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Contents

Preface xi
Contributors xv

1 Mangroves of Southeast Asia 1
M. HOLMER

1.1 Introduction 1
1.2 Mangrove forest structure and function 2
1.3 Water column biogeochemistry 3
1.4 Organic matter sources in mangrove forests 7
1.4.1 Decomposition of detritus 9
1.5 Sediment biogeochemistry 11
1.5.1 Total microbial activity in mangrove sediments 12
1.5.2 Mineralization pathways in mangrove sediments 15
1.5.3 Phosphorus cycling 23
1.6 Factors influencing the biogeochemistry 25
1.6.1 Effect of forest type and age 25
1.6.2 Influence of macrofauna 26
1.6.3 Effect of seasonal variations on mangrove forest biogeochemistry 28
1.7 Sediment biogeochemistry and implications for mangrove vegetation 29
1.8 Biogeochemistry in mangroves affected by anthropogenic activities 31
References 34

2 Coral reefs 40
M.J. ATKINSON and J.L. FALTER

2.1 Introduction 40
2.2 Coral reef morphology and zonation 41
2.3 Basic biogeochemistry 43
2.3.1 Carbon 43
2.3.2 Dissolved organic matter 47
2.3.3 Nitrogen 48
2.3.4 Phosphorus 50
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.3.5 Silica</td>
<td>51</td>
</tr>
<tr>
<td>2.3.6 Iodine</td>
<td>51</td>
</tr>
<tr>
<td>2.4 Interstitial geochemistry and hydrology of coral reef frameworks</td>
<td>52</td>
</tr>
<tr>
<td>2.5 Mass transfer-limited biogeochemical rates</td>
<td>54</td>
</tr>
<tr>
<td>2.6 Coral growth in high nutrient water</td>
<td>56</td>
</tr>
<tr>
<td>2.7 Measurement techniques</td>
<td>58</td>
</tr>
<tr>
<td>2.8 Summary statements</td>
<td>59</td>
</tr>
<tr>
<td>References</td>
<td>59</td>
</tr>
<tr>
<td>3 Fjords</td>
<td>65</td>
</tr>
<tr>
<td>J.M. SKEI, B. McKEE and B. SUNDBY</td>
<td></td>
</tr>
<tr>
<td>3.1 Introduction</td>
<td>65</td>
</tr>
<tr>
<td>3.1.1 Definition and origin of fjords</td>
<td>66</td>
</tr>
<tr>
<td>3.1.2 The public and scientific interest in fjords</td>
<td>67</td>
</tr>
<tr>
<td>3.2 Sediment diagenesis in oxic fjords</td>
<td>69</td>
</tr>
<tr>
<td>3.2.1 The Saguenay Fjord</td>
<td>69</td>
</tr>
<tr>
<td>3.2.2 Sedimentation</td>
<td>69</td>
</tr>
<tr>
<td>3.2.3 Composition of the rapidly deposited layers</td>
<td>70</td>
</tr>
<tr>
<td>3.2.4 Sulfate reduction and sulfide accumulation</td>
<td>70</td>
</tr>
<tr>
<td>3.2.5 Mercury diagenesis</td>
<td>73</td>
</tr>
<tr>
<td>3.2.6 Phosphorus and arsenic geochemistry</td>
<td>73</td>
</tr>
<tr>
<td>3.2.7 Non-steady-state diagenesis</td>
<td>75</td>
</tr>
<tr>
<td>3.3 Elemental cycling in anoxic waters</td>
<td>76</td>
</tr>
<tr>
<td>3.3.1 Chemical tracers</td>
<td>76</td>
</tr>
<tr>
<td>3.3.2 Cycling of carbon and nutrients</td>
<td>77</td>
</tr>
<tr>
<td>3.3.3 Trace element and radionuclide cycling</td>
<td>78</td>
</tr>
<tr>
<td>3.3.4 Fe–S systematics</td>
<td>81</td>
</tr>
<tr>
<td>3.3.5 Sulfate reduction and methane oxidation</td>
<td>83</td>
</tr>
<tr>
<td>3.3.6 Elemental cycling in sediments underlying anoxic waters</td>
<td>84</td>
</tr>
<tr>
<td>3.3.7 Preservation of organic matter</td>
<td>85</td>
</tr>
<tr>
<td>References</td>
<td>85</td>
</tr>
<tr>
<td>4 The Eastern Mediterranean</td>
<td>91</td>
</tr>
<tr>
<td>MICHAEL D. KROM, STEVEN GROOM and TAMAR ZOHARY</td>
<td></td>
</tr>
<tr>
<td>4.1 Introduction</td>
<td>91</td>
</tr>
<tr>
<td>4.2 History of the Mediterranean basin</td>
<td>92</td>
</tr>
<tr>
<td>4.3 Basic description of the bathymetry and physical oceanography of</td>
<td>93</td>
</tr>
<tr>
<td>the Eastern Mediterranean</td>
<td></td>
</tr>
<tr>
<td>4.3.1 Bathymetry</td>
<td>93</td>
</tr>
</tbody>
</table>
CONTENTS

4.3.2 Physical circulation of the Eastern Mediterranean 93
   4.3.2.1 Formation of LDW 94
   4.3.2.2 Formation of LIW 95
4.3.3 Recent water mass changes in the Eastern Mediterranean 96
4.3.4 Current patterns 97
4.4 Nutrients and chlorophyll distribution across the Eastern Mediterranean 98
   4.4.1 General comments 98
   4.4.2 Seasonal distributions 98
      4.4.2.1 Winter 98
      4.4.2.2 Spring into summer 100
   4.4.3 Nutrient distribution below the nutricline 100
4.5 Total chlorophyll distribution and characteristics 100
   4.5.1 Light penetration 102
   4.5.2 Species composition 102
      4.5.2.1 The prochlorophytes 102
      4.5.2.2 The unicellular cyanobacteria 103
      4.5.2.3 The eukaryotes 104
      4.5.2.4 Heterotrophic bacteria 104
4.6 Primary production 105
   4.6.1 Gradient in biomass and productivity from coastal waters to the open sea 107
4.7 Effects of mesoscale features on nutrient and chlorophyll distribution and phytoplankton productivity 108
   4.7.1 Biogeochemical processes in mesoscale features 108
      4.7.1.1 Rhodes cold-core (cyclonic) eddy 108
      4.7.1.2 Cyprus warm-core (anti-cyclonic) eddy 112
      4.7.1.3 Effects of other mesoscale features 113
4.8 Seasonal changes in phytoplankton biomass as detected by remote sensing 113
4.9 Nutrient limitation in the Eastern Mediterranean 116
4.10 Magnitude of man-induced changes in nutrient inputs and their possible effects on the Eastern Mediterranean 118
4.11 Summary and conclusions 120
Acknowledgements 121
Glossary 122
References 122

5 The Arctic seas 127
MICHAEL L. CARROLL and JOLYNN CARROLL

5.1 Summary 127
5.2 Main features 128
CONTENTS

5.2.1 Water masses 128
5.2.2 Continental shelves 131
5.2.3 Sea ice 132

5.3 Biogeochemical cycles and ecological processes 133

5.4 Environmental changes 138
5.4.1 Climate variability 138
5.4.2 Long-term climate change 140
5.4.3 Ozone and ultraviolet radiation 143
5.4.4 Contaminants 143

5.5 Natural resources and ecological services 144
5.5.1 Indigenous people 144
5.5.2 Non-indigenous regional populations 145
5.5.3 National/international/global users 146

Acknowledgements 147
References 147

6 The Arabian Sea 157
S.W.A. NAQVI, HEMA NAIK and P.V. NARVEKAR

6.1 Introduction 157
6.2 Geographical setting 157
6.3 Climate and circulation 158
6.4 Nutrients and primary production 163
6.4.1 Subsurface nutrient trap 163
6.4.2 Primary productivity 164
6.4.3 New production 166
6.4.4 Phytoplankton composition and size distribution 167
6.4.5 Chlorophyll and POC 171
6.4.6 Effect of changes in mixed layer depth 172
6.5 Heterotrophic biomass and production 174
6.5.1 Heterotrophic bacteria 174
6.5.2 Nano- and microheterotrophs 175
6.5.3 Mesozooplankton 177
6.6 Food web structure and export of material to the deep sea 179
6.6.1 Phytoplankton growth and mortality 179
6.6.2 Particle fluxes to deep sea 180
6.6.3 Role of Arabian Sea as a source or sink of carbon dioxide (CO₂) 185
6.7 Oxygen-deficient zones 185
6.7.1 Denitrification 186
6.7.2 Intermediate nepheloid layer 191
6.7.3 Other redox-sensitive elements 192
6.7.4 Biological effects 193
CONTENTS

6.8 Benthic processes 195
References 198

7 The northeastern Pacific abyssal plain 208
ANGELOS K. HANNIDES and CRAIG R. SMITH

7.1 Introduction 208
7.2 Key habitat parameters of deep seafloor communities 208
  7.2.1 Key habitat parameters 209
    7.2.1.1 Substratum type 209
    7.2.1.2 Near-bottom currents 210
    7.2.1.3 Bottom-water oxygen 211
    7.2.1.4 Sinking POC flux 211
    7.2.1.5 Redox conditions 211
  7.2.2 Variation of key habitat parameters in the
      northeastern Pacific abyssal plain 212
    7.2.2.1 Sediment types 212
    7.2.2.2 Near-bottom currents and oxygen concentrations 212
    7.2.2.3 POC flux and redox conditions 213
7.3 Northeastern Pacific abyssal zones 213
  7.3.1 The eutrophic equatorial abyss 214
  7.3.2 The mesotrophic (sub-equatorial) abyss 217
  7.3.3 The oligotrophic central gyre abyss 218
7.4 Sensitivity and resilience to natural and anthropogenic change 220
  7.4.1 General thoughts 220
  7.4.2 Potential sensitivity and resilience to specific changes 221
    7.4.2.1 Climate variation in the equatorial and
           North Pacific 221
    7.4.2.2 Global increase in atmospheric greenhouse
           gases and temperatures 223
    7.4.2.3 Manganese nodule mining 226
    7.4.2.4 Iron fertilization 229
7.5 Concluding remarks 230
Acknowledgments 231
References 231

8 Deep-sea hydrothermal vents and cold seeps 238
RICHARD J. LÉVEILLÉ and S. KIM JUNIPER

8.1 Introduction 238
  8.1.1 Deep-sea hydrothermal vents and cold seeps 238
  8.1.2 Life at hydrothermal vents and cold seeps 238
  8.1.3 Scope of this chapter 240
8.2 Deep-sea hydrothermal vents 241
  8.2.1 Distribution and general characteristics 241
    8.2.1.1 Geochemical fluxes of gases and elements from hydrothermal vents 243
    8.2.1.2 Off-axis diffuse flow versus axial venting 245
  8.2.2 Subsurface biosphere at mid-ocean ridges 246
    8.2.2.1 Evidence for a subsurface biosphere at deep-sea hydrothermal vents 246
    8.2.2.2 Biogeochemical interactions in subsurface environments 251
  8.2.3 Seafloor microbe-mineral interactions at hydrothermal vents 252
    8.2.3.1 Microbial distribution and activity at vents 252
    8.2.3.2 Biomineralisation at vents 256
    8.2.3.3 Fossilisation of microbes at vents 260
    8.2.3.4 Bacterial weathering of sulphides 260
  8.2.4 Biogeochemical interactions in hydrothermal plumes 261
    8.2.4.1 General features of hydrothermal plumes 261
    8.2.4.2 Microbial ecology of hydrothermal plumes 262
    8.2.4.3 Microbial productivity and organic carbon in plumes 263
    8.2.4.4 Biogeochemical interactions in plumes 264
  8.2.5 Biogeochemistry of off-axis vents and seafloor basalt 265
    8.2.5.1 Off-axis vents 265
    8.2.5.2 Seafloor basalts 266
  8.3 Deep-sea cold seeps 267
    8.3.1 Distribution, occurrences and general characteristics 267
      8.3.1.1 Gas hydrates 268
      8.3.1.2 Geochemical fluxes 269
    8.3.2 Biogeochemistry of seep sediment pore fluids 270
      8.3.2.1 Methanogenesis 271
      8.3.2.2 Anaerobic sulphate reduction 271
      8.3.2.3 Aerobic microbial oxidation of sulphide and methane 272
      8.3.2.4 Anaerobic oxidation of methane 273
    8.3.3 Microbial carbonates 274
  8.4 Stability and perturbations of seafloor hydrothermal vent and cold seep systems 276
    8.4.1 Geological stability of vents and seeps 276
    8.4.2 Future perturbations related to resource extraction 277
      8.4.2.1 Hydrothermal sulphides 277
      8.4.2.2 Cold seeps 278
    8.4.3 Response of cold seeps and gas hydrates to global warming 278
CONTENTS

8.5 Future work 279
8.6 Conclusion 282
References 282

9 Influence of nutrient biogeochemistry on the ecology of northwest European shelf seas 293
PAUL TETT, DAVID HYDES and RICHARD SANDERS

9.1 Introduction 293
9.2 Nutrient cycles 294
  9.2.1 Macronutrient element availability 294
  9.2.2 Sources of macronutrients 296
  9.2.3 Sinks of macronutrients 298
  9.2.4 Observed distributions of macronutrient concentrations and ratios 300
  9.2.5 Iron 301
9.3 Plankton biogeochemistry 303
  9.3.1 Taxonomy and life forms in the plankton 303
  9.3.2 Theories of floristic composition 308
    9.3.2.1 Light-nutrient-mixing explanations 309
    9.3.2.2 Biogeochemical controls 310
    9.3.2.3 Ecological controls 312
  9.3.3 Variation in nutrient element ratios and its explanation in terms of plankton biochemistry 315
  9.3.4 Quantitative theory for nutrient element ratios 320
  9.3.5 Differences in abilities to assimilate different nutrients 325
  9.3.6 Theoretical conclusions 327
9.4 Effects of ambient nutrient ratios on plankton 327
  9.4.1 Introduction 327
  9.4.2 Time series: Helgoland and the German Bight 329
  9.4.3 Mesocosm and other competition experiments 332
  9.4.4 Observations at sea 337
9.5 Discussion and conclusions 341
  9.5.1 Introduction 341
  9.5.2 Do high ambient N:Si ratios favour flagellates? 342
  9.5.3 Do non-Redfield ambient N:P ratios perturb pelagic ecosystems? 344
  9.5.4 The possibility of iron limitation in shelf seas 345
  9.5.5 Trophic consequences of ratio changes – a Panglossian conclusion? 345
  9.5.6 A flexible Redfield ratio? 347
Dedication 350
References 351

Index 364
Preface

Marine biogeochemistry is a broad, interdisciplinary subject overlapping a range of other disciplines such as marine chemistry, geochemistry, ecology, physiology and oceanography, but in its own right it has become pivotal to progress in marine research in recent years. As a key component of the ‘earth system’, marine biogeochemistry interfaces directly with terrestrial, atmospheric and geological sciences. A working definition of the subject might be ‘the processing, recycling, storage, transport and loss of chemical components within the marine environment, mediated by biological processes’.

We are said to be leaving the Holocene and entering the ‘Anthropocene’ where mankind’s cumulative impacts have significant and measurable effects on the biosphere. Biogeochemistry lies at the heart of studies on the functioning of marine provinces or types – collectively here referred to as ‘systems’ – that are crucial to understanding and predicting global change and its consequences. In the context of this great environmental and societal impact, it is the varying consequences of the same biogeochemical processes operating in marine systems under different forcing parameters that make biogeochemistry such a diverse and fascinating field.

Over the past two decades, much has been learned about the biogeochemical functioning of marine systems from large-scale, multi-partner, international and national research programmes such as are supported by the International Geosphere–Biosphere Program (IGBP), Scientific Committee on Ocean Research (SCOR), Joint Global Ocean Flux Study (JGOFS) and its regional studies, and Land–Ocean Interactions in the Coastal Zone (LOICZ). In the UK, the supporting national programmes were the Biogeochemical Ocean Flux Study (BOFS) and Land–Ocean Interaction Study (LOIS) programmes. These have been undertaken typically on ‘process’ research cruises, where the focus has been on quantifying fluxes of key components (particularly carbon) within the ocean as well as between the ocean and its boundaries (land, sediments and atmosphere). Whilst considerable information continues to be derived from such studies, the expense of such undertakings, together with the relatively low temporal and spatial coverage offered, has led some biogeochemists to develop and use new methods of data collection. These include satellite and airborne remote sensing, benthic landers, autonomous underwater vehicles, and moored and drifting sensor packages with intelligence. Many of these systems have been developed for open ocean deployment, but they are also becoming modified
for use in shallow, coastal locations. We can expect to see further developments, together with new and more robust sensors and increased data collection and transmission capacity, leading to great improvements in knowledge, operating in a synoptic fashion (for example, the new ARGO programme of drifting subsurface floats across the ocean basins).

Modelling has become ubiquitous in biogeochemistry, as in marine science more generally. Significant computing power is now available for the nesting of biogeochemical models within physical oceanographic models with high spatial resolution. Not only does this allow the generalisation of measurements made at a point in space and time, but it allows assessments and comparisons of the relative sensitivities of systems to external changes such as are caused, for example, by increased temperature, deepwater trawling or hydrocarbon exploration.

This volume provides an overview of recent research on the biogeochemistry of a diverse range of complex marine systems, each of great importance to the ‘earth system’ but for varying reasons. The systems were chosen to emphasise different forcing factors, thus offering interesting contrasts. We have been fortunate that the chapter authors reflect the diversity of academic backgrounds that typifies biogeochemical research and that they have approached their tasks from varied perspectives. Thus, the repetition of basic concepts between chapters is kept to a minimum. The book will be read by researchers and advanced students of biogeochemistry, who will enjoy the contrasts between the systems chosen, and by workers in related areas of earth science, who will find that it provides a useful point of access to the primary literature across a broad range of marine biogeochemical processes.

The first chapter deals with mangroves – key providers of biogeochemical services in large areas of tropical coastal areas that are under threat from insensitive development pressures. We stay in the tropics to consider coral biogeochemistry – also under threat in many areas from a combination of climate change, eutrophication, tourism and destructive fishing – before moving to fjords – the main interface between land and ocean in high latitudes. The eastern Mediterranean continues to attract considerable attention as a highly nutrient-poor and low productivity area, in stark contrast to the Arctic, which is light-limited during the winter months, highly productive in the summer, shows strong benthic–pelagic coupling over the shelf areas and has a productive community associated with the underside of sea ice. In the Arabian Sea, the biogeochemical system is under the control of large-scale, monsoon-linked circulation reversals with a pronounced oxygen minimum zone, and again this is an area under continuing scrutiny for its potential role in the nitrogen biogeochemical cycle. The sediments of the northeast Pacific abyss are dominated by a strong latitudinal gradient of carbon input across the equatorial divergence that has a profound effect on benthic productivity. Even in an area so remote from land, the threat of anthropogenic disturbance in the form of metal nodule mining is very real.
The penultimate chapter deals with the unique biogeochemistry of the hot and cold vents associated with plate tectonics – largely unknown until relatively recently and now thought to be of great significance in maintaining the basic chemistry of sea water. The book is completed by a modelling section, in which the ecology of planktonic organisms is examined in biogeochemical terms with an emphasis on modelling the interactions between pelagic chemistry and ecology in shelf seas, where significant recycling of sedimentary nutrients supplements direct terrestrial inputs.

We are grateful to all the authors who have contributed to this volume. Each author has original insights and approaches and so each chapter is fresh and the whole volume novel and readable. We are particularly indebted to Graeme MacKintosh and David McDade at Blackwell Publishing, who have offered every support and encouragement to this project.

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1 Mangroves of Southeast Asia
M. Holmer

1.1 Introduction

The last decade has contributed significantly to the development of research on the biogeochemistry of tropical mangrove ecosystems. Also obvious during the last decade is the continued and dramatic destruction of natural tropical mangrove resources in Southeast Asia (Fig. 1.1). The naturally high productivity of tropical mangroves has traditionally been exploited for a wide variety of purposes, both as sources of forestry or fisheries products and they have also been used for human settlement (Hatcher et al., 1989; Platong, 1998). More recently, Southeast Asian mangroves are being extensively cleared for the construction of aquaculture ponds for prawn production (Primavera, 1993). This and other consumptive uses have been estimated to cause an annual reduction of 1% of the world’s tropical mangrove resources (Hatcher et al., 1989).

Southeast Asian mangrove forests are declining at alarming rates, due to the increasing demand for land to be allocated to food, industrial production and urban settlements (Kautsky et al., 2000). More than half of the 367,900 ha of mangroves that was present in Thailand in 1961 had already been converted to prawn farms or for various other uses by 1989 (Aksornkoea, 1993), and the mangrove area was further reduced by 81,000 ha in 1996 (Platong, 1998). Mangrove forests in many other Southeast Asian countries also face the same rate of destruction, e.g. Vietnam (Kautsky et al., 2000). Changes in land use in Southeast Asia have resulted in high soil erosion rates and have yielded a major increase in transport of eroded sediments to the coastal zone. The long-term impact and the ramifications of anthropogenic disturbance, such as pollutant discharge, on the biogeochemistry of tropical mangrove forests and their associated near-shore habitats are poorly known. The aim of this chapter is to review recent findings on aspects of the biogeochemistry of Southeast Asian mangrove forests, focusing on physical and biotic processes determining the cycling of elements in mangroves. The chapter will discuss the significance of anthropogenic activities for the biogeochemical cycling of nutrients, which deserves particular attention in the study of Southeast Asian mangrove forests.
1.2 Mangrove forest structure and function

Earlier models of tropical mangrove forests proposed overwhelming influences by physical forces and processes such as the tidal regime or geomorphology on ecosystem structure and function. Mangrove ecosystem development was depicted as successional systems, where the presence of plants themselves had a significant impact on the physical environment; and such impact culminated in an alternation of growth conditions favoured by different species in time. In addition, recent findings (especially from the Indo-Pacific mangrove forests) suggest considerable influence of biotic agents and processes such as sesarmine crab feeding and bioturbation activities in shaping the ecology of tropical mangrove forests (Twilley et al., 1997). Biotic influences on mangrove forest ecosystem structure and function are expected to be more important in systems with weak external forcing or high biodiversity. Climatic features, such as the timing of monsoon periods, can give rise to strong seasonality (Alongi & Sasekumar, 1992).

Most productive mangrove ecosystems are highly effective sinks for nutrients essential to sustain high rates of plant growth, as evidenced from the fact that many such systems export refractory, particulate organic carbon but import most dissolved nutrient species (Alongi et al., 1992; Robertson et al., 1992; Hemminga et al., 1994; Rivera-Monroy et al., 1995; Alongi, 1996). Several studies have suggested that close couplings exist among benthic nutrient pools,
microbes and mangrove trees, acting as mechanisms to maximize utilization and conservation of scarce nutrients (Boto & Wellington, 1983, 1984; Kristensen et al., 1995; Alongi, 1996).

1.3 Water column biogeochemistry

Mangrove forests are highly diversified due to the large variability, for example, in geomorphology and tidal activities, and a number of different functional types of mangroves have been described (Woodroffe, 1992). The hydrodynamics in some mangrove forests are strongly influenced by river inputs, whereas others are much more dominated by the ocean, as found for fringing mangrove forests. A large number of local factors may thus influence the water column processes, which makes it very difficult to provide a generalized description of the water biogeochemistry in mangrove forests. Mangrove creeks are considered as important routes for tidal exchange of dissolved and particulate matter between the forest environment and adjacent coastal waters (Wolanski et al., 1992; Hemminga et al., 1994; Rivera-Monroy et al., 1995). The residence time of the water in the creeks is usually a useful indicator of the biogeochemical fate of the compounds in the water column (Suraswadi et al., 2003), where long residence times allow for uptake of nutrients by the vegetation, e.g. phytoplankton and mangrove trees, while short residence times leads to a larger export of materials to the ocean (Thong et al., 1993).

Hydrodynamics in the mangrove forest is controlled by tides, mangrove vegetation and geometry of the mangrove waterways (Hoguane et al., 1999). Friction from dense mangrove trees influences the tidal regime and causes tidal asymmetry (Suraswadi et al., 2003), and current velocities in a channel cross section have lateral or vertical variations due to channel geometry and bathymetry (Valle-Levinson & Atkinson, 1999). These variations in water velocity cause transverse and vertical shear stress, which are important for the mixing process in the creek water (Uncle et al., 1985). The residence time of water in mangrove forests is quite variable, determined by the forest topography, size and type, and thus hydrodynamics. It can vary from a few days in small fringe forests exposed to large tidal variation (Wattayakorn et al., 1990) to more than a month in large mangrove forests (Wolanski et al., 1990). Suraswadi et al. (2003) studied the hydrodynamics in a small mangrove forest in Thailand. The hydrodynamics was modified as a result of friction created by the mangrove vegetation, and these modifications resulted in strong ebb current, asymmetric flood and ebb tide and a time lag in the tidal phase between the upper and lower creek. The main creek was well mixed with a transient stratification during low tide and was completely mixed during high tide. This situation is similar to other mangrove estuaries (Wattayakorn et al., 1990; Wolanski et al., 1990). The hydrodynamics may be influenced by heavy rains; in this mangrove, rainfall caused an increased transport of salt water when the
rainwater pushed the creek water outward, and the period and amount of rainfall must thus be considered when the flux of solutes from the mangrove forest is determined during the wet season.

Nutrient levels in pristine tropical mangrove forests vary both in time and space as a result of differences in hydrodynamics, freshwater input, solar insolation, and productivity of phytoplankton and bacterioplankton (Ovalle et al., 1990; Alongi et al., 1992; Bava & Seralathan, 1998; Trott & Alongi, 1999; Ayakai et al., 2000). Mangrove creeks are, however, usually characterized by low nutrient concentrations due to a high capacity for retaining and recycling of nutrients within the system (Kristensen et al., 1995). Even in areas with high nutrient loading, e.g. due to urban settlement, nutrient levels are generally low (Harrison et al., 1997). Nutrient cycling in the water column is controlled by a large number of auto- and heterotrophic processes (Fig. 1.2), and the dissolved

![Fig. 1.2 Nutrient transformation processes in the water column in mangrove forests.](image)
organic matter pool especially is considered to play an important role (Alongi et al., 1989; Bano et al., 1997; Ayukai et al., 1998). Leakage of nutrient rich water from the creek banks during low tides has been suggested as an important contributor to nutrients in the mangrove waterways, and was investigated in a mangrove forest in Thailand (Kristensen & Suraswadi, 2002). Water seeping from creek banks was only enriched in inorganic phosphates and was not considered as an important source of solutes to the waterways in this forest.

The low nutrient concentrations affect the primary production in mangrove creeks, and the production has often been found to be strongly nutrient limited. Phosphorus was the limiting factor for phytoplankton growth in a mangrove creek in a tidal-dominated forest in Thailand, as indicated by a high molar ratio between dissolved nitrogen and phosphorus (~34–38) much higher than the Redfield ratio (Suraswadi et al., 2003). The degree of phosphorus limitation was less pronounced near small tributaries (~11–21), whereas the N:P ratio increased significantly (~192) near shrimp farm outlets – most likely in response to loss of dissolved nitrogen compounds from the farms (Burford & Longmore, 2001). The phytoplankton production is, however, not always nutrient limited. Due to the shallow water in many mangrove creeks and a rapid water flow in river-influenced mangrove forests the light penetration is often quite low and the phytoplankton production is just as often light limited (Harrison et al., 1997; Kristensen & Suraswadi, 2002). In a three year study of two tidal creeks on the Indus River in Pakistan, Harrison et al. (1997) found no limitation of the phytoplankton production by silicate or nitrogen, and phosphate was only limiting during large blooms. Conversely a large suspended load resulted in high light extinction coefficients and the 1% light depth ranged from <1 m to about 4 m. Consequently, primary productivity appeared to be light-limited throughout the year. There was no apparent seasonal cycle in primary productivity despite the variability in nutrient concentrations probably due to these poor light conditions. Gross primary production was also found to be only moderate in the water column in a Thailand mangrove forest dominated by tides with no pronounced spatial and temporal variations (Kristensen & Suraswadi, 2002). A large fraction of the inorganic carbon and nitrogen assimilated by the phytoplanktonic organisms was released in the form of DOC (50–90%) and DON (50–60%) indicating that primary producers were under stress or nutrient depleted. Phosphate and, occasionally, nitrogen appeared to be the limiting nutrients. However, rapid light attenuation in the turbid creek water rendered the entire water column strongly heterotrophic at all times.

The high turbidity in mangrove waterways is caused by high loads of suspended matter. Suspended matter, which originates from the erosion of soil from forests and farmlands, is discharged in large quantities from rivers, especially in the humid tropics, where heavy rainfalls occur during the wet season. Resuspension in the shallow parts of the mangrove may also contribute significantly to suspended matter in the water column, whereas import from
the ocean plays a minor role. The suspended matter contains a variety of components including nutrients such as nitrogen and phosphorus. Most of the available phosphorus in mangrove waterways occurs in bound forms, rather than in free dissolved forms in the water. The role of suspended matter in nutrient enrichment in tropical mangroves is, however, poorly documented. One study of a mangrove forest in Malaysia showed that phosphorus and iron content in the suspended matter decreased linearly with increasing salinity, reflecting the process of phosphorus release into the mangrove waterways during transportation to the sea (Tanaka et al., 1998). Iron hydroxides display a strong affinity for phosphate and are considered to be primarily responsible for phosphate adsorption in oxidized environments (Sundby et al., 1992) such as the suspended matter in mangrove forests waterways. The average C:N:P ratio of the organic substances contained in the suspended matter in waterways in the Matang Mangrove Forest was, however, estimated to be 140:16:1, which is considerably different from the ratios for mangrove litter or terrestrial sources and is rather similar to the Redfield ratio, indicating a high contribution of living organisms to the suspended matter (Tanaka et al., 1998). It is thus very likely that the suspended matter undergo important transformations during the transportation in the mangrove forests.

Except for a few recent studies (e.g. Bano et al., 1997; Harrison et al., 1997; Rivera-Monroy et al., 1998), there has been little focus on the role of microbial processes for transformations of dissolved and suspended compounds in the water column. These studies have indicated that much of the net nutrient generation within a mangrove forest originates from microbial mineralization of dissolved and particulate organic matter in tidal waters. Heterotrophic conditions in the mangrove waterways tend to result in accumulation of dissolved inorganic nutrients and dissolved organic matter, which eventually may be utilized by bacteria. Bacterial biomass and production was studied in three tidal creeks in the Indus River delta in Pakistan Bano et al. (1997), and they found a high bacterial production due to attached bacteria. The bacterial production was generally higher than the primary production, and the water columns were net heterotrophic. The microbial heterotrophs are considered to be largely supported by particulate and dissolved substrates derived from land run-off, tidal resuspension, mangrove root exudates and leachates from fallen leaves on the forest floor. In a mangrove forest in Thailand, it was, however, found that the pelagic heterotrophic community was supported primarily by exudates from primary producers (Kristensen & Suraswadi, 2002).

In view of the low nutritional quality of the mangrove detritus, the production of phytoplankton and bacterial biomasses may represent important pathways for the synthesis of high quality biomass potentially available to the grazers in the mangrove creek systems (Bano et al., 1997). On the other hand, the heterotrophic conditions may also have negative consequences for the
oxygen concentrations in the water column due to significant oxygen consumption particularly during night. Low oxygen concentrations have been measured in small tributaries in the high-intertidal forest, where the mixing of water is reduced due to low tidal influence (Suraswadi et al., 2003). Most mangroves are, however, relatively shallow, and a significant re-aeration takes place with the atmosphere promoting good oxygen conditions in the mangrove waterways for large grazing organisms (Suraswadi et al., 2003). Loading of the mangrove forest with oxygen consuming substances, e.g. released from shrimp farms may, however, give rise to problems with low oxygen tensions (Burford & Longmore, 2001).

1.4 Organic matter sources in mangrove forests

The detritus in mangrove ecosystems is either derived from autochthonous (e.g. mangrove litter, phytoplankton, benthic algae) or allochthonous sources (e.g. river run-off, anthropogenic discharges), and the fate of this detritus is recycling within or outwelling from the mangrove forest in dissolved micro-particle and macro-particle (litter) forms (Chansang & Poovachiranon, 1990; Wattayakorn et al., 1990; Ayukai et al., 1998; Kristensen et al., 2000; Wattayakorn et al., 2000). The magnitude of litter fall, which is one of the most important autochthonous sources, depends on geographical locations, seasons and tree species (Twilley et al., 1986; Woodrooffe et al., 1988; Bunt, 1995; Shunula & Whittick, 1999). The fallen litter is potentially exported from mangrove forests by tidal exchange. This process is largely influenced by mangrove vegetation, where dense trees in the mangrove stand slow down water movements, favouring trapping within the forest (Furukawa & Wolanski, 1996; Furukawa et al., 1997). Chansang and Poovachiranon (1990) emphasized the role of litter trapping processes inside a mangrove forest in Thailand, as only 0.5–15% of litter fall was exported. Moreover, feeding and burial activities of mangrove crabs can remove a substantial amount (28–100%) of leaves before litter is exported to coastal waters (Robertson, 1986; Poovachiranon & Tantichodok, 1991). Nevertheless, export of mangrove litter is an important process for nutrient transports between mangrove ecosystem and outer boundary (Chansang & Poovachiranon, 1990; Wattayakorn et al., 1990).

Only little information is available on the dynamics of the autochthonous sources (Poovachiranon et al., 2003). Litter fall was collected for a two year period along the main creek of a mixed mangrove forest in Thailand. While litter from only six mangrove species were observed within the litter fall traps, samples of tidal litter transport revealed a total of 23 mangrove species. Rhizophora apiculata and Ceriops tagal, followed by R. mucronata and Xylocarpus granatum were the most dominant species. The litter fall ranged from 8 to 12 tons ha\(^{-1}\) yr\(^{-1}\), and was mainly composed of leaves (78%).
followed by apexes, twigs and fruits (Fig. 1.3). Spatial variations in litter fall were prominent and indicated changes in mangrove and environmental conditions. While seasonal variation in leaf fall was negligible, fruit and flower fall occurred during confined periods. Year-to-year variations in litter fall, on the other hand, were prominent, with a higher rate recorded in dry than wet years. Less than 1% of total litter fall was exported from the mangrove forest, of which the net exports were highly correlated with spring tides. Twigs and fruits were major fractions of the exported litter, while leaves only comprised 28% of the total export (Fig. 1.3). Most litter was retained within the mangrove forest due to trapping effects of the dense mangrove vegetation, consumption and burial by sesarmide crabs. This mangrove forest had a high nutrient retention capacity, as less than 1% of nitrogen and phosphorus in fallen litter were directly exported out of the mangrove via litter materials. The remaining portions were efficiently recycled in the mangrove forest and subsequently outwelled from the mangrove in dissolved and micro-particulate forms. Other autochthonous sources are phytoplankton, benthic algae and macrophyte production, which are considered to be important in large lagoons with fringing mangrove forests (Robertson et al., 1992). Where shading is not severe, prop root epiphytes may be highly productive, and high benthic microalgae production has been found to be significant on creek banks and mud flats with high radiation (Kristensen et al., 1988).

![Fig. 1.3 Annual litter fall and litter transport in the Bangrong mangrove forest, Phuket, Thailand. The litter is separated into leaves, apexes, twigs, fruits and miscellaneous (misc., unidentified) material. Modified from Poovachiranon et al. (2003).](image-url)
The identification and quantification of allochthonous sources are even less documented. The increasing number of shrimp farms in Southeast Asia may contribute significantly to inputs of dissolved nutrients as well as particulate nutrients during flushing of the shrimp farms (Burford & Longmore, 2001). River-influenced mangroves may be affected by allochthonous sources, e.g. land run-off, agriculture and sewage discharges, but very limited information is available. Urbanization is rapid in Southeast Asia, and it is very likely that organic matter sources will change during the coming decades. The majority of mangrove forests, however, occur in estuarine areas, or as dense forests with tidal channels. These mangrove systems have a high productivity, and the carbon fixed by mangrove vegetation is likely to be the dominant contributor to detritus (Lee, 1999).

1.4.1 Decomposition of detritus

During the last decades, there have been a number of studies on the degradation of mangrove litter by use of litter-bags (Wafar et al., 1997; Ashton et al., 1999). These have shown rapid initial decomposition followed by low rates and accumulation of refractory compounds. The detritus is often enriched by nitrogen during the decomposition (Wafar et al., 1997; Holmer & Olsen, 2002), and recent results also show enrichment with phosphorus (Nielsen & Andersen, 2003).

The detritus derived from mangrove forests is generally low in nutrients and high in structural carbohydrates, aromatic humic compounds and geopolymers (Benner & Hodson, 1985; Kristensen et al., 1995). Nitrogen and phosphorus of mangrove leaves are re-absorbed and translocated before abscission (Woodroffe et al., 1988; Feller et al., 1999), and it has, for example, been found that the phosphorus concentration in the yellow leaves of Rhizophora sp. is only half of the content in fresh green leaves (Lugo et al., 1990). Litter fall of the evergreen mangrove trees occurs throughout the year, but often with a peak immediately before or during the wet season in monsoonal areas. The amount of leaves decomposing in and on the forest floor is a function of input (litter fall and import from adjacent areas) and output (export by tides and runoff, decomposition and removal by leaf-eating crabs). The residence times of detritus before export vary between 58–252 days in basin mangrove forests and 40–91 days for fringe and riverine forests (Twilley et al., 1986). The leaves on the forests floor range from yellow to black in colour, indicating the decomposition. Decomposition rates increase with humidity, temperature and oxygen availability, and depend on the composition of the organic matter. Often litter accumulates in the higher and less frequently inundated parts of the forest floor, while a smaller amount has been found in the lower zones of Southeast-Asian fringe forests.

The rate of decomposition of mangrove leaves varies among species. Avicennia leaves decompose at a faster rate than those of other species,
probably because the leaves are thinner and sink immediately to the sediment surface, compared to the thicker and buoyant leaves of e.g. *Sonneratia* and *Rhizophora* (Wafar *et al.*, 1997). The loss of organic matter is generally rapid during the first couple of weeks due to leaching of soluble organics (Fig. 1.4). The increase in nitrogen content, by 2–3 times, during decomposition is most likely associated with the accumulation of nitrogenous biomass of microorganisms colonizing the decaying litter (Fig. 1.4). Nitrogen fixation is generally low in mangrove sediments, diminishing the potential for this process to account for the nitrogen enrichment of the detritus (Kristensen, 1997), whereas relatively large nutrient pools provide a potential for bacterial nitrogen incorporation directly from pore water pools (Kristensen *et al.*, 1998; Holmer *et al.*, 2001).

**Fig. 1.4** Weight loss and nutrient content in the remaining litter (yellow leaves of *Rhizophora apiculata*) during a decomposition experiment in the Bangrong mangrove forest, Phuket, Thailand. The leaves were buried in surface sediment in the mangrove in litter boxes and sampled with intervals during a 3 month period. Modified from Nielsen and Andersen (2002) and Holmer and Olsen (2002).
The decay pattern of mangrove leaves shows rapid initial losses in biomass followed by a slower decrease, and a single exponential model has frequently been used to describe the decomposition process (Kristensen, 1997). The decomposition constants are generally low compared to marine detritus, and half-life ranges between 20 and 226 days depending on the type of detritus and position along the tidal gradient (Wafar et al., 1997; Kristensen, 1997; Ashton et al., 1999; de Boer et al., 2000; Holmer & Olsen, 2002). The decomposition is faster at the sediment surface compared to burial in the sediments, probably because water soaking causes leaching of labile materials and promotes leaf conditioning by microbes (Chale, 1993). The decomposition may be further enhanced by the presence of herbivorous crabs (Kristensen & Pilgaard, 2002; Thongtham et al., 2003).

A study of the decomposition of R. apiculata leaves buried in surface sediments showed that phosphorus also accumulates with time in the decomposing material (Fig. 1.4, Nielsen & Andersen, 2003). The incorporation of phosphorus into the decomposing leaves was probably associated with binding to humic acids and metals, especially iron, which also accumulated in considerable amounts in the leaves. The phosphorus most likely originated from iron-bound phosphate in the sediment as the decomposition of buried leaf litter increased the sediment microbial respiration, which led to reduced redox potential and higher dissolved reactive phosphate concentrations in the sediment pore water. This binding of phosphate to refractory organic material and the presence of oxidized iron at the sediment–water interface resulted in low release of dissolved reactive phosphate from the sediment and thus enhanced the retention of phosphorus in the mangrove forest. Similar observations have been found for nitrogen with reduced fluxes and enhanced retention in the sediments (Holmer & Olsen, 2002).

The decomposition of seagrass leaves in the mangrove, e.g. imported from the seagrass beds in front of the mangrove forests during high tide, is much more rapid than mangrove leaves. The seagrass material was degraded within the first week of the decomposition, probably because seagrass detritus is less refractory and has higher nutrient contents compared to mangrove leaves (Holmer & Olsen, 2002). Seagrass detritus may thus be an important organic matter source for the sediment microbial community and increase nutrient recycling in the mangrove forest. About 32–36% of the mineralized nitrogen from the seagrass leaves was released across the sediment–water interface, where it became available for primary producers or exported to adjacent ecosystems.

1.5 Sediment biogeochemistry

Sediment biogeochemistry in mangrove forests is just as complex as water column biogeochemistry. The sediments are highly heterogenic and the
composition varies from muddy sediments in the high-intertidal forest to coarse sands at the flats in front of the mangrove forest (Kristensen et al., 1995, 1998; Alongi et al., 1998). The sediment structure is considered to have a major impact on the abiotic processes, e.g. diffusive and advective processes, and the biotic conditions, e.g. species diversity and abundance, which among other things play a crucial role for the recycling of organic matter and the oxidation of the sediments.

The sediments are characterized by the abundance of silt and sand with minor amounts of clay (Badarudeen et al., 1996). Some mangrove sediments show enhanced contents of calcium carbonate as a result of the large quantity of shell fragments in the sediments (Badarudeen et al., 1996). The supply of organic matter to the sediments varies as described above, but the significant transportation of detritus in the mangrove creates a large potential for organic matter inputs to the sediments. The organic matter is primarily introduced through sedimentation, but bioturbating organisms may also influence the organic matter cycling. The sesarmine crabs, for example, crawl up into the forest trees, collect leaves and use these to cover their burrows. This habit adds organic matter to the sediments (Thongtham et al., 2003). The high- and mid-intertidal sediments are often densely vegetated with mangrove trees, and this may also provide a direct source of organic matter to the sediment, e.g. through root exudation and decay. Due to the large input and the refractory composition of the organic matter, mangrove sediments are often found to be organic-rich (Fig. 1.5), but as the detritus is relatively nutrient-poor and refractory, the sediments are generally characterized by low net mineralization rates (Kristensen et al., 1992, 1995).

1.5.1 Total microbial activity in mangrove sediments

Oxygen uptake and carbon dioxide production measured as fluxes across the sediment–water interface represent estimates of total microbial activity in the sediments. Sediment oxygen uptake is generally considered to be an integrated measure of aerobic bacterial respiration as well as chemical and chemoautotrophic oxidation of reduced metabolites (e.g. sulphide and ammonium). The release of carbon dioxide (CO₂) from sediments, on the other hand, may provide a reasonable estimate of total benthic carbon mineralization when no carbonate precipitation or dissolution occurs. Only very few studies of sediment oxygen uptake and CO₂ production have been undertaken in Southeast Asian mangrove forests. The benthic oxygen uptake rates in tropical mangrove forests are generally low compared to other intertidal environments at the same temperature (Kristensen et al., 1995, 1998). This is considered to be due to low microbial activity, controlled by the refractory and nutrient-poor sediment organic matter, which limits the decomposition potential (Kristensen et al., 1995). In mangrove forests, the lowest rates have been found for inundated sediments,
Fig. 1.5 Changes in sediment organic matter contents from high-intertidal mangrove forest to low-intertidal mudflats in the Bangrong mangrove forest, Phuket, Thailand. Upper panel: particulate organic carbon (POC) and nitrogen (PON), mid panel: total phosphorus content (TP) and lower panel: molar ratios between POC and PON and POC and TP. Modified from Holmer et al. (2001).

whereas air-exposed sediments generally have higher oxygen demand (Fig. 1.6). Up to 6 times higher oxygen uptake by air-exposed sediment relative to submerged sediment has been measured, and is considered to be caused by an increased area of oxic-anoxic interfaces combined with a reduced thickness of the diffusive boundary layer during air exposure (Kristensen et al., 1992).
Fig. 1.6 Changes in sediment oxygen uptake and CO$_2$ production from high-intertidal mangrove forest to low-intertidal mudflats in the Bangrong mangrove forest, Phuket, Thailand. Oxygen uptake was measured in the wet and dry season and under submerged (upper panel) and air-exposed conditions (mid panel). The CO$_2$ production was only measured under submerged conditions (lower panel). Modified from Holmer et al. (1999).
Drainage of water from sediment interstices (e.g. burrows and cracks) during low tide exposes sites that are otherwise anoxic to oxygen, thereby increasing the area of interfaces where rapid oxygen uptake can occur.

The flux of carbon dioxide from inundated mangrove sediments is generally higher than oxygen uptake (Fig. 1.6), providing community respiratory quotients (CRQ) of 0.8–3.2 (Kristensen et al., 1991, 1992, 1994, 1995; Alongi et al., 1998; Holmer et al., 2001). CRQ values higher than 1 indicate that only a fraction of the sulphide produced by sulphate reduction is reoxidized by oxygen and also suggests that anaerobic mineralization processes are important for the total mineralization of organic matter in the sediments.

The oxygen uptake and carbon dioxide production generally decrease with the degree of submergence (Fig. 1.6). Rates are highest in the high-intertidal organic-rich sediments and lowest in the mud and sand flats in front of the mangrove forests (Kristensen et al., 1995; Holmer et al., 2001). This is probably due to the large changes in physical and biological parameters along this gradient. The high-intertidal sediments are densely vegetated and have an active population of burrowing crabs, which ensures aeration of the sediments. Aerobic conditions promote the decomposition of refractory organic matter (Kristensen & Holmer, 2001). With increasing submergence, the organic matter content and the bioturbating activity decrease, and the sediments become more reduced and the microbial activity also decreases. These changes in total microbial activity along the transect from land to ocean have large effects on the nutrient regeneration within mangrove forests and will be discussed below (Holmer et al., 2001).

1.5.2 Mineralization pathways in mangrove sediments

Biogeochemical studies conducted in Thailand (Kristensen et al., 1991, 1995; Alongi et al., 1998) and Jamaica (Nedwell et al., 1994) suggest that aerobic respiration and sulphate reduction are major pathways of organic matter diagenesis in mangrove sediments, but recent studies have shown that iron reduction may also be an important respiration process (Alongi et al., 1998; Kristensen et al., 2000). Generally, the mineralization of organic matter in mangrove sediments occurs through the pathways found in marine sediments (Kristensen et al., 1995), and thus takes place with a number of electron acceptors (Fig. 1.7). Oxygen is an important and efficient electron acceptor, but is rapidly consumed and is usually only present in the upper millimetres of temperate coastal sediments (Revsbech et al., 1986). About 50% of the organic matter oxidation is considered to take place under aerobic conditions (Canfield, 1993). In the deeper layers, electron acceptors such as nitrate, iron and sulphate become important for the mineralization.

The oxygen penetration into mangrove sediments has been found to be quite limited (Andersen & Kristensen, 1988), although the penetration depth may
have been underestimated in the permeable coarse sediments of the mangrove creeks and flats in front of the mangrove forests due to methodological limitations. The oxygen penetration depth is similar to subtidal temperate coastal sediments in the order of 1–5 mm (Revsbech et al., 1986). Despite this limited penetration, the oxygen respiration appears to be very important for the organic matter decomposition in mangrove sediments (Kristensen, 1997). This is probably due to a combination of the efficiency of the electron acceptor and the presence of labile organic matter in the surface sediments.

A general characteristic of mangrove ecosystems is low levels of both particulate and dissolved (Fig. 1.5) nitrogen compounds (Fig. 1.8), suggesting that the biogeochemical cycling of nitrogenous compounds is closely coupled between assimilation and dissimilation processes. In particular, the concentration of nitrate is low in tropical sediments, and denitrification is considered to be of minor importance for the decomposition of organic matter (Kristensen et al., 1998). The primary cause for nitrogen limitation is the low nitrogen content of mangrove litter, and it has been suggested that mangrove forests are efficient in retaining and recycling nitrogen via several mechanisms that reduce export (Alongi et al., 1992). These mechanisms include re-absorption or re-translocation of nitrogen prior to leaf fall, burial of fallen detritus by crabs and rapid and efficient uptake of dissolved materials by bacteria. Nitrogen mineralization is often counterbalanced by ammonium assimilation, and the low net mineralization rates result in low pore water pools of ammonium and low release from the sediments (Fig. 1.9). The concentrations are, in particular, low in vegetated zones, where nutrients are taken up by the vegetation through the roots.
Fig. 1.8 Pore water concentrations of ammonium (upper panel, $\text{NH}_4^+$) and phosphate (lower panel, $\text{PO}_4^{3-}$) in the Bangrong mangrove forest, Phuket, Thailand during the dry season. Nitrate concentrations were <1 μM. Modified from Holmer et al. (2001).

(Kristensen et al., 1998). Although the waters flooding mangrove sediments generally are low in ammonium, there is rarely ammonium release from the sediment (Holmer et al., 2001). Ammonium fluxes are usually lower than and opposite in direction to those observed in temperate subtidal and intertidal areas. Since the profiles of pore water ammonium indicate an upward diffusive flux, rapid consumption of ammonium must occur near the sediment–water interface. The most likely agents for ammonium removal in the uppermost sediment layer are assimilation by benthic microalgae and nitrification (Kristensen et al., 1998; Holmer et al., 2001), but immobilization by an active, litter-degrading aerobic bacterial community may also contribute significantly (Holmer & Olsen, 2002).
Fig. 1.9 Changes in nutrient fluxes (nitrate, ammonium and phosphate) across the sediment–water interface from high-intertidal mangrove forest to low-intertidal mudflats in the Bangrong mangrove forest, Phuket, Thailand. Modified from Holmer et al. (2001). Negative values represent uptake.

Dynamics and fluxes of nitrate in marine sediments are primarily driven by two key processes, nitrification and denitrification. Also, the recently discovered anaerobic oxidation of ammonium coupled to nitrate reduction, producing N₂, may significantly influence the fate of nitrogen compounds (Thamdrup & Dalsgaard, 2002). The process is known as anammox and is particularly important in low activity environments, but remains to be examined in mangrove sediments. Low pore water concentrations of nitrate in mangrove sediments are probably a consequence of low nitrification rates combined with high nitrate consumption by the sediment community. Potential rates of sediment nitrification in mangrove sediments are lower than usually found in temperate coastal sediments (Kristensen et al., 1998). Although the gradient of nitrate across the sediment–water interface in mangrove forests indicates a diffusive release into the overlying water, measured fluxes are generally directed into the sediment (Fig. 1.9). Recent studies have shown that measured rates of denitrification can only account for 10–30% of the nitrate uptake by the sediment, whereas the rest is supplied from coupled nitrification–denitrification in the sediments (Kristensen et al., 1998). The fate of nitrate at the sediment–water interface in mangrove sediments is considered to be similar to ammonium: consumption by an active community of benthic microalgae or incorporation into decomposing bacteria (Holmer et al., 2001; Holmer & Olsen, 2002). These processes serve as efficient mechanisms for nutrient conservation.

The availability of sediment nutrients to microbes and plants is complicated by geochemical processes, such as the involvement of some nutrients in
adsorption reactions to clay minerals. The ammonium adsorption is low in mangrove sediments compared to temperate salt marsh sediments, probably due to higher concentration of competitive cations such as iron (Holmboe & Kristensen, 2003). A study of mangrove forest sediments in Thailand has shown that the adsorption of ammonium is negatively related to the organic content of the sediments, which is in contrast to findings for other marine sediments (Holmboe & Kristensen, 2003). It was suggested that organic material may have a diluting effect on the exchange capacity in fine-grained sediments, and that organic coatings may block ion exchange sites on clay surfaces. Ammonium availability was thus found to be relatively higher compared to temperate sediments.

Only very few studies have examined iron reduction in mangrove forest sediments, but some have been conducted in the Southeast Asian region. In subtidal sediments, rates of iron reduction have found to be positively correlated with the pool of oxidized iron (Thamdrup, 2000), and this relationship may be useful in predicting the potential of iron reduction in mangrove forest sediments. The presence of oxidized iron is considered to be controlled by the origin and the oxidation of the sediments. It can thus be expected that iron reduction will be most important in the high- and mid-intertidal sediments with a large contribution of terrigenous compounds, many bioturbating organisms and oxidation of the sediments by vegetation. This is consistent with a study of a mangrove forest in Thailand (Kristensen et al., 2000), where it was found that iron reduction accounted for up to 70–80% of the total carbon oxidation in mid-intertidal rooted mangrove forest sediments (Fig. 1.10). Similarly, Alongi et al. (1998) found that iron reduction was most important in a regenerating mangrove forest, where the iron pools were at maximum compared to older forests. The contribution from iron reduction was less in the low-intertidal sediments (30–40%) and almost absent in the seagrass sediments in front of the mangrove (<1–15%) (Fig. 1.10, Kristensen et al., 2000). The shift in dominance of electron acceptors along the tidal transect was found to be related to the presence of roots and benthic fauna, but also the sediment composition (grain size, organic content and iron content) appeared to be an important co-factor. The grain size may be an important controlling factor for the iron content, as iron oxides are adsorbed to sediment surfaces, and the decrease in iron content along the transect was coincident with an increase in the sediment particle size (Kristensen et al., 2000).

There has been relatively more focus on measurements of sulphate reduction in mangrove sediments, mainly since sulphur cycling has been intensively studied during the last three decades, but also because the sulphur cycling in mangrove sediments can have significant impacts on the benthic community due to a variety of secondary effects, e.g. associated pH changes. Sulphate reduction is not expected to be controlled by the concentration of sulphate in the mangrove forest sediments due to the high salinities generally found here.
It is much more likely that the rates are controlled by the availability of organic matter and the biological and physical processes acting on the oxidation of the sediments, e.g. bioturbation, root oxidation and tides. Sulphate reduction appears to be an important process in mangrove sediments, and relatively high rates have been found (e.g. Kristensen et al., 1995; Kristensen, 1997; Alongi et al., 1998; Holmer et al., 1999). This suggests that sulphate reduction may contribute significantly to mineralization of organic carbon and nutrient availability in
tropical mangrove sediments. Patterns in sulphate reduction rates have been found to reflect differences in physical and biological conditions in a Thailand mangrove forest (Holmer et al., 1994). Highest rates were found at the vegetated site within the mangrove (*R. apiculata*) forest, probably due to high input of labile organic matter from sedimentation of phytoplanktonic detritus among the stilt roots or by root exudates and root decay (Fig. 1.11). The contribution of sulphate reduction to CO₂ production varies among studies from about 20% up to 85%, most likely due to the heterogeneity of these sediments (Holmer et al., 1994, 1999). Sulphate reduction rates were at minimum at the high-intertidal site, and this site was characterized by a large number of crab burrows deep into the sediments and dry conditions, as the sediments were flooded only for short periods of time during high tide (Fig. 1.11). These sediments were thus highly oxidized as revealed by positive redox potentials favouring mineralization processes that employ more oxidized electron acceptors than sulphate. Sulphate reduction accounted for 11% of the CO₂ production. The rates were in between these two extremes at the mud flats in the mangrove waterways, whereas they increased again in the seagrass sediments in front of the mangrove, probably due to input of fresh organic matter from seagrasses or microphytobenthos, and sulphate reduction accounted for 20–40% of the mineralization (Holmer et al., 1999).

The accumulation of sulphur in subtidal marine sediments is primarily controlled by the rate of sulphate reduction and the oxidation state of the sediment (Thode-Andersen & Jørgensen, 1989). In tidal environments, however, additional factors must be considered. Tidal currents and wave action can affect the oxidation status of sediments directly by increased advective transport of pore water and particles. During low tide, the sediment surface desiccates and oxygen can penetrate deeper into the sediment via burrows and cracks in the surface. The presence of rooted vegetation also strongly affects the biogeochemical cycling of sulphur by vertical translocation of organic matter and oxygen (Holmer & Nielsen, 1997; Holmer & Laursen, 2002), and the cycling of sulphur is closely coupled to the reactive iron pools (Thamdrup, 2000). Reactive iron oxides present in sediments may efficiently oxidize reduced sulphides. This suggests that the cycling of reduced sulphur compounds is highly dynamic in mangrove forest sediments. Buried pools of sulphides are usually extracted in two major pools, the acid volatile (AVS) and chromium reducible (CRS) pools. The AVS pools consist primarily of dissolved H₂S and FeS compounds, and the CRS pools are mostly pyrite. AVS is considered to be the initial product formed, but the pyrite formation is also rapid, in particular in relatively oxidized sediments, such as vegetated mangrove forest sediments (Holmer et al., 1994).

Pyrite appears to be the most important inorganic sulphur component in mangrove sediments, attaining pool sizes 50–100 times higher than acid volatile pools (Kristensen et al., 1991, 1992; Holmer et al., 1994, 1999; Alongi
Fig. 1.11 Depth integrated rates of sulphate reduction (upper panel, SRR) and the contribution of sulphate reduction to total sediment metabolism measured as CO$_2$ production across the sediment–water interface (mid panel, %SR of CO$_2$ production) in the Bangrong mangrove forest, Phuket, Thailand. The depth integrated pools of total reducible sulphides are given in the lower panel (TRS pool). Results from dry and wet seasons are given. Modified from Holmer et al. (1999).
There is quite a significant burial of sulphides in the mangrove forest sediments (Fig. 1.11), in particular in the mid-intertidal sediments, where the oxidation by bioturbating organisms is low and the sulphate reduction activity high, but also the high-intertidal sediments show large accumulations below depths of bioturbation (Holmer et al., 1994). This may give rise to major problems during land reclamation, as it is often these vegetated areas which are utilized for new land or shrimp farms. The exposure of reduced sediments with high sulphur pools to oxygen produce sulphuric acid during reoxidation, and thus creates highly acidic environments not suitable for shrimp farming or agriculture (Kryger & Lee, 1995; Kautsky et al., 2000). The burial of sulphides is much less in the non-vegetated sediments of mangrove creeks and in the mud flats, probably caused by oxidation facilitated by advection during shifting tides and air exposure during low tides. Also, here pyrite is the most important sulphur pool. There are, however, large site differences in the burial of sulphides in mangrove forests. The sulphur pools were low in the Bangrong mangrove forest, Thailand, compared to other mangrove sites, e.g. the nearby Ao Nam Bor mangrove. Similarly, Alongi et al. (1998) found that the pyrite concentrations increased with forest stand age suggesting that the sulphur accumulates with time in the mangrove sediments.

In addition to the burial of inorganic sulphur compounds, an accumulation of organic sulphur has been found in the deep sediments in the inner part of mangrove forests (Holmer et al., 1994). A similar accumulation of organic sulphur has been observed in mangrove peats (Altschuler et al., 1983), but the underlying mechanisms behind this accumulation are not well understood. However, the burial of inorganic sulphur appears to be limited by the availability of iron (Holmer et al., 1994), which may favour formation of organic sulphur compounds.

As sulphate has been found to be present to deep depths in the mangrove sediments examined so far (e.g. Holmer et al., 1994; Alongi et al., 1998), methane production is not considered to be an important mineralization process in mangrove forests. Methane-producing bacteria are able to compete only with sulphate reducers for electron donors at low sulphate concentrations (<200μM), and such low concentrations have not been measured at depths of 30–50 cm examined so far. The sulphate concentration may still be as high as 8 mM at these depths (Holmer et al., 1994; Alongi et al., 1998).

### 1.5.3 Phosphorus cycling

Unlike nitrogen, iron and sulphate transformations, which are influenced by biological processes, chemical processes are more important for phosphorus transformations in aquatic environments. Phosphorus is an important element in mangrove forests, as the mangrove trees and other mangrove primary producers as well as the bacteria are often found to be phosphorus limited (Boto & Wellington,
The phosphorus dynamics in mangrove sediments are considered to be closely coupled to the activity of mineralizing iron- and sulphate-reducing bacteria. Phosphate is largely insoluble and regarded as non-reactive in the presence of oxidized iron, but is easily solubilized via chemical or biological reduction of iron under anoxic conditions. Moreover, a large fraction of the apparently reactive pool of phosphorus is prone to be immobilized by strong adsorption to clay particles (Alongi et al., 1992). Thus, phosphate is generally found in very low concentrations in mangrove waterways where suspended iron-rich clay particles are abundant (Wattayakorn et al., 1990; Trott & Alongi, 1999; Ayakai et al., 2000), and is usually also very low in the pore waters (Fig. 1.8) where it is adsorbed to the sediment particles (Tam & Wong, 1995; Alongi et al., 1998; Holmboe et al., 2001).

The flux of phosphate across the sediment–water interface is usually very low and rate measurements are constrained by large variability due to the heterogeneity of mangrove sediments and analytical precision near the detection limits (Holmer et al., 2001). In many cases, the fluxes are directed into the sediment (Fig. 1.9), and this high affinity of mangrove sediments has been ascribed to microbial uptake (Alongi et al., 1992), adsorption onto iron oxides (Holmboe et al., 2001) and binding to organic material (Hesse, 1963). The low phosphorus content of the detritus has been suggested to limit the potential for release of phosphate during mineralization (Fig. 1.5). At the same time most mangrove sediments show positive redox potentials in the surface sediments, favouring the binding of phosphate to oxidized iron. Iron-bound phosphate has been found in most mangrove sediments with highest concentrations at sites with high iron contents (Holmboe et al., 2001). In accordance with these observations, the pore water concentrations of phosphate have been found to be very low (<10 μM) in the surface sediments and increasing with depth (Alongi et al., 1998; Holmer et al., 2001). The increase with depth is considered to be due to lower diffusion to the water column and less binding of phosphate to oxidized iron. Enrichment of the sediments with organic matter (Nielsen & Andersen, 2003) or removal of vegetation (Alongi et al., 1998) has been shown to increase the pore water pools of phosphate. In both cases, this was coincident with increased mineralization of organic matter and reduced redox potentials, suggesting that the binding of phosphate to oxidized iron decreased (Alongi et al., 1998; Nielsen & Andersen, 2003).

The total content of phosphorus in mangrove sediments is usually low (Fig. 1.5) compared to temperate sediments (Alongi et al., 1998; Holmboe et al., 2001; Holmer et al., 2001), though some high values have been found in fine-grained sediments (Badarudeen et al., 1998). The content is usually higher inside the mangrove forests due to the deposition of fine particles rich in metal and organic content compared to the sand flat sediments (Holmboe et al., 2001). The surface concentrations are usually higher due to deposition and diagenesis of organic matter holding phosphorus and metals, and adsorption of phosphate
to oxidized iron (Jensen & Thamdrup, 1993). In mangrove forest sediments, however, the total phosphorus content is quite constant or increases with depth (Alongi *et al.*, 1998; Holmer *et al.*, 2001). This is probably due to the high degree of bioturbation and high redox potentials deep in the sediments.

Only very few studies have examined the inorganic forms of phosphorus in mangrove forest sediments, and the extraction schemes vary among these studies. In Southeast Asia, two detailed studies (Holmboe *et al.*, 2001; Nielsen & Andersen, 2003) are available, and these have been undertaken in the Bangrong mangrove, Thailand with the extraction method described by Jensen and Thamdrup (1993). The pools of easily exchangeable phosphorus are low, in particular in the fine-grained mangrove forest sediments. This is reflected to some extent in the higher pore water concentrations of phosphate of sand flat compared to mangrove sediments. The iron-bound phosphorus has been measured as a quantitatively important pool in many mangrove sediments; (Fabre *et al.*, 1999; Holmboe *et al.*, 2001; Nielsen & Andersen, 2003) in the Bangrong, iron-bound phosphorus comprised about 20% of the total phosphorus in mangrove and 10% in the sand flat sediments. The higher concentrations in the mangrove were correlated to higher iron pools. Phosphorus adsorbed to clay, aluminium and organic surfaces in mangrove sediments were mostly relatively low (0.4–8%) compared to the other fractions, and spatial and temporal changes were difficult to explain. The phosphorus found in the humic acid fraction was much more important, in particular in the mangrove sediments (15–42%) compared to sand flat sediments (2–8%). This is consistent with other findings of high proportions of phosphorus found in organic forms in mangrove sediments (Hesse, 1963; Alongi *et al.*, 1992). The opposite pattern is found for calcium-bound phosphorus, which is lower in mangrove compared to sand flat sediments due to the increase in CaCO₃ along this transect. The organic fraction of phosphorus was high and relatively similar among the stations (about 17% of total P), and is consistent with other findings (27–87% of total P) (Hesse, 1962; Fabre *et al.*, 1999).

### 1.6 Factors influencing the biogeochemistry

#### 1.6.1 Effect of forest type and age

Rates of nutrient transformation and recycling are presumably also dependent on forest type and age, but only few studies have examined the influence of forest type (Alongi *et al.*, 1993, 1998; Middelburg *et al.*, 1996). Early studies have suggested that some edaphic characteristics are species-specific (Nickerson & Thibodeau, 1985), but subsequent studies have shown that apparent differences between forest types are more closely related to root density and frequency of tidal inundation than to species-specific ability of mangroves to affect sediment biogeochemistry and nutrient turnover (McKee *et al.*, 1988). Nevertheless,
differences in pore water chemistry and microbial activity among different forest types have been found. Alongi \textit{et al.} (1993) studied three different forest types in Papua New Guinea: \textit{Rhizophora–Bruguiera}, \textit{Nypa} and \textit{Avicennia–Sonneratia} forests. For most variables, variations within forest type were as great as, or greater than, differences between forest types. A high-intertidal \textit{Nypa} site was most different in edaphic characteristics compared to five low-intertidal stations suggesting that differences among forest types are mainly a function of tidal elevation rather than species-specific ability of mangroves to influence redox and nutrient status.

The decomposition of organic matter has been found not to be related to the forest stand age and age-related differences in rates of forest production. There were, however, differences in the dominance of specific diagenetic pathways in different forests (Alongi \textit{et al.}, 1998). Sulphate reduction accounted for most of the total benthic mineralization (75–125\%) in the old forests (>15 years), whereas it constituted a much smaller proportion (42\%) in the younger forest (2-year old). This is probably due to the higher concentrations of organic matter in the older forests. Rates of solute efflux across the sediment–water interface and vertical profiles of dissolved manganese, nitrite and nitrate suggest that the more oxidized pathways, such as manganese reduction and denitrification–nitrification, coupled with aerobic respiration, accounted for most oxidation in the young forest.

1.6.2 Influence of macrofauna

Herbivorous crabs are important in litter processing in the Indo-West Pacific region (Robertson, 1986; Lee, 1997), whereas the detritus food web in other forests, e.g. of the Caribbean region, is primarily driven by microbial processes (Odum & Heald, 1972). Litter consumption and burial by crabs may have profound impact on the organic matter flow and nutrient dynamics within mangrove forests and affect the exchange with the adjacent coastal zone (Robertson, 1986; Twilley \textit{et al.}, 1997). Manipulative experiments with herbivorous crabs have shown that crab bioturbation significantly decreased the level of ammonium and sulphide concentrations in mangrove sediments (Smith \textit{et al.}, 1991), which in turn may improve the productivity of the mangrove forest. Crab burrows also play an important role in affecting the groundwater flow in, and the chemistry of, otherwise compact mangrove sediments (Wolanski \textit{et al.}, 1992).

Field studies of leaf removal by sesarmide crabs in mangrove forests in Thailand have shown that the crabs can remove about 75\% of the total daily litter fall and green, yellow as well as brown leaves were consumed (Fig. 1.12). It was estimated that the total population of sesarmide crabs could consume 58\% of the total leaf litter per year, in this case 1130 tons (Thongtham \textit{et al.}, 2003). A more detailed study of the economically important sesarmide crab
Neoepisesarma versicolor was done, and it was found that the crab spends most of the time during the day in its burrow or resting by the entrance, and is mainly active during the night. It mainly feeds on mangrove leaves (62%) and scraped-off food materials from sediment surface (38%). The plant material mostly comprised small pieces of mangrove leaves. Supplementary laboratory studies of leaf consumption and leaf preferences on N. versicolor showed that the crab mostly feeds on brown leaf, followed by green and yellow leaves.

A number of studies from Australia and Southeast Asia have documented that sesarmide crabs (Grapsidae) may consume 28–79% of the annual litter fall (Robertson, 1986; Robertson & Daniel, 1989). The remaining litter is either exported to adjacent waterways (Boto & Bunt, 1981; Chansang & Poovachiranon, 1990), decomposed aerobically at the sediment surface or anaerobically within the sediment (Robertson et al., 1992). The proportion of litter entering each pathway is largely determined by mangrove geomorphology, tidal flushing and type of litter (Robertson et al., 1992). Much of the litter handled by crabs will eventually enter the microbial food chain, either in the form of faecal material or as uneaten remains buried in the sediment (Giddins et al., 1986; Robertson, 1986; Lee, 1997). Intact leaves are, in contrast to faecal pellets, readily exported by tides before sinking, and thus lost from the mangrove ecosystem. Faecal pellets have been found to be more nutritious for the sediment microbes compared to refractory mangrove litter and sediment organic matter, and showed a 2 and 3–10 times faster rate of decomposition, respectively (Kristensen & Pilgaard, 2002).

Introduction of sesarmine crabs (Uca sp.) into non-bioturbated mangrove sediments has been found to enhance the sediment organic matter decomposition (Nielsen et al., 2003b). The sulphate reduction activity was in particular
enhanced. The introduction of crabs also affected the dynamics of the sulphur pools, and they were generally reduced despite stimulated sulphate reduction activity. This suggests that the crabs are able to oxidize the sediments through their construction of burrows. A direct effect from the burrow walls was, however, only found in sediments where both mangrove seedlings and crabs were introduced. Here the iron reduction became more important in the deeper layers, and the sulphate reduction activity decreased compared to the non-vegetated and non-bioturbated sediment. A detailed investigation of the sulphur and iron-dynamics in the surroundings of crab burrows showed that oxidative processes were very active in a zone of 5–10 mm from the burrow wall and the content of oxidized iron increased, whereas the content of reduced sulphides in the sediments was significantly reduced in this area.

There are many other benthic organisms of importance in Southeast Asia mangrove forests, but detailed studies of their impacts on organic matter cycling and nutrient regeneration are lacking. Benthic fauna has in particular been found to stimulate the decomposition of refractory organic matter by introducing this organic matter to aerobic degradation either by ventilation of burrows or physical movement of organic matter from the deep sediment layers to the surface (Banta et al., 1999; Kristensen & Pilgaard, 2002). It is thus likely that benthic fauna in mangrove sediments play an important role for the regeneration of nutrients from the refractory organic matter in mangrove sediments, but this remains to be explored, and this research should be initiated before it is too late. A case study of the sesarmide crab *N. versicolor* shows that this species used to be very common in Thailand’s mangrove areas but its numbers have drastically decreased due to human consumption as well as other factors (Thongtham et al., 2003). Local people recall that *N. versicolor* was dominant in the Bangrong mangrove forest, but due to deforestation for shrimp farming, land development and especially over-exploitation for human consumption, its abundance has drastically decreased. As these leaf-eating sesarmide crabs have been found to play such a significant role in litter turnover and nutrients retention in mangrove ecosystems, their disappearance is of major concern.

### 1.6.3 Effect of seasonal variations on mangrove forest biogeochemistry

Some studies have observed seasonal variations in primary production and nutrient dynamics in the tropics, but the variation is often low due to the constant environment and the intense recycling of nutrients. Enhanced outwelling during rainy seasons may affect nutrient concentrations in mangrove forests stimulating primary production in the water column (Rivera-Monroy et al., 1998), and the coupling between mineralization and immobilization in the water column has been found to shift between the wet and the dry seasons (Suraswadi et al., 2003). Heavy rainfalls may also have major effects on water
column characteristics. Thong *et al.* (1993) found that the concentrations of inorganic nitrogen in creek water increased by a factor of 10 after heavy rains. Organic nitrogen concentrations also increased under these conditions. The increase in inorganic nitrogen in the creek was greatest when the water drained off vast areas of the mangrove forest either: (a) after the flooding of high amplitude spring tides, or (b) after heavy rains. On some occasions, but not consistently, dissolved organic nitrogen and particulate nitrogen increased as water drained off the forest. In contrast, when there was no drainage due to rain and the waters were generally confined within the creek banks, either during neap or spring tides of low amplitude, the inorganic nitrogen concentrations remained relatively low. These relationships suggest that the floor of the mangrove forest is a major source of inorganic nitrogen to the creek. Export of increased nitrogen levels from the mangrove creek to the coastal waters seems likely to be greatest on occasions of high rainfall.

In addition to the low seasonal variation in parameters such as temperature and light, which are the most important factors of seasonal variations in temperate regions, the large spatial variations and the lack of long time-series in measured sediment processes contribute to the poor understanding of seasonal variation in the tropics. Most studies so far have concluded that the seasonal variations are less important compared to physical and biological processes acting on the mangrove forest sediments (Kristensen *et al.*, 1995; Alongi, 1996). Only in seagrass beds has enhanced anaerobic mineralization been found during the rainy season, probably due to lower light availability which decreases the oxidation of the sediments (Blackburn *et al.*, 1994; Holmer *et al.*, 2001).

1.7 **Sediment biogeochemistry and implications for mangrove vegetation**

The biological conditions in mangrove sediments range from aerobic through to anoxic and highly reduced. Mangrove plants growing in waterlogged soils may be adversely affected by either the strongly reduced conditions or the accumulation of soluble phytotoxins including reduced iron, manganese and organic gases (McKee, 1993). In addition, species growing in anaerobic marine sediments must also cope with toxic concentrations of sulphides (Allam & Hollis, 1972). In most wet land plants, the first line of defence against these toxic soluble ions is to render them insoluble at the root surface by oxidation with air that diffuses to the root from the photosynthesizing shoots (Armstrong *et al.*, 1994). However, Youssef and Saenger (1996) have shown that, unlike mature vegetation, roots of mangrove seedling have a very limited capacity for oxidative detoxification of the rhizosphere under laboratory conditions. Furthermore, detoxification by direct oxidation is even more
limited for seedlings under field conditions, because the seedlings are commonly partially or totally submerged or growing at low irradiances under the mature stand. Youssef and Saenger (1996) found that seedlings of the viviparous mangroves showed no significant responses to root anoxia, but sulphides inhibited photosynthetic gas exchange and caused complete stomatal closure in many species. Stomatal closure was probably the result of the damaging effect of sulphide ions on root cell membranes. It was concluded that high concentrations of sulphides in mangrove sediments may adversely affect both growth and survival of mangrove seedlings at low irradiances.

Direct oxidation of sulphides by oxygen is possible around roots of mature *Avicennia marina*, as indicated by a study by Andersen and Kristensen (1988). They measured oxygen concentration in aerial roots (pneumatophores), horizontal cable roots and surrounding sediment of *A. marina* in a mangrove forest in Thailand. The O$_2$ concentration inside pneumatophores was 63–88% of air saturation, whereas the cable roots showed a lower concentration (62–73%) indicating an O$_2$ gradient from the emerging parts to the subsurface roots. The O$_2$ concentration in the roots was highest in the outer part of the aerenchyma. There was an oxic zone of the sediment around roots, but it was thin (ca. 0.5 mm), and suggests that only little O$_2$ is released from the roots or that the oxygen is rapidly consumed by aerobic mineralization or reoxidation of reduced compounds. Also, *Rhizophora* sp. has been found to transport air to the buried portions of their roots through lenticels on the aerial portions, but there is usually no free oxygen in the sediments. There is, however, less hydrogen sulphide in the sediments under *R. mangle* and *Avicennia germinans* compared to other species, but it appears to be related to site differences (Carlson et al., 1983; Nickerson & Thibodeau, 1985). *A. germinans* plants reoxidize the sediments, as the mean sulphide concentration beneath them is nearly six times lower than that in immediately adjacent areas (Nickerson & Thibodeau, 1985), whereas *R. mangle* is only found in areas with low mean sulphide concentration not significantly different from nearby unvegetated soil.

The effect of hydrogen sulphide and metallic sulphides on mangrove vegetation during reforestation has only been briefly studied. *Avicennia* spp. with underground cable roots and pneumatophores, show clear signs of degeneration on mangrove plots, 12–14 years after reclamation of the land (Kryger & Lee, 1995). By contrast, saplings of *Rhizophora* spp. with aerial stilt roots were observed to establish within this area. It was found that concentrations of hydrogen sulphide in mangrove soils increased with the age of the soil, and it is suspected that the build-up of sulphides may affect the growth of different types of mangrove vegetation. The degeneration of *Avicennia* may be caused by the large deposition of silt, brought from inland construction areas through the inland drainage water, creating oxygen stress (Kryger & Lee, 1995). It is suspected that gaseous hydrogen sulphide may aggravate this condition of
hypoxia, hence causing *Avicennia* spp. to die. This was supported by the observation that, at the mature plot where the gaseous hydrogen sulphide content was high, the population of *Avicennia* spp. with underground cable roots was low, and seedlings of these species were not able to survive well. Conversely, *Rhizophora* spp., which have aerial stilt roots that also help in the breathing processes, were abundant. Aerial roots could help the plants to overcome the high concentration of gaseous hydrogen sulphide in the soil (Kryger & Lee, 1995).

### 1.8 Biogeochemistry in mangroves affected by anthropogenic activities

A recent review of mangrove research concludes that there is a strong bias towards subject areas such as floristic and basic plant ecology rather than ecological processes and nutrient cycling in tropical Asia (Li & Lee, 1997). Due to the capacity of mangrove forests to withstand and retain excessive nutrients, there has been considerable focus on these environments as a natural treatment facility for effluents from, e.g. aquaculture (Robertson & Phillips, 1995; Sansanayuth *et al.*, 1996; Wong *et al.*, 1997; Tam & Wong, 1999), but while various potential impacts of activities such as prawn farming have been proposed (Primavera, 1993), the effects of not only mangrove removal but also the operation of the new use remain to be addressed. Robertson and Phillips (1995) attempted to evaluate the impact of shrimp pond effluent in relation to the assimilative capacity of mangroves for nutrients (N and P). It was estimated that between 2 and 22 ha of mangrove forests are required to strip the N and P in effluent from each hectare of prawn pond. These authors nevertheless discuss that the calculation probably cannot be directly extrapolated to larger scales and direct experimentation on the response of mangrove forests to pond effluent has to be conducted. A nutrient enrichments study shows that anoxic sediment decomposition was not affected by nutrient enrichments at the level applied (2–3 times background concentration) (Holmboe *et al.*, 2001). This was substantiated by a low nutrient release from mangrove sediments and suggests a fast turnover of nitrogen and phosphorus by nutrient deficient bacteria in the mangrove sediments. Analysis of phosphorus fractions in the mangrove sediment revealed that added excess phosphate was efficiently taken up by the sediment particles and primarily retrieved in the easily exchangeable and iron-bound fractions. The mangrove forest sediments thus acted as phosphorus sinks. The long-term capacity of mangrove forests to retain excessive nutrient discharges is not known yet, but may be limited because most of the pollutants accumulate in the top layer (0–1.5 cm) of the sediment (Tam & Wong, 1999). In some cases, anthropogenic interference to mangrove forests may not always result in undesirable consequences. Li and Lee (1998) reviewed the particulate
organic matter dynamics of a small, mangrove-line embayment in the Pearl River estuary in southern China and concluded that the recent increase in waterfowl numbers supported is probably related to increased food supply from domestic sewage discharge.

Many countries in Southeast Asia have experienced almost an explosive growth in the number of shrimp farms and a corresponding reduction in the mangrove forests area (Platong, 1998; Kautsky et al., 2000). The increasing commercial shrimp farming in Thailand is considered to possess the most important threat on the stability of the coastal zone and the mangrove forests (Fig. 1.13, Platong, 1998). One of the largest problems associated with shrimp farming is the deposition and removal of the organic and nutrient rich sludge, which accumulate in the farms during the production cycle. The sludge deposits have traditionally been released through the mangrove waterways, but due to the fear of acute and long-term eutrophication problems, the recent legislation has forbidden this practice in favour of dry deposition on shore. As the onshore deposition has a high demand for resources, investigations have been undertaken to find alternative and cheaper solutions, e.g. controlled deposition where the mangrove acts as a biological filter of the enhanced nutrient loading (Robertson & Phillips, 1995; Wong et al., 1995; Sansanayuth et al., 1996; Gautier et al., 2001). Results from a study of shrimp farm impacts show that the benthic mineralization is doubled in the shrimp farm deposits compared

![Fig. 1.13 Comparison between shrimp production (metric tons) and mangrove area (10^3 ha) in Thailand from 1979 to 1996. Modified from Platong (1998).](image-url)
to untreated mangrove forests (Fig. 1.14). The enhanced mineralization was entirely due to sulphate reduction creating more reduced conditions in the sediments and possibly negative effects on the mangrove vegetation. The enhancement was, however, short-lived and after one year the carbon mineralization was already reduced to the untreated level. Introduction of burrowing crabs and mangrove seedlings in the shrimp farm deposits is essential as they improve sediment conditions in general, and accelerate reoxidation of reduced sulphide by introducing oxygen deep into otherwise anoxic sediment layers (Nielsen et al., 2003a). However, long time scales and deep and intense bioturbation are needed to observe major changes in sludge biogeochemistry, as immature vegetation and infaunal communities only have limited impact. Thus, deposition of shrimp pond sludge into mangrove areas can reduce some of environmental threats related to onshore deposition especially if deposited in areas with intense infaunal activity and high degree of vegetation. But again, the long-term environmental impacts of this practice remain unknown. Questions such as whether conversion of natural mangrove forests to shrimp ponds will lead to irreversible long-term ecological losses are still equivocal. Further research that is specifically directed towards answering practical challenges to our understanding of tropical mangrove forest ecology and biogeochemistry is urgently needed. Despite decades of increased research effort, answers to many fundamental questions concerning practical management issues of tropical mangrove forests are still largely unavailable.
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