

Groundwater

Water that is drawn up or pumped from wells from sources beneath the ground is groundwater. Wells can be an unsatisfactory source of water if badly maintained or positioned (Chapter 10), and public groundwater supplies are taken mainly from several large rock formations that are aquifers. (The word aquifer derives from the Latin and simply means water-bearer.) The main geological formations that act as aquifers in the UK are chalk, limestone and sandstone. These rocks are porous and can hold water in up to about half their total volume.

Each aquifer has a saturated and an unsaturated zone (Fig. 7.1). The top of the aquifer may have an interface with the soil, or there may be clay or other material between them. The unsaturated zone then lies between the top of the aquifer and the water table, which is the surface of the saturated zone, the usable water in the aquifer. In the saturated zone, water fills virtually the whole porosity of the rock, and it is this zone from which water is pumped for public consumption.

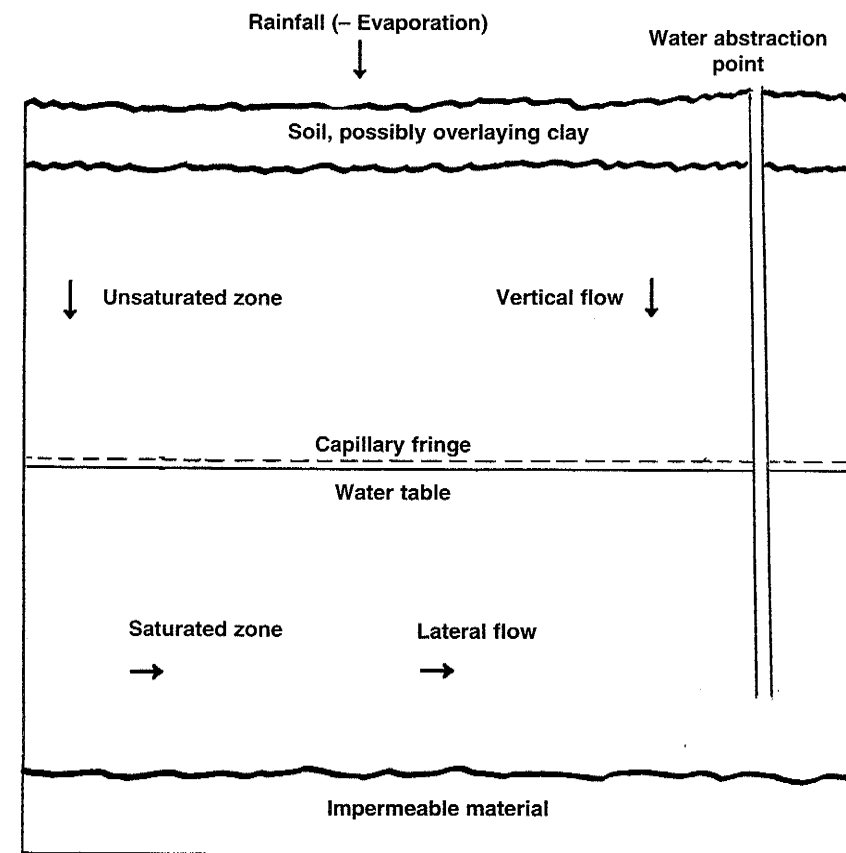


Fig. 7.1. The main features of an aquifer.

7 Nitrate in Fresh Water and Nitrous Oxide in the Atmosphere

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We saw earlier that nitrate is lost from the soil by two main processes, leaching and denitrification. Broadly speaking, leaching causes problems in the water environment, and denitrification in the atmosphere. This chapter tackles problems in fresh water and the atmosphere, while the interesting but complex effects of nitrate and other ions in coastal and estuarine waters and the sea are discussed in Chapter 8.

Nitrate in Fresh Water

Nitrate lost from the soil by leaching makes its way into groundwater or into surface waters – that is, streams, rivers and lakes – from which it may eventually reach the sea. Only a small proportion of this nitrate may have come from fertilizer. The rest will have come from mineralization in the soil (Chapter 5), some from grazing animals or the application of manures (Chapter 6), some from the ploughing up of old grassland (Chapter 10) and some, as we shall see later in this chapter, from the deposition of various forms of nitrogen from the atmosphere. The issues involved differ somewhat between ground- and surface waters, but the two categories can interact. Many streams, for example, begin in a boggy area where groundwater seeps out from an exposed aquifer.

Aquifers are an important source of water for human consumption, sometimes the only source, so there is understandable concern about possible pollution of the water contained in them. This concern is strengthened by the long periods of time involved in aquifer processes. Water passing through the unsaturated zone of a chalk aquifer moves downward at about 0.8 m/year (Young *et al.*, 1976). This implies that if a chalk aquifer has a water table 40 m below the top, a not unlikely depth, any water entering the top of the aquifer now will reach the saturated zone, from which it may be pumped, in 2053.

Farming activities above aquifers

Most of the water that enters the unsaturated zone of an aquifer has passed through the soil previously, so there is considerable interest in any farming activity on the land above the aquifer, particularly if it leads to losses of nitrate (discussed in Chapter 5). All forms of farming activity lose nitrate, but the ploughing up of old grassland was particularly interesting to Young *et al.* (1976) because it resulted in bands of nitrate moving down through the unsaturated zone, the rate of whose progress could be measured. This ploughing, the reasons for it and its consequences are discussed in Chapter 10.

Water from aquifers is used for human consumption, so the main issue raised by nitrate in aquifer water is the health issue. The evidence discussed in Chapters 9 and 10 suggests that nitrate is not only not hazardous at concentrations up to twice the European Community (EC) limit, but actually is beneficial, in that it is a key part of the body's defence system against bacteria that cause gastroenteritis and may also protect against heart disease. There are also no environmental issues that involve aquifer water unless it flows out of the aquifer into surface waters. This means that the main constraint on nitrate concentrations in aquifer water is a legislative one, in the form of the EC nitrate limit of 50 mg/l discussed in Chapter 10.

Nitrate removal from groundwater?

Denitrification can help to restrict nitrate concentrations by converting it to gases. The process is not restricted to the soil and can occur in groundwater, provided both the microbes and a suitable carbon substrate are available. The origin of the aquifer usually determines how much natural denitrification is likely (Korom, 1992). The rock surface in Triassic Sandstone, for example, may hold enough carbon substrate for measurable denitrification to occur, but rocks formed under hotter conditions will have less substrate available. The process is used in industrial plants for removing nitrate from water. Methanol is added as a substrate – subject to controls that ensure that the microbes exhaust the methanol before the nitrate. There are also reports that glucose and methanol are being introduced into aquifers for this purpose.

Surface Waters

Because water is also drawn from the larger rivers for public consumption, nitrate in surface waters, like that in groundwater, would be perceived to be a health problem were it not for the medical evidence (Chapters 9 and 10). If nitrate is a problem in surface waters it is part of the wider problem of nutrient enrichment which often manifests itself in the form of algal blooms.

Algal blooms

The blue-green algae are very small single-celled plants of the *Cyanobacteria* class of species that grow on the surface of practically anything, including water. Some of them are toxic, and others are a problem because of buoyancy conferred by the gas vesicles they contain, which enables them to rise to the surface of the water during calm conditions. The resulting 'bloom' or 'scum' is often blown by even gentle breezes to the edge of the lake or river, where it is unsightly and offensive. Algal blooms took on a greater significance a decade or so ago when it was discovered that some species of *Cyanobacteria* were toxic to humans and dogs swimming in or drinking affected water (Bell and Codd, 1996). This toxicity may seem to be a recent phenomenon, but Bell and Codd noted that the first case of its kind was in Australia in 1853. It is also a widespread problem, having occurred in more than 30 countries. Another important concern is that when algae die, the bacteria that consume them use dissolved oxygen to do so and this lessens the supply to fish and other desirable organisms, which may die as a result.

Nutrient enrichment

Plant nutrients are usually beneficial in the soil, but if they get into waters they become a nutrient enrichment problem because they trigger unwanted growth of plants, both small and large. Three terms are widely used to indicate the degree of enrichment – oligotrophic, mesotrophic and eutrophic. These imply in essence low, medium and high degrees of enrichment, and the idea has been extended to the concept of 'mean trophic rank' as a means of assessing and comparing rivers (Dawson *et al.*, 1999). The word 'eutrophication' is, of course, widely used.

The concept of the limiting nutrient

The idea of nutrient enrichment leads to the question, 'Which nutrient is the problem?' Here we need to look back to Box 1.3 to Justus von Liebig, the originator of the Law of the Minimum, the idea that plant growth is limited by the element least available in the soil. The limiting nutrient concept was extended by K. Brandt to nutrients in water in which photosynthesis may

Table 7.1. The Redfield ratios and the Law of the Minimum.

Fixed ratios of atoms found by Redfield in aquatic algae and macrophytes:

106 carbon atoms : 16 nitrogen atoms : 1 phosphorus atom

Multiplying the number of atoms of each element by its atomic weight gives the ratio on a mass basis:

40 g carbon : 7 g nitrogen : 1 g phosphorus

The law of the minimum suggests:

- When the ratio mass of available N : mass of available P exceeds 7 : 1, production of algae or macrophytes will be limited by the additions of P.
- When it is less than 7:1, production will be limited by added N.

(Carbon is freely available in carbon dioxide and unlikely to limit growth.)

occur. He correlated the abundance of plankton in lakes in Germany with nutrient concentrations. A.C. Redfield later suggested that the Law of the Minimum should be interpreted in terms of the ratios of nutrients found in living algae (Table 7.1).

The principle of the limiting nutrient is central to any discussion of nutrient enrichment of fresh water or sea water, because it provides a means of understanding the system and because it offers the possibility of controlling algae or macrophytes by managing inputs of a single nutrient. The evidence that phosphate is the limiting nutrient for algal growth in fresh water is summarized below, and the complex problem of estuarine and coastal waters and the oceans is discussed in the following chapter.

Algal growth in fresh water: limited by phosphate?

The algae that cause the blooms are *Cyanobacteria*, which can fix nitrogen from the atmosphere. This suggests that nitrogen is unlikely to be the nutrient that limits their growth. Research reviewed by Sharpley *et al.* (1994) and Ferguson *et al.* (1996) showed that algal blooms were more sensitive in freshwater lakes to the concentration of phosphate rather than to that of nitrate. Regressions relating chlorophyll concentrations (as a proxy for the quantities of algae in the water) to the phosphate concentration were valid over five orders of magnitude of the phosphate concentration (Ferguson *et al.*, 1996). The corresponding regressions for nitrate concentration were valid over only two orders of magnitude and gave a poorer fit.

One experiment in particular was decisive in establishing that phosphate was the limiting nutrient in lakes. This was a 'whole lake' study made by an international team in Canada (Schindler, 1974) in which an oligotrophic lake with two similar basins was divided by a plastic curtain. One basin was treated with carbon and nitrogen, the other with carbon, nitrogen and phosphate. The basin that was treated with just carbon and nitrogen

remained in apparently pristine condition. The other, which received phosphate as well, developed massive algal blooms.

Large water plants

Algal blooms are not the only problem caused by nutrient enrichment in surface waters. Much larger plants also grow to excess, usually with unwelcome effects. Reeds grow to excess, narrowing waterways and potentially overloading and damaging banks. The proliferation of underwater plants fouls the propellers of boats, entangles the tackle of fishermen and blocks water supply conduits, thereby damaging machinery. Although these plants need nitrogen, there is usually enough in the water, and their growth is limited by phosphate.

Nitrous Oxide in the Atmosphere

Nitrous oxide is produced in the soil as a result of incomplete denitrification or during nitrification (Chapter 3). Both arable and grassland agriculture contribute to its production, as do other sources including industry (Table 7.2). Nitrous oxide is formed during the manufacture of adipic acid, which is used in the production of nylon. Human activities contribute to atmospheric nitrous oxide slightly less than natural emissions. On a global basis, the amount of nitrous oxide-N added annually to the atmosphere is about 4.5 million tonnes greater than in pre-industrial times (Granli and Bockman, 1994). Sources cited by these authors suggest that before 1700 the concentration of nitrous oxide in air was about 285 mg/m³ but that this had risen to 310 mg/m³ by 1990, with much of the increase occurring after 1945.

Lægheid *et al.* (1999) calculated that on average about 1.25% of the nitrogen added to soil as fertilizer or manures or by biological fixation becomes nitrous oxide. This loss is trivial in agronomic or economic terms but far from

Table 7.2. Emissions of nitric oxide from human activities and natural sources worldwide. (From Lægheid *et al.*, 1999.)

Source	Nitrous oxide emitted (Mt N/year)
From human activities	
Agricultural soils	3.3
Associated with cattle	2.1
Burning of wood and other biomass	0.5
Industry	1.3
Total from human activities	7.2
Natural emissions	9.0

trivial in environmental terms. These authors also cited the Intergovernmental Panel on Climate Change (IPCC, 1997) as estimating that 2.5% of leached nitrate ended up as nitrous oxide. Fowler *et al.* (1996) described the rather complex relation between nitric and nitrous oxides near the soil surface and estimated the annual emission of nitrous oxide from soils in the UK at 27 kt N, with grassland responsible for about 60% of the emissions. They noted that soils will become the main producers when the manufacture of adipic acid ceases here.

The release of nitrous oxide to the atmosphere is an example of a global pollution problem. Nitrate lost to surface waters may pollute a lake, a river system or even a large area of coastal water such as the Gulf of Mexico, but nitrous oxide affects the atmosphere of the whole planet. It is the global nature of the problem that has encouraged the measurements of large-scale nitrous oxide emissions discussed in Chapters 5 and 6.

The layers of the atmosphere

The atmosphere is divided into two layers:

- The troposphere is the lower part of the atmosphere extending from the earth's surface to a height of about 8 km at the poles and 16 km at the equator. In the troposphere the temperature usually decreases with height.
- The stratosphere is the upper part of the atmosphere, above the troposphere and extending to a height of about 80 km. The temperature increases with height in the stratosphere.

Nitrous oxide contributes to two major atmospheric problems – the 'greenhouse effect' which is at least partly responsible for global warming at the earth's surface, and the destruction of ozone in the stratosphere.

Global warming

Global warming (Box 7.1) is regarded by many as the most serious threat to the survival of the planet and has stimulated a debate of almost religious intensity between 'believers' and 'sceptics'. This is entirely proper, because we are dealing with the ultimate in reciprocal risk problems (Chapter 12). If the believers are right, and global warming is occurring as a result of greenhouse gases released by human activities, our failure to act now to restrain the release of these gases could be disastrous for future generations. But if the sceptics are right, and the changes turn out to reflect natural cycles in the climate that are beyond human control, science, which is already suffering a slump in public trust, will be totally discredited. Worse still, the almost unimaginably large sums of money due to be spent on implementation of the Kyoto Treaty are sorely needed for development in the Third World, particularly in Africa, where they could make the difference between life

and death for the poor. A recent report stated that the money to be spent on Kyoto could provide the Third World with fresh water in perpetuity. If global warming turns out to have been no more real than the 'new ice age' about which climatologists warned us in the mid-1970s, its cost may have to be counted in millions of lives as well as billions of dollars.

Box 7.1. Global warming: a brief introduction and some questions.

Weather and climate

There is a distinction between *weather* and *climate*. This is a scale issue similar to those discussed in Chapter 5, and we are concerned with temporal rather than spatial scale.

Weather occurs in a specific area at a particular time. For example, on 4 August 2003 (when this was written), the weather was warm and sunny over the south-east of England.

Climate could be said to be weather summarized over time. The key variates in the summary are the average rainfall and average temperature. A more detailed summary would include the average run of wind, sunshine hours, number of frosts and similar data. Yearly averages are usually calculated for each month of the year and for the whole year, and long-term averages for the 30 years preceding the current year. Averages are not the whole story, and the summary needs to include deviations from the average and extreme weather events. The example could be that the south-east of England enjoys a temperate climate with about 750 mm of rain annually and a temperature that rarely exceeds 30°C or goes below 0°C.

Weather is always in the singular, but climate can be in the plural. The climates of East and West Africa, for example, differ appreciably.

The greenhouse effect

Global warming, or more specifically the 'greenhouse effect' which causes it in part, has a long and distinguished intellectual pedigree. Houghton (1992) records that it was first recognized in 1827 by the French mathematician and scientist Fourier, perhaps remembered more for his series. He pointed out the similarity between:

- The effect of the inner surface of the glass in reflecting and thereby retaining the heat energy of a greenhouse.
- The effect of the atmosphere in re-absorbing radiation reflected from the earth's surface and thereby warming the planet.

Fourier could be described as the 'father of the greenhouse effect'.

The Irish physicist Tyndall, best known for the 'Tyndall effect' observed when sunshine passes through a dusty atmosphere, measured the absorption of infra-red radiation by carbon dioxide and water vapour in about 1860. He suggested that decreases in carbon dioxide and its greenhouse effect could have caused the ice ages. This idea was pursued further in 1896 by Arrhenius, the Swedish 'founder of physical chemistry', who seems to have foreseen the possibility of global warming in the current sense. He first calculated (without a computer!) the effect of the water vapour and carbon dioxide in the atmosphere, showing that between them they increased the temperature of the earth's surface by about 33°C, from -18 to 15°C. He then calculated the effect of increasing the concentration of greenhouse gases on the warmth of the planet, and his estimate, that doubling

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the concentration of carbon dioxide would increase the global average temperature by 5–6°C, is not far out of line with assessments from the computer models used today.

The greenhouse gases

Water vapour and carbon dioxide are the gases mainly responsible for the greenhouse effect but methane, nitrous oxide, chlorofluorocarbons and ozone (in the troposphere rather than the stratosphere) also contribute to the warming effect. That order of importance is probably correct, but assigning an order is not simple. The effectiveness of a gas depends not just on how much of it is in the atmosphere but also on its residence time there and the wavelengths of radiation it absorbs. Nitrous oxide is significant as a greenhouse gas because it absorbs radiation of particular wavelengths, but it is also important environmentally as a destroyer of the ozone layer. There is considerable argument about the extent to which greenhouse gases can be controlled.

Water vapour varies greatly over time at a single location. The barometer in my living-room has during the last few years registered pressures ranging from 960 to about 1025 mbar. Nitrogen and oxygen together make up a constant 99% of the gases other than water in the atmosphere, so this substantial variation in pressure with time is due almost solely to large changes in the amount of water vapour in the air. The barometer goes down when the atmosphere is moist simply because the molecular weight of water, 18, is appreciably less than those of nitrogen and oxygen, 28 and 32 respectively. Atmospheric water vapour also varies between locations – think of the Sahara Desert and the rain-forests not far to the south of it – and it is totally beyond human control.

Carbon dioxide emissions increased by more than 20% in the last century as a result of human activity. To restrict these emissions we need to cut energy consumption, but the costs of just stabilizing them would be huge (see main text). Some, such as Stott (P. Stott, London, 2003, personal communication), doubt whether any useful control can be exerted by trying to manipulate just one variable (carbon dioxide) of the many that influence the climate. Others (e.g. Houghton, 1992) argue that we have no alternative but to try.

The concentration of methane in the atmosphere has doubled since 1880 (Houghton, 1992), but to cut emissions we would need, amongst other things, to restrict the activities of the coal, natural gas and petroleum industries, cut back on the production of rice in paddies, decrease worldwide the number of domestic animals and constrain the amount of domestic sewage treated and the amount of rubbish put into landfill. Before embarking on this ambitious project, we perhaps need to be sure that we understand the natural production of methane in wetlands and its natural removal by reactions in the atmosphere. We also need to consider the crucial alternative view of the role of methane set out in the Gaia hypothesis (Lovelock, 1995a), which is summarized in Box 7.2.

Nitrous oxide is the fourth most important greenhouse gas, but it is also important from an environmental standpoint as a destroyer of the ozone layer. There is no argument about the need to minimize losses, but we need to note the alternative view of nitrous oxide in the Gaia hypothesis (Box 7.2).

The greenhouse controversy

There is general agreement about the nature of the greenhouse effect and the gases involved but beyond that there is controversy. The international body charged with responsibility for research on climate change and the implementation of measures to counter it is the Intergovernmental Panel on Climate Change (IPCC). This is a body with

a political as well as a scientific standpoint. The view of the IPCC, that climate change is happening and that it is driven mainly by carbon dioxide emissions resulting from human activities, is now largely accepted as the orthodox view. But not all scientists agree, and some such as Stott (see above) argue strongly against it.

Some questions about the science

There is no doubt that the average global temperature is rising at present and that this temperature and atmospheric carbon dioxide were significantly correlated during the last 100 years (e.g. Kuo *et al.*, 1990). But two variables increasing simultaneously does not imply that one causes the other, even if they are correlated. During the latter half of the last century the birth rate in Europe declined, as did the population of storks – obviously implying that granny was right after all in telling you that babies were brought by storks. Most of the arguments for global warming are therefore made on the basis of computer models. These models raise a few questions.

1. All our heat comes ultimately from the sun, so the fluctuations that occur in the sun's energy output must have some influence, however small, on the temperature of the earth. Should the models take into account these fluctuations? The IPCC models do not seem to do so. There seems to be a comprehensive disagreement about the reliability and significance of the measurements of the sun's energy output. The general confusion is exemplified by a recent paper (Laut and Gundermann, 1998, cited by Lomborg, 2001). This purported to support the IPCC but stated that the increase in direct solar radiation during the last 30 years accounted for about 40% of the global warming observed, something the IPCC does not accept.
2. Carbon dioxide not only causes global warming but also is itself caused by warming. Atmospheric warming will be accompanied by soil warming, which will accelerate mineralization of soil carbon (Chapter 3), releasing more carbon dioxide into the atmosphere. We need to know which came first, the warming or the carbon dioxide. Kuo *et al.* (1990) reported that, although temperature and atmospheric carbon dioxide had been significantly correlated for the previous 30 years, changes in carbon dioxide lagged those in temperature by 5 months. Each year the increase in carbon dioxide came *after* the warming. Do the climate models simulate this lag?
3. If you plot the carbon dioxide concentration and the variation in global temperature since 1900, say, against time on the same graph, both variates show an overall upward trend, but the patterns within the trend differ considerably (Fig. B7.1.1). Apart from an annual fluctuation, the carbon dioxide concentration follows a smooth, gradually accelerating upward curve. The temperature curve, by contrast, is highly irregular and shows that a large proportion of the warming occurred before 1940, by which date only about 20% of the release of carbon dioxide from the human activities had occurred. Can the models explain this, perhaps by taking extra factors into consideration?
4. Prior to their detailed statistical study (mentioned above) on the then most recent 30 years, Kuo *et al.* (1990) divided the temperature curve from 1880 onwards into four 30-year segments. The temperature increased in only three of these segments, and in the fourth, from about 1940 to about 1970, the temperature decreased while the carbon dioxide concentration continued to rise. It was that 30-year decline in temperature that led to the last alarm about the climate. Were we entering a new ice age? We then proceeded almost seamlessly from worrying about the new ice age to worrying about global warming. How do the climate models explain that 30-year decline, which occurred in spite of rising carbon dioxide concentrations?

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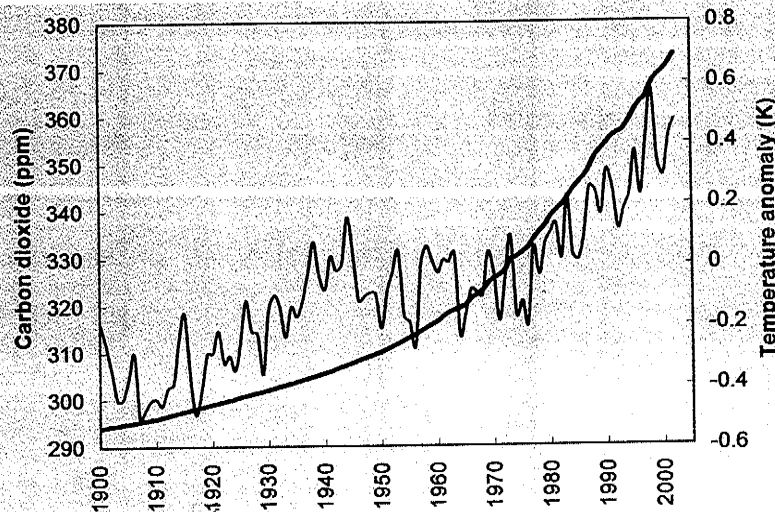


Fig. B7.1.1. The increase in the atmospheric concentration of carbon dioxide (heavy line) plotted with the global temperature anomaly (light line). (Diagram courtesy of Dr Jack Barrett.)

5. The climate models predict that the temperatures of both the land surface and the lower troposphere should rise as the carbon dioxide concentration increases. As noted in the last section, the surface temperature increased for much of the last century but decreased for about 30 years in the middle of it. The temperature in the troposphere, measured by instruments carried on balloons, did not increase between 1957 and 1976. It increased briefly in 1976 and 1977, but since 1979, when temperature measurements by satellite were started, neither type of measurement showed an increase in temperature. Thus the warming predicted by the climate models at the land surface during the last century was in reality a decrease in temperature for 30 of the last 100 years and the warming predicted in the lower troposphere hardly occurred at all. Can the climate model really be said to have been validated?

6. Another interesting question is whether the modellers should be taking more account of chaos theory. The first instance of chaos discussed by Gleick (1987) was in a weather model. One of the characteristics of a chaotic system is that it 'flips' from one form of behaviour to another, which appears to be just what we see in Fig. B7.1.1.

The climate modellers may well be able to answer these questions in due time, perhaps quite soon. But until they can, I prefer to remain 'agnostic' about global warming.

Feelings run high in the debate. The sceptics were recently pilloried as 'toxic sceptics' in a national magazine (*New Internationalist*, No. 357, June 2003, p. 13), and some scientists seem to agree with this extreme view. This bodes ill for rational debate on the topic. More worryingly, more than one of the sceptics has told me that it is difficult to get a paper published that does not agree with the orthodox view. I have given a brief introduction to the science of global warming and listed some questions about it in Box 7.1 but, as Houghton (1992) and others much more knowledgeable than myself have written books on global warming, and only a relatively

Box 7.2. The Gaia hypothesis and the greenhouse gases.

The essence of the Gaia hypothesis developed by Lovelock (1995a) is that the earth is a complex, living, self-regulating organism which he named Gaia after the Greek goddess of the Earth. In the terminology of Complexity Theory, Gaia is an emergent system. The earth as we know it is thermodynamically highly improbable and it is living matter that maintains it in this improbable state. This state is essential for the life that maintains it. The composition of the atmosphere provides one measure of this improbability. Table B7.2.1, based on Table 2 of Lovelock (1995a), compares the composition of the atmospheres of Venus and Mars with that of Earth as it is and would be without life. The most striking difference is that without life Earth would have an atmosphere made up of almost entirely carbon dioxide and would therefore be very hot.

Table B7.2.1. Comparing the composition of the atmospheres of Venus and Mars with that of Earth as it is and would be without life. (After Table 2 of Lovelock, 1995a.)

Gas/state	Atmosphere of			
	Venus	Mars	Earth with life	Earth without life
Carbon dioxide (%)	98	95	0.03	98
Nitrogen (%)	1.9	2.7	78	1.9
Oxygen (%)	Trace	0.13	21	Trace
Argon (%)	0.1	2	1	0.1
Surface temperature (°C)	477	-53	13	290 ± 50
Atmospheric pressure (bar)	90	0.064	1	60

The reason for the inclusion of this box is that three of the greenhouse gases have implications in the Gaia paradigm which differ greatly from those carried in Box 7.1.

Carbon dioxide

Lovelock (1995b) believes that there is cause for concern about the carbon dioxide emissions in terms of the Gaia paradigm, but his concern is not primarily about global warming. He feels that Gaia's regulatory system for carbon dioxide may be nearing the end of its capacity because, until the additions of the last century, the carbon dioxide concentration of the atmosphere had become rather small. This makes it a very bad time for humans to add carbon dioxide to the atmosphere, for the same reason that it is unwise to put a hypothermic animal into a warm bath. The shock of sudden change could be too much for the system at its limit. The hypothermic animal will recover if left to warm slowly, and Gaia will recover only with a slow increase in carbon dioxide. This conclusion obviously depends on the assumptions of the Gaia paradigm.

Methane

The role of methane in the Gaia paradigm is more heroic than its conventional role as the third worst greenhouse gas. Under Gaia, methane saves us, perhaps not from the flames of hell but certainly from an increased risk of combustion. Lovelock (1995a) pointed out that oxygen is a hazard because of its chemical potential. The present oxygen concentration in the atmosphere, 21%, represents a delicate balance between risk and benefit.

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Forest fires do occur, but not often enough to interfere with the level of human and other activity that 21% oxygen permits. Increasing the concentration from 21% to just 22% would greatly increase the risk of fire. The probability of a forest fire being started by a lightning flash increases by 70% for each 1% increase in oxygen concentration above the present level, and at 25% little land vegetation at any latitude would escape the inferno.

The maintenance of the oxygen concentration at 21% is clearly vital, and Lovelock (1995a) suggests that methane acts as a regulator for oxygen in two ways. Some methane reaches the stratosphere, where it is oxidized to carbon dioxide and water. The water eventually dissociates to hydrogen and oxygen, and the hydrogen escapes to space while the oxygen descends to the troposphere. In the troposphere, methane takes oxygen out of the system when it reacts with it in a series of complex reactions. Methane production is therefore important in the Gaia paradigm. It is produced by anaerobic bacteria in marshes and wetland, and also in estuaries and the seabed. Lovelock sees these zones as a key powerhouse for the maintenance of Gaia.

Nitrous oxide

Lovelock (1995a) considered nitrous oxide 'a puzzling gas' within the Gaia paradigm but he was able to suggest two roles for it. One was to complement the role of methane in oxygen regulation. Methane removes oxygen from the atmosphere but nitrous oxide brings it into the atmosphere. I think Lovelock saw the two gases as together having a 'fine tuning' function in maintaining the oxygen concentration at the appropriate level.

The other role Lovelock saw for the gas was a control on ozone in the stratosphere by the mechanisms shown in equations (7.1)–(7.3) in the main text of the chapter. He argued that too much ozone might be as undesirable as too little, and he pointed out that vitamin D was formed in the skin as a result of exposure to ultraviolet radiation. 'Too much ultraviolet may mean skin cancer,' he said, 'too little almost certainly means rickets.'

A small proportion of the warming is caused by nitrous oxide and other nitrogen oxides, Box 7.1 is the limit of the comment on the problem in this book.

I have to declare myself as 'agnostic' about global warming. I have an energy-efficient flat with cavity-wall insulation, double glazing all round, water-heating only 2 hours per day and low-energy light bulbs. I also run a small economical Skoda car, which I aim to use on only 4 days a week. But I regard these measures as stewardship of increasingly scarce energy rather than precautions against global warming. And I am not convinced that the measures undertaken at the Kyoto convention will make much difference to the mainly natural processes of climate change, particularly as the USA declines to be involved.

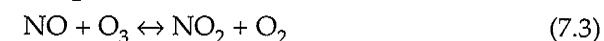
In the long run the problem may well sort itself out. Dr Roger Bentley, speaking at the Scientific Alliance conference '2020 Vision – Powering the UK's Future' in May 2003, pointed out that the resource-limited peak in oil production was likely to occur in 10 years' time and the peak in all hydrocarbons about 5 years later. Dr Bentley foresaw that the world would soon experience oil and gas shortages, and this seems to be supported by recent

events at Shell Oil, where directors have been removed as estimates of the company's oil reserves have been down-graded for the third time. An oil and gas shortage could save a lot of argument.

Nitrous oxide and ozone destruction

Nitrous oxide is very stable in air but, by an unfortunate mischance, the only processes that remove it from the atmosphere occur in the stratosphere and some involve the destruction of ozone. Ozone is an atmospheric contaminant at ground level, where it can be dangerous to people with respiratory problems and toxic to crops. Nitric oxide and nitrogen dioxide (known collectively as NO_x) catalyse its production there from volatile organic compounds (Fowler *et al.*, 1998). However, 90% of atmospheric ozone is in the stratosphere, where it forms a vital layer that protects life on the surface of the earth from ultraviolet radiation. The fluctuations in the ozone layer, particularly the hole in the layer above the South Pole, have understandably attracted widespread public concern. Nitrous oxide is not the only threat to the ozone layer. Like nitrous oxide, the chlorofluorocarbons used in refrigeration are largely inert at ground level but reactions they undergo in the stratosphere make them a threat to the ozone there.

The chemistry of nitrogen oxides in the stratosphere is somewhat complex, but the main reactions of nitrous oxide have been summarized by Granli and Bøckman (1994). Nitrous oxide reacts with excited singlet oxygen atoms (O^*) formed by the photolysis of ozone to give nitric oxide. The nitric oxide reacts with ozone to give nitrogen dioxide and oxygen:



Although it is the nitric oxide that destroys the ozone, the role of nitrous oxide is crucial. Nitric oxide, although fairly stable to decomposition, is a free radical and never reaches the stratosphere on its own because it reacts readily with other free radicals, of which there are plenty in the troposphere, before it gets to the stratosphere. Nitrous oxide travels to the stratosphere largely without reaction and therefore mainly intact. In this way it acts as a kind of 'Trojan horse' enabling nitric oxide to get into the stratosphere.

Two other reactions also remove nitrous oxide from the stratosphere but do not destroy ozone in the process (Granli and Bøckman, 1994). In one, nitrous oxide undergoes photolysis to nitrogen and a singlet oxygen atom, and in the other it reacts with an excited singlet oxygen atom to form normal molecular nitrogen (dinitrogen) and oxygen:



Table 7.3. Nitrogen species that may be present in the atmosphere and deposited on land.

Name	Chemical formula
Nitric oxide	NO
Nitrogen dioxide	NO ₂
Dinitrogen pentoxide	N ₂ O ₅
Nitrous acid	HNO ₂
Nitric acid	HNO ₃
Peroxyacetyl nitrate	CH ₃ COO ₂ NO ₂
Organic nitrates	RNO ₃
Ammonia	NH ₃

Additional species that may be present include aerosols of ammonium and nitrate and nitrate radicals formed when nitrogen dioxide reacts with ozone.

The chemistry of atmospheric nitrogen is very complex, and the main chemical species likely to be found are listed in Table 7.3. These interact with each other under the influence of photons (from sunlight), ozone and hydroxyl and peroxy radicals. Because of the influence of photons in some reactions, the chemistry in daytime differs appreciably from that at night-time. These species may be deposited on land in droplets of cloud or rain, by dry deposition, which means that they are transferred directly from the gaseous phase on to a surface, or as aerosols. Deposition on the soil surface and on vegetation both can cause problems. These are not as sensational as those caused by nitrous oxide in the stratosphere, but they merit attention.

Deposition from the Atmosphere

Deposition on farmland

Rainfall at Rothamsted was first analysed for nitrate and ammonium 127 years ago but not much was found. Between 1877 and 1915 the total deposition of nitrogen recorded was 227 kg/ha, about 6 kg/ha per year on average, but these measurements did not include all forms of deposition. More recent studies, such as those of Goulding (1990) at four sites in south-east England, included nitrate deposited on dry matter and dry deposition of nitrogen oxides, nitric acid and ammonia. These more comprehensive estimates showed an annual deposition of 35–40 kg/ha. More recent measurements at Rothamsted (United Kingdom Review Group on Impacts of Atmospheric Nitrogen, 1994) suggested that about 37 kg/ha was deposited annually on bare soil and about 48 kg/ha on soil with a well-established crop of winter wheat. The difference is due to the larger surface area for deposition offered by the crop.

The nitrogen deposited when the wheat was grown corresponded to one-quarter of the average application of nitrogen fertilizer at the time of the measurement and could be more than a quarter now. It came from industry

and motor traffic, each of which generates about half the nitrogen oxides, and from the farm and neighbouring farms, which are mainly responsible for the ammonia. The deposition occurs whether or not there are crops taking up nitrogen and can readily add to the untimely nitrate (Chapter 2) that is leached. One estimate from a model (Goulding *et al.*, 1998) suggested that about half was taken up by the crop and about 30% was leached. Some currently unpublished runs of another model (N.A. Mirza, Harpenden, 1995, personal communication) suggested that a fairly similar proportion, 25%, was leached and that it contributed about 15% of the nitrate leached overall.

This calculation implies that nitrate deposited from the atmosphere may contribute 10–15 kg/ha to annual nitrate losses from the soil. Farmers can be encouraged to view this deposition as a resource and to make allowance for it, but they can hardly be held responsible for its consequences. Assuming that the through drainage is about 250 mm, as in many parts of eastern England, its contribution to the nitrate concentration leaving the soil is about 20 g/m³, or 40% of the EC nitrate limit. This leaves farmers little room for error.

Deposition on natural vegetation

Nitrate or ammonium deposited on farmland need not be a problem, as we saw in the previous paragraph. Deposition is definitely a problem for natural vegetation and the soils on which it grows and its effects can include (United Kingdom Review Group on Impacts of Atmospheric Nitrogen, 1994):

- Loss of mosses and lichens.
- Loss of heather.
- Damage to trees from nitrate and ammonium in fog and cloud.
- Changes in species composition and loss of biodiversity.
- Decreases in tolerance of plants to stresses such as frost, drought and feeding by animals and insects.
- Changes in soil solution chemistry, including acidification and loss of cations.

Critical load and nitrogen saturation

Two concepts, critical load and nitrogen saturation, are important for understanding the problems caused by deposition of nitrate, ammonia and nitrogen oxides from the atmosphere.

A *critical load* is defined in roughly the same way as a 'no effect' level (Chapter 12) as 'an exposure below which harmful effects do not occur'. The main difference is that 'no effect' levels commonly relate to a single species or to microcosms whereas critical loads usually relate to entire ecosystems

at the landscape scale. The formal definition of a critical load, according to the United Nations Economic Commission for Europe, is 'a quantitative estimate of exposure to one or more pollutants below which significant harmful effects on sensitive elements of the environment do not occur according to present knowledge'.

The critical load for nitrogen may relate either to its acidifying effect or to its nutrient effect. The assessment can be made by calculating the critical load for each of these and using the lower value. Critical loads have been estimated for a wide variety of ecosystems including forests (Grennfelt and Thornelof, 1992) with, as the authors admit, various degrees of reliability. Their values range from 5–15 kg/ha of nitrogen per year for arctic and alpine heaths to 20–30 kg/ha for neutral or calcareous species-rich grassland. A mesotrophic, rather than an oligotrophic, fen has a critical load of 20–35 kg/ha. All these load estimates are less than the amounts of nitrogen measured by Goulding (1990) to have been deposited from the atmosphere. Goulding's measurements were in an agricultural rather than an environmentally sensitive setting, but nitrogen oxides can travel some distance in the atmosphere.

Nitrogen saturation

Nitrogen limits growth in most natural ecosystems so nitrogen deposited from the atmosphere initially increases the growth of vegetation. But ecosystems, like crops, have a limit to the amount of nitrogen they can use. Giving too much nitrogen fertilizer to a crop not only causes problems such as lodging (when the stem becomes too weak to support the weight of the crop) but also results in nitrate losses. Similarly, if more nitrogen is deposited on an ecosystem than it can use in its current state, the excess will cause some kind of change, which may well be deleterious, and nitrate will be lost from the system. Various measures of nitrogen saturation have been suggested (e.g. Grennfelt and Thornelof, 1992), but nitrate loss may be the most reliable. A small child tells you when it has had enough food by throwing the rest on the floor, and both natural and agricultural ecosystems do so by losing nitrate.

Perakis and Hedin (2002) provide excellent examples of ecosystems unsaturated and saturated with nitrogen. They showed that substantial amounts of dissolved organic nitrogen, but no nitrate, were lost in stream water flowing from pristine forests in Chile. (The nature of this organic nitrogen was discussed in Chapter 3.) These authors found that a forest in the vicinity of New York lost mainly nitrate in stream water. The second forest received a substantial load of inorganic nitrogen from the atmosphere generated probably by industry and road and air traffic.