Second edition

# PRINCIPLES OF ENVIRONMENTAL POLLUTION

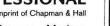
B.J. Alloway and D.C. Ayres

## Chemical Principles of Environmental Pollution

Second edition

B. J. Alloway
University of Reading, UK
and
D. C. Ayres

Queen Mary and Westfield College, University of London, UK



#### Published by Blackie Academic and Professional, an imprint of Chapman & Hall, 2-6 Boundary Row, London SE1 8HN, UK

Chapman & Hall, 2-6 Boundary Row, London SE1 8HN, UK

Chapman & Hall GmbH, Pappelallee 3, 69469 Weinheim, Germany

Chapman & Hall USA, 115 Fifth Avenue, New York, NY 10003, USA

Chapman & Hall Japan, ITP-Japan, Kyowa Building, 3F, 2-2-1 Hirakawacho, Chiyoda-ku, Tokyo 102, Japan

DA Book (Aust.) Pty Ltd, 648 Whitehorse Road, Mitcham 3132, Victoria, Australia

Chapman & Hall India, R. Seshadri, 32 Second Main Road, CIT East, Madras 600 035, India

First edition 1993 Reprinted 1994 Second edition 1997

© 1997 Chapman & Hall

Typeset in 10/12 pt Times by Thomson Press (I) Ltd, New Delhi Printed in Great Britain by Clays Ltd, Bungay, Suffolk

ISBN 0 7514 0380 6

Apart from any fair dealing for the purposes of research or private study, or criticism or review, as permitted under the UK Copyright Designs and Patents Act, 1988, this publication may not be reproduced, stored, or transmitted, in any form or by any means, without the prior permission in writing of the publishers, or in the case of reprographic reproduction only in accordance with the terms of the licences issued by the Copyright Licensing Agency in the UK, or in accordance with the terms of licences issued by the appropriate Reproduction Rights Organization outside the UK. Enquiries concerning reproduction outside the terms stated here should be sent to the publishers at the London address printed on this page.

The publisher makes no representation, express or implied, with regard to the accuracy of the information contained in this book and cannot accept any legal responsibility or liability for any errors or omissions that may be made.

A catalogue record for this book is available from the British Library

Library of Congress Catalog Card Number: 96-85900

Printed on permanent acid-free text paper, manufactured in accordance with ANSI/NISO Z39.48-1992 and ANSI/NISO Z39.48-1984 (Permanence of Paper)

#### **Preface**

Pollution is the most serious of all environmental problems and poses a major threat to the health and well-being of millions of people and global ecosystems. Other major environmental problems are also partly caused by pollution; these include global warming, climatic change and the loss of biodiversity through the extinction of many species. In the future, environmental pressures can only increase as a result of population growth and the expectation of higher living standards.

For at least thirty years people have become increasingly aware of these issues. As a result, governments and regulatory bodies have responded by taking action against grossly polluting activities and by enforcing tighter limits on the emission of pollutants into the environment. As the level of control improves so the financial costs increase exponentially, hence an effective limit must be enforced which does not impose unacceptable burdens on industrial producers.

As a consequence of the increasing economic and legal pressures which result from pollution control, there is a growing need for greater understanding of the scientific principles underlying environmental pollution. Appropriately qualified professionals will be needed in the energy, manufacturing, service and waste disposal industries and their regulatory authorities. They will be required to enforce increasingly strict standards and to monitor the environment for accidental pollution. The rapid growth in the numbers studying for undergradute and postgradute degrees and related qualifications in environmental science is a reflection of these requirements. Modules dealing with aspects of pollution have been introduced into many courses in the traditional disciplines of chemistry, biology, geography and civil engineering.

This book was written, in sympathy with these trends, for students and others with a basic knowledge of chemistry. It provides an introduction to the principles, and adopts a pollutant-oriented approach, rather than the more common one based on specific media such as air or water. All the main groups of substances are covered, and the principles relating to their nature, sources, transport, environmental behaviour and effects on targets. It is expected that readers will want to consult more advanced specialized texts dealing with particular topics, and an extensive bibliography has been included to further their studies.

The authors have been involved in teaching and researching this subject for many years and both have directed a BSc Environmental Science degree programme (at Westfield and Queen Mary and Westfield Colleges in the University of London). Their research interests include heavy metals and contaminated land (BJA), and organic pollutants and their analysis (DCA). Although both authors have come into environmental science from different subject backgrounds, in due course they both developed an interdisciplinary perspective. Nevertheless, it must be stressed that the investigation and management of environmental pollution requires the rigorous application of scientific principles. The theoretical basis of environmental pollution problems is intellectually demanding, and environmental scientists need to be able to understand the underlying principles in order to make effective decisions.

The advice of Dr Trevor Toube concerning mass spectrometry, of Dr Roger Brown on pollution monitoring and of Dr Peixun Zhang on emission spectroscopy, is gratefully acknowledged. We also thank Mr John Cross of the NRA and Ms Elizabeth Ayres for their help with the manuscript

BJA DCA

### Glossary of acronyms and abbreviations

AAS Atomic absorption spectrophotometry (analysis)

ACGIH American Conference of Governmental Industrial

Hygienists

ADI allowable daily intake (toxicology)
AEA Atomic Energy Authority (UK)
AGR advanced gas-cooled reactor
ALARA as low as reasonably achievable
ALARP as low as reasonably possible

AMU atomic mass unit

ANOVA analysis of variance (statistical test)
APEs alkyl phenol ethoxylates (chemicals)

AQA analytical quality assurance

BATNEEC best available technology not entailing excessive cost

BBP butyl benzyl phthalate (chemical)
BCF biological concentration factor
BHA butylated hydroxyanisole (chemical)
BHC benzene hexachloride (chemical)
BHT butylated hydroxytoluene (chemical)

BOD biochemical oxygen demand

BPEO best practicable environmental option

BPM best practicable means
BSI British Standards Institution

BTEX benzene, toluene, ethyl benzene and xylene (suite of

organic chemicals)

BWR boiling water reactor (nuclear)

CAMP Continuous Air Monitoring Programme (USA)

CANDU
CEC cation exchange capacity (soil chemistry)
CEC Commission of the European Communities
CERCLA Comprehensive Environmental Response

Compensation and Liability Act (US) (1980)

('Superfund') – see also SARA

CFCs chlorofluorocarbons (chemicals)

CHCs chlorinated hydrocarbon compounds (chemicals)

Ci curie

CIMAH Control of Industrial Major Accidents Regulation

(1984) (UK)

CNS central nervous system
COD chemical oxygen demand

COPA Control of Pollution Act (UK) (1974)

COSHH Control of Substances Hazardous to Health (UK)

CPs chlorophenols (chemicals)

CRM certified reference material (analytical)

CTB chemical time bomb

DBP di-*n*-butyl phthalate (chemical)
DCE dichloroethene (chemical)

DDE dichlorodiphenyl dichloroethene (chemical)
DDT dichlorodiphenyl trichloroethane (chemical)
DEHP bis(2-ethylhexyl) phthalate (chemical)

DNA deoxyribonucleic acid (biochemical: genetic code

material)

DNAPL dense non-aqueous-phase liquid DOCs dissolved organic compounds

DoE Department of the Environment (UK)

DoE Department of Energy (US)

DTPA diethyltriaminepentaacetic acid (chemical reagent) EDTA ethylenediaminetetraacetic acid (chemical reagent)

EIA Environmental Impact Assessment (also

EA: environmental assessment)

EPA Environmental Protection Agency (US) EPA Environmental Protection Act (UK) (1990)

EQO environmental quality objective

ETA-AAS electrothermal activation-atomic absorption

spectrometry (elemental analysis)

EU European Union (formerly European Community)

FGD flue gas desulphurization GC gas chromatography (analysis)

GC-MS GC combined with mass spectrometry (analysis)

GDP gross domestic product

GFAAS graphite furnace atomic absorption spectro-

photometry (also referred to as ETA-AAS) (analysis)

GIS geographical information systems
GLC gas—liquid chromatography (analysis)

GLP good laboratory practice Gy the Gray (100 rads)

HCFC hydrogen-containing chlorofluorocarbon (chemical)

HCH hexachlorohexane (chemical)

HMIP Her Majesty's Inspectorate of Pollution (UK) HPLC high-pressure liquid chromatography (analysis)

also high performance liquid chromatography

HSE Health and Safety Executive (UK)
IAEA International Atomic Energy Authority
IARC International Agency for Research on Cancer
ICP-OES inductively coupled plasma optical emission

spectrometry (analysis)

ICP-MS inductively coupled plasma mass spectrometry

(analysis)

ICRP International Commission for Radiological

Protection

INES International Nuclear Event Scale
IPC Integrated Pollution Control (Europe)
IPCC International Panel for Climate Change
ISO International Standards Organization

JET Joint European Taurus

LAAPC Local Authority Air Pollution Control LC<sub>50</sub> lethal concentration for 50% survival

LD<sub>50</sub> lethal dose for 50% survival

LFG landfill gas

LMFBR liquid metal fast-breeder reactor LNAPL light non-aqueous-phase liquid

LOAEL lowest observable adverse effect level (toxicology)

LOEL lowest observable effect level (toxicology)

LPG liquefied petroleum gas
LULU locally unwanted land use

LUST leaking underground storage tank

MAC maximum allowable concentration (USA)
MAFF Ministry of Agriculture, Fisheries and Food

MCP monochlorophenol (chemical)

MEL maximum exposure limit (toxicology)

MSW municipal solid waste

NAAQS National Air Quality Standards (USEPA)

NAPL non-aqueous-phase liquid

NBS National Bureau of Standards (US): supplier of

**CRMs** 

MCP monochlorophenol (chemical)

NIMBY 'not in my back yard'

NIOSH National Institute of Occupational Safety and

Health (USA)

NOAEL no observable adverse effects level (toxicology)

NOEL no observable effects level (toxicology)
NPEs nonyl phenol ethoxylates (chemicals)

NRA National Rivers Authority (UK) (Incorporated into

Environmental Agency 1996)

NRPB National Radiological Protection Board (UK)

NTA nitriloacetic acid (chemical)

ms and abbreviations	
NTP	normal temperature (273.15 K) and pressure (101/325 Pa)
ODP	ozone depletion potential
OECD	Organization for Economic Co-operation and
	Development
OEL	occupational exposure limit (toxicology)
OES	occupational exposure standard
OP	organophosphorus
OSHA	Occupational Safety and Health Administration
PAH	polycyclic (or polynuclear) aromatic hydrocarbon
	(chemical)
PAN	peroxyacetyl nitrate (chemical)
PCB	polychlorinatedbiphenyl (chemical)
PCDD	polychlorodibenzo-p-dioxin (chemical)
PCDF	polychlorodibenzofuran (chemical)
PCP	pentachlorophenol (chemical)
PEL	permissible exposure limit (toxicology)
$PM_{10}$	particulate matter smaller than 10 µm
PMTWI	provisional maximum tolerable weekly intake
	(toxicology)
POMP	persistent organic micropollutant
PRA	probabilistic risk analysis
PTWI	provisional tolerable weekly intake (toxicology)
PVC	polyvinyl chloride (chemical)
PWR	pressurized water reactor
QA	quality assurance
QC	quality control
QSAR	quantity, structural activity relationship
Rad	absorbed radiation of 0.01 J/kg
RCRA	Resource, Conservation and Recovery Act (US)
	(1976)
Rem	Roentgen equivalent humans
RNA	ribonucleic acid (biochemical: genetic code material)
SARA	Superfund Amendments and Reauthorization Act
	(US) (1986): amendment to CERCLA (1980)
SMR	standardized mortality ratio (epidemiology)
STP	standard temperature and pressure
STEL	short-term exposure limit (toxicology)
TBT	tributyltin (chemical)

**TCB** trichlorobiphenyl (chemical)

**TCDD** tetrachlorodibenzo dioxin (chemical)

**TCE** trichloroethene (chemical)

tolerable daily intake (toxicology) TDI

**TDS** total dissolved solids

**TEF** toxic equivalent factor (toxicology) TEL tetraethyl lead (chemical)

TEQ toxic equivalent quantity (TEF × concentration)

THORP thermal oxide reprocessing plant

TLV threshold limit value

TOMP toxic organic micropollutant
TSP total suspended particles
TWA time-weighted average
UARG Urban Air Review Group

VCM vinyl chloride monomer (chemical)

VOC volatile organic compound

Waldsterben forest death

WDA Waste Disposal Authority (UK)
WHO World Health Organization

XRD X-diffraction (mineralogical analysis)
XRF X-ray fluorescence (elemental analysis)

#### **Contents**

Preface			xi
G	lossa	ry of acronyms and abbreviations	xiii
P	ART	ONE BASIC PRINCIPLES	
1	Intr	roduction	3
		Pollution in the modern world Definition of pollution Air pollution Environmental literature Population pressures Energy demand Wastes Concluding remarks erences ther reading	3 5 7 9 10 11 13 13 14
2	Tra	nsport and behaviour of pollutants in the environment	17
	2.1	A basic model of environmental pollution	17
	2.2	Sources of pollutants	17
	2.3	The pollutants	18
		<ul><li>2.3.1 Classification of hazardous substances in the USA</li><li>2.3.2 European Community Dangerous Substances</li></ul>	20
		Directive	22
		2.3.3 UK priority list of pollutants	22
		2.3.4 Pesticides 2.3.5 Indoor pollution	24
	2.4		26
	2.4	Physical processes of pollutant transport and dispersion 2.4.1 Transport media	27
		2.4.2 Transport fielda 2.4.2 Transport of pollutants in air	27
		2.4.3 Some important types of reaction which pollutants undergo	27
		in the atmosphere	34
	2.5	Dispersion of pollutants in water	36
		2.5.1 Physical transport in surface waters	36
		2.5.2 Dispersion of pollutants in groundwaters	39
		2.5.3 Biochemical processes in water (involving microorganisms)	46
	2.6	The behaviour of pollutants in the soil	53
		2.6.1 The composition and physico-chemical properties of soils	53
		2.6.2 Cation and anion adsorption in soils	55
	2.5	2.6.3 Adsorption and decomposition of organic pollutants	58
	2.7	Overview of the fate of soil pollutants	62
		rences	63
	Furth	her reading	64

3	Tox	icity and risk assessment of environmental pollutants	65
	3.1	Basic principles of toxicology	65
	3.2	Effect of pollutants on animals and plants	68
		3.2.1 Effect of pollutants on humans and other mammals	68
		3.2.2 Teratogenesis, mutagenesis, carcinogenesis and immune	
		system defects	69
		3.2.3 Ecotoxicology	75
	3.3	Assessment of toxicity risks	75 73
		3.3.1 Pollutants in contaminated land	81
		3.3.2 Pollutants in drinking water 3.3.3 Toxic or explosive gases and vapours	84
	Dofo	3.3.3 Toxic or explosive gases and vapours rences	84
		her reading	85
	run	ner reading	0.
4	Ana	lysis and monitoring of pollutants	86
	4.1	Introduction	86
	4.2	Chromatography	87
	4.3	Thin-layer chromatography	88
		4.3.1 Separation of pesticides by HPLC	89
		4.3.2 Separation of metal cations by HPLC	89
	4.4	Gas-liquid chromatography	90
		4.4.1 Detection of eluted substances 4.4.2 Principal parameters	93 93
		4.4.2 Principal parameters 4.4.3 Optimum operating conditions	9.
		4.4.4 Capillary columns for GLC	98
		4.4.5 Analysis of urban air pollution	99
		4.4.6 Detection by mass spectrometry	99
		4.4.7 Analysis of common pollutants	109
	4.5	High pressure liquid chromatography	113
		4.5.1 The components	114
		4.5.2 Detectors	115
		4.5.3 Analysis of polluted air	117
		4.5.4 Analysis of polluted water	120
		4.5.5 Trace enrichment followed by GLC analysis	121
	4.6	Pollution by metals – atomic absorption spectroscopy	123
		4.6.1 Historical introduction	123
		4.6.2 Basic theory of atomic absorption and emission	124
		4.6.3 The Lambert–Beer law	125
		4.6.4 Instrumental details 4.6.5 Interferences	126 127
		4.6.6 The determination of sodium in concrete	128
		4.6.7 Sample preparation	129
		4.6.8 Precision and accuracy of measurement	130
		4.6.9 Graphite furnace atomization	130
	4.7	A plasma source	131
		4.7.1 Method development in ICP-OES (ICP-AES)	133
		4.7.2 Determination of metals in environmental samples	135
		4.7.3 ICP-mass spectrometry	137
	4.8	Analytical quality assurance	137
	4.9	Environmental monitoring	139
		4.9.1 Introduction	139
		4.9.2 Air pollution monitoring	141
		4.9.3 Water pollution monitoring	143
		4.9.4 Soil pollution monitoring	146
		4.9.5 Plant sampling and analysis	149
		4.9.6 Sampling and analysis of animals and animal tissue	150
		4.9.7 The use of biological indicators in environmental monitoring	150

	Further reading			152 153
P	ART	TWO	THE POLLUTANTS	
5	Ino	rganic p	oollutants	157
	5.1	Ozone		157
		5.1.1	Historical introduction	157
		5.1.2	Formation	157
		5.1.3	Physical properties and structure	157
		5.1.4	The ozone layer	158
		5.1.5 5.1.6	Factors which disturb the natural environment	159
		5.1.7	Chemistry of stratospheric CFC Control measures (American Conference of Government	161
		3.1.7	Industrial Hygienists, 1990)	162
		5.1.8	Ozone in the troposphere	162
		5.1.9	Diurnal variations of ozone levels	163
		5.1.10		164
	5.2	Oxides	of carbon, nitrogen and sulphur	164
		5.2.1	Carbon dioxide	165
		5.2.2	Oxides of nitrogen	174
	<i>5</i> 2	5.2.3	Oxides of sulphur	179
	5.3	Heavy 5.3.1		190
		5.3.1	General properties	190
		5.3.3	Biochemical properties of heavy metals Sources of heavy metals	191 192
		5.3.4	Environmental media affected	192
		5.3.5	Heavy metal behaviour in the environment	200
		5.3.6	Toxic effects of heavy metals	207
		5.3.7	Analytical methods	211
		5.3.8	Examples of specific heavy metals	211
	5.4		metals and inorganic pollutants	217
		5.4.1	Aluminium	217
		5.4.2	Beryllium	218
	5.5	5.4.3 Radion	Fluorine	219
	3.3	5.5.1		220
		5.5.2	History and nomenclature Types of radioactive emission	220 220
		5.5.3	Units of energy and measurement of toxicity	220
		5.5.4	Radioactive potassium	223
		5.5.5	Production of radionuclides by artificial means	223
		5.5.6	Nuclear fission	223
		5.5.7	Power generation in nuclear reactors	225
		5.5.8	Nuclear reactor types	226
		5.5.9	The future of nuclear power	231
		5.5.10 5.5.11	Observations on major accidents	233
		5.5.11	Social aspects of nuclear power generation Power from thermal fusion	237
		5.5.13	Cold fusion	238 239
	5.6		I fibres and particles	240
		5.6.1	General aspects	240
		5.6.2	Examples of mineral pollutants	241
		rences		242
	Furt	her readir	ng	245
6	Orga	anic pol	lutants	247
	6.1	Smoke		247
	6.2		e and other hydrocarbons - coal and oil as sources	252

		6.2.1 The formation of coal	252
		6.2.2 Petroleum	253
		6.2.3 Methane	258
		6.2.4 Higher alkanes	259
		6.2.5 Polycyclic aromatic hydrocarbons (PAHs)	267
	6.3	Organic solvents	271
		6.3.1 Adhesives	272
		6.3.2 Coatings and inks	273
		6.3.3 Aerosol sprays	274
		6.3.4 Metal cleaning	275
		6.3.5 Dry cleaning of clothes	275
		6.3.6 Solvent toxicology	276
		6.3.7 Organochlorine compounds	277
		6.3.8 Detergents	279
	6.4	Organohalides: pesticides, PCBs and dioxins	282
	50.2	6.4.1 Historical note	282
		6.4.2 Organochlorine production	282
		6.4.3 DDT (dichlorodiphenyl trichloroethane)	283
		6.4.4 Lindane, hexachlorocyclohexane	284
		6.4.5 Some other chlorinated pesticides	285
		6.4.6 Organochlorine herbicides	287
		6.4.7 Toxic effects of insecticides	288
		6.4.8 Control of pesticides	291
		6.4.9 Vinyl chloride and polyvinyl chloride ( <i>Kirk-Othmer</i> , 1996)	292
			293
		6.4.10 Polychlorobiphenyls	
		6.4.11 Toxic substances in herbicides 6.4.12 Metabolism of chloroaromatic compounds	297
			305
		6.4.13 Disposal of organochlorine compounds	305
		6.4.14 Cremation or burial of wastes	307
		6.4.15 Use of biodegrading microorganisms	307
	6.5	Natural, organophosphorus and carbamate pesticides	307
		6.5.1 Naturally occurring pesticides	307
		6.5.2 Organophosphorus pesticides	312
		6.5.3 Carbamate pesticides	318
	6.6	Odours	322
		6.6.1 Important properties of odours	322
		6.6.2 Methods of odour control	323
	_	6.6.3 Methods of odour treatment	323
		rences	324
	Furt	ner reading	327
7	Indo	or pollution	329
•			
	7.1	Volatile organic compounds	329
		7.1.1 Oxidized forms of VOCs	331
	7.2	Ozone	333
	7.3	Oxides of nitrogen	334
	7.4	Carbon monoxide	335
	7.5	Other gaseous oxides	336
	7.6	Cigarette smoking	336
		7.6.1 <i>N</i> -Nitrosocompounds	337
		7.6.2 Polycyclic aromatic hydrocarbons	338
		7.6.3 Other mutagens	339
	7.7	Asbestos fibres	340
	*******	7.7.1 Analysis	341
		7.7.2 Toxicity	341
		7.7.3 Other particulate pollutants	343
	7.8	Lead	344
	7.9	Radon	346
			3.40

Contonto	1
ontents	IX

	Dofe	7.9.1 Cancer risk 7.9.2 Remedial measures	346 348 348
	0.0000	ther reading	350
PA	ART '	THREE WASTE AND OTHER MULTIPOLLUTANT SITUATIONS	
8	Was	stes and their disposal	353
	8.1	Introduction	353
	8.2	Amounts of waste produced	353
		8.2.1 Industrial wastes	354
	0.2	8.2.2 Municipal wastes	354
	8.3	Methods of disposal of municipal wastes	354
		8.3.1 Landfilling 8.3.2 Incineration	354
			358
		8.3.3 Composting 8.3.4 Recycling	359
	8.4	Sewage treatment	359
	8.5	Hazardous wastes	360
	0.5	8.5.1 The nature and amount of hazardous waste produced	365 365
		8.5.2 Hazardous waste management	366
		8.5.3 New technologies for waste disposal	368
	8.6	Long-term pollution problems of abandoned landfills containing	300
		hazardous wastes	369
		8.6.1 Love Canal, New York, USA	369
		8.6.2 Lekkerkirk, near Rotterdam, the Netherlands	371
		8.6.3 The Chemstar fire at Carrbrook, Cheshire	371
		8.6.4 Abandoned waste tips	372
	8.7	Tanker accidents and oil spillages at sea	372
	8.8	Other multipollutant situations	373
		8.8.1 Pollution from warfare and military training	374
	8.9	Chemical time bombs	376
	Refe	rences	377
Ap	pendi	x Table of units and conversions	379
Ind	Index 3		

### **Part One**Basic Principles