THE CHEMISTRY AND MICROBIOLOGY OF POLLUTION

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Preface

Despite all that has been said and written in recent years about pollution and the environmental crisis, there has been a conspicuous lack of a comprehensive text dealing with the chemistry and microbiology of the subject. It is this deficiency that has prompted the writing of this book, which is aimed at both undergraduates and graduates studying environmental sciences. We hope that the specialist will also find the book useful even though he may discover insufficient detail in some areas; this must be inevitable in a book of this size covering such a variety of topics. Reference is made, where appropriate, to more comprehensive texts.

There is no attempt at a detailed discussion of the moral and philosophical aspects of environmental pollution which have been argued at great length elsewhere. We hope, however, that the reader will find in this volume a balanced view of the current state of chemical and microbiological knowledge and that the gaps in mankind's understanding will be apparent to him. These must be filled by further research if we are to adopt a rational approach to the increasingly serious pollution problems resulting from a rapidly expanding population and a concomitant desire for higher standards of living.

Finally, we should like to thank Dr. R. B. Cain for access to his review on surfactant degradation prior to its publication, our patient wives for typing and proof-reading, the publishers for many helpful suggestions and Dr. Hugo Z. Hackenbush for keeping us sane throughout the past months.

University of Kent,
July, 1975

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Introduction

The biosphere is dominated by a reactive mixture of hydrogen, carbon, oxygen, nitrogen, phosphorus and sulphur compounds—all in a continuous state of synthesis, decomposition and transformation. It is upon this dynamic equilibrium that the success or failure of our ecosystem depends. The functions of microorganisms in these processes include fixation, assimilation, and the degradation of organic residues to release nutrients in a suitable form for uptake by plants. This last process is described as mineralization and is a key reductive step in the recycling of elements.

The apparently unfailing capacity of bacteria to mineralize naturally occurring organic matter was described by Beijerink as "microbial infallibility". To a large extent man-made organic substances are also degraded by microorganisms although, in some instances, the time required for total breakdown is considerable. However, some synthetic chemicals appear resistant to both biological and non-biological decay, representing not only the immobilization of elements but also the accumulation of toxins.

Some ecologists believe that a pollutant-induced disruption of biological cycles may lead to irreversible damage to the environment. It is probable, however, that all ecosystems have some degree of flexibility and can absorb quite severe shocks without permanent displacement of their equilibria. Notwithstanding, some toxic compounds are not only recalcitrant but also exhibit mobility within the biosphere; a combination which may have undesirable ecological consequences.

1. Origin and Dispersal of Pollutants

Environmental pollutants, defined as those chemicals having a detrimental effect on man and his environment, are derived from three main sources (Table 1.1).

TABLE 1.1
Origin of pollutants

A. Naturally occurring	B. Transformed and Concentrated	C. Synthesized
Oxides of nitrogen	Sewage	Pesticides
Nitrate	Fertilizers	Surfactants
Nitrite	Acid Waste	Radionuclides
Asbestos	Fuel combustion products	Synthetic polymers
Heavy metals	Heavy metals	Petrochemicals
Radionuclides	Radionuclides	
Hydrocarbons and their derivatives	Pesticides	
Allergens	Surfactants	
	Hydrocarbons	
	Petrochemicals	

In the first instance they may arise quite naturally to form part of the background level of toxic substances in the environment. Constant distribution and genetic selection has ensured that these compounds cause few problems and even if absorbed by plants and animals are rapidly excreted or detoxified. Pollutants may also be produced by the concentration and transformation of naturally occurring materials during their domestic and industrial use. Finally, some novel chemicals are synthesized by man.

From their point of origin pollutants may spread laterally and vertically to all components of the environment and their persistence can be measured in minutes (sulphur dioxide), days (alkoxy-alkyl-mercury), years (DDT) or even centuries (plutonium-239). The capacity of a chemical to persist and become a pollutant rests upon its inherent physico-chemical properties, its resistance to removal by chemical, physical and biological mechanisms and its toxicity to microorganisms, plants and animals.

2. Environmental Problems

It has been said that mankind's concern for his environment is directly related to the ability of the chemist to detect low levels of toxic chemicals. To some extent this is true, in the sense that our understanding of the consequences of contaminating the biosphere has somewhat paralleled the development of analytical techniques. Nevertheless, the dangers of pollutants to man and his environment are real enough (Table 1.2) and we are all familiar with phenomena such as eutrophication, during which aquatic systems are deoxygenated by the introduction of reduced effluents and inorganic

TABLE 1.2

The effect of pollutants on man

Pollutants may affect man by:

1. his inhalation of contaminated air
2. his ingestion of contaminated food and water
3. damaging his livestock and crops
4. increasing levels of radiation
5. causing climatic changes
6. inhibiting the flora and fauna and disrupting biological stability
7. affecting microorganisms, plants and animals responsible for mineral cycles
8. disrupting amenities

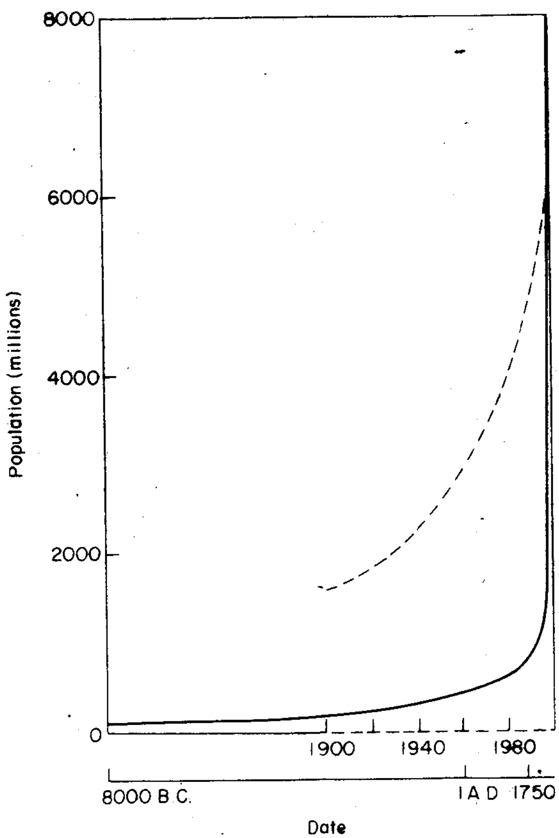

Fig. 1.1. Human population growth.

nutrients. Additionally, DDT, cyclodiene insecticides, mercury and cadmium may become concentrated in animal tissues and cause the disruption of a variety of normal metabolic and physiological functions whilst the hazards of air pollution have been dramatically demonstrated.

On the other hand, over-reaction has resulted in the total condemnation of many chemicals before any assessment of real value versus real or potential dangers has been made. In recent years a highly critical and somewhat emotional spotlight has been directed at phosphates, methyl mercury, nitrate, organo-chlorine insecticides and others

In the broadest sense it is difficult to divorce pollution problems from those posed by a rapidly expanding population (Fig. 1.1). In the simplest terms this means more people: more food; an equation that is becoming increasingly difficult to balance. It has been estimated that some 50% of the world's potential agricultural land is already being used and that the cultivation of the remainder will prove extremely difficult. The potential agricultural acreage will, of course, decrease with population growth and, at present productivity levels and predicted population demands, will have ceased to produce enough food by the end of the century. Some have forecast that increasing the yield four-fold (fertilizers, pesticides, genetic manipulation) will only delay the nutritional catastrophe for two generations. Additionally, the greater material expectations and energy consumption of many societies puts pressure upon industries whose products and by-products contribute significantly to pollution.

It is readily apparent that we need to (i) improve our understanding of both the short- and long-term effects of pollutants and (ii) investigate alternative technologies (e.g. biological control). The former will only result from a comprehensive understanding of the molecular structure of pollutants, their chemical and physical properties, their mobility and partitioning in the hydrosphere, atmosphere, lithosphere and biosphere, and their rate of and susceptibility to biological and non-biological decay.

Recommended Reading

Articles on Human Population. (1974). *Scientific American* 231 No. 3. W. H. Freeman.

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2
Pesticides

INTRODUCTION

Pesticides can be defined as those chemicals employed by Man to destroy or to inhibit life forms which he has decided are a nuisance. Of course, this may often be a subjective assessment in that one man's weed is another's wild flower.

Used as a collective noun, the word pesticide embraces herbicides, fungicides, insecticides, nematocides, rodenticides, molluscicides, bacteriocides and others (Fig. 2.1). Compounds which have been and which are being used for biological control include naturally occurring organics (antibiotics, pyrethrins), synthetic organics (chlorinated hydrocarbons, thiocarbamates) and inorganics (copper sulphate, mercuric chloride). Since 1945 the production and use of organic pesticides in particular, has increased at an enormous rate (for example see Table 2.1) and the prominence of the subject in the public mind is, to a large extent, due to any associated environmental hazards.

Pesticide pollution is not, however, a new problem. Prior to the Second World War pesticides were inorganic, made up of arsenic, mercury, selenium and lead compounds amongst others and routinely applied at dosage rates in excess of 200 kg ha^{-1}. Even at

Fungicides		Fungi
Insecticides		Insects
Herbicides		Green Plants
Nematacides	INHIBIT OR KILL	Nematodes
Molluscicides		Molluscs
Bacteriocides		Bacteria
Rodenticides		Rodents

Fig. 2.1. What are pesticides?

TABLE 2.1

Production of organochlorine insecticides in the U.S.A.

	kg x 10^{-6}	
	DDT	Cyclodienes
1945	15.9	
1950	34.1	
1955	59.1	36.4
1960	75.0	43.2
1965	63.6	52.4
1969	60.5	50.0

this time there was some concern over the accumulation of insoluble heavy metal residues in soil (see Chapter 7). However, in the postwar period, with the introduction of organic herbicides such as 2,4-dichlorophenoxyacetic acid (2,4-D) and the chlorinated hydrocarbon insecticides like DDT, the use of inorganic chemicals for pest control declined rapidly. In addition, the whole approach to pest control was revolutionized with the development of highly selective and efficient compounds which could be used at low application rates (1–20 kg ha^{-1}). Moreover, it was hoped that, since organic compounds are readily metabolized by microorganisms, toxic residue problems would be negligible. Unfortunately, it has since become apparent that microorganisms are far from infallible in their ability to degrade each and every organic substrate presented to them. As a result, whilst most organic pesticides are transient some may remain unchanged in the environment for long periods of time (1–20 years) whilst others may be converted to equally persistent toxic substances. In the early 1950's environmentalists were beginning to voice their concern over the apparent persistence of these "biodegradable" organic compounds and, as a group, the chlorinated hydrocarbon insecticides (DDT, aldrin, dieldrin, heptachlor) were the subject for many of these misgivings.

It was not, however, until the early 1960's that the public at large became aware of the deleterious effects of pesticide residues in the environment. Around this time Rachel Carson, a scientific and literary figure of some repute, published "Silent Spring" a book in which she dramatically described the catastrophic effects on wild life arising from the indiscriminate use of pesticides. The remarkable outcome of this book was that, in addition to becoming a best seller, it focused public attention on the potential problems associated with pesticide use, specifically in relation to non-target animals.

CHEMISTRY

Pesticides include a vast array of substances with widely different formulae and chemical and physical properties. In this discussion only the major groups of compounds are introduced and the reader is referred to the bibliography at the end of the chapter for a more detailed account.

On a chemical basis pesticides may be conveniently divided into three major groups: inorganic compounds, organic compounds containing metal ions, and organic compounds.

1. Inorganic Pesticides

1.1. Insecticides

Inorganic arsenic compounds, in addition to their use as herbicides, have also found favour as non-selective insecticides. The first of these compounds was Paris Green, ($Cu(C_2H_3O_2)_2 \cdot 3Cu(AsO_2)_2$) introduced in 1865 to control the Colorado Potato Beetle. Probably the most widely used and the safest of the arsenicals since that time has been lead arsenate ($PbHAsO_4$), traditionally mixed with sodium arsenate and suitable for controlling a wide spectrum of insect pests. Compounds of fluorine have been utilized as insecticides in the past but have not proved very effective.

1.2. Fungicides

Salts of copper, zinc, mercury, potassium and sulphur have been used as fungicides for many years. In the second half of the eighteenth century solutions of copper sulphate ($CuSO_4 \cdot 5H_2O$) were used to protect wheat seed and wood from fungal attack. Bordeaux mixture, a formulation of copper sulphate and calcium carbonate, was introduced in 1885 and, as an effective mildew-controlling fungicide, is still in use today. Zinc oxide (ZnO) is commonly used in fungicide preparations and has proved particularly useful in the treatment of superficial mycoses such as Athlete's Foot.

Mercuric chloride ($HgCl_2$) was introduced in 1890 as a fungicide for treating cereal seeds and had been used prior to this as a bacteriocide. However, due to its chronic and acute mammalian toxicity, it was never widely adopted in agricultural practice. Mercuric cyanide ($Hg(CN)_2$) or corrosive sublimate, however, has been used in the treatment of fungal and insect pathogens of potatoes, cabbages, cucumbers and fruit trees although it is also extremely poisonous to Man.

Potassium sulphide solutions are effective substitutes for Bordeaux mixture in the control of powdery mildews whilst sulphur and sulphur-lime have been used to alleviate fungal infections of stone fruit (such as peaches and plums) and as insecticides for cattle dips.

1.3. Herbicides

A variety of inorganic compounds are used as herbicides. Arsenic trioxide (As_2O_3), sodium arsenite ($NaAsO_2$) and calcium arsenate ($Ca_3(AsO_4)_2$) have been applied as soil sterilants and non-selective contact and systemic herbicides. However, in recent years, they have been largely replaced by organic arsenicals which are more selective to plants and, at the same time, less toxic to mammals.

Sodium chlorate ($NaClO_4$) is widely used for the destruction of deep-rooted perennials. This chemical is a strong oxidizing agent, a useful characteristic in the firework industry but one presenting a not inconsiderable hazard when used as an herbicide. Consequently sodium chlorate is often mixed with various borate salts and substituted ureas, both to decrease its combustibility and increase its weed-killing efficiency.

Boron compounds (as sodium tetraborate or borax, $(Na_2B_4)_7 \cdot 10H_2O$) are extremely toxic to plants and may persist in the soil for a considerable time. Unlike sodium chlorate however borax herbicides are non-flammable, non-corrosive, non-volatile and non-poisonous.

Calcium cyanamide ($CaCN_2$) is a fertilizer, defoliant and herbicide. Other inorganic herbicides include sodium cyanate ($NaOCN$), potassium cyanate ($KOCN$), ammonium sulphamate ($H_2NS(O)_2ONH_4$) and magnesium chlorate ($Mg(ClO_3)_2 \cdot 6H_2O$).

1.4. Fumigants

Several simple inorganic compounds, such as carbon bisulphide (CS_2), carbon tetrachloride (CCl_4), hydrogen cyanide (HCN) and sulphur dioxide (SO_2), function as fumigants to destroy a variety of pests.

2. Organo-Metallic Pesticides

The dangers involved in handling mercuric chloride prompted the introduction in 1915 of chlorphenol mercury ($ClC_6H_3OH \cdot Hg \cdot OSO_3Na$), the first of the organic mercurial pesticides. Subsequently a variety of compounds were synthesized all having the general formula of RHgX, where R = aryl-, aryloxy-, alkyl-, alkyloxyethyl-, and X = chloride, acetate, lactate, urea of hydroxyl. Examples include methoxyethylmercury chloride ($CH_3O . CH_2 . CH_2 . HgCl$), hydroxymercurychlorophenol ($Cl . C_6H_4 . O . HgOH$), phenylmercuric acetate ($C_6H_5Hg . O . CO . CH_3$) and ethylmercuric chloride ($C_2H_5 . HgCl$). Most of these substances have been used as seed treatments for fungal control for once in the soil they decompose to yield the active fungicidal agent, either metallic mercury or a mercury salt. Unfortunately mercury compounds are rapidly absorbed through the skin, mouth and respiratory tract and show both an acute and a chronic toxicity to mammals. These pesticides also pose a broader environmental hazard, since they are concentrated in food chains as biologically-formed dimethylmercury (see Chapter 7).

Since 1950 a series of organo-tin compounds has been developed and, although as a group they tend to be rather general biocides, they are safer fungicides than the organo-mercury compounds. The organo-tins include tributyl-tin hydroxide ($(C_4H_9)_3SnOH$), triphenyl-tin acetate ($(C_6H_5)_3SnOCOCH_3$) and triphenyl-tin disulphide ($(C_6H_5)_3SnS{-}SSn(C_6H_5)_3$). Triphenyl-tin compounds have the lowest toxicity to higher plants of the derivatives so far synthesized and can be used as foliar fungicides.

Cacodylic acid, monosodium methane-arsonate and disodium methane-arsonate are all arsenic-containing organic herbicides.

3. Organic Pesticides

This group accounts for the majority of pesticides in present day use.

3.1. Insecticides

Table 2.2 presents the formulae of a variety of organic insecticides.

3.1.1. Naturally Occurring Compounds. Nicotine, in the form of dried tobacco leaves and stems, was employed to control aphids on currants and gooseberries as long ago as 1763. It was thus one of the earliest organic pesticides and is still used today. It is, however, acutely toxic to Man and other animals but since it is rapidly broken down is not considered a chronic hazard.

The main pyrethroid insecticides are synthetic analogues of the naturally occurring pyrethrins from *Chrysanthemum* species. They have extremely low mammalian toxicities since they are rapidly metabolized in the mammalian body. Insects are also capable of