Introduction

1

1.1 What is environmental chemistry?

It is probably true to say that the term environmental chemistry has no precise definition. It means different things to different people. We are not about to offer a new definition. It is clear that environmental chemists are playing their part in the big environmental issues—stratospheric ozone (O_3) depletion, global warming and the like. Similarly, the role of environmental chemistry in regional-scale and local problems—for example, the effects of acid rain or contamination of water resources—is well established. This brief discussion illustrates the clear link in our minds between environmental chemistry and human beings. For many people, 'environmental chemistry' is implicitly linked to 'pollution'. We hope this book demonstrates that such a view is limited and shows that 'environmental chemistry' has a much wider scope.

Terms like *contamination* and *pollution* have little meaning without a frame of reference for comparison. How can we hope to understand the behaviour and impacts of chemical contaminants without understanding how natural chemical systems work? For many years a relatively small group of scientists has been steadily unravelling how the chemical systems of the Earth work, both today and in the geological past. The discussions in this book draw on a small fraction of this material. Our aim is to demonstrate the various scales, rates and types of natural chemical processes that occur on Earth. We also attempt to show the actual or possible effects that humans may have on natural chemical systems. The importance of human influences is usually most clear when direct comparison with the unperturbed, natural systems is possible.

This book deals mainly with the Earth as it is today, or as it has been over the last few million years, with the chemistry of water on the planet's surface a recurrent theme. This theme emphasizes the link between natural chemical systems and organisms, not least humans, since water is the key compound in sustaining life itself. We will start by explaining how the main components of the near-surface Earth—the crust, oceans and atmosphere—originated and how their broad chemical composition evolved. Since all chemical compounds are built from atoms of individual elements (Box 1.1), we begin with the origin of these fundamental chemical components.

1.2 In the beginning

It is believed that the universe began at a single instant in an enormous explosion, often called the *big bang*. Astronomers still find evidence of this explosion in the movement of galaxies and the microwave background radiation once associated with the primeval fireball. In the first fractions of a second after the big bang, the amount of matter and radiation, at a ratio of about 1 in 10^8, was fixed. Minutes later the relative abundances of hydrogen (H), deuterium (D) and helium (He) were determined. Heavier elements had to await the formation and processing of these gases within stars. Elements as heavy as iron (Fe) can be made in the cores of stars, while stars which end their lives as explosive supernovae can produce much heavier elements.

Hydrogen and helium are the most abundant elements in the universe, relics of the earliest moments in element production. However, it is the stellar production process that led to the characteristic cosmic abundance of the elements (Fig. 1.1). Lithium (Li), beryllium (Be) and boron (B) are not very stable in stellar interiors, hence the low abundance of these light elements in the universe. Carbon (C), nitrogen (N) and oxygen (O) are formed in an efficient cyclic process in stars that leads to their relatively high abundance. Silicon (Si) is rather resistant to photodissociation (destruction by light) in stars, so it is also abundant and dominates the rocky world we see about us.

1.3 Origin and evolution of the Earth

The planets of our solar system probably formed from a disc-shaped cloud of hot gases, the remnants of a stellar supernova. Condensing vapours formed solids that coalesced into small bodies (planetesimals), and accretion of these built the dense inner planets (Mercury to Mars). The larger outer planets, being more distant from the sun, are composed of lower-density gases, which condensed at much cooler temperatures.

As the early Earth accreted to something like its present mass some 4.5 billion years ago, it heated up, mainly due to the radioactive decay of unstable isotopes (Box 1.1) and partly by trapping kinetic energy from planetesimal impacts. This heating melted iron and nickel (Ni) and their high densities allowed them to sink to the centre of the planet, forming the core. Subsequent cooling allowed

Box 1.1 Elements, atoms and isotopes

Elements are made from atoms—the smallest particle of an element that can take part in chemical reactions. Atoms have three main components: protons, neutrons and electrons. Protons are positively charged, with a mass similar to that of the hydrogen atom. Neutrons are uncharged and of equal mass to protons. Electrons are about 1/1836 the mass of protons, with a negative charge of equal value to the (positive) charge of protons.

Atoms are electrically neutral because they have an equal number (Z) of protons and electrons. Z is known as the atomic number and it characterizes the chemical properties of the element.

The atomic weight of an atom is defined by its mass number and most of the mass is present in the nucleus.

$$\text{Mass number} = \text{number of protons } (Z) + \text{number of neutrons } (N) \qquad \text{eqn. 1}$$

Equation 1 shows that the mass of an element can be changed by altering the number of neutrons. This does not affect the chemical properties of the element (which are determined by Z). Atoms of an element which differ in mass (i.e. N) are called isotopes. For example, all carbon atoms have a Z number of 6, but mass numbers of 12, 13 and 14, written:

$$^{12}\text{C},\ ^{13}\text{C},\ ^{14}\text{C} \text{ (isotopes of carbon)}$$

In general, when the number of protons and neutrons in the nucleus are almost the same (i.e. differ by one or two), the isotopes are stable. As Z and N numbers become more dissimilar, isotopes tend to be unstable and break down by radioactive decay (usually liberating heat) to a more stable isotope. Unstable isotopes are called radioactive isotopes (see Section 2.8).

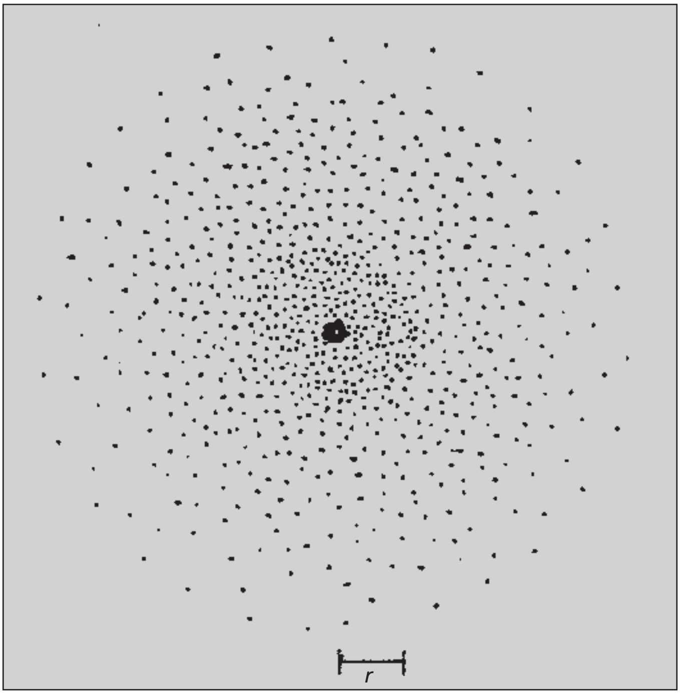


Fig. 1 Representation of the hydrogen atom. The dots represent the position of the electron with respect to the nucleus. The electron moves in a wave motion. It has no fixed position relative to the nucleus, but the probability of finding the electron at a given radius (the Bohr radius, r) can be calculated; $r = 5.3 \times 10^{-5}$ µm for hydrogen.

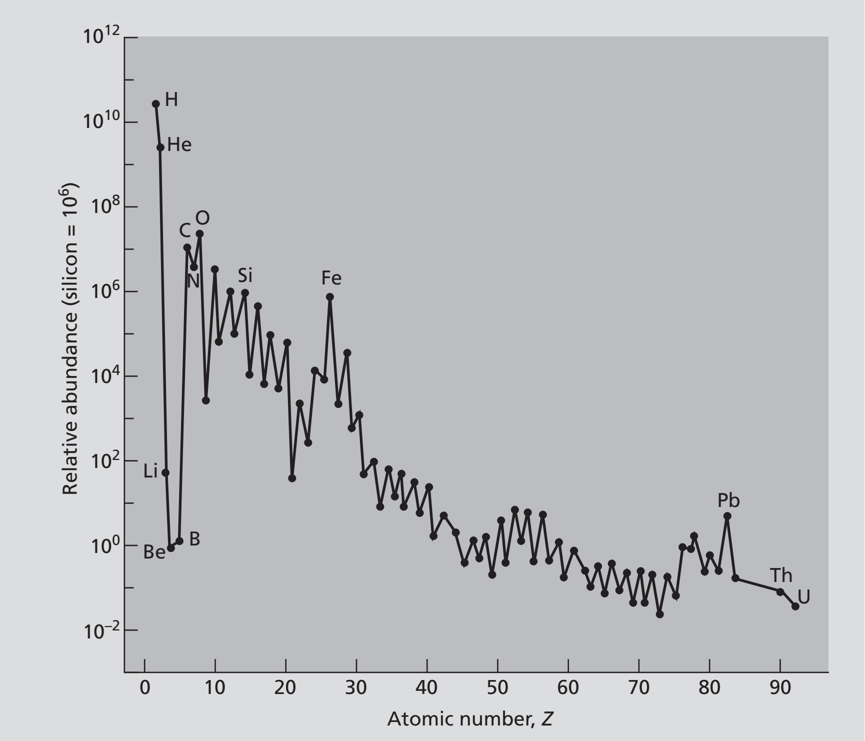


Fig. 1.1 The cosmic abundance of elements. The relative abundance of elements (vertical axis) is defined as the number of atoms of each element per 10^6 atoms of silicon and is plotted on a logarithmic scale.

solidification of the remaining material into the mantle of $MgFeSiO_3$ composition (Fig. 1.2).

1.3.1 Formation of the crust and atmosphere

The crust, hydrosphere and atmosphere formed mainly by release of materials from within the upper mantle of the early Earth. Today, ocean crust forms at mid-ocean ridges, accompanied by the release of gases and small amounts of water. Similar processes probably accounted for crustal production on the early Earth, forming a shell of rock less than 0.0001% of the volume of the whole planet (Fig. 1.2). The composition of this shell, which makes up the continents and ocean crust, has evolved over time, essentially distilling elements from the mantle by partial melting at about 100 km depth. The average chemical composition of the present crust (Fig. 1.3) shows that oxygen is the most abundant element, combined in various ways with silicon, aluminium (Al) and other elements to form silicate minerals.

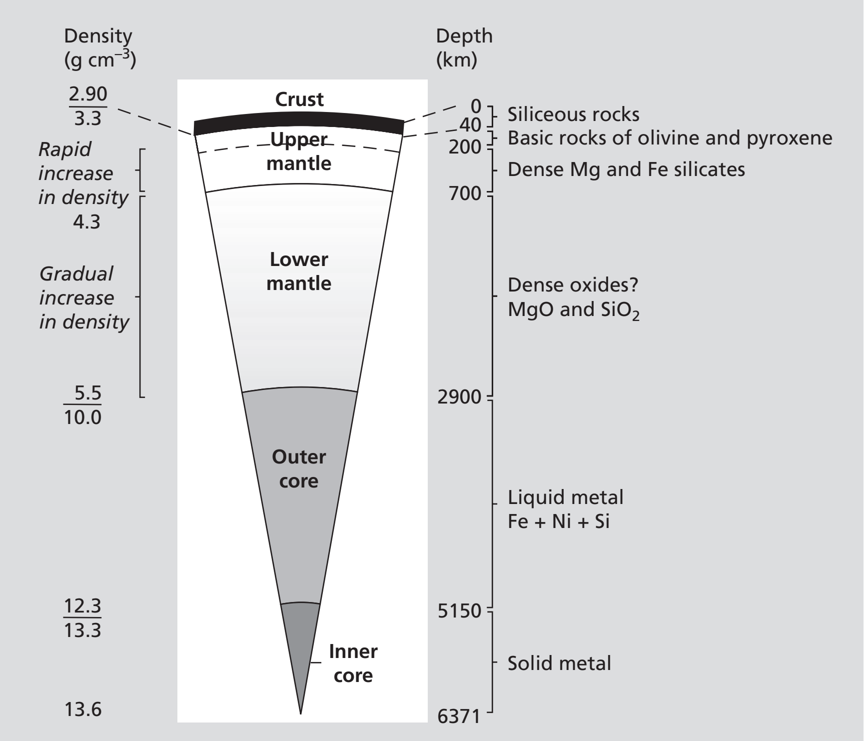


Fig. 1.2 Schematic cross-section of the Earth. Silica is concentrated in the crust relative to the mantle. After Raiswell *et al.* (1980).

Various lines of evidence suggest that volatile elements escaped (degassed) from the mantle by volcanic eruptions associated with crust building. Some of these gases were retained to form the atmosphere once surface temperatures were cool enough and gravitational attraction was strong enough. The primitive atmosphere was probably composed of carbon dioxide (CO_2) and nitrogen gas (N_2) with some hydrogen and water vapour. Evolution towards the modern oxidizing atmosphere did not occur until life began to develop.

1.3.2 The hydrosphere

Water, in its three phases, liquid water, ice and water vapour, is highly abundant at the Earth's surface, having a volume of 1.4 billion km^3. Nearly all of this water (>97%) is stored in the oceans, while most of the rest forms the polar ice-caps and glaciers (Table 1.1). Continental freshwaters represent less than 1% of the total volume, and most of this is groundwater. The atmosphere contains comparatively little water (as vapour) (Table 1.1). Collectively, these reservoirs of water are called the *hydrosphere*.

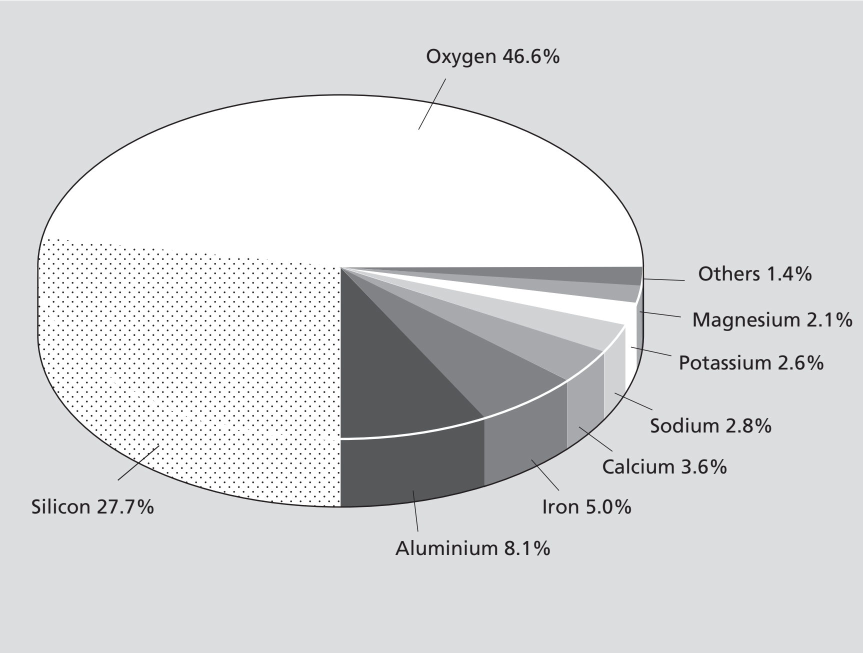


Fig. 1.3 Percentage of major elements in the Earth's crust.

Table 1.1 Inventory of water at the Earth's surface. After Speidel and Agnew (1982).

Reservoir	Volume (10^6 km^3)	Percentage of total
Oceans	1350	97.41
Ice-caps and glaciers	27.5	1.98
Groundwater	8.2	0.59
Inland seas (saline)	0.1	0.007
Freshwater lakes	0.1	0.007
Soil moisture	0.07	0.005
Atmosphere*	0.013	0.001
Rivers	0.0017	0.0001
Biosphere	0.0011	0.00008
Total	1385.9	100

*As liquid equivalent of water vapour.

The source of water for the formation of the hydrosphere is problematical. Some meteorites contain up to 20% water in bonded hydroxyl (OH) groups, while bombardment of the proto-Earth by comets rich in water vapour is another possible source. Whatever the origin, once the Earth's surface cooled to 100°C, water vapour, degassing from the mantle, was able to condense. Mineralogical evidence suggests water was present on the Earth's surface by 4.4 billion years

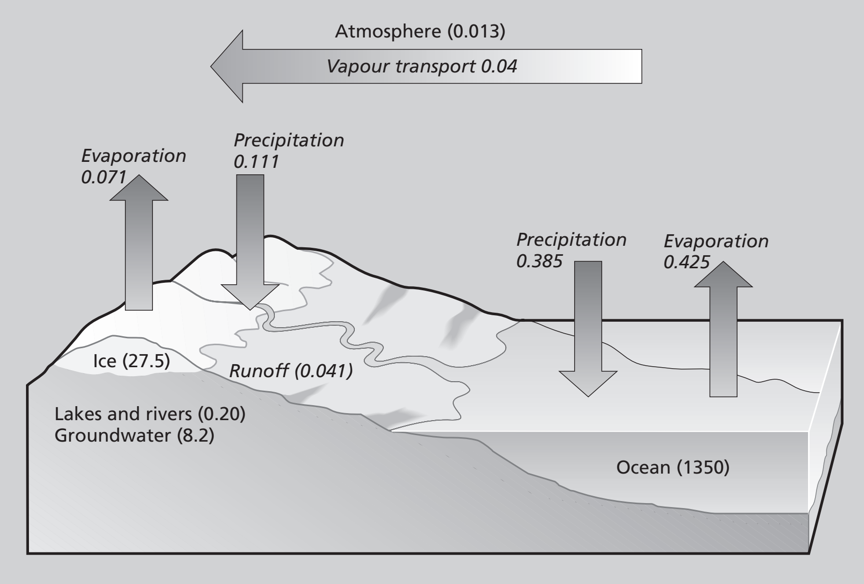


Fig. 1.4 Schematic diagram of the hydrological cycle. Numbers in parentheses are reservoir inventories ($10^6 km^3$). Fluxes are in $10^6 km^3 yr^{-1}$. After Speidel and Agnew (1982).

ago, soon after accretion, and we know from the existence of sedimentary rocks laid down in water that the oceans had formed by at least 3.8 billion years ago.

Very little water vapour escapes from the atmosphere to space because, at about 15 km height, the low temperature causes the vapour to condense and fall to lower levels. It is also thought that very little water degasses from the mantle today. These observations suggest that, after the main phase of degassing, the total volume of water at the Earth's surface changed little over geological time.

Cycling between reservoirs in the hydrosphere is known as the *hydrological cycle* (shown schematically in Fig. 1.4). Although the volume of water vapour contained in the atmosphere is small, water is constantly moving through this reservoir. Water evaporates from the oceans and land surface and is transported within air masses. Despite a short residence time (see Section 3.3) in the atmosphere, typically 10 days, the average transport distance is about 1000 km. The water vapour is then returned to either the oceans or the continents as snow or rain. Most rain falling on the continents seeps into sediments and porous or fractured rock to form groundwater; the rest flows on the surface as rivers, or re-evaporates to the atmosphere. Since the total mass of water in the hydrosphere is relatively constant over time, evaporation and precipitation must balance for the Earth as a whole, despite locally large differences between wet and arid regions.

The rapid transport of water vapour in the atmosphere is driven by incoming solar radiation. Almost all the radiation that reaches the crust is used to evaporate liquid water to form atmospheric water vapour. The energy used in this transformation, which is then held in the vapour, is called *latent heat*. Most of the

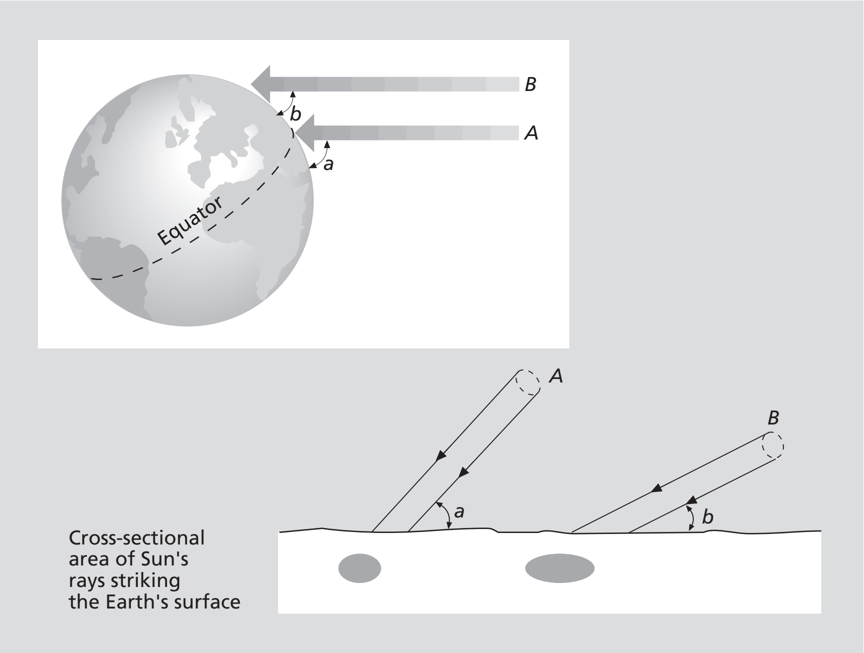


Fig. 1.5 Variation in relative amounts of solar radiation (energy per unit area) with latitude. Equal amounts of energy *A* and *B* are spread over a larger area at higher latitude, resulting in reduced intensity of radiation.

remaining radiation is absorbed into the crust with decreasing efficiency with increasing latitude, mainly because of the Earth's spherical shape. Solar rays hit the Earth's surface at 90 degrees at the equator, but at decreasing angles with increasing latitude, approaching 0 degrees at the poles. Thus, a similar amount of radiation is spread over a larger area at higher latitudes compared with the equator (Fig. 1.5). The variation of incoming radiation with latitude is not balanced by an opposite effect for radiation leaving the Earth, so the result is an overall radiation imbalance. The poles, however, do not get progressively colder and the equator warmer, because heat moves poleward in warm ocean currents and there is poleward movement of warm air and latent heat (water vapour).

1.3.3 The origin of life and evolution of the atmosphere

We do not know which chance events brought about the synthesis of organic molecules or the assembly of metabolizing, self-replicating structures we call organisms, but we can guess at some of the requirements and constraints. In the 1950s there was considerable optimism that the discovery of deoxyribonucleic acid (DNA) and the laboratory synthesis of likely primitive biomolecules from experimental atmospheres rich in methane (CH_4) and ammonia (NH_3) indicated a clear picture for the origin of life. However, it now seems more likely that the synthesis of biologically important molecules occurred in restricted, specialized environments, such as the surfaces of clay minerals, or in submarine volcanic vents.

Best guesses suggest that life began in the oceans some 4.2–3.8 billion years ago, but there is no fossil record. The oldest known fossils are bacteria, some 3.5 billion years old. In rocks of this age there is fossil evidence of quite advanced metabolisms which utilized solar energy to synthesize organic material. The very earliest of autotrophic (self-feeding) reactions were probably based on sulphur (S), supplied from volcanic vents.

$$CO_{2(g)} + 2H_2S_{(g)} \rightarrow \underset{\substack{\text{(organic}\\\text{matter)}}}{CH_2O_{(s)}} + 2S_{(s)} + H_2O_{(l)} \qquad \text{eqn. 1.1}$$

However, by 3.5 billion years ago photochemical splitting of water, or photosynthesis was happening.

$$H_2O_{(l)} + CO_{2(g)} \rightarrow CH_2O_{(s)} + O_{2(g)} \qquad \text{eqn. 1.2}$$

(If you are unfamiliar with chemical reactions and notation, see Chapter 2.)

The production of oxygen during photosynthesis had a profound effect. Initially, the oxygen gas (O_2) was rapidly consumed, oxidizing reduced compounds and minerals. However, once the rate of supply exceeded consumption, O_2 began to build up in the atmosphere. The primitive biosphere, mortally threatened by its own poisonous byproduct (O_2), was forced to adapt to this change. It did so by evolving new biogeochemical metabolisms, those that today support the diversity of life on Earth. Gradually an atmosphere of modern composition evolved (see Table 3.1). In addition, oxygen in the stratosphere (see Chapter 3) underwent photochemical reactions, leading to the formation of ozone (O_3), protecting the Earth from ultraviolet radiation. This shield allowed higher organisms to colonize the continental land surfaces.

In recent decades a few scientists have argued that the Earth acts like a single living entity rather than a randomly driven geochemical system. There has been much philosophical debate about this issue, often called the Gaia hypothesis, and more recently, Gaia theory. This view, suggested by James Lovelock, argues that biology controls the habitability of the planet, making the atmosphere, oceans and terrestrial environment comfortable to sustain and develop life. There is little consensus about these Gaian notions, but the ideas of Lovelock and others have stimulated active debate about the role of organisms in mediating geochemical cycles. Many scientists use the term ‘biogeochemical cycles’, which acknowledges the role of organisms in influencing geochemical systems.

1.4 Human effects on biogeochemical cycles?

In discussing the chemistry of near-surface environments on Earth it is important to distinguish between different types of alteration to Earth systems caused by humans. Two main categories can be distinguished:

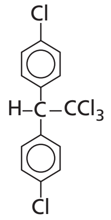
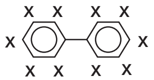
1 Addition to the environment of exotic chemicals as a result of new substances synthesized and manufactured by industry.
2 Change to natural cycles by the addition or subtraction of existing chemicals by normal cyclical and/or human-induced effects.

The first category of chemical change is probably easiest to understand. Some examples of substances which are found in the environment only as a result of human activities are given in Table 1.2 and include pesticides, such as 2,2-bis(*p*-chlorophenyl)-1,1,1-trichloroethane (DDT), which is broken down by bacteria in the soil to produce a number of other exotic compounds; polychlorinated biphenyls (PCBs), which have many industrial uses and are slow to degrade in the environment; tributyl tin (TBT), which is used in marine paints to inhibit organisms from settling on the hulls of ships; many drugs; some radionuclides; and a range of chlorofluorocarbon compounds (CFCs), which were developed for use as aerosol propellants, as refrigerants and in the manufacture of solid foams.

The list in Table 1.2 is by no means complete. It has been calculated that the chemical industry has synthesized several million different chemicals (mainly organic) never previously seen on Earth. Although only a small fraction of these chemicals are manufactured in commercial quantities, it is estimated that approximately a third of the total production escapes to the environment.

The impact of these exotic substances on the environment is difficult to predict, since there are often no similar natural compounds whose behaviour is

Table 1.2 Examples of substances found in the environment only as a result of human activities.

Name	Formula	Use	Environmental impact
DDT (2,2-bis (*p*-chlorophenyl)-1,1,1-trichloroethane		Pesticide	Unselective poison, concentrates up food chain
PCBs (polychlorinated biphenyls)	 (x are possible chlorine positions)	Dielectric in transformers; hydraulic fluids and many other uses	Resistant to breakdown carcinogens
TBT (tributyl tin)	$(CH_3(CH_2)_3)_3Sn$	Antifouling agent in marine paints	Affects sexual reproduction of shellfish
CFCs (chlorofluorocarbons)	e.g. F-11, CCl_3F	Aerosol propellant, foam blower	Destruction of stratospheric ozone

understood. A new substance may be benign, but our lack of knowledge can lead to unforeseen and sometimes harmful consequences. For example, because of the chemical inertness of the CFCs, when they were first introduced it was assumed that they would be completely harmless in the environment. This was true in all environmental reservoirs except the upper layers of the atmosphere (stratosphere), where they were broken down by solar radiation. The breakdown products of CFCs led to destruction of ozone (O_3), which forms a natural barrier, protecting animal and plant life from harmful ultraviolet (UV) radiation coming from the sun (see Section 3.10).

The second category of chemical changes is concerned with natural or human-induced alterations to existing cycles. These types of changes are illustrated in Chapter 7 with the elements carbon and sulphur. The cycling of these elements has occurred throughout the 4.5 billion years of Earth history. Furthermore, the appearance of life on the planet had a profound influence on both cycles. As well as being affected by biology, the cycles of carbon and sulphur are also influenced by alterations in physical properties, such as temperature, which have varied substantially during Earth history—for example, between glacial and interglacial periods. It is also clear that changes in the cycles of carbon and sulphur can influence climate, by affecting variables such as cloud cover and temperature. In the last few hundred years, the activities of humans have perturbed both these and other natural cycles. Such anthropogenic changes to natural cycles essentially mimic and in some cases enhance or speed up what nature does anyway.

In contrast to the situation for exotic chemicals described earlier, changes to natural cycles should be easier to predict, since the process is one of enhancement of what already occurs, rather than addition of something completely new. Thus, knowledge of how a natural system works now and has done in the past should be helpful in predicting the effects of human-induced changes. However, we are often less able at such predictions than we would like to be, because of our ignorance of the past and present mode of operation of natural chemical cycles.

1.5 The structure of this book

In the following chapters we describe how components of the Earth's chemical systems operate. Chapter 2 is a 'toolbox' of fundamental concepts underpinning environmental chemistry. We do not expect all readers will need to pick up these 'tools', but they are available for those who need them. The emphasis in each of the following chapters is different, reflecting the wide range of chemical compositions and rates of reactions that occur in near-surface Earth environments. The modern atmosphere (see Chapter 3), where rates of reaction are rapid, is strongly influenced by human activities both at ground level, and way up in the stratosphere. In terrestrial environments (see Chapters 4 & 5), a huge range of solid and fluid processes interact. The emphasis here is on weathering processes and their influence on the chemical composition of sediments, soils and continental surface waters. Human influence in the contamination of soils and natural waters is also a strong theme. Terrestrial weathering links through to the oceans (see Chapter 6) as the major input of constituents to seawater. It soon becomes clear, however, that the chemical composition of this vast water reservoir is controlled by a host of other physical, biological and chemical processes. Chapter 7 examines environmental chemistry on a global scale, integrating information from earlier chapters and, in particular, focusing on the influence of humans on global chemical processes. The short-term carbon and sulphur cycles are examples of natural chemical cycles perturbed by human activities. Persistent organic pollutants (POPs) are used as examples of exotic chemicals that persist for years to decades in soils or sediments and for several days in the atmosphere. Their persistence has allowed them to be transported globally, often impacting environments remote from their place of manufacture and use. In all of these chapters we have chosen subjects and case studies that demonstrate the chemical principles involved. To help clarify our main themes we provide information boxes that describe, in simple terms, some of the laws, assumptions and techniques used by chemists.

1.6 Internet keywords

There is now a wealth of information available on the Internet (worldwide web, www). In an environmental chemistry context there are many thousands of sites that provide quality information. Information ranges from lecture notes and problems set by university and college staff, through society web pages, to pages managed by government institutions. These pages have the advantage of many excellent colour illustrations and photographs. The information can be used to consolidate on material covered in this book, or as way of starting to explore a subject in more depth. To help you find material on the Internet, at the end of each chapter we have included a list of keywords or phrases as input for search engines. We use keywords rather than specific site addresses as website addresses change rapidly and would soon become dated in a book. The keyword lists are not intended to be complete, but are based on the main themes discussed in each chapter. You will be able to adapt the keywords or think up your own. We have personally checked each of the keywords included in the lists and know they give sensible outcomes.

We do, however, ask you to take care in your Internet searches. Remember, unlike scientific books and papers, there has been no peer review of material. If you are unsure about the quality of information on a specific site do check with your course teachers. They will be able to advise you on the validity of information.

Finally, when using search engines we advise you to use a variety of search options. Advanced search options that search for exact word strings are better for finding specific factual sites, whereas wider, less-constrained searches, usually find more diverse sites. Be as specific as you can. For example, if you are interested in ion exchange in soils use the phrase ‘ion exchange soil’ rather than ‘ion exchange’. This will help you home in to the subject of interest much more efficiently.

1.7 Further reading

Allegre, C. (1992) *From Stone to Star*. Harvard University Press, Cambridge, Massachusetts.

Broecker, W.S. (1985) *How to Build a Habitable Planet*. Lamont-Doherty Geological Observatory, Columbia University, Palisades, New York.

Lovelock, J. (1982) *Gaia: A New Look At Life on Earth*. Oxford University Press, Oxford, 157pp.

Lovelock, J. (1988) *The Ages of Gaia*. Oxford University Press, Oxford, 252pp.

1.8 Internet search keywords

big bang
formation chemical elements
elements stars
elements isotopes
differentiation Earth
origin atmosphere
origin hydrosphere
hydrological cycle
origin life earth
photosynthesis
Gaia theory