

## Trace Metals in the Environment and Living Organisms

The British Isles as a Case Study

Trace metals play key roles in life – all are toxic above a threshold bioavailability, yet many are essential to metabolism at lower doses. It is important to appreciate the natural history of an organism in order to understand the interaction between its biology and trace metals. The countryside and indeed the natural history of the British Isles are littered with the effects of metals, mostly via historical mining and subsequent industrial development. This fascinating story encompasses history, economics, geography, geology, chemistry, biochemistry, physiology, ecology, ecotoxicology and, above all, natural history. Examples abound of interactions between organisms and metals in the terrestrial, freshwater, estuarine, coastal and oceanic environments in and around the British Isles. Many of these interactions have nothing to do with metal pollution. All organisms are affected, from bacteria, plants and invertebrates to charismatic species such as seals, dolphins, whales and seabirds. All have a tale to tell.

**Philip S. Rainbow** has more than 40 years' experience of research into the biology of trace metals. As lecturer, reader and professor at Queen Mary University of London, he taught students at undergraduate, master's and PhD levels, and often ran courses overseas. From 1997 to 2013, he was Keeper of Zoology and subsequently the head of the Department of Life Sciences at the Natural History Museum in London. He has published more than 250 refereed scientific publications, including two co-authored and seven edited books, and also upwards of 30 popular articles. In 2002, he was awarded the Environmental Pollution Kenneth Mellanby Review Award.





# Trace Metals in the Environment and Living Organisms

The British Isles as a Case Study

PHILIP S. RAINBOW

Natural History Museum





#### CAMBRIDGE UNIVERSITY PRESS

University Printing House, Cambridge CB2 8BS, United Kingdom

One Liberty Plaza, 20th Floor, New York, NY 10006, USA

477 Williamstown Road, Port Melbourne, VIC 3207, Australia

314-321, 3rd Floor, Plot 3, Splendor Forum, Jasola District Centre, New Delhi - 110025, India

79 Anson Road, #06-04/06, Singapore 079906

Cambridge University Press is part of the University of Cambridge.

It furthers the University's mission by disseminating knowledge in the pursuit of education, learning, and research at the highest international levels of excellence.

www.cambridge.org

Information on this title: www.cambridge.org/9781108470933

DOI: 10.1017/9781108658423

© Cambridge University Press 2018

This publication is in copyright. Subject to statutory exception and to the provisions of relevant collective licensing agreements, no reproduction of any part may take place without the written permission of Cambridge University Press.

First published 2018

Printed in the United Kingdom by TJ International Ltd. Padstow Cornwall

A catalogue record for this publication is available from the British Library.

Library of Congress Cataloging-in-Publication Data

Names: Rainbow, P. S., author.

Title: Trace metals in the environment and living organisms: the British isles as a case study / Philip S. Rainbow, Natural History Museum, London.

Description: Cambridge, United Kingdom; New York, NY: Cambridge University Press, 2018. | Includes bibliographical references and index.

Identifiers: LCCN 2018017273 | ISBN 9781108470933 (hardback) | ISBN 9781108456869 (paperback)

Subjects: LCSH: Metals–Environmental aspects–British isles.
Classification: LCC QH545.M45 R35 2018 | DDC 572/.51–dc23
LC record available at https://lccn.loc.gov/2018017273

ISBN 978-1-108-47093-3 Hardback

Cambridge University Press has no responsibility for the persistence or accuracy of URLs for external or third-party internet websites referred to in this publication and does not guarantee that any content on such websites is, or will remain, accurate or appropriate.



### **CONTENTS**

	eface <i>page</i> xiii	2.3.8 Manganese 29	
Ac	cknowledgements xvi	2.3.8.1 Pyrolusite 29	
		2.3.9 Tungsten 29	
1	Introduction 1	2.3.9.1 Wolframite 29	
	1.1 Metals 2	2.3.9.2 Scheelite 29	
	1.2 Metals and Humans 4	2.3.10 Antimony 29	
	1.3 Sources and Global Cycles of Metals 10	2.3.10.1 Antimonite, Jamesonite and	
	1.4 Trace Metals and Living Organisms 17	Bournonite 29	
	1.5 Pollution Hazard and Environmental	2.3.11 Cobalt, Nickel and	
	Regulation 21	Molybdenum 29	
		2.3.12 Uranium 30	
2	Metals and Mining 22	2.3.13 Gold 30	
	2.1 Introduction 24	2.3.14 Aluminium 30	
	2.2 Geological Origin of Metal Ores 24	2.3.14.1 Bauxite 30	
	2.3 Ores 27	2.4 Geographical Distribution of Ores	
	2.3.1 Tin 27	and Mining Districts 30	
	2.3.1.1 Cassiterite 27	2.4.1 Cornwall and Devon 31	
	2.3.1.2 Stannite 27	2.4.2 Pennines 31	
	2.3.2 Copper 27	2.4.3 Wales 33	
	2.3.2.1 Chalcopyrite 27	2.4.4 Scotland 33	
	2.3.2.2 Chalcocite 27	2.4.5 Other Mining Regions 34	
	2.3.2.3 Malachite 27	2.5 History of Mining for Metals in the	
	2.3.2.4 Azurite 27	British Isles 34	
	2.3.2.5 Cuprite 27	2.5.1 Bronze Age and Iron Age 34	
	2.3.2.6 Tenorite 27	2.5.2 Roman Britain 35	
	2.3.3 Arsenic 27	2.5.3 The Middle Ages 35	
	2.3.3.1 Arsenopyrite 27	2.5.3.1 Pennines 36	
	2.3.4 Lead 28	2.5.3.2 Cornwall and Devon 37	
	2.3.4.1 Galena 28	2.5.3.3 Lake District 39	
	2.3.4.2 Other Lead Ores 28	2.5.3.4 Scotland and Wales 39	
	2.3.5 Zinc 28	2.5.3.5 Iron 39	
	2.3.5.1 Sphalerite 28	2.5.4 Sixteenth and Seventeenth	
	2.3.5.2 Smithsonite, Hemimorphite	Centuries 40	
	and Calamine 28	2.5.4.1 Lake District 40	
	2.3.6 Silver 28	2.5.4.2 Cornwall and Devon 41	
	2.3.6.1 Argentiferous Galena 28	2.5.4.3 Pennines 42	
	2.3.6.2 Acanthite 29	2.5.4.4 Scotland 42	
	2.3.7 Iron 29	2.5.4.5 North Wales, Staffordshire and	
	2.3.7.1 Pyrite 29	the Mendips 43	

2.3.7.2 Other Iron Ores 29

2.5.4.6 Iron 43



νi

3

#### **Table of Contents**

2.5.5 Eighteenth and Nineteenth	3.7 Biomarkers 115
Centuries 44	3.7.1 Community Effects 120
2.5.5.1 Cornwall and Devon 45	3.8 Tolerance 121
2.5.5.2 Pennines 53	
2.5.5.3 Wales 55	4 Terrestrial Environment 124
2.5.5.4 Scotland 57	4.1 Introduction 128
2.5.5.5 Lake District 58	4.2 Metal Concentrations in Soils 135
2.5.5.6 Shropshire, Staffordshire and	4.2.1 Mining Sites 135
Somerset 59	4.2.2 Smelter and Refinery Sites 139
2.5.5.7 Isle of Man 60	4.2.3 Smelter and Refinery Emissions 139
2.5.5.8 Ireland 60	4.2.4 Other Anthropogenic Input into
2.5.5.9 Iron 61	Soils 140
2.5.6 Twentieth Century Forward 62	4.2.5 Bioavailability of Trace Metals in
2.5.6.1 Cornwall and Devon 63	Soils 140
2.5.6.2 Pennines 65	4.2.6 Bioaccessibility 144
2.5.6.3 Lake District 65	4.2.7 Trace Metals and Soil Types 145
2.5.6.4 Wales 65	4.2.7.1 Calcicoles and Calcifuges 14!
2.5.6.5 Scotland 66	4.2.7.2 Aluminium and Laterites 147
2.5.6.6 Ireland 66	4.2.7.3 Serpentine Group of
2.5.6.7 Aluminium Smelting 66	Soils 147
2.5.6.8 Avonmouth 66	4.3 Microbial Community 148
2.5.7 Conclusions 67	4.4 Lichens 151
	4.4.1 Metallophytic Lichen
Biology of Trace Metals 68	Assemblages 152
3.1 Introduction 74	4.4.2 Detoxification of Trace
3.2 Evolution and Trace Metals 75	Metals 155
3.3 Uptake of Trace Metals 76	4.5 Mosses and Ferns 156
3.4 Bioavailability 79	4.5.1 Mosses 156
3.4.1 Dissolved Bioavailability 80	4.5.2 Ferns 158
3.4.2 Effects of Physiology 83	4.6 Flowering Plants 158
3.4.3 Bioavailability from Food 85	4.6.1 Uptake, Accumulation and
3.4.4 Uptake from Sediments 89	Detoxification 158
3.5 Accumulation 90	4.6.2 Metallophytes 160
3.5.1 Metabolic Requirements for Essential	4.6.3 Accumulation from Metal-Contaminated
Trace Metals 94	Soils 162
3.5.2 Detoxification 95	4.6.3.1 Mining Sites 162
3.5.3 Accumulation, Detoxification and	4.6.3.2 Smelter Emissions 164
Toxicity 98	4.6.3.3 Roadside Lead 166
3.5.4 Accumulation Patterns 99	4.6.4 Hyperaccumulation 167
3.5.5 Biodynamic Modelling 104	4.6.5 Metal tolerance 172
3.5.6 Food Chains and Trace	4.6.5.1 Occurrence of Tolerant
Metals 106	Populations 172
3.5.7 Significance of Bioaccumulated Trace	4.6.5.2 Evolution of Tolerance 173
Metal Concentrations 108	4.6.5.3 Mechanisms of Tolerance 175
3.6 Biomonitors 111	4.6.6 Aluminium 176



**Table of Contents** 

vii

4.7 Invertebrate Herbivores 177	4.12.1 Avonmouth Smelter 244
4.7.1 Slugs and Snails 177	4.12.2 Merseyside Smelter 248
4.7.1.1 Detoxification 178	4.12.3 Spoil Tips 250
4.7.1.2 Biomonitoring 180	4.12.3.1 Northern Pennine Lead
4.7.2 Insect Herbivores 181	Mines 250
4.8 Invertebrate Detritivores 183	4.12.3.2 Tamar Valley 251
4.8.1 Earthworms 184	4.12.4 Sewage Sludge Application 254
4.8.1.1 Trace Metal	4.12.5 Hyperaccumulation: Ecological
Accumulation 186	Effects 258
4.8.1.2 Detoxification of Trace	4.12.6 Ecotoxicological Risk
Metals 190	Assessment 259
4.8.1.3 Ecotoxicology: Tolerance and	4.12.6.1 Chemical Criteria 259
Resistance 191	4.12.6.2 Biological Criteria 265
4.8.2 Woodlice 193	4.13 Livestock 270
4.8.2.1 Trace Metal Accumulation 193	4.13.1 Ecotoxicology 270
4.8.2.2 Detoxification 195	4.13.1.1 History 270
4.8.2.3 Ecotoxicology 198	4.13.1.2 Critical Soil
4.8.3 Collembolans 199	Concentrations 272
4.8.4 Millipedes 200	4.13.2 Deficiency 273
4.9 Invertebrate Predators 202	4.14 Human Health 275
4.9.1 Spiders 203	4.14.1 Risk to Human Health 275
4.9.2 Pseudoscorpions 206	4.14.1.1 Environmental Geochemistry
4.9.3 Centipedes 206	and Human Health 275
4.9.4 Beetles 206	4.14.1.2 Food 276
4.9.5 Parasitoid Wasps 208	4.14.1.3 Drinking Water 279
4.10 Mammals 209	4.14.1.4 Soil 279
4.10.1 Small Mammals 209	4.14.1.5 Dust 280
4.10.1.1 Kidneys 210	4.14.1.6 Soil Guideline Values 283
4.10.1.2 Livers 219	
4.10.1.3 Whole Bodies 220 <b>5</b>	Freshwater 286
4.10.1.4 Hair 221	5.1 Introduction 289
4.10.1.5 Ecotoxicology 222	5.1.1 Biology of Trace Metals in
4.10.2 Bats 225	Freshwater 290
4.11 Birds 225	5.2 Metal Concentrations in
4.11.1 Birds of Prey 226	Freshwater 292
4.11.2 London Pigeons 230	5.3 Metal Concentrations in Freshwater
4.11.3 Pheasants, Partridges and Lead	Sediments 293
Shot 234	5.4 Metal-Contaminated Freshwater
4.11.4 Biomonitoring and	Systems 295
Ecotoxicology 234	5.4.1 Southwest England 299
4.11.4.1 Feathers 234	5.4.1.1 River Carnon 299
4.11.4.2 Blood 239	5.4.1.2 River Hayle 304
4.11.4.3 Eggs 241	5.4.1.3 Red River 305
4.12 Environmental Effects: Community	5.4.1.4 River Gannel 305
Ecotoxicology 243	5.4.1.5 River Tamar 306



viii

#### **Table of Contents**

5.4.2 Wales 306	5.11.1.3 Lake District 327
5.4.2.1 Afon Goch 306	5.11.2 Accumulation and
5.4.2.2 Rivers Ystwyth and	Biomonitoring 328
Rheidol 307	5.12 Flowering Plants 334
5.4.2.3 River Conwy 308	5.13 Invertebrates 334
5.4.3 Northern Pennines 309	5.13.1 Stoneflies 344
5.4.3.1 River Nent 310	5.13.2 Mayflies 348
5.4.3.2 River West Allen 310	5.13.3 Caddisflies 352
5.4.3.3 River Derwent 310	5.13.4 Chironomid Midges 358
5.4.4 Derbyshire 311	5.13.5 Further Insects 360
5.4.4.1 River Ecclesbourne 311	5.13.5.1 Blackflies 360
5.4.5 Lake District 311	5.13.5.2 Craneflies 360
5.4.5.1 Threlkeld, Keswick 311	5.13.5.3 Dagger Flies 361
5.4.6 Scotland 312	5.13.5.4 Alderflies 361
5.4.6.1 Leadhills 312	5.13.5.5 Dragonflies 361
5.4.6.2 Tyndrum 312	5.13.5.6 Beetles 361
5.4.7 Isle of Man 312	5.13.6 Crustaceans 362
5.5 Concentration and	5.13.6.1 Amphipods 362
Bioavailability 313	5.13.6.2 Isopods 362
5.5.1 Dissolved Bioavailability 313	5.13.7 Oligochaetes 365
5.5.2 Sediment Bioavailability 314	5.13.8 Molluscs 366
5.6 Acid Mine Drainage 315	5.13.8.1 Gastropods 366
5.7 Iron-Rich Streams 317	5.13.8.2 Bivalves 367
5.8 Aluminium 318	5.14 Fish 369
5.9 Microscopic Life 319	5.14.1 History of Fish in
5.9.1 Bacteria 320	Metal-Contaminated River
5.9.2 Periphyton 320	Systems 370
5.9.2.1 Diatoms 320	5.14.2 Accumulation 372
5.9.3 Meiofauna 322	5.14.2.1 Metals in the Flesh of
5.10 Algae 323	Freshwater Fish 377
5.10.1 Blue-Green Bacteria 323	5.15 Birds 378
5.10.2 Green Algae 323	5.15.1 Mercury 379
5.10.2.1 Mid-Wales 324	5.15.2 Cadmium 380
5.10.2.2 Northern Pennines 324	5.15.3 Lead 381
5.10.2.3 Cornwall 325	5.15.3.1 Lead Shot 382
5.10.3 Red Algae 325	5.16 Mammals 384
5.10.4 Golden-Brown Algae 325	5.17 Community Ecotoxicology 386
5.10.5 Accumulation and Detoxification in	5.17.1 Metal-Resistant Species 387
Algae 326	5.17.2 Community Analysis and Biotic
5.11 Bryophytes 326	Indices 388
5.11.1 Mining-Affected Streams and	5.17.3 Biomonitors, Bioaccumulated
Rivers 326	Metal Guidelines and
5.11.1.1 Mid-Wales 326	Ecotoxicological
5.11.1.2 Northern Pennines 327	Effects 390



6

Cambridge University Press 978-1-108-47093-3 — Trace Metals in the Environment and Living Organisms Philip S. Rainbow Frontmatter <u>More Information</u>

5.17.3.1 Is There an Easier Way? 390

**Table of Contents** 

6.8.2 Arenicola marina: The Lugworm 452

iх

5.17.4 Biomarkers 391	6.9 Deposit-Feeding Bivalves 455
5.17.5 Tolerance 393	6.9.1 Scrobicularia plana: The Peppery
5.17.6 Water Framework Directive 394	Furrow Shell 455
5.17.6.1 Environmental Quality	6.9.2 Macoma balthica: The Baltic
Standards 395	Tellin 461
5.17.7 Weight of Evidence (WOE) 398	6.10 Deposit-Feeding Amphipod
5.18 Human Health 399	Crustaceans 464
	6.10.1 Corophium volutator 464
Estuaries 401	6.11 Suspension Feeders 465
6.1 Introduction 403	6.11.1 Mussels 465
6.2 Metal Concentrations in the Waters of	6.11.1.1 Biomonitoring 466
Estuaries 404	6.11.1.2 Bioaccumulation and
6.2.1 Speciation and Bioavailability 409	detoxification 471
6.3 Metal Concentrations in Estuarine	6.11.1.3 Ecotoxicology 473
Sediments 411	6.11.2 Oysters 474
6.3.1 Bioavailability of Sediment-Associated	6.11.2.1 Accumulation and
Metals 417	detoxification 474
6.3.2 Organometals in Estuarine	6.11.2.2 Ecotoxicology 479
Sediments 419	6.11.3 Cockles 480
6.4 Trace Metals in Selected British	6.11.4 Clams 484
Estuaries 420	6.11.5 Scallops 484
6.4.1 Restronguet Creek 421	6.11.6 Importance of Family 486
6.4.2 Hayle 423	6.11.7 Slipper Limpets 492
6.4.3 Gannel 423	6.11.8 Barnacles 494
6.4.4 Looe 424	6.11.8.1 Accumulation and
6.4.5 Tamar and Tavy 424	Detoxification 495
6.4.6 Dulas Bay 425	6.12 Grazing Gastropods 499
6.4.7 Thames 426	6.12.1 Periwinkles 499
6.4.8 Severn 428	6.12.1.1 Detoxification of
6.4.9 Mersey 430	Accumulated Trace
6.4.10 Humber 432	Metals 504
6.4.11 South Wales 434	6.12.1.2 Tolerance and
6.4.12 Poole Harbour 435	Ecotoxicology 506
6.5 Salt Marshes and Seagrasses 436	6.12.2 Limpets 506
6.6 Seaweeds 436	6.12.2.1 Limpets as Biomonitors 507
6.7 Meiofauna 441	6.13 Detritivores in the Strandline 510
6.8 Deposit-Feeding Polychaetes: Ragworms and	6.13.1 Talitrid Amphipod
Lugworms 442	Crustaceans 510
6.8.1 Hediste diversicolor: A Ragworm 442	6.13.1.1 Body Concentrations of Trace
6.8.1.1 Bioaccumulation 443	Metals 511
6.8.1.2 Biomonitoring 444	6.13.1.2 Talitrids as Trace Metal
6.8.1.3 Tolerance and	Biomonitors 512
Ecotoxicology 451	6.14 Predators 515



X

#### **Table of Contents**

6.14.1 Polychaete Worms 515	7.2.1 Coastal Waters 569
6.14.1.1 Catworms 516	7.2.2 Ocean Profiles 571
6.14.1.2 Glycerids 517	7.3 Plankton 573
6.14.2 Whelks 517	7.3.1 Phytoplankton 573
6.14.2.1 Dogwhelks 519	7.3.1.1 Trace Metal Uptake and
6.14.2.2 Other Neogastropods 523	Accumulation 574
6.14.3 Prawns and Shrimps 523	7.3.1.2 Adaptations of Oceanic
6.14.3.1 Accumulation and	Phytoplankton 576
Regulation 523	7.3.1.3 Deficiency and Toxicity 577
6.14.3.2 Copper 526	7.3.2 Zooplankton 578
6.14.3.3 Cadmium and Lead 527	7.3.2.1 Calanoid Copepods 578
6.14.3.4 Chromium 527	7.4 Pelagic Animals 581
6.14.4 Crabs 527	7.4.1 Krill 582
6.14.4.1 Copper 528	7.4.2 Deep Sea Decapods and Copper
6.14.4.2 Zinc 531	Deficiency 584
6.14.4.3 Cadmium and Lead 532	7.4.3 Cadmium and Oceanic
6.14.4.4 Detoxification 532	Invertebrates 587
6.14.4.5 Ecotoxicology 533	7.4.3.1 Hyperiid Amphipods 587
6.14.5 Fish 533	7.4.3.2 Squid 588
6.14.5.1 Flounder 533	7.4.3.3 Ocean Striders 589
6.14.5.2 Eelpout 535	7.4.4 Zinc-Tipped Arrow Worms 589
6.14.5.3 Eels 536	7.5 Horn-Headed Amphipods and a Dietary Iron
6.15 Wading Birds 537	Challenge 590
6.15.1 Trace Metals in Waders 538	7.5.1 Stegocephaloides christianiensis 590
6.16 Community Effects 540	7.5.2 Parandania boecki 591
6.16.1 Case Studies 541	7.6 Sea Squirts and Vanadium 592
6.16.2 Weight of Evidence 543	7.7 Polychaetes and Predator
6.16.2.1 Biomonitors 544	Deterrence 595
6.16.2.2 Environmental Quality	7.7.1 Fan Worms 595
Standards 545	7.7.1.2 Arsenic 596
6.16.2.3 Biomarkers 547	7.7.1.3 Vanadium 597
6.16.2.4 Tolerance 550	7.7.2 Copper in Melinna palmata 598
6.16.2.5 Toxicity Tests 550	7.8 Sediments 599
6.16.2.6 Community Structure 552	7.8.1 Sediment Metal Concentrations 599
6.17 Fouling and Antifouling 553	7.8.2 Dump Sites 599
6.17.1 Resistance, Invasive Fouling Species	7.8.2.1 Firth of Clyde 603
and Tolerance 556	7.8.2.2 Liverpool Bay 604
6.17.2 Tributyl Tin 559	7.8.2.3 Outer Thames 606
6.17.2.1 Imposex and	<b>7.8.2.4</b> Other dump sites 607
Dogwhelks 560	7.8.3 Hypoxia, Manganese and Scampi 608
	7.9 Fish 609
7 Coastal Seas and Oceans 565	7.9.1 Trace Metals in Fish 610
7.1 Introduction 568	7.10 Seafood 614
7.2 Metal Concentrations in Coastal and Oceanic	7.10.1 Fish 616
Waters 569	7.10.2 Crabs, Lobsters and Shrimps 618



**Table of Contents** 

хi

	7.10.3 Molluscs 622
	7.10.3.1 Whelks 622
	7.10.3.2 Scallops 622
	7.10.3.3 Cockles and mussels 624
	7.10.3.4 Oysters 625
7.11	Seabirds 626
	7.11.1 Trace Metal Accumulation in
	Seabirds 627
	7.11.1.1 Cadmium 630
	7.11.1.2 Mercury 632
	7.11.1.3 Ecotoxicology 637
7.12	Marine Mammals 639
	7.12.1 Trace Metals and Marine
	Mammals 645
	7.12.1.1 Copper and Zinc 646
	7.12.1.2 Cadmium 646
	7.12.1.3 Lead 646
	7.12.1.4 Mercury 647
	7.12.1.5 Organotin 648

7.12.1.6 Ecotoxicology 649

Epilogue 655
8.1 Biology of Trace Metals 655
8.2 Effects of Trace Metals and the Natural
History of the British Isles 657
8.2.1 Past 658
8.2.2 Present 659
8.2.2.1 TBT and Antifouling 660
8.2.2.2 Mercury in Tuna 661
8.2.3 Future 662
8.2.3.1 Rehabilitation and
Restoration 662
8.2.3.2 Conservation 666
8.2.3.3 Climate Change and Seawater
Acidification 667
8.2.3.4 Ecotoxicology 668
8.3 Postscript 669

8

References 671 Index 720 Colour plates can be found between pages 368 and 369





#### **PREFACE**

This is a book about the natural history of metals. Without metals, there would be no life, and there are habitats in the world where, because of metals, there is no life. This is neither a story of metals in their elemental form, not a discourse on a lump of lead or an ingot of gold. It is a tale of how metals, whether in ionic form in a salt such as zinc chloride, or bound in a molecule as is iron in the protein haemoglobin in our red blood cells, have an all-important role in the biology of life around us.

This is a story of the biology of so-called trace metals, the metals that are to be found in very small 'trace' amounts in the physical environment of the rocks, soils, sediments and waters of the world, and in all forms of life from bacteria to algae and land plants, to fungi, and to invertebrates and vertebrates. The actors in this story are metals such as copper, zinc, lead, iron, manganese, tin, silver, cadmium and arsenic. Pedantic chemists will query whether some of the elements to be considered in this book fall strictly into a precise chemical definition of a metal, and will favour the term metalloid for the likes of arsenic. That argument can be left to another place and another time. There are other metals, the socalled major metals, such as sodium, potassium, calcium and magnesium, that occur in greater abundance on earth, including in living organisms, but again this book is not about them. Trace metals have a biological importance in stark contrast to their tiny concentrations in the physical and biological compartments of the world. All are toxic to life above a threshold concentration, a concentration that may still be staggeringly small to our first impressions, for these toxic concentrations often register only on a parts per million scale. And yet, many of these same metals are actually essential to life at doses below this toxic threshold – in the case of selenium, not far below this toxic threshold. Without enough of an essential metal such as zinc, copper or iron, organisms suffer deficiency symptoms and ultimately just cannot survive without a minimum supply. We have not found (if we ever will) an essential role in metabolism, as part of an enzyme or a key biological molecule such as haemoglobin, for the non-essential metals such as lead or mercury, but these metals are still taken up into organisms with the potential to interfere with life's processes. The division into non-essential or essential is not a division into toxic or non-toxic. All trace metals are toxic if present in high enough concentrations, and indeed some essential metals, for example copper, are amongst the most toxic metals known, if present above that toxic threshold.

The biology of trace metals is not a simple story. Life has evolved in the presence of these toxic metals, and indeed life has evolved because of the presence of these metals. Trace metals have a vast range of potential chemical reactions with the likes of proteins and other key molecules in the metabolism of organisms. The resulting chemical associations have provided a fantastic resource for the action of natural selection on the evolution of the biochemistry of life in all its variants. The biochemical basis of our respiration to deliver energy could not exist without the binding of iron to key molecules called cytochromes, nor could many of our enzymes function without the incorporation of a trace metal to play a key catalytic role. And yet, simultaneously there have evolved the systems within organisms to stop these potentially



xiv

Preface

vital, but potentially toxic, metals binding in the wrong place to the wrong protein at the wrong time. We have evolved in a toxic world but have the systems to cope.

So how have different organisms coped with and exploited trace metals in their biology? The answer is wonderfully and diversely, and this book explores many such examples. Why do some animals contain huge concentrations of some trace metals and not others, while even relatively closely related animals have very different metal concentrations in their bodies? Why do oysters and mussels handle zinc so very differently, so that what is a very low zinc concentration in an oyster would be off the scale in a mussel? Why do some hymenopteran insects concentrate zinc in their ovipositors, and some polychaete worms copper in their jaws? Do other worms concentrate arsenic to deter the feeding efforts of would-be fish predators, and does the high vanadium content of the outer surface of some sea squirts stop them being fouled by barnacles and other sessile marine organisms? Why do some oceanic seabirds have fantastic concentrations of toxic metals in their kidneys, even in the absence of metal pollution? In the sea, how do chitons store potentially toxic amounts of iron before its transport to the radula to harden the developing teeth which will be used to rasp the surface of rocks to scrape off the algae growing there?

All such questions have an effect on the natural history of the organisms concerned, and in turn are affected by the natural history of these organisms. To understand the mechanisms controlling the uptake, accumulation and toxicity of trace metals in organisms, it is necessary to understand the role of natural history in these processes. Many specific aspects of the biology of an animal, such as its method of feeding and respiration or burrowing activity, critically affect how an animal interacts with metals. It is crucial to appreciate the importance of natural history in understanding the interaction of metals and organisms.

There is also an applied aspect to such a discussion, given the ability of metals to play such a significant ecotoxicological role in habitats affected by the output of historical activities such as mining or by other modern industrial effluents. How do some organisms cope better than others in streams or estuaries affected by metal-rich mining waste? How do communities change in such circumstances, and so what?

The British Isles offer an ideal template to explore such questions. The countryside and indeed the natural history of Britain are littered with the effects of metals, mostly via historical mining. The tale to be told encompasses history, geography, geology, chemistry, biochemistry, physiology, ecology, ecotoxicology and, above all, natural history.

The book is a natural history voyage from the ancient mines of Britain, usually situated in upland areas, through the catchments of the surrounding terrestrial regions, to streams, rivers, estuaries, coastal waters and the oceans. It is a story of how metals are found in ores, how they have been mined and consequently enter the local environment with consequences for the growth of plants and terrestrial animals associated with those plants, before affecting the life of upland streams by direct runoff or via the metal-rich sediments that are transported into these streams, either deliberately or accidentally. What changes occur to local freshwater communities, and what are the adaptations of those organisms that survive? From stream to river to estuary. Many of the estuaries in Cornwall, for example, are full of metal-rich sediments washed down in the heyday of local copper mining in the second half of the nineteenth century, lying there still and affecting the local biota. Out to sea, there are fewer examples of the metal-associated effects of humankind, but many examples of how marine organisms handle the metals that inevitably enter their bodies naturally and the physiological



**Preface** 

χv

uses to which they may be put. Finally, oceanic life is still interacting with metals. While there is some entry of anthropogenically derived metals transported in the atmosphere into the ocean, particularly in polar regions, charismatic marine organisms such as whales still have remarkable physiological methods of handling the trace metals that are taken up quite normally from their often metal-rich diets. Similarly, the kidneys of some oceanic seabirds have no right to function given their naturally accumulated huge loads of the poisonous metal cadmium.

Many of the interactions between trace metals and organisms have nothing to do with metal pollution. All organisms are affected, from bacteria, plants and invertebrates to charismatic species such as seals, dolphins, whales and seabirds. All have a tale to tell.



#### **ACKNOWLEDGEMENTS**

I have relied on the help, collaboration and friendship of many people over many years in order to arrive at a position to undertake the writing of this book. First and foremost, my very good friend Sam Luoma, who was my co-author on a tome on metal contamination in aquatic environments, has been an outstanding guide and colleague, as we have worked together to stress the role of biology in the chemistry-dominated world of metal ecotoxicology, and indeed put more 'eco' into 'ecotoxicology'. Claude Amiard-Triquet and Jean-Claude Amiard have similarly influenced my knowledge and thinking considerably, in our happy and productive research collaborations in the worlds of metal ecophysiology and ecotoxicology since the turn of the millennium. Wen-Xiong Wang has been another strong collaborator and friend, generous with his time and resources, as we have exploited the natural laboratory that is the coastal region of Hong Kong as a source of metal-related environmental questions. Over a longer period stretching further back in time, I have learnt so much marine biology from my great friend Geoff Moore. Bill Langston is a continuing source of good sense on the biology of trace metals, and the sadly now late Dave Phillips was a forceful and appreciated collaborator on research projects and a book on biomonitoring in the 1990s. I also owe debts of gratitude to Stephen White, Jason Weeks, Dayanthi Nugegoda, Paul O'Brien, Darren Martin, Michael Depledge, Carmen Casado-Martinez, Wojciech Fialkowski, Farhan Khan, Judit Kalman and Islay Marsden for their productive research collaboration over many years. I would have achieved little without the support of Brian Smith over the last twenty years, and I gratefully acknowledge his considerable contribution.

It is a pleasure to thank Christopher Rainbow for the use of his colour photographs, and for his time and patience in their acquisition. I am also grateful to the Natural History Museum for permission to include colour photographs under their copyright. I thank Harry Taylor for these beautiful illustrations. My thanks too to Kevin Brix and Charlie Arneson for their kind permission to use their photographs. Mike Rumsey, Hölger Thues, Jeff Duckett and Emma Sherlock of the Natural History Museum provided much appreciated guidance through the worlds of ores, lichens, bryophytes and earthworms respectively. William Yeomans is to be thanked for his interest in the black-tailed trout of Leadhills, which he brought to my attention. Paul Henderson kindly read draft chapters for me, but remaining errors are down to me.

Arguably, this book is a culmination of research experience over a career of forty years. All would have been impossible without the love and support of my family, particularly my wife Mary. I am forever in her debt.