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*Editors*

SOIL BIOLOGY

# Advances in Applied Bioremediation

 Springer

# Soil Biology

Volume 17

Series Editor

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# Advances in Applied Bioremediation

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Soil Biology ISSN: 1613–3382  
ISBN: 978-3-540-89620-3 e-ISBN: 978-3-540-89621-0  
DOI 10.1007/978-3-540-89621-0  
Springer Dordrecht Heidelberg London New York

Library of Congress Control Number: 2008944089

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*Cover design:* SPi Publisher Services

Printed on acid-free paper

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# Preface

The utilization of naturally occurring and mainly prokaryotic organisms in soil for detoxifying and rehabilitating polluted soils provides an effective, economical, versatile and eco-compatible means of reclaiming polluted land. Soil microbial communities are relatively evenly distributed in unpolluted environments. In the soil, microorganisms may develop various mechanisms to access sorbed compounds on soil particles and sediments, as well as to utilize water-insoluble pollutants, facilitating the development of new equilibrium states. These mechanisms may create concentration gradients, bring about micro-environmental pH shifts, and cause secretion of extracellular enzymes and production of surfactants, emulsifiers, solvents or chelators in order to partition chemicals from the non-aqueous phase liquid to the water phase, and to promote degradation of exposed substituents. The purpose of soil remediation is not only to enhance the degradation, transformation, or detoxification of pollutants, but also to protect the quality and capacity of the soil to function within ecosystem boundaries, to maintain environmental quality and sustain biological productivity.

It is difficult to evaluate this market with any specificity, but the international market for remediation is estimated to be around US \$25–30 billion. It is challenging to establish such estimates, as many countries have not undertaken comprehensive identification of contaminated sites. Remediation markets usually develop after a country has considered and addressed its air, water and waste management priorities. The US, Canada, Western Europe, Japan and Australia are considered to be the dominant international markets for remediation, with an established presence of a large number of environmental companies, products and services. Emerging economies of some more developed Asian, Eastern European and Latin American countries will represent significant medium-term remedial market opportunities.

Soil remediation processes may be implemented using a variety of different engineered configurations applicable in situ, at the surface or subsurface, and to the excavated soils. Biological remediation technologies require knowledge of interdisciplinary sciences, involving microbiology, chemistry, hydrogeology, engineering, soil and plant sciences, geology and ecology. Biological processes are typically implemented at a relatively low cost, and biological remediation methods have been successfully used to treat polluted soils, oily sludges, and groundwater contaminated by petroleum hydrocarbons, solvents, pesticides and other chemicals.

This volume, “Advances in Applied Bioremediation”, of the series Soil Biology is a selection of topics related to biological processes, with an emphasis on their use in remediation of soil pollutants. Topics include an overview of the global soil remediation market and available biotechnology solutions, the bioavailability of contaminants in soil, the role of biosurfactants in bioremediation, metabolism of nitroaromatics, bioremediation of explosive- contaminated soils, biodegradation of petroleum hydrocarbons, bioremediation of benzene-contaminated aquifers, microbial remediation of metals in soil, biotransformation of toxic metals and metalloids, biomining microorganisms and phytoremediation technologies, application of bacterial soluble di-iron monooxygenases and fungal enzymes, and advanced molecular tools for monitoring biological processes in soil remediation.

Experts in the area of environmental microbiology, biotechnology and bioremediation, from diverse institutions worldwide have contributed to this book. This book should prove to be useful to students, teachers and consulting professionals in the disciplines of biotechnology, microbiology, biochemistry, molecular biology, and soil and environmental sciences.

We gratefully acknowledge the cooperation and support of all the contributing authors, and the valuable advice and encouragement provided by Ajit Varma and Jutta Lindenborn throughout the preparation of this volume.

Canada  
Canada  
India  
February 2009

Ajay Singh  
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# Chapter 1

## Biological Remediation of Soil: An Overview of Global Market and Available Technologies

Ajay Singh, Ramesh C. Kuhad, and Owen P. Ward

### 1.1 Introduction

Due to a wide range of industrial and agricultural activities, a high number of chemical contaminants is released into the environment, causing a significant concern regarding potential toxicity, carcinogenicity, and potential for bioaccumulation in living systems of various chemicals in soil. Although microbial activity in soil accounts for most of the degradation of organic contaminants, chemical and physical mechanisms can also provide significant transformation pathways for these compounds. The specific remediation processes that have been applied to clean up contaminated sites include natural attenuation, landfarming, biopiling or composting, contained slurry bioreactor, bioventing, soil vapor extraction, thermal desorption, incineration, soil washing and land filling (USEPA 2004).

Biological remediation using microorganisms and plants is generally considered a safe and less expensive method for the removal of hazardous contaminants. The microorganisms have the primary catalytic role in degrading or mineralizing various contaminants and converting non-toxic by-products during soil bioremediation processes (Seshadri and Heidelberg 2005; Head et al. 2006; Gomez et al. 2007). Plants have an inherent ability to detoxify some xenobiotics in soil by direct uptake of the contaminants, followed by subsequent transformation using enzymes similar to detoxification enzymes in mammals, transport and product accumulation (Macek et al. 2008). Phytoremediation, with the associated role of rhizospheric microorganisms, is therefore an important tool in bioremediation processes. Various bioremediation configurations as options for treatment of different classes of chemicals have been evaluated (Hughes et al. 2000). Natural attenuation and electron

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donor delivery were considered as options for remediation of chlorinated solvents, biostimulation for treatment of chlorinated solvents and phenols, bioventing for polycyclic aromatic carbons (PAHs); landfarming or composting were options for nitroaromatics, phenols, monoaromatic hydrocarbon and PAHs (Prince 1998; Mishra et al. 2001). Slurry bioreactor processes were considered suitable for treatment of all of the above mentioned chemicals. Optimizing the environmental conditions in bioremediation processes ensures that the physiological and biochemical activities are directed towards biodegradation of the target contaminants. Environmental factors influencing biological activity include moisture, temperature, pH, oxygen, soil type and chemical nature of contaminant for aerobic degradation and redox potential for anaerobic degradation (Van Hamme et al. 2003).

Bioremediation of some recalcitrant xenobiotic chemicals may require a combination of chemical, physical and biological steps to increase the efficacy of contaminant destruction. Risk assessment is an emerging multi-disciplinary scientific practice used to evaluate health and ecological risks posed by chemical contaminants. Such evaluation helps in devising risk-based management plans to achieve target risk reduction. However, to develop a cost-effective remedial action plan, there is a need to introduce a systematic and scientifically sound methodology to assess the associated risks at a site and identify appropriate remediation technologies.

## 1.2 Global Remediation Market

In 2001, the global environmental market, including hazardous waste management and disposal, approaches to brownfield redevelopment and site remediation was reported to be of the order of \$1 trillion (Masons Water Yearbook 2000–2001). Based on current literature, the international market for the remediation sector is estimated to be in the range US\$30–35 billion. The application of bioremediation and phytoremediation cleanup technologies is rapidly expanding and according to an estimate, worldwide demand for these biological technologies is thought to be valued in the region of \$1.5 billion per annum. The soil remediation sector has a ready market in countries such as the US, Canada, Western European countries, Japan and Australia. More developed Eastern European, Latin American and Asian countries represent emerging markets for the remediation sector. Understandably, it is not as easy to quantify the value of these emerging remediation markets, especially since comprehensive catalogues of contaminated sites in these countries have not been established. Remediation markets usually develop after a country has dealt with air, water and waste management priorities. The US is possibly the only country that has undergone such an extensive assessment of contamination for federal sites which contributes to solid market evaluation data. As a result, market figures for many jurisdictions are variable, limited and/or inexact.

Nevertheless, the global remediation business is undergoing a process of change and is exhibiting indications of attaining a state of market maturity. Many contaminated sites are in the post-remedial action phase, and have benefited from better and more



reliable technology and the availability of greater process performance information. Many other contaminated sites have been characterized as essentially ready for implementation of a preferred remediation process. Clearly, many other contaminated sites have yet to be formally identified, declared or characterized. There has also been a shift in the general factor(s) motivating remedial action. Up to the mid-1990s, implementation of cleanup of contaminated properties was driven by regulatory compliances, and guided by clean-up end points or residual limits which bore little relationship to the proposed use of the remediated land. More recently, great attention has been placed on relating remedial action to the intended use of the property, as well as remediation economics and risk assessment. Analysis of international environmental markets in the following subsections clearly shows that substantial growth will occur over the next decade in markets throughout the world. The discussion on marketing potential is assembled mainly from data cited by CTCS (2002), The Delphi group (2003), AEGIS (2003), USEPA (2004), Statistics Canada (2004), EcoLog Group (2005), JETRO (2007) and Industry Canada (2008).

### ***1.2.1 North America***

The current estimated hazardous remediation market in the United States is pegged at around \$12 billion, which represents about 30% of global demand. Based on currently applicable regulatory standards in the United States, an estimated quarter of a million sites require some form of remediation, but the number of contaminated sites is larger than that if all brownfield sites are taken into account (see below). Most of these sites have one or combinations of the most common contaminants – solvents, petroleum products, VOCs and heavy metals, the nature and concentrations of which will influence technology choice. These contaminated sites can be divided into seven groups depending on which government agency/regulations have enforcement and/or decontamination responsibility: Superfund, Resource Conservation and Recovery Act (RCRA) Corrective Action, Underground Storage Tanks (UST), Department of Defense (DOD), Department of Energy (DOE), Civilian Federal Agencies, and States (USEPA 2004). The majority of these sites requires the collaboration of multiple stakeholders for successful cleanup, as well as the development and implementation of innovative remedial solutions. The United States Environmental Protection Agency (USEPA) enforcement of the Superfund program is still encouraging remediation by potentially responsible parties at the majority of highly contaminated sites. This is evident based on USEPA's precedent-setting order requiring General Electric to pay nearly half a billion dollars for the cleanup of polychlorinated biphenyls (PCBs) in the Hudson River.

EPA estimates that up to \$100 billion will be spent during the next 30 years to meet new underground storage tank regulations. The USEPA brownfield development program promotes the remediation and redevelopment of industrial sites by enhancing the acceptance of cleanups based on the concept of risk-based standards and restricted future land use. The USEPA estimates that over half a million brownfield

sites exist across the United States. The brownfield market continues to be an area of growth for many remediation firms because of the opportunities to partner with property owners and developers.

The Canadian environment industry has annual sales of over \$20 billion, and contributes 2.2% to Canada's GDP. Remediation is considered a part of the solid and hazardous waste management sector, comprising the second largest component (24%) of Canada's environment industry. Based on provincial programs such as Environment Canada's Green Plan, rising awareness of the need to clean-up public lands, and the expected positive image gained from establishing/enforcing regulations which mirror those of the USEPA, the Canadian market is expected to reach \$1 billion for soil and groundwater remediation. Current Canadian demand for soil remediation services and products is estimated at \$250–500 million. There are positive signs for further growth in Canada given the government's commitments for the next ten years of \$3.5 billion for remediation of federally owned contaminated sites, \$500 million for specific contaminated sites of concern across Canada for which it has shared responsibility, e.g., the Sydney Tar Ponds, and a budget of \$150 million for redevelopment of municipal brownfields under the management of the Federation of Canadian Municipalities.

Canada has an estimated 30,000 contaminated sites, and approximately two-thirds of these sites can be economically cleaned up and redeveloped. Nevertheless, there is still great uncertainty with regard to the extent and number of contaminated sites in Canada. There is also no national legislation on contaminated land to coordinate approaches between provincial and territorial jurisdictions and create common approaches and standards. Awareness of the problem of contaminated sites is growing in Canada, as is effort to address them. According to Statistics Canada, Canadian revenues from the international environment market are in excess of \$1.6 billion for exports of solid and hazardous waste management services. For large Canadian environmental consulting and engineering firms involved in remediation, approximately 10–30% of their business can come from export markets.

### ***1.2.2 Europe***

Although technologies for soil and groundwater remediation are at an advanced stage in Europe, the European Commission (EC) has recognized a need for strengthening innovation of environmental technologies in order to increase competitiveness in a global market and to achieve a more sustainable development. The European Co-ordination Action for Demonstration of Efficient Soil and Groundwater Remediation (EURODEMO), an EC-funded initiative, has been launched to promote investigations and application for innovative technologies for supporting these goals. EURODEMO is expected to bring together formerly isolated national-scale knowledge to build a greater confidence in remediation technologies while providing a platform for innovation potential (Spira et al. 2006).

Western Europe's estimated overall environmental market is around US\$227 billion. Highest growth rates are forecast in areas such as waste management,

environmental consultancy, cleaner technologies and renewable energy sub-sectors. The number of contaminated sites in the Western Europe is estimated to be over 600,000, the remediation of which will cost an estimated €50 billion, over an extended clean-up duration. Potentially 0.5–1.5% of GDP is likely to be spent per annum to clean up the contaminated sites. Among the Western European countries, the United Kingdom (UK), France and the low-lying Netherlands have spent the most money to date for remediation. The UK environmental market is forecast to grow to £21 billion by 2010. Key contaminants are typical of other industrialized countries and include hydrocarbons, pesticides, radio-nuclides, localized contamination from abandoned industrial plants/land, past industrial spills or improper municipal and industrial waste management.

Environmental business opportunities in jurisdictions tend to parallel economic growth and prosperity and in the period 2000–2010, Central and Eastern Europe (CEE) is experiencing substantial economic development. Substantial investments opportunities are associated with waste management, water and wastewater treatment and contaminated land remediation. Overall, the environmental markets in CEE are forecast at US\$15 billion by 2010 at a growth rate of 6.6%. Thus, the countries which have experienced the more successful economic transformations, for example the Czech Republic, Slovakia, Hungary, Poland and Slovenia, have likewise exhibited faster rates of environmental market growth than other Eastern European countries.

### ***1.2.3 Australia and New Zealand***

Regulatory and environmental policies are relatively well developed in Australia and New Zealand, and trends similar to European markets are emerging – including the need to improve resource use efficiency, minimize waste and reduce greenhouse gas emissions. The economies have performed well over the last few years, with a growth rate around 3% per annum. This growth is reflected in environmental market forecasts which are projected to be around US\$13 billion in 2010 in the larger sectors of water and wastewater treatment, waste management and air pollution control. Higher growth is forecast in sectors such as water re-use technologies, environmental monitoring, renewable energy, energy management, cleaner technologies and environmental consulting over the next 10 years.

### ***1.2.4 Asia***

In Asia there has been high market demand for site assessment/soil testing services and for treatment technologies for oil decontamination, PCB destruction, bioremediation, and especially for in-situ technologies that permit the surface structure to remain intact, hazardous wastes from dry cleaners and gas filling stations.

The Japanese environmental market is relatively well developed and mature in areas such as water and wastewater treatment, waste management and air pollution

control. Overall, the environmental market is growing at around 2% per annum to an estimated US\$113 billion by 2010. In Japan, the number of contaminated sites is estimated to be over 500,000. The Japanese remediation market is expected to grow to \$3 billion by 2010. Site remediation and groundwater treatment are expected to grow substantially.

Over the past 30 years and dominated by their rich petrochemical resources and associated revenues, the Middle Eastern countries have experienced unprecedented economic growth. Traditionally, this region's health and environmental standards have substantially lagged behind those of North American and European jurisdictions. However, environmental pressures from the latter jurisdictions which import and consume large volumes of Middle Eastern oil are growing, based both on motivations related to achieving global environmental sustainability and also to ensure a level playing field with respect to competition among industries located in different jurisdictions, so that poor environmental practice does not afford a competitive advantage. The overall environmental markets in the region are forecast to approach US\$8 billion in 2010, representing annual growth of greater than 4%. Significant developments in environmental regulations and cultural attitudes towards the environment are needed in order to achieve this growth.

East and South East Asian countries such as Malaysia, Indonesia, Singapore, the Philippines, Thailand, South Korea, Taiwan and Hong Kong require major investments in environmental infrastructure in order to alleviate significant public health impacts of pollution. Environmental markets in the East and South East Asia region are forecast to reach US\$27 billion in 2010.

Perhaps the greatest environmental impact derives from human population growth and human population density and associated economic development. In this regard, the greatest environmental impact may be expected from the two countries with the largest populations; China with a population of about 1.25 billion, and India with a population exceeding 1 billion and expected to surpass that of China by 2050. Furthermore, these two countries are currently experiencing extraordinary annual economic growth rates (8–10%) through rapid industrialization. Both these economies will surpass the US as leading world economies within the next few years. As elsewhere, environmental market growth in these countries is driven by the growing environmental impacts associated with economic growth, rapid industrialization and indeed intensive agricultural practices, including widespread use of inorganic fertilizers and pesticides. Environmental challenges are exacerbated by the existence of very large urban populations and associated high levels of urban pollution. There is a limited infrastructure for mitigating the negative environmental impacts, which in turn leads to serious impacts on human and animal health and raises concerns regarding long-term environmental sustainability. The true potential size of the environmental sectors in these countries is not known.

The current environmental market in India is valued at approximately US\$4 billion. China's environmental market approximately doubled from US\$3 to 6 billion from 1995 to 2000, and is expected to double again by 2010, representing an annual growth of over 8%. In terms of size, the market is dominated by water and wastewater treatment, followed by waste management, site remediation and air pollution control.

### ***1.2.5 Latin America and Africa***

Overall, the environmental market in Latin America is forecast to grow from approximately US\$9.7 billion in 2000 to US\$15 billion by 2010, representing an annual growth of around 4.5%. The bulk of the market activity will relate to water and wastewater treatment and waste management activities, and related sectors such as environmental instrumentation and environmental consultancy. Sectors such as contaminated land remediation and marine pollution control are, at present, lower priorities, but opportunities in these fields are anticipated to emerge in the next 5 years plus. Although enforcement of environmental regulations is still limited, other market drivers are strong — notably the need to address the health impacts of environmental pollution, and increases in international donor aid for environmental improvement in the less developed countries.

Environmental degradation is one of the major factors constraining economic development in North and Sub-Saharan Africa. Substantial investments are required in basic water and waste management infrastructures — for example, an estimated US\$80 billion to US\$100 billion is needed just in basic water services in the next 10 years. International aid programs will help to provide a proportion of the funding requirements. Much of the environmental investment throughout Africa over the next decade will involve relatively ‘low tech’ equipment to address environmental problems and pressing human health needs.

## **1.3 Major Environmental Contaminants of Concern**

The huge expansion of the chemical and petroleum industries in the twentieth century has resulted in the generation of a vast array of chemical products for daily use. According to an estimate, there are somewhere between 8 and 16 million molecular species of natural or man-made organic compounds present in the biosphere, of which as many as 40,000 are pre-dominant in our daily lives (Hou et al. 2003).

Since soil and groundwater are preferred sinks for complex contamination, various chemical and biological soil properties are profoundly altered, which affects biodiversity and soil function. The organic contaminants include the alkanes, monoaromatics, monocyclic and polycyclic aromatic compounds, chlorinated hydrocarbons, including the polychlorinated biphenyls, nitroaromatics and nitrogen heterocycles. Often the organic contaminants are present as complex mixtures of different chemical species, as are present in petroleum on sites including petroleum refineries, petrochemical plants, gas stations, leaking storage tanks, and exploration and production well-heads. Halogenated chemicals are potentially found in chemical manufacturing plants or disposal areas, pesticide/herbicide mixing areas, contaminated marine sediments, firefighting training areas, vehicle maintenance areas, landfills and burial pits, and oxidation ponds/lagoons. Explosive contaminants such as TNT, DNT, RDX and other nitroaromatics may be found on sites like artillery/impact areas, contaminated marine sediments, disposal wells, landfills, burial pits, and TNT washout lagoons.

Sites contaminated by heavy metal include battery disposal areas, burn pits, chemical disposal areas, contaminated marine sediments, electroplating/metal finishing shops, and firefighting training areas, as well as landfills and burial pits. Excessive levels of inorganic fertilizer-related chemicals introduced into soil, such as ammonia, nitrates, phosphates, and phosphonates, which accumulate there or lead to contamination of water courses and air, have resulted in significant environmental deterioration. Undesired contamination of soil with radionuclides represents an additional environmental hazard to all life forms. Radioactive and mixed waste disposal areas are the major sites for radionuclide contaminants.

The return of environmentally contaminated sites to pristine conditions is quite challenging, and often not achievable (Kostelnik and Clark 2008). Currently available remediation techniques do not completely eliminate hazardous waste, but rather only concentrate and contain the contaminants of concern (Table 1.1). Since most of the remedial decisions concerning these complex challenges often focus on mitigation actions to reduce risk to human health and the environment, the problem frequently remains with the residual waste at many sites even after regulatory-approved

**Table 1.1** Soil remediation technologies

Soil remediation processes	Specific technologies	Comments
Biological processes	Landfarming	Involves excavation of soil and by placing on lined landfarms, and stimulation of natural microbial population by providing nutrients, water, bulking agents and tilling
	Ex situ bioremediation	
	Biopile, biocells, bioheaps Biomounds, compost cells Ex situ bioremediation	Involves excavation of soil and placing in heaps or aerated piles, and stimulating microbial activity by providing nutrients, water and oxygen
	Slurry bioreactor	Involves excavation of soil and treatment in a contained environment such as tanks/reactors
	Ex situ bioremediation	by providing oxygen, water and nutrients under controlled conditions for accelerated biodegradation
	Bioleaching	Clean up of heavy metal contaminated soil using acidophilic bacteria that oxidize reduced sulfur compounds to sulfuric acid. Performed either in slurry or by heap leaching system
	Enhanced bioremediation In situ bioremediation	Achieved by creating a favorable environment to stimulate the natural or inoculated population of microorganisms. Biodegradation rate is influenced by biostimulation, bioaugmentation or cometabolism
	Bioventing In situ bioremediation	Involves injection of air or water to supply oxygen and nutrients into the underground contaminated mass
	Biosparging	Addition of air/oxygen and nutrients to enhance biodegradation of groundwater contaminants. Also potentially improves biodegradation in the unsaturated zone

(continued)

**Table 1.1** (continued)

Soil remediation processes	Specific technologies	Comments
	Anaerobic biodegradation	Anaerobic degradation of polychlorinated organic pollutants in sediments. Generally followed by an aerobic process for further dechlorination of the pollutants
	Phytoremediation	Higher plants are used either to degrade contaminants, to fix them in the ground, to accumulate them within plant tissue or to release them to the atmosphere
	Monitored natural attenuation	A strategy of allowing natural processes to reduce contaminant concentrations over time, involving physical, chemical and biological processes with continuous monitoring
Chemical processes	Oxidizing agents (oxygen, ozone, UV, H <sub>2</sub> O <sub>2</sub> , chlorine gas, etc.); reduction agents (Al, Na and Zn metals, alkaline polyethylene glycols, etc.)	Oxidation and reduction processes can treat a range of contaminants including organic compounds and heavy metals
	Dechlorination	Reduction reagents remove chlorine atoms from hazardous chlorinated molecules (PCBs, pesticides)
	Chemical extraction with inorganic acids (HCl, H <sub>2</sub> SO <sub>4</sub> , HNO <sub>3</sub> ), organic acids (acetic, tartaric, citric), chelating compounds (EDTA, DTPA, NTA)	Inorganic and organic acids are used to decrease the pH of contaminated soil to release the heavy metals; chelating compounds are used to form water-soluble metal-ion complexes
	Solvent extraction using organic solvents	An organic solvent that has a high solubility for the pollutants is intensively mixed with the soil. The solvent is recovered and reused and pollutant is concentrated
	Solidification/stabilization agents such as Portland cement, fly ash, silicates, lime, clays, and polymers	Achieved by solidifying contaminated soil, converting contaminants into a less mobile chemical form and/or by binding them within an insoluble matrix to reduce leaching
	Asphalt batching	An alternative stabilization/solidification method treats hydrocarbon-contaminated soils by incorporating petroleum-contaminated soils into hot asphalt mixtures as a partial substitute for stone aggregate and utilizing the mixture for paving
Physical processes	Soil washing	Uses water or surfactant solution and mechanical processes to scrub soils
	Soil flushing	Achieved by flooding contaminated soils with an extraction fluid that moves the contaminants to a particular area. Generally used in conjunction with activated carbon, biodegradation, or pump-and-treat

(continued)

**Table 1.1** (continued)

Soil remediation processes	Specific technologies	Comments
	Soil vapor extraction	Removes gases and organic volatile or semi-volatile contaminants from soil atmosphere by vacuum pumping; also stimulates bioremediation process in the unsaturated zone
	Electrokinetic remediation	An in situ process induced by electrolysis, electroosmosis and electrophoresis through an array of electrodes embedded in the soil to move contaminants in the pore water towards the electrodes
	Wet classification	Two steps involve an intensive mixing of sediment to disintegrate agglomerates of sediment particles, and a mechanical separation step
	Encapsulation	Physical isolation and containment of the contaminated soils by low permeability caps, slurry walls, grout curtains, or cutoff walls
Thermal processes	Thermal desorption	Heating to 600 °C results in evaporation of volatile contaminants and subsequent removal from the exhaust gases by condensation, scrubbing, filtration or destruction
	Incineration	Involves heating of excavated soil to temperatures of 880–1,200°C to destroy or detoxify contaminants
	Vitrification	Heating of excavated soil to temperature range of 1,000–1,700°C resulting in vitrification of the soil, forming a monolithic solid glassy product
	Wet oxidation	The oxidation process occurs in the water phase at high temperatures and high pressures, but below the supercritical temperature and pressure of water
	Supercritical oxidation	Temperature and pressure above the critical point of water result in higher solubility of oxygen and toxic organic compounds in the water phase, and a higher oxidation rate

environmental remediation operations are complete. Chapter 2 in this volume provides a discussion on the holistic environmental merit of soil remediation to complement risk assessment, using two assessment software models, and tips and tools on how to improve remediation.

## 1.4 Biological Remediation of Contaminated Soils

The utilization of naturally occurring prokaryotic organisms in soil (around 4,600 distinct genomes in one gram of soil) for detoxifying and rehabilitating polluted soils provides an effective, economical, versatile and eco-compatible means of



reclaiming polluted land (Hunter-Cevera 1998; Van Hamme et al. 2003). Soil microbial communities are relatively evenly distributed in unpolluted environments. The general assumption stands that higher microbial diversity is proportional to an increased catabolic potential. This can be extrapolated to imply that high species diversity leads to more effective removal of metabolites and pollutants from a substrate. In the soil, microorganisms may develop various mechanisms to access sorbed compounds on soil particles and sediments, as well as to utilize water-insoluble pollutants by facilitating a new equilibrium state, creating concentration gradients, bringing about micro-environmental pH shifts, secreting extracellular enzymes, producing surfactants, emulsifiers, solvents, and chelators to partition chemicals from the non-aqueous phase liquid to the water phase, and degrading exposed substituents (Van Hamme et al 2006; Singh et al. 2007). Chapter 3 provides a detailed discussion on geochemical conditions, coupled biodegradation–sorption models, correlations between bio-resistant and desorption-resistant fractions of contaminant, and facilitated bioavailability. Chapter 4 outlines biosurfactant chemical characterization, physiological roles, applications in bioremediation, and both in situ and ex situ biosurfactant production.

Use of plants for transfer, accumulation and removal of pollutants from the environment is called phytoremediation. The approach can be used for removal of both inorganic and organic xenobiotics and pollutants present in the soil, water and air. The type of contaminants range from inorganic fertilizers to pesticides, from heavy metals and trace or radioactive elements to explosives, oil spills to PAHs and PCBs.

Biological remediation technology for restoration of a polluted site may be utilized in situ or ex situ. In situ treatment allows soil to be treated without being excavated and transported, but it requires longer time periods and extensive monitoring due to variability in soil and aquifer characteristics. Examples of in situ treatment methods are enhanced microbial bioremediation, bioventing and phytoremediation. Ex situ treatment generally requires shorter time periods with better process implementation and monitoring controls but requires excavation of soils, leading to increased engineering cost. Landfarming, biopiling, composting and slurry bioreactors are examples of ex situ technologies.

### ***1.4.1 In Situ Biological Remediation***

Enhanced microbial bioremediation is achieved by creating a favorable environment to stimulate the natural or inoculated population of microorganisms and exploit their catabolic potential to grow and consume the contaminants as a food and energy source. Among the most important of the enzymes used by bacteria in degradation of organic compounds are oxygenases. Recent advances in understanding of the diversity, distribution and physiology of monooxygenases are discussed in Chapter 5. Biodegradation or biotransformation rate is influenced by the type and concentration of specific contaminant present, oxygen supply, moisture, temperature, pH, nutrient supply or biostimulation, bioaugmentation with strains containing desired catabolic properties, and cometabolism (de Lorenzo 2006; Borden and Rodriguez 2006).