POLLUTION of our ATMOSPHERE

B Henderson - Sellers

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A Note on SI Units

Perhaps the most important aspect of a quantitative approach is the correct and sensible use of a units system. In modern science the SI system (Système International) is advocated. In this system the basic units of interest† are:

length	metre (m)
mass	kilogram (kg)
temperature	kelvin (K)
time	second (s)
amount of substance	mole (mol).

Three useful derived units are:

force	newton (N) ($1\ N = 1\ kg\,m\,s^{-2}$)
energy	joule (J) ($1\ J = 1\ kg\,m^2\,s^{-2} = 0.2388\ cal$)
power	watt (W) ($1\ W = 1\ J\,s^{-1}$).

Perhaps the two most used units in air pollution literature are those of length and concentration (amount of substance in a given volume). Although lengths (in the SI) should be given in metres, many of the sizes encountered (e.g. sizes of respirable particulates) would require a large negative power of ten and hence smaller units (in multiples of $10^{\pm 3}$) are permitted in the system. Thus

$$10^6\ \mu m\ \text{(micrometre)} = 10^3\ mm\ \text{(millimetre)} = 1\ m.$$

Similarly for mass

$$10^6\ \mu g = 10^3\ mg = 1\ g\ = 10^{-3}\ kg$$

i.e. $$10^9\ \mu g = 10^6\ mg = 10^3\ g = 1\ kg.$$

†The other two basic units are electric current (ampere), luminous intensity (candela)

Preface

Pollutant emissions to the atmosphere change temporally and spatially as a result of technology, social attitudes, population movement and increase or decrease, economic pressure, fuel usage etc. The existence of an air pollution problem results largely from public perception of the environment and people's concern that existing technology could be used to improve the air quality of their locale. There is thus no absolute quantitative definition of air pollution—both legal standards and socially acceptable concentrations depend upon the political and socioeconomic structure of a country and its degree of industrial development. Indeed it is often observed that during the early stages of industrialisation, economic pressures completely overwhelm environmental concerns. Pollutant control can be costly, and only when all industries feel themselves to be economically established can they afford the time and money to consider implementation of controls over their waste products (with the exception of those industries where the wastes contain economically recoverable constituents). Within this scenario, we can consider that guidelines for pollution have already been established by the industrialised world during centuries of development but adoption of these 'standards' by the Third World remains an open question. The examples given are, largely of necessity (due to the greater availability of data on all aspects of air pollution and pollution control), limited to Europe and North America. However air pollution knows no political or geographical boundaries; long range transport of sulphur dioxide, for example, leads to international exchange of pollutants as typified by the acid rain problems of Canada and Scandinavia. In all countries (developed or developing) the chemistry and physics remain the same. In many cases too the technology is immediately transferable between countries. Hence the use of a restricted data set in no way restricts the applicability of the conclusions. To further the international relevance of this text SI units are used throughout (in the author's view a necessity in modern science).

The material in this volume is based largely on a series of lectures given at the University of Salford to a group of students studying environmental science with special emphasis on the health effects of pollution within the urban environment. It is almost impossible for any student entering upon this course of study to possess background knowledge of sufficient depth to encompass the many aspects of this subject without first the whole class being directed to revision or review material in order to establish a common base. The choice of this I leave to the individual tutor or course leader. The material in this book can also be (and has been) used in courses on Environmental Chemical Engineering and Environmental Resources at final year Honours and Masters degree level, but in this case the text supplies basic information which is then supplemented by reference to papers from the current research literature.

The text follows a structure which, it is hoped, will be found useful for a wide variety of atmospheric pollution courses. It covers all aspects of the subject: physics, observational techniques, health effects, fuels and industrial combustion, prevention, control and legislation—all subjects about which the environmental scientist dare not be ignorant, even if his expertise is highly specific. Chapter 1 describes the historical development of pollution and the chemical pollutants of interest. Some emissions figures are also given. Chapter 2 introduces basic air pollution meteorology and climatology. Chapter 3 looks at the problem of stack emissions (the predominant industrial source). This includes quantitative analysis of diffusion, plume rise and pollutant removal. Chapter 4 then describes the methods of assessing pollutant concentrations, together with some recent results for ambient values. The next link, from emissions through transport to removal and measurements, is described in Chapter 5 in which the deleterious effects on plants, animals and man are considered in detail. Chapter 6 then describes pollutant creation (i.e. before emission) in terms of fuels, combustion chemistry, furnaces and boilers. Chapter 7 deals with the modern day problem of mobile sources including photochemical smog formation and Chapter 8 with the technology of pollution control (including a section on the legislative requirements in different countries).

This text could not have been completed without the assistance and encouragement of many people: colleagues at both Salford University and Woods Hole Oceanographic Institution where the text was completed and also student groups over the years. Specific thanks go to Professor P Slawson, Dr P Brimblecombe, Dr D Trout, Dr D S Munro and Dr J W Bacon for reading the draft manuscript. I wish to thank Alan Abbott for the cover photograph and figure 3.15; Bert Pade for figure 1.8; Sara Whiteley for figure 1.13; Kendal McGuffie for figures 3.1 and 3.2; Tom Lyons for figure 3.3 (lower); Alex Alexander for figure 4.4 (right) and my brother Peter for figure 3.12 (left).

Finally thanks to my wife Ann for her love and patient understanding without which this project could never have been completed.

Brian Henderson-Sellers
Louvain-la-Neuve, April 1983

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Introduction—Background and Source Types

Pollution—the very word is emotive. In the study of pollution of our atmosphere it is necessary to see through this emotion to the facts beneath. A definition of our subject matter is necessary. Air pollution is defined in as many ways as there are authors, for example:

'Air pollution means the presence in the outdoor atmosphere of one or more contaminants, such as dust, fumes, gas, mist, odour, smoke, or vapour in quantities, of characteristics, and of duration, such as to be injurious to human, plant or animal life or to property, or which unreasonably interferes with the comfortable enjoyment of life and property' (quoted in Perkins 1974)

'An unfavourable alteration to the environment' (Hodges 1973)

'The presence in the atmosphere of a substance or substances added directly or indirectly *by an act of man* [author's italics], in such amounts as to affect humans, animals, vegetation, or materials adversely' (Williamson 1973).

Dictionary definitions of the act of polluting are several and include

'to make or render unclean; to defile, desecrate, profane' (*Websters*)

'to make foul; to desecrate; to corrupt' (*Collins*)

'to destroy the purity or outrage the sanctity of' (*Shorter Oxford*).

Taking an overview of these definitions leads to two fundamental questions. If air pollution is defined, in some way, as the addition of undesirable substances to the atmosphere, then we need to know the composition of the 'undefiled' atmosphere. Although it is a moot point as to what is natural it could be argued that only a world without man was unpolluted. The origin and evolution of life itself probably caused the most traumatic chemical change in the atmosphere: the introduction of free oxygen. Indeed the atmospheric composition given in table 1.1 has been determined largely by biological, rather than inorganic, processes. Notwithstanding, it is usual to present data from an unpolluted atmosphere which is based largely on an Earth before industrialisation. The values in table 1.1 are given as a volume ratio (i.e. % or ppm) and show the predominance of gaseous oxygen and the relatively inert gas nitrogen. Also in the table are found the background values for the 'pollutants' such as SO_2, NO_2 and O_3—values in excess of those quoted here indicate local pollution.

Table 1.1 The composition of the dry atmosphere (after Schidlowski 1980).

Constituent	Chemical formula	Abundance by volume
Nitrogen	N_2	78.084 ± 0.004 %
Oxygen	O_2	20.948 ± 0.002 %
Argon	Ar	0.934 ± 0.001 %
Water vapour	H_2O	variable (%–ppm)
Carbon dioxide	CO_2	325 ppm
Neon	Ne	18 ppm
Helium	He	5 ppm
Krypton	Kr	1 ppm
Xenon	Xe	0.08 ppm
Methane	CH_4	2 ppm
Hydrogen	H_2	0.5 ppm
Nitrous oxide	N_2O	0.3 ppm
Carbon monoxide	CO	0.05–0.2 ppm
Ozone	O_3	variable (0.02–10 ppm)
Ammonia	NH_3	4 ppb
Nitrogen dioxide	NO_2	1 ppb
Sulphur dioxide	SO_2	1 ppb
Hydrogen sulphide	H_2S	0.05 ppb

Alternatively, if substances are added to the atmosphere, not by man but by another part of the biosphere or by natural catastrophe, should this be regarded as natural air pollution, in contrast to industrial/domestic or *anthropogenic* air pollution? It is deemed worthwhile to discuss both these types of air pollution. It will be shown, perhaps surprisingly, that natural emissions of many so-called pollutants are in fact much greater than anthropogenic emissions; yet this book will deal almost exclusively with the latter. Why is this justified? To answer this question it is necessary to trace the historical tale.

For the present discussion let us assume *pollution* encompasses natural and man-made sources. Historically natural sources have always been present in the form largely of volcanoes, forest fires, dust storms, sea-salt spray etc. Volcanoes add excess dust and gases such as sulphur dioxide and carbon dioxode to the atmosphere. Forest fires, perhaps initiated by lightning, add large quantities of smoke (carbonaceous particles), unburned hydrocarbons (any chemical compound containing hydrogen and carbon),

carbon monoxide and oxides of nitrogen to the atmosphere. Such fires may be visible for several hundred kilometres. A dust storm is a natural phenomenon, creating large amounts of suspended particulate matter as a natural 'pollutant'.

HISTORICAL ASPECTS

As soon as man first 'tamed' the element of fire, anthropogenic pollution became possible—but with very limited (both spatial and temporal) effects. Indeed polluting one's own immediate environment is considered socially acceptable—it is with increasing population and more 'sophisticated' technology that man pollutes his neighbour's environment and his pollution then becomes a problem.

Fire, or more technically *combustion*, is responsible for over ninety per cent of air pollutants. The domestic fires of our cave-dwelling ancestors developed into congregations of fires in the urban environments of the Roman Empire† and the communal fires of the mediaeval manor and subsequently, industrialised Europe and America. Smoke (and other byproducts of combustion) rose from the fires, making the air in the immediate vicinity 'heavy laden'. The burning of fires indoors lead to the invention of the *chimney*, creating both a draught and an outlet for removing smoke from the place of origin (figure 1.1). Chimneys do nothing for air pollution control (see Chapter 8) but are simply designed to redistribute the pollution out of the ken of the originator. The domestic chimney is not always successful in this aim, being relatively squat, but the industrial chimney is designed to be tall enough to spread its correspondingly greater emission over a large area (at the same time ensuring it dilutes sufficiently to be of little harm—see Chapter 3).

Combustion-generated pollutants are determined by the nature of the fuel (see Chapter 6). In Britain, wood was the prime fuel for both domestic and industrial use until the end of the thirteenth century. The first recorded instance of smoke pollution from coal burning would appear to have been in 1257, when emissions from coal being used in the building works for the renovation of Nottingham Castle were so great that Queen Eleanor (Henry III's wife) was forced to leave Nottingham for the less polluted rural surroundings of Tutbury Castle. By the early fourteenth century the use of coal had started to become common, particularly as an industrial fuel. Although it is thought that coal was first used in Britain around 1500 BC in the Bridgend (Glamorgan) area, it was not until 1180 AD that systematic

†In 61AD Seneca reported 'As soon as I had gotten out of the heavy air of Rome and from the stink of the smoky chimneys, thereof, which being stirred, poured forth whatever pestilential vapours and soots they had enclosed in them, I felt an alteration in my disposition.'

mining began and by 1228 coal was being shipped regularly to London from the Newcastle area. Dick Whittington's cat was, in reality, a coal barge! Another source of coal was seafloor coal extrusions which were subject to marine erosion. Coal was deposited on beaches—hence its early name of sea coal—a name commemorated in Seacoals Lane in London.

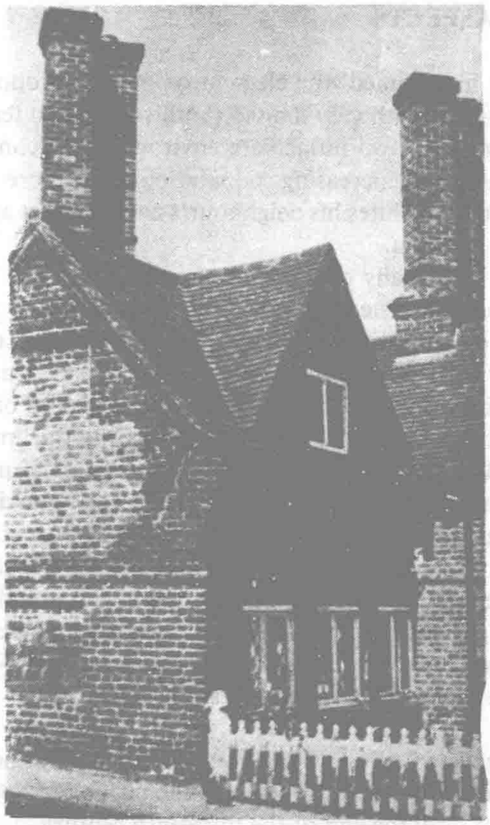

Figure 1.1 Tudor chimneys, Harefield, Middlesex (UK).

In 1273 Edward I took the first legal steps to alleviate atmospheric pollution by prohibiting coal burning in London. This apparently had no long term effect as an identical proclamation was given by Elizabeth I. At one time (under Edward II) the use of coal carried the death penalty. By the seventeenth century King Charles II was sufficiently concerned about London's smoke (the city today is still referred to familiarly as 'The Smoke') to commission a report by John Evelyn entitled *Fumifugium, or the Inconvenience of the Aer, and Smoake of London Dissipated (together with some remedies humbly proposed)*—a work which is still worth reading and which, happily, was reprinted recently.

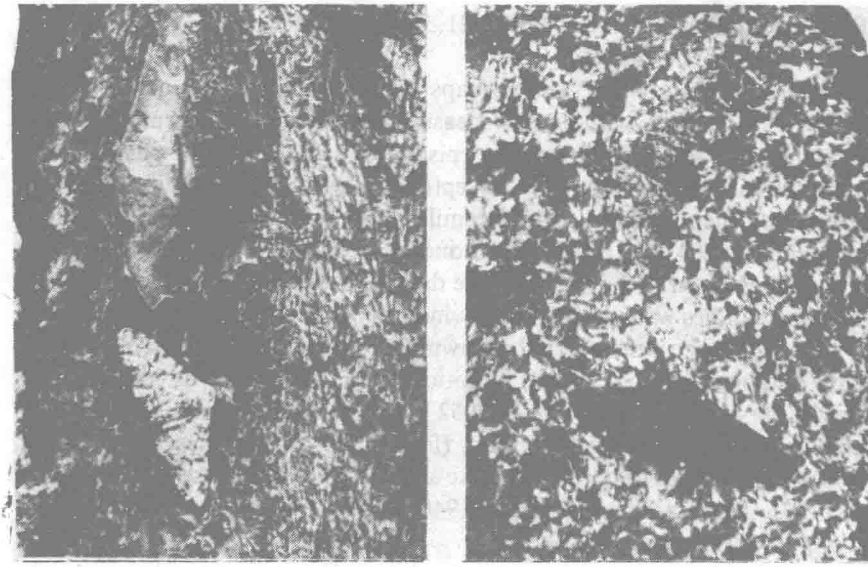

Figure 1.2 Melanism in the peppered moth. Photographs by John Haywood, University of Oxford, Department of Zoology.

Before the Industrial Revolution, coal-consuming industries were on a small scale, largely confined to metallurgy, lime burning, ceramics, preservation of animal products, bricks and leather tanning. Coke did not become important in metallurgical processes until 1700. The harnessing of steam power following inventions such as Watt's reciprocating steam engine in 1784 resulted in greatly increased consumption of coal over more widespread geographical areas. Governmental concern began to increase in the late nineteenth centry. The first Public Health Act of 1848 was followed by the Alkali Act of 1863. American legislation was first directed at industrial and locomotive emissions although in both countries a smoking chimney was regarded as a symbol of a successful business! Much US legislation was either municipal or state legislation: in 1867 the city of St Louis demanded that chimneys should be 20 feet (about 6 metres) higher than adjoining buildings. However an Act against smoke passed in 1893 was unable to be enforced until 1902. In Britain, Manchester led the way in air pollution control. Although the Corporation initiated a Nuisance Committee on Smoke in 1801, powers were not given to the police for control of smoke until the Manchester Police Act of 1844. Although some progress was made, the first sighting of the melanic form of the peppered moth (*Biston betularia*) (figure 1.2) occurred in Manchester in 1848. Black smoke emissions did not become an offence until 1866, and even the legislative enforcement of fines of £10 in 1882 were by no means preventative. The concept of smokeless zones was first raised in Manchester by Mr Gandy in 1934—plans for which were delayed until 1946 by the Second World War.

Before the Clean Air Act of 1956, 221.5 hectares of Manchester had already been declared 'smokeless'.

The Ringelmann chart was perhaps the first attempt to quantify emissions. This concern with smoke measurement and smoke abatement was accelerated by the London smog† episode of 1952. London 'pea-soupers' were by that time infamous and accepted as part of everyday life—Dickens referred to them as the London 'familiar'. In *A Christmas Carol*, written in December 1843, he describes a London afternoon: 'The city clocks had only just gone three, but it was quite dark already: it had not been light all day: and candles were flaring in the windows of the neighbouring office, like ruddy smears upon the palpable brown air'. Cattle deaths at the Smithfield show had been attributed to air pollution since 1873. This was compounded during the period December 4–8 1952 by human deaths calculated at 4000 over and above the expected figures (figure 1.3). Other extended pollution periods or *episodes* to note were those at Seraing in the Meuse Valley (3 days in 1930), Donora, Pennsylvania (1948) and the US east coast (Thanksgiving, November 22–25 1966).

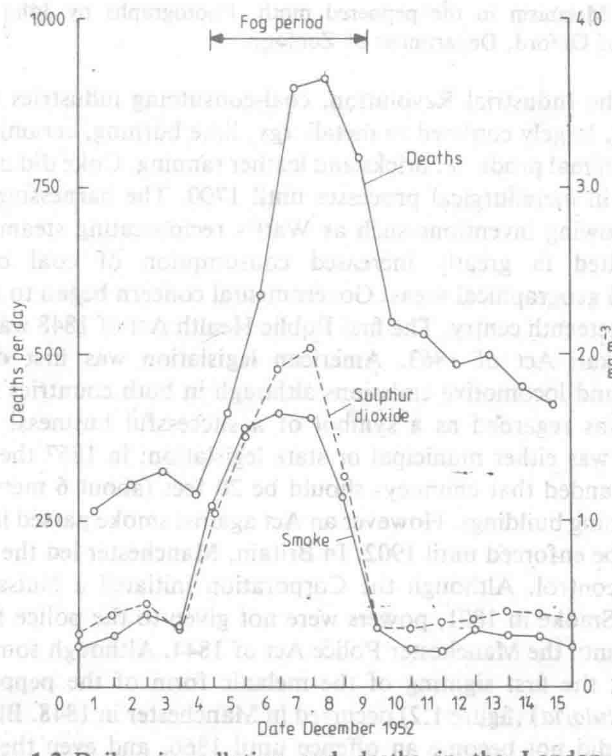

Figure 1.3 Daily air pollution and deaths in the London smog, December 1952. From Wilkins (1954)

†The word smog (smoke + fog) is usually attributed to Dr Des Voeux around 1910.

The most immediate result of the 1952 London episode was the establishment of the Beaver Committee. Their recommendations led directly to the Clean Air Act of 1956—a landmark in British legislation. This empowered local authorities to establish smokeless (Clean Air) zones, thus attempting to eliminate smoke pollution from both industrial and domestic sources. The effect of the Clean Air Act has been augmented or, arguably, superceded, by the socioeconomic pressures resulting in the coincident trend away from the use of coal in domestic heating.

Thus both air pollution and the degree of perception of pollution as a problem have changed and will continue to change. Steam locomotives (figure 1.4) have been replaced by electric and diesel locos in many countries; oil has replaced coal in many industries and yet with the impending

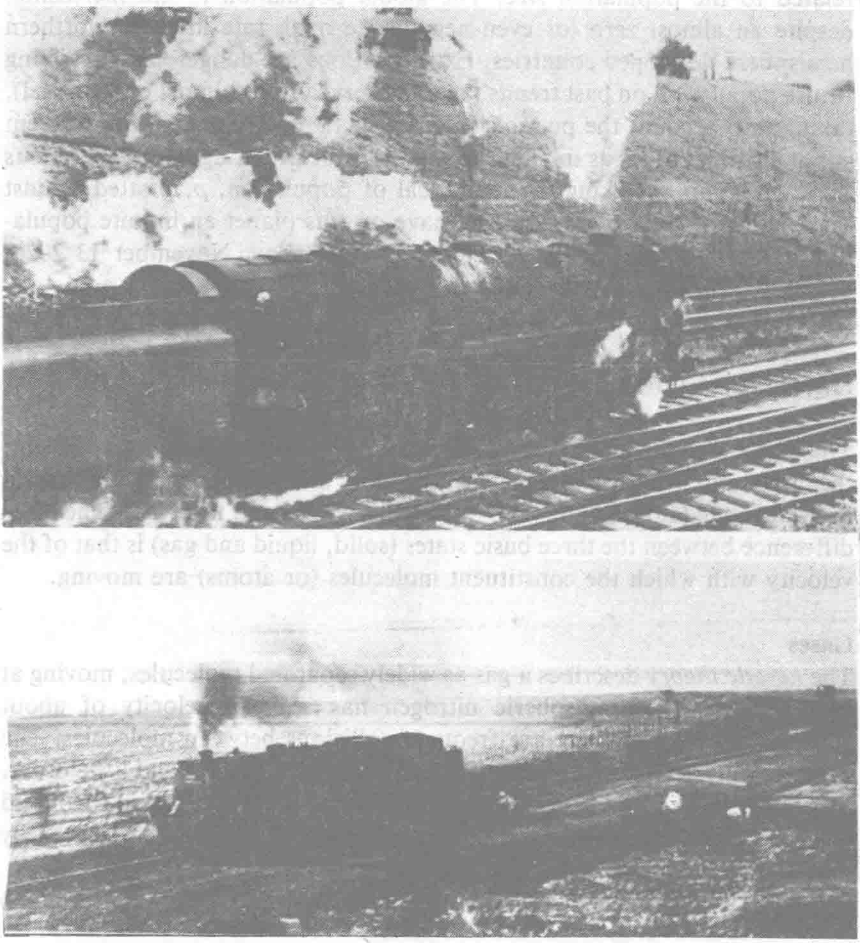

Figure 1.4 Steam locomotives in the UK in the 1960s (top) and South Africa in the late 1970s (bottom).

shortage of oil a new chapter in fuel usage is beginning to be written. (The debate continues as to the relative merits of nuclear power, alternative or renewable resources and a return to a coal economy†—possibly including the reintroduction of domestic coal fires and steam locomotives.) Pollution from vehicles (hydrocarbons, carbon monoxide and oxides of nitrogen) is of increasing concern; as is the formation of photochemical smogs (Chapter 7) in urban areas. Increasing trends over the last few centuries, reported by many as being exponential, may have been severely moderated by the 'Oil Crisis' of 1972–3 and the impending 'Energy Crisis' of the 1990s. An increasing per capita energy use has been associated with a higher standard of living (and often a higher degree of energy wastage) and a developing industry and economy. An increasing total consumption is thus further related to the population size. The global population is still increasing, despite an almost zero (or even negative) growth rate in many northern hemisphere developed countries. Extrapolations are dangerous. Predicting future population on past trends (again observed to be almost exponential), taking into account the possible increase in family planning and different social attitudes towards smaller families, is difficult. Hodges (1973) presents the calculation by taking the reciprocal of population, p, plotted against time. When $1/p$ becomes zero, we have on this planet an infinite population. This, Hodges calculates, will occur on Friday, November 13 2026, when most of us will still be alive!

NOMENCLATURE

The *phase state* of an element or compound is often related to its weight; the larger and heavier a molecule is, the more likely it is to exist in the solid or liquid state (although this is by *no* means a hard and fast rule). The basic difference between the three basic states (solid, liquid and gas) is that of the velocity with which the constituent molecules (or atoms) are moving.

Gases

The *kinetic theory* describes a gas as widely separated molecules, moving at high speeds (e.g. atmospheric nitrogen has a mean velocity of about $500\ \mathrm{m\,s^{-1}}$) in which there are frequent collisions between molecules. The gas mass has no shape (unless confined within a container) and little order. More ordering results from lower velocities and is exemplified in the liquid or, eventually, the solid state. (This decrease in velocity can be easily brought about by, for instance, decreasing the temperature.)

For a gas, one mole occupies a volume of $22.4 \times 10^{-3}\ \mathrm{m}^3$ (=22.4 litres)

†The *World Energy Outlook*, recently published by the OECD, forecasts a doubling of coal production and use by the year 2000.