

CHAPTER 1

Introduction

ROY M. HARRISON

Division of Environmental Health and Risk Management, School of Geography, Earth and Environmental Sciences, University of Birmingham, Edgbaston, B15 2TT, Birmingham, UK

1.1 THE ENVIRONMENTAL SCIENCES

It may surprise the student of today to learn that ‘the environment’ has not always been topical and indeed that environmental issues have become a matter of widespread public concern only over the past 20 years or so. Nonetheless, basic environmental science has existed as a facet of human scientific endeavour since the earliest days of scientific investigation. In the physical sciences, disciplines such as geology, geophysics, meteorology, oceanography, and hydrology, and in the life sciences, ecology, have a long and proud scientific tradition. These fundamental environmental sciences underpin our understanding of the natural world and its current-day counterpart perturbed by human activity, in which we all live.

The environmental physical sciences have traditionally been concerned with individual environmental compartments. Thus, geology is centred primarily on the solid earth, meteorology on the atmosphere, oceanography upon the salt-water basins, and hydrology upon the behaviour of freshwaters. In general (but not exclusively) it has been the *physical* behaviour of these media which has been traditionally perceived as important. Accordingly, dynamic meteorology is concerned primarily with the physical processes responsible for atmospheric motion, and climatology with temporal and spatial patterns in physical properties of the atmosphere (temperature, rainfall, *etc.*). It is only more recently that *chemical* behaviour has been perceived as being important in many of these areas. Thus, while atmospheric chemical processes are at least as important as physical processes in many environmental problems such as stratospheric ozone depletion, the lack of chemical knowledge has been

extremely acute as atmospheric chemistry (beyond major component ratios) only became a matter of serious scientific study in the 1950s.

There are two major reasons why environmental chemistry has flourished as a discipline only rather recently. Firstly, it was not previously perceived as important. If environmental chemical composition is relatively invariant in time, as it was believed to be, there is little obvious relevance to continuing research. Once, however, it is perceived that composition is changing (*e.g.* CO₂ in the atmosphere; ¹³⁷Cs in the Irish Sea) and that such changes may have consequences for humankind, the relevance becomes obvious. The idea that using an aerosol spray in your home might damage the stratosphere, although obvious to us today, would stretch the credulity of someone unaccustomed to the concept. Secondly, the rate of advance has in many instances been limited by the available technology. Thus, for example, it was only in the 1960s that sensitive reliable instrumentation became widely available for measurement of trace concentrations of metals in the environment. This led to a massive expansion in research in this field and a substantial *downward* revision of agreed typical concentration levels due to improved methodology in analysis. It was only as a result of James Lovelock's invention of the electron capture detector that CFCs were recognised as minor atmospheric constituents and it became possible to monitor increases in their concentrations (see Table 1). The table exemplifies the sensitivity of analysis required since concentrations are at the ppt level (1 ppt is one part in 10¹² by volume in the atmosphere) as well as the substantial increasing trends in atmospheric halocarbon concentrations, as measured up to 1990. The implementation of the Montreal Protocol, which requires controls on production of CFCs and some other halocarbons, has led to a slowing and even a reversal of annual concentration trends since 1992 (see Table 1).

Table 1 *Atmospheric halocarbon concentrations and trends^a*

Halocarbon	Concentration (ppt)		Annual change (ppt)		Lifetime (years)
	Pre-industrial	2000	To 1990	1999–2000	
CCl ₃ F (CFC-11)	0	261	+9.5	−1.1	50
CCl ₂ F ₂ (CFC-12)	0	543	+16.5	+2.3	102
CClF ₃ (CFC-113)	0	3.5			400
C ₂ Cl ₂ F ₄ (CFC-113)	0	82	+4–5	−0.35	85
C ₂ Cl ₂ F ₄ (CFC-114)	0	16.5			300
C ₂ ClF ₅ (CFC-115)	0	8.1		+0.16	1700
CCl ₄	0	96.1	+2.0	−0.94	42
CH ₃ CCl ₃	0	45.4	+6.0	−8.7	4.9

^a Data from: World Meteorological Organization, *Scientific Assessment of Ozone Depletion: 2002*, WHO, Geneva, 2002.

1.2 ENVIRONMENTAL CHEMICAL PROCESSES

The chemical reactions affecting trace gases in the atmosphere generally have quite significant activation energies and thus occur on a timescale of minutes, days, weeks, or years. Consequently, the change to such chemicals is determined by the rates of their reactions and atmospheric chemistry is intimately concerned with the study of reactions kinetics. On the other hand, some processes in aquatic systems have very low activation energies and reactions occur extremely rapidly. In such circumstances, provided there is good mixing, the chemical state of matter may be determined far more by the thermodynamic properties of the system than by the rates of chemical processes and therefore chemical kinetics.

The environment contains many trace substances at a wide range of concentrations and under different temperature and pressure conditions. At very high temperatures such as can occur at depth in the solid earth, thermodynamics may also prove important in determining, for example, the release of trace gases from volcanic magma. Thus, the study of environmental chemistry requires a basic knowledge of both chemical thermodynamics and chemical kinetics and an appreciation of why one or other is important under particular circumstances. As a broad generalisation it may be seen that much of the chapter on atmospheric chemistry is dependent on knowledge of reaction rates and underpinned by chemical kinetics, whereas the chapters on freshwater and ocean chemistry and the aqueous aspects of the soils are very much concerned with equilibrium processes and hence chemical thermodynamics. It should not however be assumed that these generalisations are universally true. For example, the breakdown of persistent organic pollutants in the aquatic environment is determined largely by chemical kinetics, although the partitioning of such substances between different environmental media (air, water, soil) is determined primarily by their thermodynamic properties and to a lesser degree by their rates of transfer.

1.3 ENVIRONMENTAL CHEMICALS

This book is not concerned explicitly with chemicals as pollutants. This is a topic covered by a companion volume on *Pollution Science*. This book, however, is nonetheless highly relevant to the understanding of chemical pollution phenomena. The major areas of coverage are as follows:

- (i) *The chemistry of freshwaters*. Freshwaters comprise three different major components. The first is the water itself, which inevitably contains dissolved substances, both inorganic and organic. Its properties are to a very significant degree determined by the

inorganic solutes, and particularly those which determine its hardness and alkalinity. The second component is suspended sediment, also referred to as suspended solids. These are particles, which are sufficiently small to remain suspended with the water column for significant periods of time where they provide a surface onto which dissolved substances may deposit or from which material may dissolve. The third major component of the system is the bottom sediment. This is an accumulation of particles and associated pore water, which has deposited out of the water column onto the bed of the stream, river, or lake. The size of the sediment grains is determined by the speed and turbulence of the water above. A fast-flowing river will retain small particles in suspension and only large particles (sand or gravel) will remain on the bottom. In relatively stagnant lake water, however, very small particles can sediment out and join the bottom sediment. In waters of this kind, sediment accumulates over time and therefore the surface sediments in contact with the water column contain recently deposited material while the sediment at greater depths contains material deposited tens or hundreds of years previously. In the absence of significant mixing by burrowing organisms, the depth profile of some chemicals within a lake bottom sediment can provide a very valuable historical record of inputs of that substance to the lake. Ingenious ways have been devised for determining the age of specific bands of sediment. While the waters at the surface of a lake are normally in contact with the atmosphere and therefore well aerated, water at depth and the pore water within the bottom sediment may have a very poor oxygen supply and therefore become oxygen-depleted and are then referred to as anoxic or anaerobic. This can affect the behaviour of redox-active chemicals such as transition elements, and therefore the redox properties of freshwaters and their sediments are an important consideration.

- (ii) *Salt waters.* The waters of seas and oceans differ substantially from freshwaters by virtue of their very high content of dissolved inorganic material and their very great depth at some points on the globe. These facets confer properties, which although overlapping with those of freshwaters, can be quite distinct. Some inorganic components will behave quite differently in a very high salinity environment than in a low ionic strength freshwater. Historically, therefore, the properties of seawater have traditionally been studied separately from those of freshwaters and are presented separately, although the important overlaps such as in the area of carbonate equilibria are highlighted.

- (iii) *The chemistry of soils and rocks.* There are very significant overlaps with freshwater chemistry but the main differences arise from the very large quantities of solid matter providing very large surfaces and often restricting access of oxygen so that conditions readily become anoxic. However, many of the basic issues such as carbonate equilibria and redox properties overlap very strongly with the field of freshwater chemistry. Soils can, however, vary very greatly according to their location and the physical and chemical processes which have affected them during and since their formation.
- (iv) *Environmental organic chemistry.* Much of the traditional study of the aquatic and soil environment has been concerned with its inorganic constituents. Increasingly, however, it is recognised that organic matter plays a very important role both in terms of the contribution of natural organic substances to the properties of waters and soils, but also that specific organic compounds, many of them deriving from human activity, show properties in the environment which are not easily understood from traditional approaches and therefore these have become a rather distinct area of study.
- (v) *Atmospheric chemistry.* The atmosphere contains both gas phase and particulate material. The study of both is important and the two interact very substantially. However, as outlined previously, chemical processes in the atmosphere tend to be very strongly influenced by kinetic factors, and to a large extent are concerned with rather small molecules, which play only a minor part in the chemistry of the aquatic environment or solid earth. Inevitably, there are important processes at the interface between the atmosphere and the land surface or oceans, but these are dealt with more substantially in the companion volume on *Pollution Science*.

1.4 UNITS OF CONCENTRATION

1.4.1 Atmospheric Chemistry

Concentrations of trace gases and particles in the atmosphere can be expressed as mass per unit volume, typically $\mu\text{g m}^{-3}$. The difficulty with this unit is that it is not independent of temperature and pressure. Thus, as an air mass becomes warmer or colder, or changes in pressure, so its volume will change, but the mass of the trace gas will not. Therefore, air containing $1 \mu\text{g m}^{-3}$ of sulfur dioxide in air at 0°C will contain less than $1 \mu\text{g m}^{-3}$ of sulfur dioxide in air if heated to 25°C . For gases (but not particles), this difficulty is overcome by expressing the concentration of

the trace gas as a volume mixing ratio. Thus, 1 cm^3 of pure sulfur dioxide dispersed in 1 m^3 of polluted air would be described as a concentration of 1 ppm. Reference to the gas laws tells us that not only is this one part per 10^6 by volume, it is also one molecule in 10^6 molecules and one mole in 10^6 moles, as well as a partial pressure of 10^{-6} atm. Additionally, if the temperature and pressure of the air mass change, this affects the trace gas in the same way as the air in which it is contained and the volume-mixing ratio does not change. Thus, ozone in the stratosphere is present in air at considerably higher mixing ratios than in the lower atmosphere (troposphere), but if the concentrations are expressed in $\mu\text{g m}^{-3}$ they are little different because of the much lower density of air at stratospheric altitudes. Chemical kineticists often express atmospheric concentrations in molecules per cubic centimetre (molec cm^{-3}), which has the same problem as the mass per unit volume units.

Worked Example

The concentration of nitrogen dioxide in polluted air is 85 ppb. Express this concentration in units of $\mu\text{g m}^{-3}$ and molec cm^{-3} if the air temperature is 20°C and the pressure 1005 mb ($1.005 \times 10^5 \text{ Pa}$). Relative molecular mass of NO_2 is 46; Avogadro number is 6.022×10^{23} .

The concentration of NO_2 is $85 \mu\text{L m}^{-3}$. At 20°C and 1005 mb,

$$\begin{aligned} 85 \mu\text{L NO}_2 \text{ weigh } 46 \times \frac{85 \times 10^{-6}}{22.41} \times \frac{273}{293} \times \frac{1005}{1013} \\ = 161 \times 10^{-6} \text{ g} \end{aligned}$$

NO_2 concentration = $161 \mu\text{g m}^{-3}$
This is equivalent to 161 pg cm^{-3} , and

$$\begin{aligned} 161 \text{ pg NO}_2 \text{ contain } 6.022 \times 10^{23} \times \frac{161 \times 10^{-12}}{46} \\ = 2.1 \times 10^{12} \text{ molecules} \end{aligned}$$

and NO_2 concentration = $2.1 \times 10^{12} \text{ molec cm}^{-3}$.

1.4.2 Soils and Waters

Concentrations of pollutants in soils are most usually expressed in mass per unit mass, for example, milligrams of lead per kilogram of soil. Similarly, concentrations in vegetation are also expressed in mg kg^{-1} or $\mu\text{g kg}^{-1}$. In the case of vegetation and soils, it is important to distinguish

between wet and dry weight concentrations, in other words, whether the kilogram of vegetation or soil is determined before or after drying. Since the moisture content of vegetation can easily exceed 50%, the data can be very sensitive to this correction.

In aquatic systems, concentrations can also be expressed as mass per unit mass and in the oceans some trace constituents are present at concentrations of ng kg^{-1} or $\mu\text{g kg}^{-1}$. More often, however, sample sizes are measured by volume and concentrations expressed as ng L^{-1} or $\mu\text{g L}^{-1}$. In the case of freshwaters, especially, concentrations expressed as mass per litre will be almost identical to those expressed as mass per kilogram. As a kind of shorthand, however, water chemists sometimes refer to concentrations as if they were ratios by weight, thus, mg L^{-1} are expressed as ppm, $\mu\text{g L}^{-1}$ as ppb and ng L^{-1} as ppt. This is unfortunate as it leads to confusion with the same units used in atmospheric chemistry with a quite different meaning.

1.5 THE ENVIRONMENT AS A WHOLE

A facet of the chemically centred study of the environment is a greater integration of the treatment of environmental media. Traditional boundaries between atmosphere and waters, for example, are not a deterrent to the transfer of chemicals (in either direction), and indeed many important and interesting processes occur at these phase boundaries.

In this book, the treatment first follows traditional compartments (Chapters 2, 3, 4, and 5) although some exchanges with other compartments are considered. Fundamental aspects of the science of atmosphere, waters, and soils are described, together with current environmental questions, exemplified by case studies. Subsequently, the organic chemistry of the environment is considered in Chapter 6, and quantitative aspects of transfer across phase boundaries are described in Chapter 7, where examples are given of biogeochemical cycles.

REFERENCES

1. For readers requiring knowledge of basic chemical principles R.M. Harrison and S.J. de Mora, *Introductory Chemistry for the Environmental Sciences*, 2nd edn, Cambridge University Press, Cambridge, 1996.
2. For more detailed information upon pollution phenomena *Pollution: Causes, Effects and Control*, 4th edn, R.M. Harrison (ed), RSC, Cambridge, 2001 or R.M. Harrison (ed), *Introduction to Pollution Science*, RSC, Cambridge, 2006.