p.p.b.) molar basis if the lead is present in elemental form. A similar figure has been set by the EPA in the US. There has been a dramatic reduction in lead release over the last thirty years since unleaded petrol came into widespread use (see next section). Even so, the annual release of lead into the atmosphere in the US is 1300 tons. It is believed that releases of this order are sufficient to be harmful, especially to children. A calculation similar to those done previously for VOC and for carbon monoxide follows.

Equating tons to tonnes for the purpose of a rough calculation
annual US release of lead = 1300×10^3 kg

Uniformly dispersed this will give:

$(1300 \times 10^3 / 5.1 \times 10^{18}) \times 10^{14} \times 28.8/207$ parts per hundred trillion volume basis

= 3.5 parts per hundred trillion

We might reasonably judge a rise of the order of parts per hundred trillion to be negligible when the ambient standard is 0.3 parts per billion or thereabouts. This is so and is an encouraging result of the change from leaded to unleaded petrol. There is scope for lowering this figure further by addressing lead paints. Lead from automobiles is further discussed in the next section. We also note that minuscule amounts of lead can be present in coals, perhaps milligrams or a few tens of milligrams per kilogram of coal. This is another way in which lead can find its way into the atmosphere.

7.1.2   Leaded petrol as a source of atmospheric lead

About 40 years ago there was major concern about lead in the atmosphere arising from use of lead tetraethyl as an octane enhancer for gasoline. Since then lead tetraethyl has very largely been replaced with organic materials which serve the same purpose. These include methyl tertiary butyl peroxide (MTBE). The ability of lead tetraethyl to improve engine performance was discovered in the 1920s by General Motors and was soon implemented. Concern about health effects was immediately expressed, and by 1927 the Surgeon General of the United States had set a limit on the proportion of lead tetraethyl in gasoline. As late as the 1960s, levels as high as about 2.5 gram of lead tetraethyl per gallon. By the mid 1980s standards were an order of magnitude lower than this.

The gigantic amounts of lead released over the decades when use of leaded gasoline was prevalent[12] would on the basis of a simple calculation like that above be expected to have led to ambient levels exceeding by an order of magnitude or more those currently enforced had they simply entered the atmosphere and remained there. However lead, being a heavy atom, does not disperse totally. Some of the lead emitted by car exhausts is quickly deposited and some of that which does enter the air subsequently deposits. In this way nature controls amounts of lead in the atmosphere

7.2   Mercury

7.2.1   Levels and amounts

Background levels of mercury in the atmosphere are typically 2 to 3 ng m^{-3} ($\equiv$ 0.3 parts per trillion). About 40% of the release of mercury into the atmosphere is from natural sources including volcanic eruptions. Forest fires also contribute significantly. 'Human' sources include power generation, trace amounts of mercury in fuels finding their way into the atmosphere. Incineration of household waste is a further source. A group of experts met in Bangkok in November 2007 in order to discuss mercury contamination of the atmosphere and prepared a report for the United Nations Environmental Programme. Mercury from coal combustion was amongst the sources identified for future reduction, as was waste incineration.

It has been estimated [1] that over the last 130 years about 200000 tons of mercury have been released into the atmosphere and that 2% of this resides in the atmosphere. The remainder is distributed between the soil and the oceans. A concentration for mercury like the one for lead in the previous section follows. The calculation uses the figures quoted from [1].

Equating tons to tonnes as previously:

Total mercury in the atmosphere = 200000×10^3 kg

Uniform dispersion will give:

$(200000 \times 10^3 \times 0.02/5.1 \times 10^{18}) \times 10^{12} \times 28.8/201$ parts per trillion volume basis

= 0.1 parts per trillion.

This is in order-of-magnitude agreement with the air quality
standard for mercury previously given.

The background level given above is sometimes well exceeded locally. In the early years of the 21st Century levels exceeding that by an order of magnitude were observed at least for part of the time in Beijing.

7.2.2 Health effects of mercury

These are well known, and only one will be mentioned here. It is believed that mercury is linked to autism, and that the closer a child lives to a power station burning coal with traces of mercury the more likely the child is to develop autism.

7.3 Cadmium

7.3.1 Levels and amounts released

Background levels of typically 0.5 ng m^{-3} ($\approx$ 0.1 parts per trillion molar basis) of cadmium occur in the atmosphere. Again volcanic eruption is a 'natural' source and coal combustion and waste incineration are 'human' ones. Total annual release in the US is believed to be of the order of 25000 US tons, and that up to 50% of that is of 'human' origin.

7.3.2 Carcinogenicity of cadmium

There is evidence from animal experiments and from studies of 'affected populations' that cadmium causes cancer. As an example, particles containing cadmium were secretly dropped from RAF planes over the English city of Norwich on several occasions in the 1960s. At that time England considered itself under threat from germ warfare, and the particles were used to simulate micro-organisms used in such warfare in order to predict dispersion patterns. In the early 2000s the facts relating to the spraying of cadmium particles over Norwich became known and there was concern that there had been cases of cancer attributable to the cadmium. The organisation 'Families against Cancer' alleged [2] that incidences of oesophageal cancer in the area over which the particles had been sprayed were significantly higher than average. The carcinogenicity was, 'Families against Cancer' assert, known at the time that the spraying took place. Moreover, a surprising proportion of the deaths from oesophageal cancer in the Norwich area had been of non-smokers (see below).

7.3.3 Cadmium in cigarette smoke

An individual who smokes 20 cigarettes a day will in so doing inhale about a microgram of cadmium, half of which will be retained by the body, the remainder being exhaled into the atmosphere where it is a danger to 'passive smokers'. This is examined in the calculation in the shaded area below.

Cadmium taken up per day by a twenty-a-day smoker = 0.5 µg

An adult inhales about 10 m^3 of air per day, therefore for a background level of 0.5 ng m^{-3} the cadmium inhaled from the atmosphere in one day by a non-smoker is:

$$0.5 \text{ ng m}^{-3} \times 10 \text{ m}^3 = 5 \text{ ng} \equiv 0.005 \text{ µg}$$

On the reasonable basis that the risk of ill effects from the cadmium is directly proportional to the amount inhaled, the increased risk due to smoking is:

$$0.5/0.005 = 100$$

The calculation has made the assumption that all of the cadmium inhaled from the atmosphere is retained, which is almost certainly not so. If we postulate that half of it is the figure in the bottom line becomes 200. The realities of 'passive smoking' are brought home when one considers the figures above. The half-life of cadmium once it is inside the body is long, of the order of tens of years.

7.4   Nickel

7.4.1   Occurrence in fuels

Nickel occurs in coal and, when coal is exported, its level can be a factor in the pricing. Export coals commonly have nickel contents in the range 1 to 20 mg kg^{-1} (1 to 20 parts per million weight basis). It comes from nickel in the original plant material from which the coal is derived and not (as is true of some inorganics in coals) from marine incursion into a deposit during coalification. Crude oil contains nickel at much higher levels than those, typically hundreds of p.p.m.

7.4.2   Atmospheric levels

A typical concentration of nickel in the atmosphere would be 0.003 μg m^{-3} (1 part per trillion molar basis). A related calculation follows in the shaded area.

The world consumes 80 million barrels of crude oil per day. If we make the approximation that it is all, either as distillate or residue, burnt and we use a value of 100 p.p.m. for the nickel content, the quantity of nickel released per day is:

80×10^6 bbl $\times$ 0.159 m^3 bbl^{-1} $\times$ 950 kg m^{-3} $\times$ (100/10^6) kg = 1208400 kg

Rise in the level of nickel in the atmosphere due to one day's oil usage =

(1208400/5.1 $\times$ 10^{18}) $\times$ (28.8/59) $\times$ 10^{12} parts per trillion volume basis

= 0.1 parts per trillion volume basis.

In reviewing this calculation we note the following. First, the assumption that all of the crude oil is burnt is incorrect in that it disregards the proportion diverted to petrochemical manufacture. However, a fair proportion of such petrochemicals are used to make polymers which in turn are the basis of such things as single-use plastic wrappings which have a fairly short life expectancy before incineration. This reduces the effect of the approximation on the accuracy of the calculation. Secondly, 0.1 parts per trillion is of the order of a tenth of the ambient level. The calculation is taken a step further below.

In the limit where all of the nickel in the atmosphere is taken to be from petroleum products, the residence time of one particle of nickel in the atmosphere before deposition, dry or with the rain water, is:

(1 part per trillion/0.1 part per trillion per day) = 10 days.

A point which the reader can easily confirm for him/herself is that particles in the atmosphere frequently <u>do</u> have residence times of the order of days, so again a semi-quantitative calculation has given a correct bottom line and, possibly, provided guidance for a more precise calculation where for a particular scene of nickel release numbers with only a moderate plus-or-minus are available. Two further points will be made in relation to the above calculations. First, the assumption that all of the nickel in the atmosphere is derived from petroleum sources is, for the purposes of a rough calculation, not an unreasonable one given the high nickel content of crude oils. Secondly, for the purpose of the reasoning underlying the calculations it is not necessary to assume that nickel exists in the atmosphere as elemental nickel.

7.5   Arsenic[13]

7.5.1   Concentrations in the air

Arsenic in the air is partly from natural sources, notably volcanic activity, and partly from 'human sources' including fuel utilisation. Levels in the atmosphere are of the order of 1 ng m^{-3} ($\equiv$ 0.4 parts per trillion molar basis). The world's most aberrant place in terms of arsenic levels in the atmosphere is Dhaka, Pakistan, where a level of 463 ng m^{-3} (0.18 p.p.b.) has been recorded. Even in Los Angeles levels of around 70 ng m^{-3} have been observed.

Typically, standards for arsenic in water are about 10 p.p.b. weight basis, and 10 p.p.m. weight basis in the soil. Each of those is much higher than the amount expected in air. One effect of a hurricane is that it transfers mass from earth and water to the air, and after Hurricane Katrina in 2005 there was concern about levels of arsenic in the air in the Gulf Coast states [3].

7.5.2   Arsenic as a carcinogen

Inhalation of arsenic from the atmosphere can cause lung cancer (and its ingestion from water can lead to cancer in organs including the liver and the bladder). Here again 'passive smokers' are placed at risk. Arsenic-containing pesticides are used at tobacco plantations and residues from these find their way into smoking materials.

The arsenic from a cigarette tends to be in the side stream smoke, that which is discharged into the atmosphere without having been inhaled [4]. Such smoke is rich in condensibles, as it has not passed through the filter tip of the cigarette. It would appear that the arsenic therefore threatens active and passive smokers equally. There is evidence that arsenic itself, unlike cadmium, is in liquid-vapour form in the side stream smoke. For this to happen under phase equilibrium conditions (as has in fact been asserted [4]) would not be possible under the temperature-pressure conditions of the cigarette smoke. This does not however preclude the co-existence of liquid arsenic and vapour any more than the co-existence of ice and liquid water is precluded in a room at 25°C. In either case the system will come to equilibrium eventually but it is the non-equilibrium situation in the meantime that is of practical interest. This section concludes with a calculation apropos of arsenic as a carcinogen.
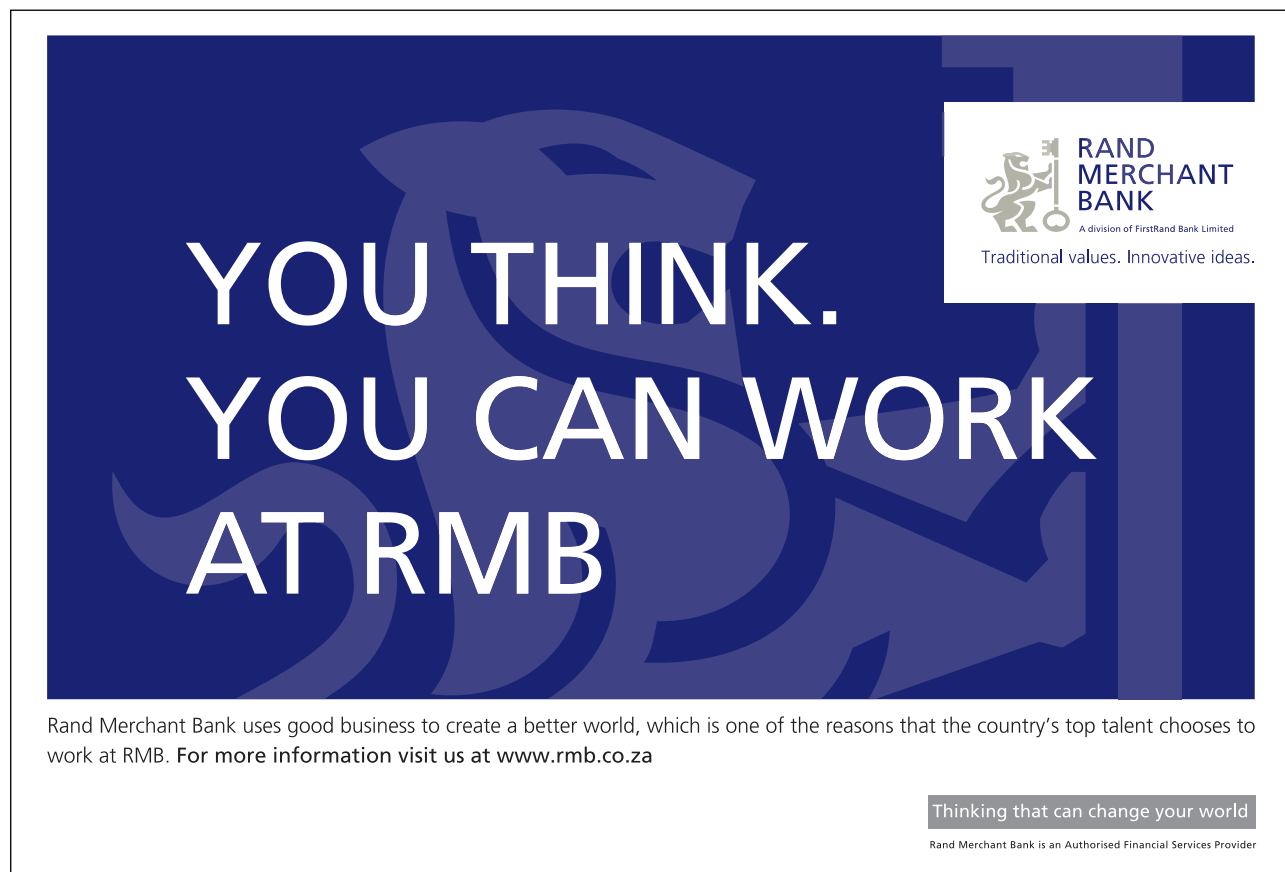
It has been estimated [5] that an upper bound on cancer risk due to arsenic in the atmosphere is 3×10^{-3} per µg m^{-3} of arsenic in the air. On that basis, if the standard quoted above of 1 ng m^{-3} is conformed to the excess deaths per million will be:

$$3 \times 10^{-3}\ [\text{µg m}^{-3}]^{-1} \times 10^{-3}\ \text{µg m}^{-3} \times 1000000\ \text{excess deaths}$$

$$= 3\ \text{excess deaths}.$$

For the conditions prevailing in Dhaka the figure will be ≈ 1400 excess deaths.

7.6   Analysis of air for metallic elements

The most common approach to such analysis is Atomic Absorption (AA) spectroscopy. In AA the element of interest is got into atomic form, usually in a flame. Light from the same element, having been produced in a hollow cathode tube, is directed at the flame. Light entering the flame is absorbed by the target element, and this is the basis of the signal. In many cases more than one spectral line is produced by the element in the cathode tube, so there is a choice of which one is selected for absorption measurement by the corresponding atoms in the flame (see below). There are variants on the basic AA technique; for example, the well known Zeeman effect can be used to resolve the signal into a number of components by application of a magnetic field, in which case the term Zeeman Atomic Absorption (ZAA) applies. Applications to three of the elements discussed in this chapter will be outlined in the concluding paragraph below.

Arsenic displays more than one spectral line. If that at 228.8 nm is used in atomic absorption spectroscopy there is the difficulty that cadmium also has a spectral line at this exact wavelength. 'Slits' are sometimes incorporated into atomic absorption devices which can resolve closely similar wavelength emissions from different atoms in the flame, but such a slit can only separate lines at least half a nanometre apart so cannot resolve the arsenic and cadmium lines referred to. The spectral line from arsenic at 193.7 nm is therefore often used in atomic absorption. The line at 189 nm might be used as an alternative. Finally when mercury is measured ZAA is often preferred for ambient level measurement distant from a releaser. ZAA devices for mercury analysis are available which have a detection limit down to 2 ng m^{-3}, the spectral line to which the magnetic field is applied being at 254 nm.

7.7   References

[1]   http://www.masgc.org/mercury/abs-moore.htm

[2]   http://www.familiesagainstcancer.org/?id=297

[3]   http://epa.gov/air/katrina/arsenic-screening.html

[4]   http://www.rsc.org/Publishing/ChemScience/Volume/2005/12/Toxic_smoke.asp

[5]   http://oehha.ca.gov/air/toxic_contaminants/html/Inorganic%20Arsenic.htm

8   Chlorinated Pollutants

8.1   Hydrogen chloride

8.1.1   Introduction

A chlorinated hydrocarbon will burn according to:

$$C_xH_yCl_z + [x + 0.25(y - z)]\,O_2 \rightarrow xCO_2 + zHCl + 0.5(y - z)H_2O$$
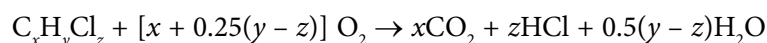
The primary pollutant arising from this is hydrogen chloride. There will of course be side-products including dioxins. Each of these will be discussed.

8.1.2   Sources of hydrogen chloride in the atmosphere

The most important 'human source' is incineration as explained above. For example, polyvinyl chloride (PVC) is a significant component of household waste and, when such waste is incinerated, will form hydrogen chloride. The generalised equation above becomes, for PVC:

$$[CH_2{=}CHCl]_n + 2.5nO_2 \rightarrow 2nCO_2 + nHCl + nH_2O$$
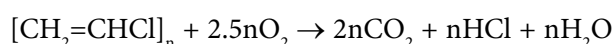
The presence of hydrogen chloride in the products necessitates neutralisation. Lime is the usual choice of base for this purpose. Notwithstanding these precautions some hydrogen chloride from incineration processes does enter the atmosphere.

Not only 'chlorinated waste' gives rise to hydrogen chloride. Cellulosic substances contain minuscule amounts of chlorine. Massive volumes of cellulosics are incinerated and their total release of hydrogen chloride is far from being negligible. Coals contain trace amounts of chlorine and this is another source of hydrogen chloride.

8.1.3   Background levels of HCl in the atmosphere

There are numerous standards relating to levels of hydrogen chloride in **workplace** atmospheres where hydrochloric acid is being used. A 'time-weighted average' (TWA) might be of the order of 5 p.p.m. However, in the atmosphere generally it might be exceedingly difficult to detect any hydrogen chloride at all. This is because any which might be released is very rapidly dissolved in water to form hydrochloric acid. Sulphur dioxide and nitric oxide are the anhydrides of weak acids, that is, acids in which the extent of dissociation in solution is a long way short of being total. When these dissolve therefore the result is a solution which is largely of the undissociated acid. By contrast hydrochloric acid is a strong acid and dissolution of hydrogen chloride leads to a fully ionic solution of the acid. This is the reason for the absence of gaseous hydrogen chloride from the atmosphere. We'd intuitively expect hydrogen chloride release to be a major factor in acid rain, and this is discussed in the following section.

8.1.4   Hydrogen chloride and acid rain

It is believed that hydrogen chloride does play a part in acid rain, but not a major one because the fact that hydrogen chloride is a strong acid is offset by the low levels of release when compared to sulphur dioxide and nitric oxide. The total hydrogen chloride release for the US in 2003 was just over a quarter of a million US tons (over ninety per cent of which was from fuel combustion to make electricity). The sulphur dioxide release was about two orders of magnitude higher and (as is clear from what has been said in Chapter 3) oxide of nitrogen release also hugely exceeds the hydrogen chloride release. It is for these reasons that hydrogen chloride is not a major factor in acid rain. A related calculation follows.

> The area of the lower 48 states of the US is 8 million km² approx. If we estimate the rainfall
> across the landmass as 12 inches (0.3 m) per year, the volume of rain in a year is:
>
> $0.3\ m \times 8 \times 10^{12}\ m^2 = 2.4 \times 10^{12}\ m^3$ or 2.4×10^{15} litres.
>
> Annual release of HCl $\approx 0.25 \times 10^6$ tonne $\equiv 6.8 \times 10^9$ mol
>
> If all of the HCl dissolves in rain water which is initially neutral,
> the concentration of hydrogen ions would be:
>
> $(6.8 \times 10^9\ mol/2.4 \times 10^{15}\ litre)$ mol litre^{-1} = 2.8×10^{-6} mol litre^{-1}
>
> pH = 5.5
>
> and this is about a unit of pH higher (i.e., a unit less acidic)
> than the values for acid rain given earlier in this volume.

The 'object lesson' of this calculation is that hydrogen chloride alone, in amounts which are actually released, would not bring the pH down to harmful levels. In fact so sensitive is the pH scale to adventitious acid that one would not expect tap water or even distilled water to have a pH of 7, and the value above is indicative of no more than background acidity. A further point is that if, as is actually the case, hydrogen chloride entered water already acidic because of oxides of sulphur and nitrogen the hydrogen ions from it would not simply add arithmetically to those from the other acids. This is because addition of the hydrogen chloride would cause extents of dissociation of the weaker acids to adjust in a way which could be calculated from their pK_a values.

8.2   Chlorofluorocarbons (CFCs).

8.2.1   Chemical structures of CFCs

Table 8.1 below gives details of CFCs which, it will be appreciated, are very simple compounds.

Chemical name	Chemical formula	Other names
trichlorofluoromethane	CCl_3F	CFC-11; Freon-11; Refrigerant 11.
dichloro difluoromethane	CCl_2F_2	CFC-11; Freon-12; Refrigerant 12.
trichloro trifluoroethane (strictly 1,1,2 trichloro 1,2,2 trifluoro ethane)	$CFCl_2ClF_2$	CFC-113
dichloro tetrafluoroethane (strictly 1,2 dichloro tetrafluoroethane)	CCl_2FCF_2Cl	Refrigerant 114
chloropentafluoroethane	$CClF_2CCl_3$	CFC-115: Freon 115; Refrigerant 115

Table 8.1 CFCs

Note that in all of the examples in the table the alkane structure, be it methane or ethane, is fully substituted with halogen atoms to the complete exclusion of hydrogen. Structures in which substitution is not total are known as hydrochlorofluorocarbons (HCFCs).

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8.2.2   CFCs and ozone

Uses of CFCs include refrigeration and air conditioning. Some leakage into the atmosphere occurs and this is of concern because of the effects on the ozone layer. The point was made in a previous chapter that whereas ozone close to the earth is a pollutant that at about 20 km above the earth's surface – the 'ozone layer' – needs protecting as it filters out parts of solar radiation which are harmful to persons. CFCs contribute significantly to ozone layer depletion, and this has led to restrictions in their use.

The way in which CFCs deplete ozone is by release of chlorine atoms. These can then react with ozone according to:

$$Cl + O_3 \rightarrow ClO + O_2$$
$$ClO + O \rightarrow Cl + O_2$$
$$\text{----------------------------}$$
$$\text{Net result: } O_3 + O \rightarrow 2O_2$$
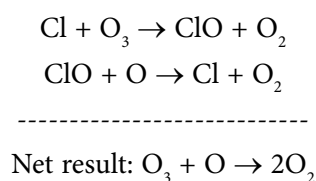
Important in understanding the potency of the chlorine atom in ozone depletion is that it is regenerated in the mechanism shown above.

8.2.3   The Montreal Protocol

This is a treaty whereby nations co-operate in controlling the release of ozone-depleting substances into the atmosphere. Since the treaty came into being in 1987 it has been revised several times, and over 190 nations have become signatories to it. Not only CFCs and HCFCs but also halons, used in fire extinguishment, come within its scope. Examples of halons are Halon 1211 (CF_2ClBr), Halon 1301 ($CBrF_3$) and Halon 2402 (CBr_2FCF_3). These are clearly distinguished from CFCs and HCFCs by the fact that they contain bromine. Countries having signed the treaty are required to limit CFC and Halon usage and production. CFCs and halons can be classified according to ozone depletion potential (ODP). Phasing out of particular CFCs and particular Halons is on a time scale which depends on the ODP and on the availability of suitable substitutes.

8.3   Elemental chlorine

8.3.1   Amounts and origin

Elemental chlorine is present in air at typically 2.5 parts per trillion. This is re-expressed on a weight basis below.

$$(2.5 \times 10^{-12} \times 40) \text{ mol m}^{-3} \times 71 \text{ g mol}^{-1} \Rightarrow 7 \text{ ng m}^{-3}$$

Most of the chlorine in the atmosphere comes from sea spray, according to:

$$2H^+ + 2Cl^- + 0.5O_2 \rightarrow H_2O + Cl_2$$
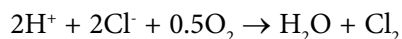
It is believed [1] that about 2 billion tonne per year of chlorine is formed in this way. This and the concentration information above provide a basis for estimating the residence time of elemental chlorine in the atmosphere.

2.5 parts per trillion molar basis = 71/28.8 × 2.5 parts per trillion
weight basis = 6 parts per trillion weight basis.

Weight of Cl_2 in the atmosphere = $6 \times 10^{-12} \times 5.1 \times 10^{18}$ kg ≈ 3×10^7 kg

Rate of chlorine production = 2×10^9 tonne per year ≡ 4×10^6 kg per minute

Lifetime = 3×10^7 kg/4×10^6 kg per minute = 7.5 minutes.

A reader can verify for him/herself from Web sources that it is known that the lifetime of a chlorine molecule in the atmosphere before it goes on to react is of the order of minutes. Here again a simple calculation has 'delivered the goods'. By the same token the reader must be aware that this is only a rough calculation. For example, the residence time will not be single-valued but will have a distribution.
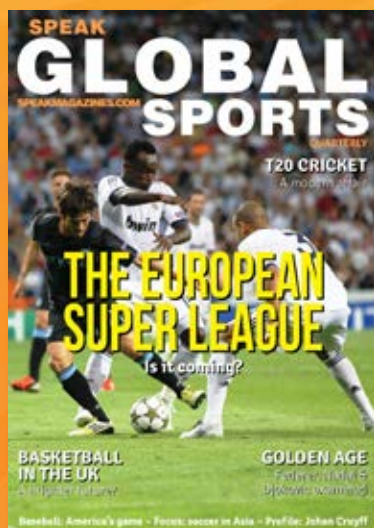
8.4 Dioxins

8.4.1 Definition

The term 'dioxin' has more than one meaning. Often it refers to a specific chemical compound, namely 2,3,7,8 tetrachloro dibenzo *p* dioxin. The chemical structure of this is very well known and is in any case available from very many conventional and electronic sources, so it will not be reproduced here. The term dioxin, possibly in plural form, also includes compounds having the same organic structure but with fewer chlorines or with the same number of chlorines orientated in an unsymmetrical way. Dioxins so defined are the most harmful chemical to human health known. However, the compounds which make up 'dioxins' do differ in their toxicity and the less toxic ones can be assigned a fractional value of the toxicity of 2,3,7,8 tetrachloro dibenzo *p* dioxin. This is the basis of TEQ – **t**oxic **eq**uivalent – amounts of dioxins, which is the conventional way of reporting quantities of dioxins.

8.4.2 Sources and amounts

It was mentioned earlier that in PVC incineration dioxins are produced. Wherever a chlorinated substance is burnt this is so. Similarly, when an organic substance is undergoing chlorination dioxins will be formed. These are 'human' sources: additionally there are natural sources, in particular forest fires. Because of the extreme hazards of dioxins, emission and ambient standards which apply are many orders of magnitude lower than for any other atmospheric pollutant. Ambient standards in air are of less than 1 picogram[14] per cubic metre of air, TEQ basis [2].

> From [2] we take a value of 0.1 picogram per cubic metre of air for the dioxin concentration. This represents a weight fraction of:
>
> $$10^{-13}/(40 \times 28.8) = 9 \times 10^{-17}$$
>
> If this figure is taken to apply to the entire atmosphere the total amount of dioxins in the atmosphere is:
>
> $$9 \times 10^{-17} \times 5.1 \times 10^{18} \text{ kg} = 450 \text{ kg}$$

We infer from this that the entire dioxin concentration of the atmosphere is only of the order of a tonne or less. It follows that sudden release of a quantity of the order of a kg would be a major incident. Also, when releases of dioxins from an activity which produces them are summed nationwide they are expected to be of the order of grams or at most tens of grams per year.

8.4.3 Measurement of dioxins

A reader of the previous section might wonder how dioxins in picogram quantities can be measured. In fact MS-GC[15] is routinely used to measure dioxins at these levels. Good resolution of the various compounds which comprise 'dioxins' can be achieved. If the effluent for a particular process is monitored for dioxins over a period, the measurements can be summed to give a total release over that period.

8.5 References

[1] http://www.eurochlor.org/index.asp?page=90

[2] http://www.epd-asg.gov.hk/textonly/english/report/dioxin02.php

9 Greenhouse Gases Part I: Background

9.1 Introduction to the greenhouse gas chapters

It is obvious that this matter is at present powerfully influencing world affairs. This will be so when those in infancy at this time are in old age, and beyond then. Carbon dioxide targets have already been set for the year 2100, so such emissions are certain to remain high on the international agenda throughout the 21st Century. Article after article, report after report, thesis after thesis and commentary after commentary are being produced on global warming, and it is doubtful whether to 'review the field' would be possible. That it would be hopelessly *im*possible on the scale of this text is certain.

It does not follow from what has been said in the previous paragraph that to attempt a short discourse on such matters would be unjustifiable. Quite the contrary. A writer with a long background in related matters who has himself been able to make one of two modest utterances on the matter of global warming (e.g., [1], [2]) might be able to prepare a useful synthesis of information which is focused on the related scientific principles. The value of such a synthesis is that media comments on the matter of global warming can be checked against it for scientific acceptability. It will also serve as a useful introduction to the subject for someone becoming professionally involved in it for the first time. These at any rate are the aspirations of the author as he sets about the two chapters of this book concerned with greenhouse matters.

9.2 Gas radiation

Many gases are transparent to thermal radiation across its entire spectrum. Those which do absorb radiation are known as participating gases. They include carbon dioxide and hydrocarbon gases such as methane. There is an important distinction between radiation from a solid and that from a gas. The interior of a solid does not of course participate in thermal radiation, which is a surface effect only. By contrast the space between gas molecules is transparent to thermal radiation and so radiation from gases is a volumetric effect. Also, radiation emission from gases is due to transitions within the molecular structure which are at particular levels, so radiation is in bands and not in a continuum.

9.3   Why 'greenhouse'?

Why is the effect of the carbon dioxide referred to as a greenhouse effect? We first consider how a greenhouse works. The glass or plastic panels of a greenhouse are transparent to visible radiation, and to radiation across a significant wavelength range beyond the ultra-violet and below the infra-red. Once this radiation is inside the greenhouse it is absorbed, possibly after a number of attenuating reflections. This causes the contents of the greenhouse to warm, and they in turn emit radiation characteristic of their temperature which is at much longer wavelengths than the solar radiation received. The glass or plastic panels are opaque to radiation of such wavelengths. They therefore absorb this radiation instead of transmitting it and the greenhouse interior is further heated as a result.

The comparison between a greenhouse and the action of so-called greenhouse gases is not totally rigorous. It is valid in that the greenhouse gases transmit solar radiation and retain terrestrial radiation like the panes in a greenhouse do. However, such retention is not the only factor in the 'greenhouse effect'. There is also emission of short-wavelength radiation by the greenhouse gases.

9.4   A simplified model for the emissivity of the troposphere

The troposphere extends to 11 km above the earth's surface. At that height the pressure is 0.23 bar and the temperature 216K [3]. In a simple, illustrative calculation we take the height at which T = 273K, which is 2.3 km, and approximate the troposphere to a spherical envelope extending to that height above the earth's surface. We take this to have a uniform carbon dioxide concentration of 350 p.p.m.[16] at a total pressure [3] of 0.76 bar. Accordingly we proceed to calculate the emissivity of such a layer. A reader requiring background on the principles of thermal radiation should go to [4] or equivalent.

Letting the radius of the earth be r_i and that of the troposphere envelope r_t:

$$V/A = (1/3)[\ (r_t^3 - r_i^3)/\ (r_t^2 + r_i^2)]$$

where V is the envelope volume and A its area, the latter being the sum of the outer and inner areas. Now for such a layer the path length *L* for radiation purposes is given by [4]:

$$L = 3.6V/A = 1.2[\ (r_t^3 - r_i^3)/\ (r_t^2 + r_i^2)]$$

Using a value of 6378 km for r_o, a value of 6380.3 km is obtained for r_t from which:

$$L = 4 \text{ km.}$$

Now the pressure 'p' of carbon dioxide is 0.76 × 350 × 10^{-6} bar

$$= 0.00027 \text{ bar}$$

The product p*L* is then 1.1 bar metre = 3.5 bar foot.

Now from charts [4], [5] this path length at 273 K (491°R) corresponds to an emissivity of 0.2 to one significant figure.

Hence it has been shown how an atmosphere containing carbon dioxide at hundreds of p.p.m. level can have a very significant emissivity. The calculation can be taken one step further in the following way.

Rate of radiation from the gas = esT^4 W m^{-2} [4]

where e is the emissivity (0.2), s the Stefan-Boltzmann constant
(5.7×10^{-8} W m^{-2}K^{-4}) and T the gas temperature (273K). This is a flux per unit area of the source and not per unit area of the earth's surface.

Inserting numbers:

Rate of radiation from the gas = 63 W m^{-2}

This is about 5% of the solar flux which the earth receives at high sun and can reasonably be correlated with 'radiative forcing'. The radiative forcing in units of W m^{-2} can be defined as the change in the solar flux divided by 4 and multiplied by 0.7. The above figure gives when so processed gives 11 W m^{-2} or 0.8% of the solar constant. It would be facile or even misrepresentative to compare this with arbitrarily selected values for the carbon dioxide radiative forcing from the literature, but that this is about the expected value there is no question. (A very brief search on the Web will confirm this.)

An interested reader might like to repeat the calculations with other values of the quantities. There is the difficulty that the radiation charts for carbon dioxide do not go to temperatures below 273K, and of course the temperature of the troposphere at heights greater than that used in the calculation goes well below 273K. Extrapolation of the charts over a few tens of degrees would probably be justifiable.

9.5   Levels of carbon dioxide in the atmosphere

The level is currently about 370 p.p.m. In the early nineteenth century it was about 280 p.p.m. In the first century A.D. it was about 260 p.p.m. These data are known from 'ancient air' trapped in bubbles of known age in the Antarctic ice layer. A rise of 90 p.p.m. over two hundred years converts simply to 0.45 p.p.m. per year but this is not in fact the case: the rise is faster than linear and in the early 21st Century it well exceeds 1 p.p.m. per year. This is shown in the calculation below.

In 2005 the amount of carbon dioxide released into the atmosphere from combustion processes was 28192.74 million tonne [6]. As an annual increase in the carbon dioxide content of the atmosphere p.p.m. volume or molar basis this is:

$[28192.74 \times 10^9/(5.1 \times 10^{18})] \times 10^6 \times 0.0288/0.044 = 3.5$ p.p.m. approx.

This figure will be revisited in the next chapter when the Kyoto targets are discussed.

9.6   The distinction between fossil fuel and non-fossil fuel carbon dioxide

Carbon dioxide in the atmosphere is taken up by plants and converted to glucose and from there to cellulose. When the cellulose is burnt the carbon dioxide is simply being put back where it came from and there is no net increase in the carbon dioxide level of the atmosphere and the fuels are said to be carbon neutral. By contrast when fossil fuels are burnt carbon dioxide not having, on any time scale of interest, previously existed in the atmosphere is put there. Combustion of such fuels therefore raises the carbon dioxide content of the atmosphere and these fuels are not carbon neutral. A related calculation follows which is taken from previous work [7] by the present author.

Suppose it is required to produce heat at 10 MW. The amount of carbon dioxide per hour will this produce if the fuel is bituminous coal of carbon content 85% and calorific value 30 MJ kg^{-1} is calculated below.

Rate of requirement of fuel = $(10^7$ J $s^{-1}/30 \times 10^6$ J $kg^{-1}) \times 3600$ s $hour^{-1}$
=1200 kg $hour^{-1} \Rightarrow$ 1020 kg $hour^{-1}$ of carbon burnt $\Rightarrow$ 3740 kg CO_2

If the fuel is wood waste of carbon content 55% and calorific value 17 MJ kg^{-1} the hourly carbon dioxide production is:

$(10^7$ J $s^{-1}/17 \times 10^6$ J $kg^{-1}) \times 3600$ s $hour^{-1}$
= 2117 kg $hour^{-1} \Rightarrow$ 1164 kg $hour^{-1}$ of carbon burnt $\Rightarrow$ 4270 kg CO_2

There is the anomaly that the carbon neutral fuel produces significantly more carbon dioxide than the fossil fuel per unit heat produced. The above calculation uses arbitrary though typical values for the quantities involved, and that wood fuel produces more carbon dioxide than coal other things being equal is in fact a general result. The wood fuel is preferred on carbon dioxide emission terms because, unlike the carbon in the coal, that in the wood fuel was in the recent past carbon dioxide in the atmosphere. This means that when the wood is burnt carbon dioxide is simply being put back where it came from, as discussed in the previous paragraph.

9.7   Carbon dioxide emissions from natural gas and petroleum fuels

Natural gas can often be approximated in composition to pure methane which burns according to:

$$CH_4 + 2O_2 \ (+7.52 \ N_2) \rightarrow CO_2 + 2H_2O \ (+ \ 7.52 \ N_2)$$
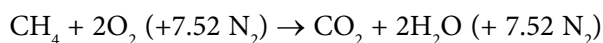
with calorific value[17] 55 MJ kg^{-1} for the reaction as written.

Where carbon dioxide and water vapour are both 'participating', contributing to the emissivity of the gas, the ratio of carbon dioxide to water needs to be known. For methane then the ratio of carbon dioxide to water molar basis in the products is 1:2. Plots the gas emissivity against the temperature for different pL values analogous to those used for carbon dioxide alone in section 9.4 are also available (from the same sources, e.g., [4], [5]) for gas containing carbon dioxide and superheated water in the ratio 1:2. Consider now the combustion of a liquid hydrocarbon of generalised formula C_nH_m:
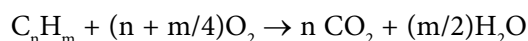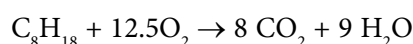
$$C_nH_m + (n + m/4)O_2 \rightarrow n\ CO_2 + (m/2)H_2O$$

where for clarity the nitrogen has been omitted from the equation. Clearly for methane n = 1 and m = 4. For n-octane for which n = 8 and m = 18:

$$C_8H_{18} + 12.5O_2 \rightarrow 8\ CO_2 + 9\ H_2O$$

The point being made is that as 'n' and therefore 'm' get larger in going from short chain hydrocarbons to long chain ones 'n' approaches 'm/2' and the ratio of carbon dioxide to water vapour in the product gas approaches unity. For the post-combustion products of liquid fuels therefore it is taken that the two participating gases are equimolar and plots of the emissivity against the temperature for different pL values are for this composition. These too are available from sources including [4] and [5].

9.8   Methane as a greenhouse gas

The current level of methane in the atmosphere is 1745 p.p.b. (parts per billion). The level was about 40% lower than this in pre-industrial times. It is released as escaped natural gas, from gas fields and from pipelines, and also from coal mines including disused ones. 'Natural gas hydrates' are currently seen as a possible 'beyond oil' source of energy. These consist of methane molecules trapped in ice in a clathrate structure and occur on the seabed and on the continental shelf. It is **certain** that the amount of methane contained in the gas hydrate resources of the world exceeds the known conventional natural gas reserves by at least three orders of magnitude. Natural gas hydrates therefore contribute to the background methane levels of the atmosphere. Cellulosics form methane on decomposition and this is another source. Methane in the atmosphere is eventually oxidised to oxides of carbon and water, but very slowly; the half life of methane in the atmosphere is 7 years.

Methane is a more powerful greenhouse gas than carbon dioxide. This can be explained to a limited degree in the following way. Methane has five atoms but carbon dioxide only three. There will therefore be more modes of vibration with methane than with carbon dioxide, and it is the vibrational functions of the molecular structure that absorb in the infra-red. This reasoning can only be rough because not all vibrational modes of molecules are infra red active but as an intuitive guide it is valid.

9.9   Sources of carbon dioxide other than fossil fuel combustion

These include seepage from carbon dioxide fields. Such fields are natural reserves of carbon dioxide, and include those in Utah, Oklahoma and Colorado many of which are owned and operated by oil companies. The McElmo Dome field in Utah holds an estimated 3×10^{11} m³, of carbon dioxide, equivalent to 5×10^8 tonne. Carbon dioxide from such fields can be used in enhanced oil recovery, a topic discussed at greater length in the next chapter. Like so many pollutants, carbon dioxide is produced by volcanic activity. We have already seen that long before industrialisation there were considerable levels of carbon dioxide in the atmosphere.

9.10   References

[1]   Jones J.C. 'Greenhouse gases and non-grey behaviour' Journal of Chemical Education 82 837 (2005)

[2]   Jones J.C. 'On the reduction of atmospheric carbon dioxide levels' Open Thermodynamics Journal 2 12 (2008)

[3]   http://hurri.kean.edu/~yoh/calculations/standatm/StdAtm.html

[4]   Holman J.P. 'Heat Transfer' McGraw-Hill NY, any available edition.

[5]   Perry's Chemical Engineers' Handbook, any available edition.

[6]   http://www.eia.doe.gov/pub/international/iealf/tableh1co2.xls

[7]   Jones J.C. 'Reflections on combustion principles as they relate to a miscellany of practical fuels' Chemical Journal of Armenia 60 (2) 174–185 (2007)

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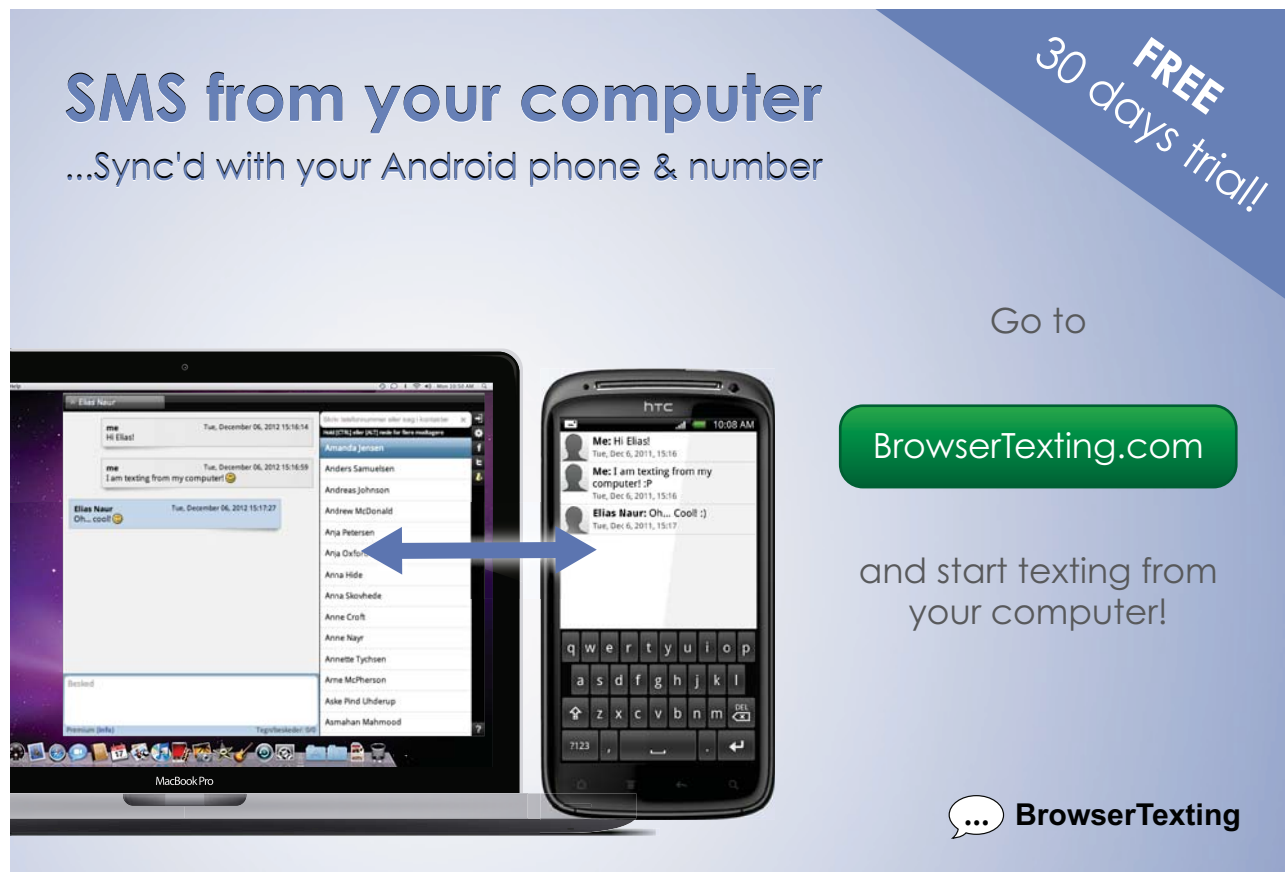
10 Greenhouse gases Part II: Mitigation measures, emission targets and carbon trading

10.1 Introduction

Countries have set targets for carbon dioxide reductions, some in conformity with the Kyoto Protocol. This is an international agreement setting limits on emissions of carbon dioxide and other greenhouse gases. It originated at an assembly in Kyoto, Japan, in 1997. Targets vary by region: in the UK a 12.5% reduction on the 1990 emissions by 2012 is aimed for. What were initially recommendations were actually enforced in 2005 in the countries – 141 in all – which had ratified the Kyoto protocol. The US had not ratified it, neither had Australia which nevertheless has its own quite ambitious CO_2 reduction targets.

10.2 Reduction of carbon dioxide emissions from power generation

10.2.1 Introduction

Electricity generation makes a very large contribution to annual carbon dioxide amounts. We saw in the previous chapter how substitution of carbon neutral fuels for fossil fuels can bring about a reduction in carbon dioxide release. This theme is extended in this section in two ways: by consideration of co-firing of coal biomass and by examining effects of turbine efficiency on carbon dioxide emissions.

10.2.2 Co-firing of coal and biomass

Thermal generation of electricity contributes a great deal to the annual carbon dioxide release. One way of reducing such emissions is by co-firing of biomass with coal. This is explained in the shaded area below.

We return to the calculation in section 9.6 in which heat is being produced at 10 MW from coal. We now consider the case [1] where the coal-derived CO_2 has to be reduced by 5% to comply with local non-fossil-fuels requirements. This is done by co-firing with biomass of calorific value 17 MJ kg^{-1} and carbon content 55%. The amounts of coal and biomass per hour required and their carbon dioxide releases can be calculated.

Coal-derived CO_2 to be reduced from 3740 kg per hour to 3553 kg per hour.

Carbon burnt to be reduced from 1020 to 969 kg per hour.

Coal burnt reduced from 1200 to 1140 kg per hour.

Heat to be provided by the biomass per hour

$= 60 \times 30$ MJ $= 1800$ MJ requiring
$1800/17 = 106$ kg biomass releasing
$(106 \times 0.55 \times 44/12)$ kg $CO_2 = 214$ kg CO_2.

Total CO_2 release per hour $= (3553 + 214)$ kg $= 3766$ kg

There is therefore a slight increase (0.7 of 1%) of total CO_2 due to partial substitution of the biomass for coal but a reduction as required of 5% of the CO_2 from coal. The objective of the co-firing is therefore achieved. Wood in various forms, including forest thinnings, can be used in such co-firing. Cotton waste has also been used. An important example of co-firing of coal and biomass is Drax Power Station in West Yorkshire. This is the UK's largest coal fired per station and will by the end of 2009 have replaced 10% of its coal with biomass.

10.2.3 Enhanced turbine efficiency

Where a steam cycle (Rankine cycle) is used to make electricity, some reduction in carbon dioxide release can be achieved by changing the turbine conditions, for example by using superheated steam instead of saturated steam in the work-releasing step of the cycle. Imagine that a turbine operating on a Rankine cycle without superheating achieves an efficiency of 30%. Superheating is then introduced and this raises the efficiency to 35%. The fuel is natural gas, calorific value 55 MJ kg^{-1}. We calculate in the shaded area below the carbon dioxide release per TJ (10^{12}J) of energy from the cycle in each case. (This choice of reference value of the energy will be justified in a follow-up calculation.)

Calling the efficiency of the cycle expressed fractionally h:

Per TJ of energy from the cycle (1/h) TJ of heat are required from the fuel.

Returning to the chemical equation for the combustion:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

From an examination of the above equation:

1 molar unit of CH_4 weighing 0.016 kg

$\downarrow$

1 molar unit of CO_2 weighing 0.044 kg

1 kg methane burnt $\rightarrow$ (0.044/0.016) = 2.75 kg carbon dioxide

No superheating, efficiency 30%

Per TJ of energy from the cycle:

$(10^{12}/0.3)$ J $= 3.3 \times 10^{12}$ J of heat needed requiring:

$[(3.3 \times 10^{12})/(55 \times 10^6)]$ kg methane yielding:

$2.75 \times 3.3 \times 10^{12}/(55 \times 10^6)$ kg carbon dioxide

= 165000kg (165 tonne)

With superheating, efficiency = 35%

Per TJ of energy from the cycle:

$(10^{12}/0.35)$ J $= 2.86 \times 10^{12}$ J of heat needed requiring:

$[(2.86 \times 10^{12})/(55 \times 10^6)]$ kg methane yielding:

$2.75 \times (2.86 \times 10^{12})/(55 \times 10^6)$ kg carbon dioxide

= 143000 kg (143 tonne) , a 13% reduction on the simple cycle without superheating.

10.3   Carbon credits

10.3.1   Illustrative calculation

We continue to consider the calculation immediately above and first note that a turbine producing 100 MW of power would produce 1 TJ in just under 3 hours hence the TJ is a reasonable basis for the calculation.

In the above calculations, over a three hour period the reduction in carbon dioxide emissions is 22 tonne. Monetary value = $US 22 x where x is the value of one carbon credit in units $ per tonne.

Scaled to one year, this becomes $US 0.064 x million

Values of carbon credits vary widely from place to place and from time to time. Negotiation and brokerage occur. The basis of carbon credits is discussed below.

10.3.2   Allocation and distribution of carbon credits

Any country in attempting to meet its greenhouse targets imposes limits on the amount of carbon dioxide which may be released by a particular organisation. If that organisation exceeds the quota it has been assigned, it must purchase credits from another organisation which has produced a quantity of carbon dioxide, over the period to which the quota applies, lower than that assigned to it. We might say that the former organisation is in the red and the latter in the black, so transfer of 'credit' from the latter to the former keeps the books balanced. In such a transfer cash is traded for carbon dioxide emission allowances. This is the basis of carbon credits and there is a great deal of trading in them as previously noted. Carbon credit trading between countries is quite standard practice and this helps keep prices competitive.

Carbon trading is a major part of the budget of any big organisation. For example, it was reported that in 2006 the National Health Service had exceeded its allowance and had to rectify that by purchasing carbon credits and that the cost of those credits would have provided the salaries for a significant number of newly hired nursing staff.

10.4   Carbon dioxide from vehicles

10.4.1   Introductory calculation

Imagine a motor vehicle operating at 50 miles per (Imperial) gallon of gasoline fuel. Per mile travelled the quantity of fuel used is:

$$1/50^{th} \text{ of a gallon} \equiv 9 \times 10^{-5} \text{ m}^3$$

The density of such a fuel will be $\approx 800 \text{ kg m}^{-3}$, so the weight of gasoline consumed per mile is:

$$9 \times 10^{-5} \text{ m}^3 \times 800 \text{ kg m}^{-3} = 0.07 \text{ kg}$$

Now we saw in the last chapter that a liquid fuel such as a gasoline will to a fair approximation give an equimolar carbon dioxide/water combustion product. This means that the empirical formula is:

$$C_nH_{2n}$$

In a quantity of 1 kg of such a fuel there are 857 g of carbon and 143 g of hydrogen. When therefore 0.07 kg of the fuel is burnt (that is, the car travels 1 mile) there are:

$$0.07 \times 857 \times 44/12 \text{ g carbon dioxide produced} = 219 \text{ g CO2}$$

So the carbon dioxide release is 219 g per mile or 137 g per km.

In fact in 1998 in the EU a target figure for 2008 was set at 140 g per km [2], almost exactly the figure arrived at in the above calculation. It would appear therefore that fuel consumption of 50 miles per gallon is required for this target to be reached.

10.4.2   Carbon dioxide levies on vehicle registration

Motor cars in the UK which use gasoline or diesel are subject to a levy on the annual registration fee according to the carbon dioxide release. This release is determined for particular makes and models and appears on the registration document in units either of g per km or g per kWh. No levy applies to a vehicle emitting less than 100 g per km of carbon dioxide. An annual levy of £35 (June 2008 reckoning) applies to vehicles emitting in the range 101 to 120 g per km, and this rises over five increments to £400 for a car emitting in excess of 225 g per km. An emission of 140 g per km, obtained in the calculation above, would attract a levy of £120 per year.

A current statistic [3] is that an 'average' private motorist in the UK drives 13438 km per year and in so doing adds 2.246 tonne of carbon dioxide to the atmosphere. This converts to 167 g per km, for which a registration levy of £170 per year would be payable.

10.4.3   Carbon-neutral fuels for vehicles

For spark ignition engines ethanol, or gasoline-ethanol blends, are becoming very widely used. A common example is E85which is 85% ethanol balance gasoline. Ethanol can be obtained from corn or (increasingly in the US) from sorghum and, originating with biomass, is carbon neutral. Methanol is also a good fuel for spark ignition engines. However, the carbon neutrality of methanol is ambiguous. If it is made from pyrolysis of biomass or from gasification of biomass it is of course carbon neutral. However, a great deal of methanol on the world market is made from natural gas which is not carbon neutral, therefore neither is the methanol made from it.

For compression ignition engines biodiesels are becoming more and more prevalent. When biodiesel is being used to power a diesel engine its cetane index has to be of the correct value (about 50). If this is not so with the oil as extracted the cetane number can be brought to the required value by esterification. This however adds to the cost of the fuel and, more seriously, and if the methanol used as a reagent in the esterification was made from natural gas the esterified product loses about 10% of its carbon neutrality. There is nothing at all new about the fuels discussed in this section. A version of the Ford Model T, the world's first mass produced car, was available which would run on ethanol. The Japanese Navy used biodiesel in WW2.

10.5   Carbon dioxide from aircraft

10.5.1   Amounts released

Each year 600 million tonnes of carbon dioxide are released from commercial aircraft. From a calculation of the sort carried out several times previously in this book which will therefore not be given in detail here, it is easily shown that this is sufficient to raise the carbon dioxide content of the atmosphere by about 0.08 p.p.m. annually.

> The annual rise in CO_2 is about 3.5 p.p.m., as stated in an earlier chapter.
>
> Percentage due to commercial aircraft = (0.08/3.5) × 100 = 2% to the nearest whole number.
>
> It is in fact widely known that only about 2% of the total carbon
> dioxide release is from commercial aircraft.

Release of carbon dioxide from jet aircraft is of the order of 100 g per passenger kilometre, comparable to the figure from a singly occupied motor car. Aircraft operators are assigned carbon credits and are involved in buying and selling them. For example, British Airways have been assigned carbon credits of 16.1 million tonne per year, yet produce carbon dioxide at about 16.8 million tonne per year. A fiscal calculation follows.

> Carbon credits needing to be bought by BA on the basis of the
> figures in the previous paragraph = 0.7 million.
>
> Average price of a carbon credit = £25 per tonne
>
> Price of the credits required = £17.5 million
>
> This is equivalent to 3 to 4% of the after-tax annual profit of the airline.

The conclusion of the rough calculation is that when the airline is exceeding its carbon dioxide allocation by a mere 4% the cost is an equivalent percentage of the annual profits. Little wonder that BA has expressed concern to the European Commissioner for the Environment about the need to obtain carbon credits at a time when the aviation industry is being affected by unprecedentedly high oil prices.

Many airlines enable passengers who wish to do so to meet the 'carbon cost' of their journey[18]. We consider Qantas (Australia), who operate such a scheme, as an example. At say 100 g carbon dioxide per km, a 5000 km trip generates half a tonne per passenger. This is paid for at the going rate for a carbon credit. At a credit price of typically $A50 per tonne, $A25 are payable for a 5000 km trip. Money so raised is diverted to approved activities for offsetting carbon dioxide emissions.

10.5.2 Possible use of carbon neutral fuels in jet aircraft

The fuel used in aircraft jet engines is petroleum material in the kerosene boiling range. The view of the author is substitution of this with a carbon neutral fuel should not be difficult, and he is supported by a recent trial trans-Atlantic crossing of a Virgin aircraft powered by biodiesel. Interchangeability of fuels in jet aircraft would be expected to be technically simple. This is because a jet engine, being a gas turbine, is not an internal combustion engine: all combustion is external to the turbine cycle. It is the hot post-combustion gases which enter the turbine where their sensible heat is converted to work, and the nature and quality of the fuel are fairly immaterial. When for example biodiesel is being used to power a diesel engine its cetane index has to be the correct value as discussed previously. When biodiesel is used as the fuel for a jet engines it is difficult to see how the cetane number would be at all relevant to performance, so processing would be not be required. The fact that the mineral counterpart of biodiesel, that is diesel itself, is in a different boiling range from kerosene is also irrelevant.

10.6   Carbon dioxide from shipping

There are said to be of the order of 70000 vessels on the oceans of the world using 200 million tonnes of hydrocarbon fuel per year.

> If again we take it that the fuel corresponds to the empirical formula CH_2,
> a tonne of the fuel contains 12/14 tonne carbon = 0.86 tonne
>
> 200 million tonnes fuel → (0.86 × 200 × 44/12) million tonnes CO_2
>
> = 630 million tonnes.
>
> This is a somewhat higher figure than for commercial aircraft.

Passenger shipping can have a major advantage over land or air transport in terms of carbon economy as the calculation below shows.

> The recently laid up QE2 ocean liner travelled about 40 feet per gallon of fuel
>
> In SI this converts to 2700 m per m³ of fuel or about 3 m per kg of fuel
>
> This converts to 1 m per 0.33 kg of fuel or 1 m per (12/14)
> × 0.33 kg carbon burnt = 0.28 kg carbon
>
> ⇓
>
> 280 × 44/12 g CO_2 per m travelled = 1030 g per m
>
> Now the QE2 could hold up to 1800 passengers therefore CO_2 per
> passenger m = 1030/1800 g = 0.6 g per passenger m.
>
> This is comparable to such figures for land and air transport. If the number
> of crew members (up to 1000) is added to the number of passengers
> the figure for the QE2 becomes correspondingly lower.

The above calculation does in fact require qualification. A large passenger ship like QE2 does not only convey passengers: it accommodates, feeds and entertains them and in cold weather keeps them warm. When the carbon costs of these are factored in it is possible for the gap between the gram per passenger kilometre for air and sea to close altogether. A passenger ferry, which does merely transport passengers, might well in its carbon footprint to approximate to the calculation above.

10.7   Miscellaneous sources of carbon dioxide

These are given in table 10.1 below. It must in all cases be recognised not only that different practices apply in different places but that R&D into reduction of carbon dioxide emissions is continual with the result that figures such as those given tend to go out of date very quickly.

Source	Magnitude of CO2 release.
Railways.	e.g., Amtrak (USA): 180 g per passenger mile. This can be compared with figure for road, air and sea travel given previously in this chapter.
Oil refining.	35 to 40 million tonne per day internationally.
Household waste incineration.	A weight of carbon dioxide equal to that of the waste incinerated.
Airports, air transport movements (ATM) and stationary aircraft.	e.g., Stanstead Airport, London (» 0.21 million ATM per year and 24 million passengers per year): 5 million tonnes of CO_2 per year.
Residential natural gas installations.	80 million tonnes per year in the UK.
Car production.	Half a tonne to a tonne of CO_2 per car manufactured. A car will subsequently release an equivalent amount over 5000 to 10000 km of travel.

Table 10.1 Miscellaneous carbon dioxide releasers.

10.8   Uptake of carbon dioxide by vegetation

A widely applied rule is that a tree traps a tonne of CO_2 in 40 years.

Some trees, notably in the Sequoia forest in the US, have been known to have existed for over 2000 years. Such a tree will therefore have trapped :

(2000/40) tonne = 50 tonne over its life span.

In the rain forests of the world an estimated 1050 million trees per year are felled for timber. The loss of this to the carbon sequestration capacity of the planet is easily calculated to be 26 million tonne per year.

About a billion trees were planted across the world in 2007 [4]. These when fully grown will add:

$(10^9/40)$ tonne = 25 million tonne

to the carbon sequestration capability of the planet.

It is in fact straightforward to estimate to what extent the forests of the world are able to cope with carbon dioxide emissions using the figure [4] of 4 billion hectares of forest on the world's surface and [5] of 6 tons of carbon dioxide removed from the atmosphere per hectare of forest per year. Simple multiplication gives a figure of 24 billion tonne, which is of the same order of magnitude as the total release annual though smaller than it. Clearly the forests of the world have a critical role to play in protection from the effects of carbon dioxide. Illegal felling of trees, referred to above, is much more serious than simply misappropriation of the timber.

10.9   Carbon dioxide sequestration

10.9.1   Introduction

The capture and storage of carbon dioxide is an increasingly important practice in the struggle to keep carbon dioxide levels down. We return to the calculation in section 9.6 in which 3740 kg of carbon dioxide per hour are produced in the generation of electricity from coal at 10MW and imagine that carbon dioxide sequestration is to be applied to this.

> The carbon dioxide per day requiring sequestration is:
>
> 3740×24 kg = 90000 kg $\equiv 2 \times 10^6$ mol or 50000 m^3 at 1 bar 288 K.
>
> 50000 m^3 is equivalent to a cube of 37 m side.

Storage of carbon dioxide as a liquid as a liquid is possible.

> Using a value of 950 kg m^{-3} for liquid carbon dioxide, the calculation above can be extended:
>
> 90000 kg per day $\equiv$ approx 100 m^3 per day, a cube of 4.5 m side.

10.9.2   Case study: Drax power station

Drax power station featured previously in this volume. It has recently been reported [6] that there are proposals under way for the carbon dioxide from Drax as well as that from other major releasers in that region of England to be stored in depleted oil and gas fields in the nearby north sea. These are of course already linked by infrastructure to the mainland.

10.9.3   Enhanced oil recovery (EOR)

When carbon dioxide is admitted to an oil well for storage the internal pressure is raised and this can have the effect of forcing oil out in what is called enhanced oil recovery. This has taken place at a number of fields including the Sleipner Field in the North Sea and the Weyburn Field in Saskatchewan. Carbon dioxide pressure required are in excess of 100 bar.

10.10   Concluding remarks

That the issues discussed in this chapter and the previous one will continue to dominate the international agenda is not in doubt. I expect that students – undergraduates and postgraduates – will be amongst the readers of this book (although it is directed at other audiences as well). Such students when they enter careers in engineering and technology will find that so many of the decisions they are responsible for have to be justified in 'carbon' terms. These chapters have not gone far at all with this enormous topic, but sometimes the perspectives and emphases of a discourse can be more important than its degree of detail. The scientific principles invoked are not abstruse. The principles of thermal radiation were formulated in the 1870s. About 50 years before then the French mathematician and physicist Fourier asserted that gases in the atmosphere could raise the temperature of the earth [7]. The ramifications – economic, social and political – of 'global warming' are very complex, but their complexity should not have the effect of banishing from the minds of those professionally involved in such matters that the science is simple to understand.

10.11   References

[1] Jones J.C. 'Reflections on combustion principles as they relate to a miscellany of practical fuels' Chemical Journal of Armenia 60 (2) 174–185 (2007)

[2] http://www.vcacarfueldata.org.uk/information/cars-and-carbon-dioxide.asp

[3] http://www.carplus.org.uk/carclubs/car-clubs-&-carbon-savings.htm

[4] http://www.unep.org/billiontreecampaign/FactsFigures/QandA/index.asp

[5] http://aede.osu.edu/people/sohngen.1/forests/effectc.pdf

[6] 'The Chemical Engineer' July 2008 p. 8.

[7] Jones J.C. 'Fourier and Napoleon' International Journal of Mechanical Engineering Education 35 (3) 182 (2007)
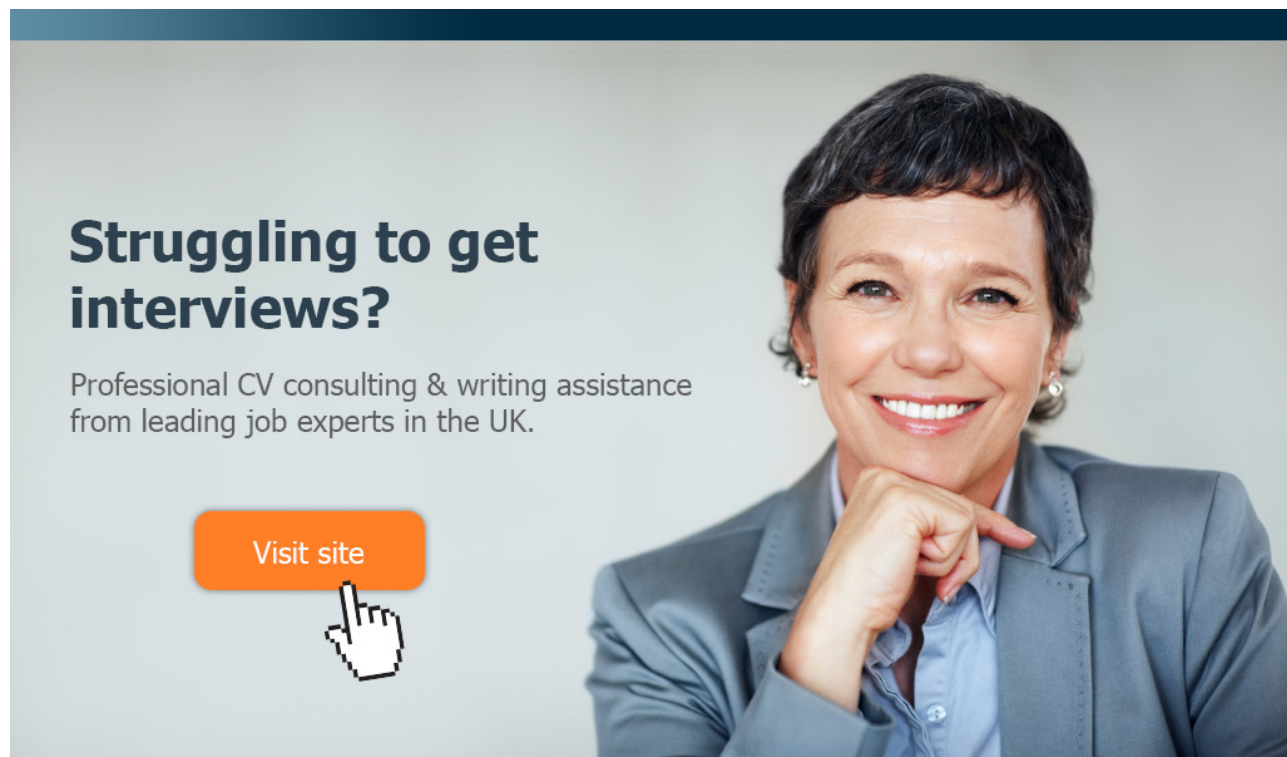
11 Radioactivity in the Atmosphere

11.1 Radon

One of the inert gases (a.k.a. as noble gases) radon occurs in air and is radioactive. The process of interest is:

$$^{222}\text{Rn} \rightarrow {}^{218}\text{Po} + \alpha \text{ particle}$$
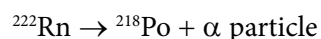
with a half-life ($t_{1/2}$) of 3.8 days. Radon is believed to cause lung cancer, consequently standards apply. One such is 4 picocuries (pCi) per litre of indoor air. This is explained more fully in the shaded area below.

1 pCi ≡ 2.2 disintegrations per minute

Disintegration is according to:

$$m/m_o = e^{-0.18t}$$

where m_o is the initial mass of radon and m is the mass at time t days. The factor of 0.18, which has units day^{-1}, is simply:

$$\ln 2/t_{1/2}$$

The radioactivity of 4 pCi becomes 12672 disintegrations per day. Now putting t = 1 day into the above equation:

$$(m_o - 12672)/m_o = 0.835$$

$$\Downarrow$$

$$m_o = 80000 \text{ approx.}$$

Having regard to the fact that the radioactivity in pCi relates to a litre of air, the number obtained above can be understood as 80000 radon atoms per litre of air.

A concentration of 80000 atoms per litre corresponds to a fraction:

$$80000/(40 \times 10^{-3} \times 6 \times 10^{23}) = 3 \times 10^{-18}$$

The quantity calculated above appertains, as has been noted, to a fairly stringent standard for indoor air. Radon occurs in certain building materials, notably fly ash, and this makes such standards necessary. Ambient levels of radon vary widely and can be significantly higher than this, an order of magnitude or more. Radon occurs in the ground and is transferred from there to the air. It is sometimes transferred to water and concentrates there before release into air. Hot springs in particular are sources of radon, necessitating monitoring of the air for radon in locations close to hot springs.

11.2   Uranium

Distant from sites of uranium activity, the element is present in the atmosphere at typically 10^{-2} pCi per litre. 'Ambient' levels of radon can be as high as or in excess of 50 pCi per litre, so the ratio is 5000. This figure has been **broadly** reproduced in a comparative health physics study of the effects of the two [1]. Of the natural isotopes of uranium that with the shortest decay half life is Uranium-234. The half life is nevertheless 2.5×10^5 years (9×10^7 days). The natural abundance, fractional basis, is 5.5×10^{-5}. The atmospheric radiation due to uranium is about 10^{-2} pCi or 0.022 disintegrations per minute. For the purposes of the calculation, which is concerned with times of the order of one day, we attribute this to solely to the isotope with the shortest half-life. These data then provide the basis for a calculation similar to the one above for radon.

Disintegration is according to:

$$m/m_o = e^{-0.0000000077t}$$

where m_o is the initial mass of radon and m is the mass at time t days.

The radioactivity of 0.022 pCi becomes 32 disintegrations per day. Now putting t = 1 day into the above equation:

$$(m_o - 32)/m_o = 0.9999999923$$

$$\Downarrow$$

$$m_o = 4 \times 10^9$$

This number signifies 4×10^9 Uranium-234 atoms per litre of air or 7×10^{13} atoms of uranium summed across the isotopes. This can be re-expressed:

The concentration of radium in the earth's crust is 2.4 p.p.m. weight basis. The calculated value above for air is about two orders of magnitude lower than this, which is intuitively reasonable.

11.3   Thorium

This element is present in earth and rock, a small amount finding its way into the atmosphere. The most abundant isotope is ^{232}Th, which disintegrates according to:

$$^{232}\text{Th} \rightarrow {}^{228}\text{Ra} + \alpha \text{ particle}$$
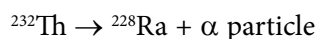
with accompanying gamma rays. The half life of the above process is 14 billion years. This exceedingly high value keeps the level of ^{232}Th in the atmosphere constant.

Radon, uranium and thorium have been considered separately, and polonium will be considered below. The four of course closely inter-related when radioactive processes are considered.

11.4   Polonium

This undergoes processes including:

$$^{210}\text{Po} \rightarrow {}^{206}\text{Pb} + \alpha \text{ particle}$$
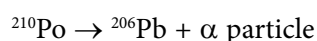
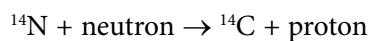the half-life for this process being 138 days. Polonium is present in the earth's crust at a fraction 10^{-15}, very much lower than the proportion of uranium. Polonium tends to concentrate in phosphate rock, which forms one ingredient of fertiliser for tobacco cultivation. Accordingly polonium enters the atmosphere from smoking materials. Levels of polonium in the region of 0.5 pCi per gram have been found in USA-grown tobacco.

About 25 litres of smoke-contaminated air will result from complete smoking of a cigarette of say 1 g tobacco content. The radioactive process involving polonium is independent of temperature and not affected in any way by the chemical history of the cigarette on smoking. The figure of 0.5 pCi per gram becomes 0.5 pCi per 25 litre, or 0.02 pCi per litre of

smoke-contaminated air released by the smoker.

11.5   Cosmic rays

These are not actually 'rays', that is, they are not a component of the electromagnetic spectrum. They are particles, with protons in a high preponderance. There are also alpha particles and beta particles. Cosmic rays enter the atmosphere at very high speeds. They can be seen as the debris from nuclear processes at the sun and elsewhere in the universe. Their most important role is in creating carbon-14:

$$^{14}N + neutron \rightarrow {}^{14}C + proton$$

A fuller discussion of carbon-14 follows.

11.6   Carbon-14

This decays with release of a beta particle, the half-life being 5700 years. However the half-life in a different sense (used previously in this volume), the time taken for half a quantity of carbon-14 to be transferred from the air to other parts of the biosphere, is only about 6 years. The carbon-14 in the entire atmosphere provides approximately 3.8 million curies of radiation. A related calculation follows.

Using again the data in Section 9.4 and retaining the symbols:

Radius of the earth = 6378 km (r_o)

Radius of the earth when enveloped by a spherical troposphere = 6380.3 km (r_t)

Volume of the troposphere = $(4/3)p\ (r_t^3 - r_o^3) \approx 1 \times 10^9$ km$^3 \equiv 10^{21}$ litre

Radiation due to carbon-14 = $(3.8 \times 10^6/10^{21})$ curies per litre or:

0.004 pCi per litre.

The value obtained above for the radioactivity due to carbon-14 in the atmosphere can be compared with values for the other radioactive elements considered.

11.7   Iodine

Until now, this chapter has dealt with naturally occurring radioactive substances. By contrast the iodine isotope I-131 is formed when uranium and plutonium are used as nuclear fuels. It decays with beta particle release and gamma radiation with a half-life of 8 days. There have been massive, sudden releases of I-131 where nuclear weapons have been tested. On a smaller scale, I-131 is released when there is loss of containment at a nuclear plant. I-131 in a quantity of 150 million curies was released during nuclear tests in Nevada over the period 1952–1970 [2].

The 1979 Three Mile Island accident released I-131 in an amount of about 20 curies [2]. Now the radioactivity in curies is proportional to the mass of decaying isotope, and the equation:

$m/m_o = e^{-lt}$

where m_o is the initial mass of I-131 and m is the mass at
time t days applies. The quantity l is given by:

$\ln 2/t_{1/2} = 0.087$ day^{-1}

Hence the quantity released at Three Mile Island would have decayed from 20 curies to 1 curie in:

- $(1/0.087)\ln(1/20)$ days = 34 days.

For the residual 1 curie to decay to a picocurie would have taken:

- $(1/0.087)\ln(10^{-12})$ days = 318 days.

Adding the two times together, the release would have been
down to picocurie level after about a year.

The 1986 Chernobyl disaster involved I-131 release at megacurie (MCi) level.

The isotope I-129 also decays with beta particle release, and has a half-life of 16 million years. Its existence in the atmosphere is due to cosmic ray interaction with Xenon and (as with I-131) to its being a product of uranium and plutonium fission.

11.8   Caesium

The isotopes Cs-137 and Cs-134 are radioactive, decaying with beta particle emission. These isotopes do not occur naturally but are products of nuclear fuels. The 1986 Chernobyl disaster involved release of radioactive caesium at about microcurie (µCi) level.

11.9   Some nuclear incidents

Summaries of selected incidents having led to release of radioactive material into the atmosphere are given in Table 11.1 below.

Date and location.	Details of release.
Windscale UK, 1957.	Release of 20,000 curies of I-131 into the atmosphere. Other radioactive isotopes released included plutonium and polonium.
Chelyabinsk USSR, 1957.	Chemical explosion at a nuclear waste processing facility which resulted in release of the nuclear material to the extent of 20 megacuries (MCi).
Nevada USA, 1970.	Underground nuclear test in which there was accidental leakage of radioactive substances to the extent of 6.7 MCi through cracks in the ground. A moratorium placed on nuclear tests in the USA as a result.
Three Mile Island PA, 1979.	See section 11.7.
Chernobyl, 1986.	See sections 11.7 and 11.8.

Table 11.1 Nuclear accidents.

'Nuclear accidents' most commonly involve acute exposure to persons close to the source. Those which result in leakage to the atmosphere are much rarer. Those in the table are all from that category.

11.10   References

[1] Shawky S., Hany A.A., Hussein M.I., El-Mahdy Z., Mustafa M. Journal of Environmental Monitoring 4 588–591 (2002)

[2] http://www.iodine131.org/q3.htm

Postscript

Aristotle (384–322 BC) was a promoter of the four-element idea of the universe, that is, that there are four elements which make up the physical world. These are earth, air, fire and water. Inclusion of air amongst these is an indication of how important it is and how deeply, in periods hugely distant in time and in culture from our own, human beings were conscious of this importance.

Those of us occupying the planet in this early 21st Century are still relatively close in history to the start of the industrial period although, of course, it has long passed out of living memory. Environmental responsibility was not evident over the first century or so of industrialisation, partly because the knowledge and expertise upon which environmental protection depends were not available at that time. Even so to conclude that there was some very insensitive neglect of the effects of using the atmosphere as a dump for the gaseous or gas-borne effluents from industry is reasonable. The blackening of buildings in English cities in Victorian times was surely evidence of the harmful potential of the pollutants. In the first half of the twentieth century there was much activity and progress in cleaning the air and reversing the damage done previously. Enhanced life expectancy of human beings has been the most obvious benefit.

There is now the added dimension of carbon dioxide emissions which, as already stated more than once in this volume, is a matter of the highest possible importance in the ordering of world affairs. A person in middle age or older is likely to sense that there was a discontinuity, a 'fault line of history', in the closing years of the twentieth century and the opening years of the twenty-first. Over that short period an awareness that the planet itself was threatened developed internationally. No country or organisation could consider itself responsible which did not examine itself in terms of greenhouse gas emissions. There has since been a proliferation of legislation whereby accountability and compliance with standards are enforced.

History has gone from pre-Christian to Christian to post-Christian on the time scale of a couple of millennia. We are going from 'pre-greenhouse' to 'greenhouse' in the sense that we have entered the period when the danger to the planet is recognised and measures to save it have to be put into effect. By analogy with the Christian model, we have passed 0 AD. Will the 'post-greenhouse' era ever come? The Kyoto protocol has set limits for the year 2100 of 550 p.p.m. of carbon dioxide. If and when such limits are achieved, what follows? Is a decline below 550 p.p.m. back to the levels of pre-industrial times hoped for over a period of several centuries? Will the world be in the 'post-greenhouse era' when that happens? Will commitment to greenhouse gas control be sustained by generations as yet unborn? Or will interest be lost, and the 'post-greenhouse era' be entered simply by default? Will the time come when such things as carbon neutral fuels, wind farms and photovoltaic cells have expanded to such an extent that without loss of 'quality of life' energy demands are being met without major carbon dioxide emissions? He or she would be a very brave expert who claimed to have more than speculative answers to such questions, but they are questions which naturally occupy the minds of thinking people at this time.

Endnotes

1. 1 US ton = 0.907 tonne.

2. In the US non-SI units are still widely used in such applications.
   1 BTU (British Thermal Unit) = 252 calorie

3. Also the conversion factor 1 US gallon = 3.785 litre

4. Although the success of the recent Olympic Games in Beijing must be seen as a considerable plus for the country. There was considerable cleaning up of the air in Beijing in readiness for the Games.

5. A value of 3.6 has been observed at a particular location in Taiwan.

6. The word 'contaminant' is probably more widely used in the industry.

7. With NOx measured as NO.

8. May 2008

9. Page numbers not given in the electronic form consulted by the author.

10. A 'latex paint' despite its name does not contain natural rubber. The term is simply a way of describing the consistency of the paint before use.

11. The figure is more precise than the author realised when he first arrived at it. Reference [1] gives a figure of 51% for carbon monoxide release in the US from road vehicles and a figure of 55% of that from 'cars and motorcycles'. The contribution from cars is then:

    $$0.51 \times 0.55 = 0.3$$

    So to one place of decimals and agreement is exact.

12. About 75 million tonnes in the US between the 1920s and the 1980s.

13. A 'metalloid'.

14. 1 picogram (pg) = 10^{-12} g.

15. Mass spectrometry-gas chromatography

16. See section 9.5.

17. For gaseous fuels the calorific value is more commonly expressed on a volume basis, unit volume being measured at 288K and 1 bar. The value so expressed for methane is 37 MJ m^{-3}.

18. An equivalent way of expressing that would be that such a passenger removes the carbon footprint left by his or her journey.