Chapter 1
Principles of Phytoremediation

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Abstract Phytoremediation, a form of bioremediation, is one viable option for removing pollution from contaminated soil and water. Bioremediation was developed as an inexpensive, environmentally friendly, and sustainable alternative to traditional chemical and physical pollution remediation methods. Bioremediation began with the use of bacteria and later other microorganisms, to extract or degrade inorganic and organic contaminants in soil and water in situ. It then evolved to other applications in combination with traditional chemical and physical remediation methods. Phytoremediation was came about from basic research studies on the physiology of halophytic and hyperaccumulating plants. At first, plants provided successful for extracting salts, metals, and radionuclides from soil and water. Further, studies discovered that plant roots and the rhizosphere were capable of extracting or degrading organic pollutants such as pesticides and petrochemicals. The in situ case studies showcased in this book demonstrate how phytoremediation is a sustainable means of pollution remediation in economically emerging countries and is consistent with the United Nations Sustainable Development Goals.

Keywords Bioremediation · Environmental pollution · Phytoremediation · Phytotechnology · Traditional remediation

1.1 Introduction

Phytoremediation is a means of applying the plant sciences to the better of human living conditions. It makes use of plant physiology and rhizosphere organisms as inexpensive and reliable approaches to removing some of the most hazardous or persist pollutants in regions with few financial resources available for pollution remediation in soils or waterways (Schwitzguébel et al. 2011). Some of these applications can be adapted to remediating airborne pollutants (Argawal et al. 2019). Phytoremediation is not a fad and it is most applicable when costly pollution remediation methods

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and technologies are not available (Bandari 2018). This view is supported by early efforts to accelerate the technology transfer of phytoremediation research (Boyajian and Carreira 1997; Salt et al. 1998). Aside from remediating customary pollution sites, phytoremediation has gained the interest of groups and governments evaluating community-based phytoremediation in grassroots efforts to remediate contaminants in community gardens, densely populated slums, farmlands, municipal parks, rural communities, and small towns (Smith 2015).

1.1.1 Origins of Phytoremediation

Humans and plants have coevolved since the hominid lineage branched from its Australopithecus ancestors (Martin and Li 2017). As societies progressed, people learned that a methodical understanding of plants was essential for their survival of people starting in Neolithic times, about 3000 BCE. This ancient knowledge, or protobotany, allowed people to use plants for food, medicines, and the construction of homes and tools (Day 2019). Archeological studies provide no doubts that ancient people made rational decisions about food plants that were applicable for cultivation and long-term subsistence. The use of plants for other purposes varied based on environment and culture. Plants used for building structures and burning were often selected based on the climate and the available of plants in a particular location (Garrison 1998). Medicinal uses of plants did not start out as a scientific pursuit and were primarily based on anecdotal evidence, non-controlled quasi-experimental, or cultural beliefs (Petrovska 2012).

The modern field of scientific botany, or plant sciences, was first published on papyrus documents around 400 BCE in Greece. During that period, Aristotle and Theophrastus developed a systematic characterize plants. Similar efforts on plant classification were recorded in China around 60 CE (Hardy and Totelin 2015). It is generally accepted in the European literature that Carolus Clusius heralded in modern botany around the 1500s CE. Clusius' work paved the way for a host of studies on plant anatomy, physiology, and reproduction carried out in Europe in the 1600s and 1700s CE based on microscopic studies and simple chemical analysis experiments (Egmond 2010). The 1800s CE was noted advances in plant diseases and inheritance. The advent of molecular biology brought forth more advances in botany including precise plant physiology investigations, genomics studies, and genetic modification (Iriti 2013). During this period, a rapid growth of biotechnology applications and innovations was developed leading to the first attempt at phytoremediation in 1983 by hyperaccumulating plants (Hakeem 2014).

Phytoremediation is a specific category bioremediation that makes use of metabolic processes in plants and in the rhizosphere to remove polluting substances from the environment (DeLorenzo 2018). Initially, bioremediation was developed as an alternative to traditional chemical and physical methods of remediating pollution contaminating soils and water, such as chemical neutralization or bulk soil removal (Conesa et al. 2012). Later, bioremediation efforts were adapted to removing air pollution (Devinny et al. 2017). Anthropogenic environmental contamination is an expected outcome of human activities in any type of societal survival strategy. Hunter-gatherer societies typically avoiding the buildup of pollution by migrating away from contaminated sites. The simplest forms of pollution, food waste, and human excrement became problematic for people during the first confirmed human urban settlements established by (Hershkovitz et al. 2018). This was determined by evidence of rodent infestation remains plaguing second millennium BCE archeological sites in the Near East (Weissbrod et al. 2014).

1.1.2 History of Pollution Remediation

Pollution mitigation in human population centers was first developed around 800 BCE by the Romans. This was evident in the aqueduct systems and excrement collection procedures that involving transporting the pollutants from the population centers for dilution in waterways or dispersal on agricultural lands (Markham 1994). Municipal waste pollution was less of a problem in ancient times and was typically buried or burned very much as it done today in many regions. Globally, other pollutants associated with early crafting, manufacturing, mining, smelting, and tooling were not considered hazardous and accumulated in the environment often with harmful effects on the environment and on human population (Zalasiewicz et al. 2010).

Environmental decay due to anthropogenic activity was likely recognized by ancient civilizations, but there was not much that could be done at the time to remediate any problems. Unfortunately, like in many regions of the world today, pollution was tolerated as a requisite consequence of commerce and settlement lifestyles. Pollution started becoming a grave problem around 1000 CE with the birth of the coal-burning era and expansion of mining operations. Societies in the medieval period saw worsening pollution which led to public concerns and calls for political action. It was not until the 1600s CE when Europe showed the first records of pollution control methods that typically involved pollution fines and the development of early technologies for pollution remediation such as sewage septic systems in the middle 1800s CE (Hughes 2016). The amount of pollution produced globally started increasing dramatically since the early 1900s CE; any efforts for pollution control focused on various strategies to contain or reduce pollution.

Almost all of the modern strategies for reducing pollution were expensive and involved either penalties, transport to specialized landfills, or manufacturing practices that reduced or recycled wastes. Prosperous industrialized nations benefited from these practices which were unfeasible to practice in emerging nations. It was not until the 1980s CE that pollution remediation became a concern primarily in the USA with the development of the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA), or Superfund (Beins and Lester 2015). The strategies needed to carry out environmental remediation as proposed in CERCLA were even more costly than pollution prevention and pollutant storage (Markham 1994). Again, countries with emerging did not have the economies to model remediation efforts in the USA and similar programs in Europe. By the 2000s CE, prosperous industrialized nations were seeing great improvements in environmental quality while pollution in countries with emerging economies was worsening remaining a persistent problem (Fig. 1.1).

A factor exacerbating pollution in countries with emerging economies is the pollution haven hypothesis. The pollution haven hypothesis is global economy observation in which differences in environmental regulations will cause the inter-country relocation of dirty industries to countries that are already heavily impacted by protracted pollution problems (Xiang et al. 2018). Potential pollution haven regions that have been identified are Central East European Countries (Martínez-Zarzcoso et al. 2016), Southern Africa (Nahman and Antrobus 2005), Asia (Shaprio 2013), and Latin America (Birdsall and Wheeler 1993; Sapkota and Bastola 2017). The susceptibility of a country or region becoming a pollution haven is calculated using the Kuznets curve which is a correlation between environmental quality and economic development (Fig. 1.2). In certain situations, indicators can predict that pollution gets worse as the modernization of a country's economy increases. This trend continues until the average income reaches a certain level as development progresses (Kaika and Zervas

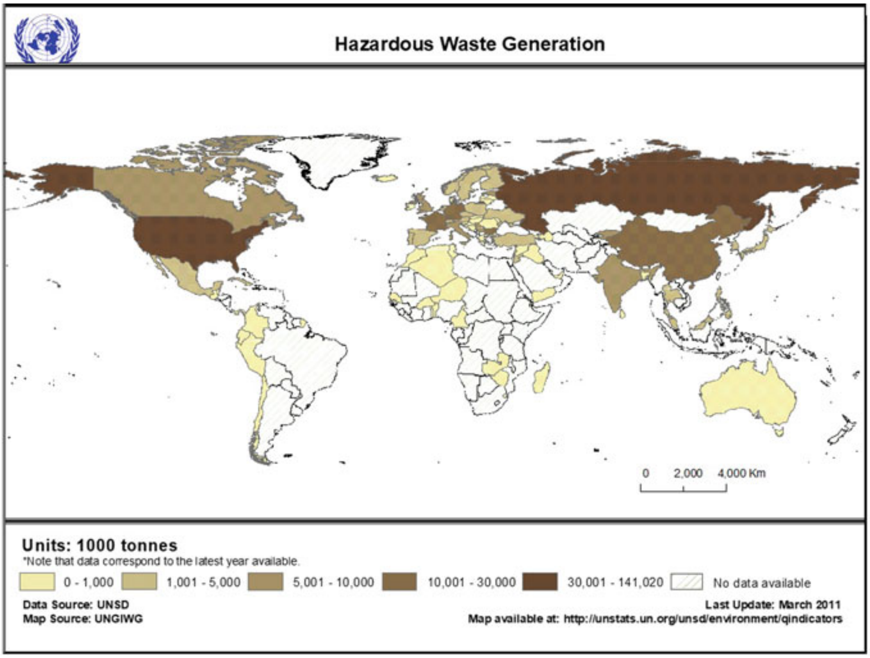

Fig. 1.1 Hazardous waste production is not equally distributed worldwide. Many of the nation that produce the wastes lack the resources to reduce, store, and remediate hazardous waste pollution. Image courtesy of the United Nations Statistics Division

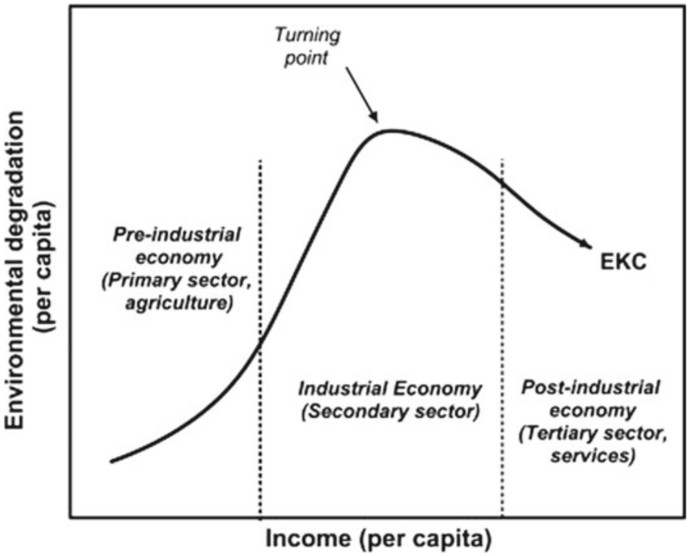

Fig. 1.2 The Kuznets curve helps predict the susceptibility of a region to being a pollution haven. Image from Kaika and Zervas (2012). The environmental Kuznets curve (EKC) theory—Part A: Concept, causes, and the CO_2 emissions case. The environmental Kuznets curve (EKC) theory—Part A: Concept, causes, and the CO_2 emissions case. Energy Policy. 62:1392–1402

2012). Pollution haven regions would benefit the most from inexpensive and sustain pollution prevention and remediation efforts.

The mounting pollution problem in emerging economies was formally recognized by the United Nations Environment Program at the United Nations Conference on the Human Environment (Stockholm Conference) in June 1972 (Brisman 2011). According to Brisman, "the main purpose of the conference was to serve as a practical means to encourage and provide guidelines for action by Governments and international organizations designed to protect and improve the human environment." In 2017, the fifteenth meeting of the Chemical Review Committee of the Rotterdam Convention concluded that "the Stockholm Convention provides an effective and dynamic framework to regulate POPs throughout their lifecycle, addressing the production, use, import, export, releases, and disposal of these chemicals worldwide. However, inadequate implementation is a key issue that has been identified in the evaluation. Mechanisms and processes required by the Convention to support Parties in meeting their obligations have all been put in place, with the exception of procedures and mechanisms on compliance." The key challenge for emerging economy countries was the financial infrastructure needed to support the pollution remediation initiatives outlined by the United Nations (UN 2018). It appears that the Stockholm Conference differentially benefited countries with the means to reduce environmental pollution.

Pollution problems have been officially recognized by the United Nations as one consequence of the country's non-sustainability. In June 1992, the United Nations Conference on Environment and Development (UNCED), also known as the Rio de Janeiro Earth Summit, generated a comprehensive action plan for building global partnerships for sustainable development to improve human living conductions and protect the environment from anthropogenic activities and natural disasters (Dodds et al. 2016). The action plan is divided into seventeen sustainable development goals, three of which are directly applicable to reducing environmental pollution using sustainable methods: Goal 6—Clean Water and Sanitation, Goal 14—Life Under Water, and Goal 15—Life on Land. Goal 10, Reduce Inequalities, sets best practices for reducing economic equities that hinder access to pollution remediation and increase the likelihood of becoming a pollution haven (Gaffney 2014). In the sustainable development goals, phytoremediation is one of the recommended sustainable pollution remediation best practices, particularly for counties with emerging economies (Haller et al. 2018).

1.2 Traditional Methods of Removing Contaminants

1.2.1 Traditional Soil Remediation

As discussed earlier, soil contamination, or land pollution, is an ancient problem that has become more complex with the advent of industrialization and urbanization. Typically, soil contamination is defined as the occurrence of hazardous materials at harmful concentration levels to humans or to the environment in soils. Some contaminants, such as arsenic or sulfates, are natural pollutants. However, most remediation efforts focus on anthropogenic contaminants from a variety of sources (Mirsal 2008). The most common soil contaminants are minerals and metals, organic compounds, and xenobiotics directly and indirectly from agricultural, industrial, and municipal sources (Duarte et al. 2018). Future technologies and increasing global urbanization will be exacerbating soil pollution problems with higher levels of contaminants and emerging pollutants (Noguera-Oviedo and Aga 2016).

There are many traditional on-site, or in situ, and off-site chemical and physical soil remediation methods used today (Nyer 1998). Traditional soil remediation begins with mapping the contamination site to determine the probable extent of the contamination plume. The next step is collecting homogenized soil samples in the potential plume area. Soil sampling is typically done with non-contaminated augers, shallow sampling tubes, or deep sub-soil probes. Sampling can also be done with scoops, shovels, or spades (Couch et al. 2000). Commonly, samples are preserved and transported to chemical testing laboratories. On-site testing can also be done using portable testing laboratories. Soil pollution screening tests usually involve standard assays that characterize the pollutant and determine pollutant levels; this task varies in complexity, particularly if the area has many sources of contamination (EPA 2018;

ASTM 2019). Containment in a contaminated site is a standard procedure before any remediation can proceed (Zhang 2009).

The simplest method of soil pollution remediation is removing the soil using the physical removal method of dredging or excavation (Wang and Leonard 1976). This process involves digging up the contaminated soil and transporting it off-site for disposal or treatment. Soils with hazardous contaminants are normally disposed in either a hazardous waste landfill or hazmat holding facility. The major limitations of this method are safe and affordable storage and transportation of the contaminated soil. Studies show that this model of soil pollution remediation is not optimal or preferred for economically emerging countries due to deficiencies in hazardous materials handling technologies and safe handling practices. However, it is more economical than other traditional remediation strategies (Manap and Voulvoulis 2015).

In many situations, it is not prudent to remove and transport contaminated soil. Soil removal can spread and worsen contamination in an area. Plus, the storage or future remediation of the soil transported off-site is often costly. Solidification and stabilization is a process that encloses the pollution on-site for storage or future remediation (Scullion 2006). This process involves using some type of chelating agent to stabilize the pollutant in the soil, to reduce leaching, followed by solidification of the soil with binding agents or soil amendments that made the soil impermeable and immobile. Soil stabilization varies with the chemical characteristics of the contaminant. Chemical methods can be used to react with the pollution, typically forming precipitants or compounds that bind to the soil. Metal oxides (Komárek et al. 2013), phosphates (Hettiarachchi et al. 2000), and clays such as palygorskite (Álvarez-Ayuso and Garcıa-Sánchez 2003) are common stabilizers for heavy metal pollutants in soil. Organic pollutants, such as PCBs and pesticides, are less likely candidates for soil stabilization (Uqab et al. 2016). They are best stabilized using physical methods that absorb and trap the contaminants. Studies have used activated carbon, plant polymers, liquefied humus, and iron nanoparticles to bind and stabilize organic pollutants (Singh and Misra 2016). Current solidification agents also vary based on the soil structure and nearby geological features. Cement was the first material used for soil stabilization (Glasser 1997). Cement-free methods using clay are being tested for solidification to reduce soil compaction and reduce solidification costs (Wang et al. 2019). The greatest limitations of this method are the depth of the soil and future use of the site. Structures constructed over the site might compromise the integrity of the solidification (Stojić et al. 2018).

During thermal desorption, the contaminated soil is heated in a chamber to vaporize the soil contaminants. This can be done off-site or on-site depending on cost-effectiveness. In addition, it is effective for removing heavy metal (Sierra et al. 2016) and organic (Kastanek et al. 2016) pollutants. It has been tested with some effectiveness at removing pollutants on-site from contaminated agriculture soils proposed for further food production (O'Brien 2016). Vaporization takes place in rotary dryer or thermal screw dryer. Rotary dryers indirectly heat the soil in a rotating cylinder, while thermal screws circulate hot oil or steam directly on the soil as it passes through an auger. Thermal desorption can be achieved using low temperatures (LTTD) or high temperatures (HTTD). Organic pollutants are usually removed from soil using

LTTD; the off-gassed contaminants are collected in vapor condensation systems and are not fully degraded into nonhazardous byproducts. Heavy metals are removed with HTTD; the off-gas is collected using air pollution scrubber units that require further treatment to reduce any toxicity. There are several limitations for thermal desorption in economically emerging countries. A primary limitation is the cost of the thermal desorption unit as well as the added cost of heating the unit. Another limitation is the off-gas usually has to be treated as a hazardous material and requires further remediation (Zhou et al. 2019).

The process of in situ oxidation is a flexible chemical method of removing contaminants from soils, particularly contamination that spreads to contiguous groundwater. An off-site strategy called ex situ soil oxidation is an alternative method requiring transportation to a treatment facility (Zhang 2009). It is best used with volatile and semivolatile organic contaminants and has been used extensively on US Superfund sites (EPA 2017; Tsitonaki and Bjerg 2008). This process involves pumping oxidizing compounds into an injection well inserted into the contaminated soil. Oxidants such as hydrogen peroxide, ozone, permanganate, and persulfate are commonly used. In certain soil, iron catalysts may be needed to facilitate oxidation (EPA 2017). The site is recurrently sampled until the contaminants are degraded in situ. This method can be done in an off-site facility; the soil can be reused once the contaminants are degraded. Limitations are primarily related to the effectiveness of oxidation in different types of soils and in complex heterogeneous contamination events. Its applicability in emerging economies is promising, but still under investigation (Pac et al. 2019).

The emerging strategy of electroremediation can be used along or in combination with other remediation efforts to remove soil contaminants (Page and Page 2002). This process is most feasible in situ and uses a low-voltage direct current charge to remediate heavy metals in soils. The electrodes are inserted into slotted PVC-lined wells dug around the contaminated site. The anodes and cathodes set up an electrokinetic migration potential that attracts the heavy metals which then become immobilized in wells. The electrodes also facilitate migration of the heavy metals by producing acidic pH conditions in the contaminated soil (the US Army Environmental Center 2000). Limitations in producing an adequate electrokinetic field and a uniform soil pH in many types of soils restrict the utility of this process. Plus, the procedure is not practicable in large remediation sites likely found in countries with emerging economies (Cameselle and Reddy 2019).

Nanoremediation is the newest of the traditional soil remediation methods that use chemical or physical separation of pollutants from soil. This technology uses a variety of nanoparticles to degrade or immobilize soil contaminants. In current applications of nanoremediation, the nanoparticles are composed of zero-valent iron particles. The zero-valent iron either acts like a catalyst to facilitate contaminant degradation or alters the soil matrix to immobilize the contaminants (Machado et al. 2017). Currently, nanoparticles are used for remediating heavy metal contamination (Gil-Díaz et al. 2017). Nanoremediation has been combined with electroremediation to remove organic pollutants (Gomes et al. 2016). Its application in emerging economies is restricted for various reasons, primarily due to the cost of purchasing or synthesizing the volume of zero-valent iron nanoparticles needed for large remediation sites (Gavaskar et al. 2005).

1.2.2 Traditional Methods of Removing Water Contaminants

Water pollution is often defined as the presence of anthropogenic or naturally occurring harmful substances, primarily biological or chemical, in groundwater or surface water. As with soil pollution, the anthropogenic contamination of ground and surface water is an ancient problem that was exacerbated by the growth of human settlements during Paleolithic times (Armelagos 2009). Unlike soil pollution, water pollution can disperse rapidly and globally through the water cycle. Global industrialization greatly intensified the severity of water pollution. Particularly, harmful anthropogenic water pollutants were synthetic pesticides and plastics (Bell et al. 2019; Markham 1994). Unfortunately, water pollution control up until the 1980s CE was not adequate and reducing or remediating water pollution and remains inadequate in many countries with emerging economies (Goel 2006).

Many entities involved in water quality management characterize water pollution into the following categories: chemical, effluent, industrial specific, microbiological, and radiochemical. Chemical pollution is typically divided into inorganic and organic pollutants. The environmental impacts of chemical pollutants can alter pH, increase chemical oxygen demand, and alter salinity and toxicity. Effluent pollution is usually associated with municipal activities and is often made up of an unpredictable combination of pollutants. Industrial specific pollution would include sediment and thermal pollution (Helmer and Hespanhol 2019).

Traditional water pollution remediation strategies are often divided into two groupings: groundwater remediation and surface water remediation (Bell et al. 2019). Several of the methods used in soil remediation also apply to the removal of contaminants from groundwater. Surface water strategies are facilitated by having easier access to the pollution; however, the pollutants are difficult to contain after a contamination event.

1.2.2.1 Traditional Groundwater Remediation

Strategies for traditional groundwater remediation can be done within ex situ or in situ processes. The simplest and most common ex situ remediation method is to physically pump contaminated water out of the soil through a well and then collect the water in containers for disposal or cleanup processing. Pumping systems are relatively simple and inexpensive to operate and ideal for countries with emerging economies (Dermatas 2017). Unfortunately, there is no generalized method for pumping the water out of the soil. Pumping systems and well designs vary greatly with the site characteristics including soil type and the local of the water in the soil profile (EPA

2017). Pumping permits flexibility in that the contaminated water can be treated on-site or off-site. Ex situ treatments of groundwater use standard on-site or off-site water treatment for the storage or neutralization of liquid hazardous wastes (LaGrega et al. 2010).

In situ air sparging is a remediation technique developed for saturated soils and shallow groundwater pollution conditions. In the literature, it is also called air stripping and volatilization. Its utility has been expanded to aquifers by enhancing the technique with surfactants (Kwon et al. 2019). Organic pollutants are currently the only target contaminant that works with air sparging. Air sparging is achieved by injecting air directly into the groundwater. The air bubbles volatize the contaminants so that the pollutants can be extracted by vapor phase technologies. The process could be enhanced with chemical decomposition methods such as oxidation (Brusseau and Maier 2004). The major limitation of the process is site-specificity based on soil makeup and the degree of water saturation. Air injection wells must be designed for the particular site. Its use is promising for countries with emerging economies (Naidu 2013).

In situ remediation of groundwater can be achieved with mixed success using the solidification and stabilization processes applied to soil remediation. Studies by the EPA demonstrated that solidification and stabilization is effective for groundwater contaminated with heavy metals, radioactive materials, semivolatile organics, and nonvolatile organics. It was ineffective for volatile organics (EPA 2009). As discussed earlier, the greatest limitations of this method are the depth of the soil and future use of the site. This process of groundwater remediation is feasible in countries with emerging economies as a stopgap effect. It is not environmentally or economically sustainable for large-scale groundwater pollution (Dermatas 2017; EPA 2009).

Also, discussed earlier was in situ oxidation as an adaptable chemical method of removing pollutants from soils that also have contaminated groundwater. Specific applications of in situ oxidation have been tested on various groundwater pollution cases (Siegrist et al. 2011). As with the treatment of soils, limitations are primarily related to the effectiveness of oxidation in different types of groundwater environments and in situation with complex heterogeneous contamination of the groundwater. Its applicability in emerging economies is promising and still under investigation.

Electroremediation has also be tested as a strategy for in situ groundwater remediation. Early tests on aquifers (Shiba et al. 2000) shallow groundwater situations (Fallgren et al. 2018) were promising for inorganic and organic pollutants. The process is more sophisticated than the electroremediation of soils; however, it appears to be cost-effective for countries with emerging economies.

The feasibility of using nanoremediation on groundwater pollution is still under consideration as far as its cost and environmental safety (Bardos et al. 2018). This method is best for remediating soils contaminated with heavy metals. As discussed earlier with soil remediation, the nanoparticles used to trap or degrade pollutants are composed of zero-valent iron particles (Machado et al. 2017). This technique is effective in sites contaminated with a mixture of heavy metals that may actually be cost-effective in the future for groundwater treatment in countries with emerging economies (Liu et al. 2015).

Prevention of nonpoint and point source pollution events in surface waters definitely outweighs costs and outcomes any remediation option, particularly in countries with emerging economies. Unlike groundwater, surface water is simple and rapid to collect using wide-ranging pumping systems and highly adaptable containment booms. Unfortunately, the containment of pollutant plumes in flowing water and large non-flowing bodies of water is minimal or nonexistent and the plumes disperse as micropollutants which are difficult to recover and are subject to biomagnification (Schwarzenbach et al. 2006). Traditional methods of surface water pollution treatment vary greatly based on the environmental fluid dynamics, or water hydraulics, of the body of water (Singh and Hager 1996). Important factors for effective and sustainable surface water remediation are containment, hydrodynamics, microbial load, sediment load, and water quality (Mekala and Davidson 2015). Hydrodynamic characteristics are the major factor because it is possible to enclose the pollution lentic systems, non-flowing bodies of water, whereas in lotic systems, flowing bodies of water, there are negligible pollution containment possibilities.

1.2.2.2 Traditional Surface Waters Remediation

The simplest traditional method of remediating lotic aquatic systems, such as rivers and tidal regions, is through purification. Purification involves injecting clean water into the aquatic system to flush the pollutants downstream or into the tidal outflow while diluting the pollution plume. This process does not remover the pollutants. Rather, it dilutes the pollutants to subthreshold levels of environmental and human toxicity and facilitates natural biological, chemical, and physical degradation processes. This process can be enhanced using optimal control theory to improve water quality efficiently (Alvarez-Vázquez et al. 2009). This is an underexploited technology in many economically emerging countries. Purification can be supplemented with in situ oxidation (Andreottola and Ferrarese 2008) and nanoremediation (Rasalingam et al. 2014) with significant success at improving degradation of the pollutants with a considerable cost to the process.

In another traditional remediation process, polluted lotic water can be diverted to retention ponds or pumped into containers for on-site or off-site treatment using a variety of wastewater purification processes (Ramalho 2013) and hazardous materials neutralization or disposal methods (Wang et al. 2004). A major problem with the dilution and diversion methods is that they only reduce the pollutants from the water and do not remove pollutants in the soils of the river banks and benthic regions (Domínguez et al. 2016). Initial methods for addressing the complete contamination issue of lotic water and adjacent soils were studied in small-scale and field-scale experiments (Sheng et al. 2012).

As mentioned earlier, pollutants in lentic systems are contained systems and it is somewhat of a simpler remediation process using many of the traditional methods for cleaning flowing waters. In addition, in situ flocculation, used alone and in conjunction with other traditional remediation methods, has been shown effective in large lakes (Chen et al. 2015). As with lotic systems, pollutants in lentic systems do not remove pollutants in the soils of the littoral zone soils and benthic regions (Domínguez et al. 2016). However, there are traditional in situ, such as capping and neutralization (Zoumis et al. 2001), and ex situ, such as dredging (Cooke et al. 2005), methods of sediment remediation for lentic systems. Overall, surface water traditional remediation methods vary in their success and cost. Most of these remediation methods are not sustainable in any country and do not impart resiliency to further contamination. However, early studies showed that it is possible to combine traditional remediation with emerging strategies in the bioremediation of soils and water to improve and possibly reduce the cost of pollution mitigation (Lynch and Moffat 2005).

1.3 A Survey of Bioremediation

In contrast to the chemical and physical methods used in traditional pollution remediation, bioremediation is based on the principle that all organisms remove inorganic and organic substances from the environment to carry out their growth, metabolism, and reproduction. Bioremediation using natural, selectively bred, genetically modified organisms can be used to clean unwanted substances from air, soil, raw materials, and water for pollution management and industrial processing (Shmaefsky 1999). It is typically divided into bacterial bioremediation, mycoremediation, and phytoremediation. Protists currently play a small role in bioremediation except in applications where they facilitate the bioremediation of other organisms (Rubenstein et al. 2015).

1.3.1 History of Bioremediation

Ancient Babylonians were actually the first to make use of rudimentary bioremediation around 4000 BCE. They deposited human feces and urine into large cesspools where the sewage biologically degraded until it was diluted with freshwater and passed through hydraulic systems that fed the wastewater into waterways (George 2015). Sewage treatment remained somewhat unchanged until the 1800s CE in France and the United Kingdom with the development of the first septic system designed to biodegrade sewage into a quality of water similar to modern secondary treatment (Cotteral and Norris 1969).

The first recorded trial study on bioremediation was performed in the 1960s CE by petroleum engineer George M. Robinson. He used various mixtures of bacteria to degrade petroleum produces vitro and in holding tanks (Sonawdekar 2012). Robinson's work was supported by actual field experiments on petroleum-contaminated groundwater in the 1970s CE (Raymond et al. 1975). In the 1970s CE, Robinson commercialized his discovery and made use of various strains of Pseudomonas to clean fuel from decommissioned Queen Mary passenger ship's fuel storage tanks, clean oil residues in restaurant grease traps, remove odors from zoo animal wastes, and supplement sewage treatment. However, Robinson's major contribution was the use of Pseudomonas to remediate petroleum pollution in soils and water (Adams et al. 2015); other naturally occurring bacteria were recruited into bioremediation based on particular metabolic pathways suitable for specific pollutants. Following Pseudomonas, other commonly used bioremediation bacteria were *Alcanivorax borkumensis*, *Dechloromonas aromatic*, *Deinococcus radiodurans*, *Methylibium petroleiphilum*, and *Phanerochaete chrysosporium* (Antizar-Ladislao 2010). The arrival of genetically modified bacteria brought about the desire to produce bacteria specifically engineered for bioremediation (Kumar et al. 2013). Bacteria have proved successful in the in situ and ex situ bioremediation of inorganic and organic pollutants in soil and water and are cost-effective for countries with emerging economies.

Experiments using fungi as bioremediation organisms got its start in the 1990s CE and led to the first trials on mycoremediation. Fungi were exploited because, compared to bacteria, they showed a greater diversity of enzymes capable of degrading pollutants and xenobiotic compounds (Kulshreshtha et al. 2014). Dozens of fungi, both mycelial and yeast forms, have been tested. The most studied fungi for mycoremediation are *Agaricus*, *Bjerkandera*, *Irpex*, *Lentinula*, *Pestalotiopsis*, *Phanerochaete*, *Pleurotus*, and *Trametes*. They are equally effective to bacteria at remediating inorganic and organic pollutants. The literature shows that they are superior at colonizing various substrates in a wide variety of natural and artificial environments. However, organic substrates, such as algal polymers or wood chips, are often needed for mycoremediation of water contaminants (Harms et al. 2011; Rhodes 2014). As with bacterial bioremediation, mycoremediation appears cost-effective for countries with emerging economies.

1.3.2 Mechanisms of Bioremediation

The metabolic mechanisms of bacterial and fungal bioremediation include intrinsic enzymatic activities that degrade food sources or deactivate environmental toxins. Microorganisms can also be genetically engineered to express enzymes that alter or break down xenobiotic chemicals. A primary limitation of bacterial bioremediation is the bioavailability of enzymes that biologically convert many substances into innocuous products and byproducts (Kang 2014). To degrade the pollutant, a majority of the bioremediation microbes carry out metabolic reactions involved in aerobic metabolic pathways that use oxygen as an electron acceptor. Anaerobic bioremediation microbes use carbon dioxide, certain metals (Fe^{3+} and Mn^{4+}), nitrate, and sulfate as electron acceptors (Hatzikioseyian 2010). The role of the contaminants in nascent bioremediation applications is either an organic source of carbon dioxide or a source of electrons for the microorganisms. In a cometabolism pathway, the contaminant undergoes a process similar to detoxification. Cometabolism requires a primary food source for the microorganisms to degrade the contaminant (Frascari et al. 2015). The established methods making use of microorganisms in bioremediation include bioaugmentation, biofiltration, ex situ bioreactors, biostimulation, bioventing, composing, and landfarming (Baker and Herson 1994; Adams et al. 2015).

Bioaugmentation is the in situ or ex situ addition of bioremediation enzymes or organisms on contaminated materials. Bacteria and bacterial enzymes are most often used in bioaugmentation. It is commonly used to facilitate the remediation of wastewater and has been applied extensively in petroleum cleanup and landfill maintenance. In agriculture, bioaugmentation is used to remove excess nutrients from farm runoff. Bioaugmentation is often used in countries with emerging economies (Hernandez-Soriano 2013).

Biofiltration can be used in two different applications. One form of biofiltration is a specialized application of bioremediation used to remove organic vapors from volatile emissions. Microorganisms are embedded in a biofilter matrix that captures and traps the vapors for microbial degradation. Another form of biofiltration uses biofilters placed in holding tanks to remove contaminants from materials through the filter or trapped in the filter. Inexpensive biofiltration units have been used successfully in countries with emerging economies (Mara 2013).

Bioreactor remediation typically uses large environmentally controlled mixing tanks as a container for ex situ bioremediation. Biodegradation in bioreactors can be achieved with a mixture of microorganisms or a cocktail of specific enzymes. Bioreactors are often associated with the remediation of excavated soils, solid wastes, and pumped contaminated water. It is very simple to monitor the rate and accomplishment level of the degradation or detoxification processes (Robles-González et al. 2008). Automated bioreactors tend to be very costly, but there are designs that are inexpensive and relay on manual techniques to operate and monitor the bioremediation process. They are usually too costly to use in countries with emerging economies except in situations where the extracted contaminant has a large economic value that compensates for the cost of the unit.

Biostimulation is an economically feasible bioremediation process that uses nutrients, such as fertilizer or nutrient molecules, or substrates, such as enzyme cofactors, to stimulate the naturally occurring organisms in the contaminated site. The process is mostly done in situ, but it has also been used ex situ off-site. It is most useful in sites with low levels of contaminants. In some situations, biostimulation is encouraged adding small amounts of a related pollutant to the remediation site. Biostimulation is economically feasible for emerging economy countries in situations of low levels of contaminants (Adams et al. 2015). Bioventing is related to biostimulation. It differs in that the naturally occurring organisms in the contaminated are stimulated by oxygen vented to the contaminated site. It is used primarily in situ for contaminated soils. It is a relatively inexpensive technique, but it is not suitable for remediating halogenated gases (Lui et al. 2017).

Composting and landfarming are two inexpensive bioremediation processes that stimulate naturally occurring or supplemented bioremediation microorganisms. Compositing is typically performed ex situ and involves mixing contaminated soil or water with compose that contains bioremediation microorganism. Once the process is done, the compost can be used for soil supplementation or disposed in a sanitary landfill. Landfarming in an in situ process that using soil amendment and tilling practices to stimulate the bioremediation organisms added to contaminated soils. Both of these processes are most effective against organic pollutants at low to moderation contamination levels (Bandyopadhyay et al. 2018).

1.4 A Survey of Phytoremediation

1.4.1 Phytoremediation Defined

The focus of this chapter is the use of plants, phytoremediation, as a bioremediation agent. Phytoremediation is considered a subset of phytotechnology according to the International Phytotechnology Society. The official definition of phytoremediation is defined as "the uses plants to absorb pollutants from soils or from water." Phytotechnology is defined as "the science of using plants to solve environmental problems such as pollution, reforestation, biofuels, and landfilling" according to the International Phytotechnology Society (International Phytotechnology Society 2019).

1.4.2 History of Phytoremediation

It is generally accepted that the idea of using plants for bioremediation was formalized by Robert Richard Brooks research studies on hyperaccumulating plants in the 1960s CE (Brooks 1998). Hyperaccumulating is naturally capable of growing in soils or water with high concentrations of metals that would normally harm other plants. They can tolerate large concentrations of the metals in their tissues while exhibiting no signs of cytotoxicity. Some of these plants have specialized metal transporter proteins that facilitate the uptake of metals that are typically not transported into cells (Rascio and Navari-Izzo 2011). Brooks directly and indirectly contributed to the discovery of hundreds of hyperaccumulating plants selectively capable of up-taking and accumulating various metals as aluminum, arsenic, cadmium, cobalt, copper, chromium, lead, manganese, mercury, molybdenum, nickel, selenium, thallium, and zinc (Brooks 1998). Later, it was discovered in a host of studies that certain hyperaccumulating plants could uptake radioactive materials (Fulekar and Singh 2010).

Studies conducted in the 1990s by academic researchers and the US Environmental Protection Agency paved the way for using plants for the bioremediation of organic contaminants in soil and water. These plants were not the bioaccumulation plants used for remediating metals; rather, these plants were capable of degrading or detoxifying a variety of organic chemical pollutants in soil and water. The organic chemicals these plants could remediate included crude oil, explosives, herbicides, landfill leachates, pesticides, petrochemicals, and wastewater components (Tsao 2003).

1.4.3 Mechanisms of Phytoremediation

The mechanisms of phytoremediation include phytoextraction, phytostabilization, phytotransformation, phytovolatilization, and rhizodegradation. These physiological processes are similar to traditional chemical remediation methods and microbial bioremediation mechanisms. Plus, phytoremediation is subject to some of the constraints of other remediation methods, such as optimal concentration of the contaminants, environmental pH, and soil or sediment composition. Many phytoremediation plants have unique needs in that they may require a cometabolism relationship with microorganisms in order to carry out remediation (Hooda 2007).

Phytoextraction, as described earlier, makes use of hyperaccumulating plants that naturally uptake, translocate, accumulate, and sometimes metabolically degrade contaminants using unique carrier proteins, transporters, and enzymes. It is one of the earliest of the phytoremediation methods and is primarily effective for the remediation of metals and radioisotopes. This number of plants suitable for phytoextraction keeps growing and includes alga, ferns, and mosses (Singh and Ma 2007). Phytodesalination is a variation phytoextraction that uses halophytic plants to uptake and sequester salts from soil or water (Jlassi et al. 2013).

Phytostabilization relies on plants that have the ability to stabilize or immobilize metals in soils. It is typically used to reduce leaching of contaminants from soils and decrease soil erosion and runoff. This is achieved with root exudates that bind to soil particles, metals, and certain organic molecules. The root exudates are usually a complex mixture of amino acids, carbohydrates, enzymes, lipids, organic acids, and phenolic compounds. Sometimes, a combination of plants is used to achieve a particular composition of exudates (Hillel 2005).

Phytotransformation, also known as phytodegradation, refers to the use of plants to break down organic contaminants. The plants used in phytotransformation take up the organic materials through the roots and perform the bioremediation intracellularly. Biodegradation is typically achieved using hydroylases that attach hydroxyl functional groups to the contaminant molecules or oxidases that modify the contaminant functional group. The contaminants are often modified with the second phase of metabolism using detoxification enzymes. Phytotransformation is relatively inexpensive and has been shown effective against atrazine, PCPs, pesticides, petrochemicals, and TNT.

Phytovolatilization exploits transpiration and sometime phytotransformation to remove contaminants from soil and water. In this process, plants uptake the contaminants in the roots. The contaminants are then transported to the leaves where the contaminant is removed by transpiration as a volatile substance. Many of the compounds are degraded or detoxified before being transpired. This process is most effective on organic pollutants. Phytovolatilization has also be used to remediate mercury which is converted to its elemental form. Other studies used phytovolatilization to remove arsenic and selenium from soil and water (Arya et al. 2017).

Rhizodegradation, often called phytostimulation, takes advantage of the plant–soil interactions in the rhizosphere that degrade contaminants. The rhizosphere is a thin region of soil modified by a complex mixture of root exudates and a unique microbiome made of up bacteria, fungi, and protists. Rhizosphere dynamics has been the subject of basic ecological research for many years. However, it is only recently that these findings are being applied to agriculture, land management, and phytoremediation. The plant-microbiome environment is proving effective at degrading metals, organic pollutants, radionuclides, and xenobiotic compounds (Dzantor 2007). Rhizofiltration is a variation of rhizodegradation for remediating groundwater and surface waters. In this application of bioremediation, the rhizosphere acts as a filter that uptakes and degrades water contaminants (Hanus-Fajerska and Koźmińska 2016).

1.5 Genetic Modification and Phytoremediation

Advances in producing genetically modified organisms (GMOs) have contributed greatly to the plant sciences, particularly early in the history of phytotechnology (Cherian and Oliveira 2005). Genetic engineering provides the opportunity to impart phytoremediation properties into any plant increasing. This increases the options for selecting native plants to carry out phytoremediation more effectively than introduced plants not fully acclimatized to the remediation site as evident in plant physiology studies (de Mello-Farias et al. 2011). Genetic engineering also permits the use of crop plants (Agnihotri and Seth 2019) or other commercially useful plants (Das et al. 2016) for phytoremediation in which the spent plants are repurposed.

Researchers have currently isolated several groups of "phytoremediation genes" that can be transfected into host plants to impart phytoremediation properties. These include genes for cytochromes, mono-oxidases, specific reductases, and specific synthetases for biodegradation. A wide array of genes are available for inducing hyperaccumulation or phytoextraction including alpha-glutamyl-cysteine (alpha-Glu-Cys) synthetase, ATP sulfurylase, cysteine synthase, glutathione reductase, metallothionein, phytochelatin synthase, serine acetyltransferase, and metal-specific transferases (Cherian and Oliveira 2005).

One drawback to integrating GMO plants or microorganisms into phytoremediation is resistance by governments or the public about releasing GMOs into the environment (Shmaefsky 2010). Another disadvantage to GMO phytoremediation is the commercialization (Qaim 2009) and economics (Barragán-Ocaña et al. 2019) of using in economically emerging countries.

1.6 The Reality of Phytoremediation

Phytoremediation as an exclusive or supplemental means of remediating soil and water pollution is very promising for countries with emerging economies, as well as economically advantaged countries. In economically emerging countries, phytoremediation as a sole remediation method is inexpensive compared to traditional chemical and physical remediation methods and requires a minimum of engineered technologies (Prabakaran et al. 2019). Supplementing phytoremediation with traditional remediation technology in any country can improve the expediency of severe pollution situations as is evident in trial applications on the US Superfund sites (Rock and Sayre 2007) and military remediation operations (Siebielec and Chaney 2012). Urban areas in economically emerging countries can chiefly benefit from hybrid phytoremediation efforts (Banjoko and Eslamian 2015). It appears from the literature that the diversity of plants used for phytoremediation may exceed the variety of bioremediation microorganisms and can be used in conjunction with traditional chemical and physical remediation as well as phytoremediation (Ijaz et al. 2016).

Consequently, there is abundant potential for using phytoremediation in a spectrum of climates and in extreme environmental conditions. Invasive plants, when grown in a contained site, are proving highly effective for countries that do not have native phytoremediation plants (Prabakaran et al. 2019). All countries have the option of encouraging technology transfer opportunities for phytoremediation green technologies. Even, early assessments of phytoremediation showed that each country can tailor the technology transfer agreements based on the specific needs and economic limitations (Flathman and Lanza 1998; Sridhar et al. 2002). Recent assessments of phytoremediation as a viable green technology are supporting this view (Gerhardt et al. 2017).

Phytoremediation has its technical limitations as is true for any other remediation strategy. One strategic consideration is the long growth periods needed for plant growth or acclimatization. Another tactical concern is that the contaminants must be in close proximity to the plant roots. Plus, the concentration of the contaminants impacts the success of roots absorbing or degrading the contaminants (Ansari et al. 2015). As mentioned earlier about microbial bioremediation, soil or water chemistry and composition can inhibit phytoremediation. Also, plants may be more susceptible than bacteria and fungi to the toxic effects of high levels of contaminants. In spite of these limitations, phytoremediation is equivalent to traditional in situ remediation and may be more environmentally sound than traditional ex situ remediation (Gatliff et al. 2016).

In support of phytoremediation, there are efforts to improve the utility of phytoremediation by recycling or repurposing the plants after they have served their bioremediation purpose. Typically, after a phytoremediation treatment is completed, the plants need to be disposed in some way. Depending on the nature of the contaminant, the plants are placed in a municipal landfill, incinerated, or disposed as hazardous materials. It would be worthy to somehow reuse or recycle the plants. Early studies recognized the feasibility of reclaiming metals that were accumulated in the biomass of harvested phytoextraction plants (Cunningham and Ow 1996). This is particularly valuable for retrieving the rare earth metals electronic waste sites undergoing phytoremediation effects. Studies on various phytodegradation and phytostabilization plants show that harvested plants have the potential of being used as animal feed (Ghaly et al. 2005). Similar attempts are being investigated using harvested phytodegradation and phytostabilization plants for human consumption (Mitton et al. 2016). The use of energy crops, for producing biofuels or combustible biomass, has also been investigated (Pandey et al. 2016). Spent phytoremediation plants have shown value as a feedstock for anaerobic digestion products (Cao et al. 2014).

One caution about the economics of phytoremediation is ensuring that phytoremediation is equally effective as and less costly than traditional chemical and physical remediation. Cost-benefit calculations on phytoremediation are available and show that researchers must be aware of bias favoring phytoremediation over other remediation methods. Overall, on study concluded that "Considering the loss caused by environmental pollution, the benefits of phytoremediation will offset the project costs in less than seven years" for economically emerging countries (Wan et al. 2016). Calculations are also available for measuring the sustainability and resiliency value of phytoremediation. Sustainability and resiliency values will be specific for each circumstance and will be dependent on a society's environmental ethics and political views (An et al. 2016).

It is important to consider the public perceptions of any new technology when assessing its feasibility. Biotechnology still faces negative public sentiments which inhibit the growth of certain facets of the industry. Phytoremediation as a remediation method is viewed positively by the public and seen as an environmentally friendly. However, people do not trust remediation processes in general because the public believes that site may still have harmful levels of some of the known contaminants or may harbor an unidentified contaminant (Weir and Doty 2014).

The in situ case studies in this book represent a small body of successful phytoremediation efforts that are particularly relevant to countries with emerging economies or economically advanced countries seeking viable options for sustainable and resilient remediation efforts (Balkema et al. 2002). Phytoremediation is not a fad or a panacea. It is another individual strategy or supplemental strategy for environmental remediation. Likely, the future of phytoremediation will involve a combination of strategies that improve the economic sustainability of environmental remediation and increase the resilience from potentially damaging pollution events (Farraji et al. 2016).

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