Phytoremediation: A Multidimensional and Ecologically Viable Practice for the Cleanup of Environmental Contaminants

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Abstract

The humungous load of pollutants added to the environment every day by the human activities is one of the major menaces facing by the world. Toxic substances released into the ecosystems are said to create imbalance to the equilibrium of the environment. Phytoremediation is a set of processes which have been considered as one of the most sustainable approaches to combat the problem of contaminants. Phytoremediation is considered to be more effective in comparison with traditional techniques because of the added benefits provided by the plants. The mechanisms adapted by the plants for extraction, accumulation, stabilization and degradation of contaminants from the polluted sites have been explored in this chapter. Various floral species which have been reported by several researchers that have the potential to remediate contaminated sites are listed in this report. The bioenergy crops, medicinal plants, trees and weeds have been found to be the best options for phytoremediation. Phytoremediation has proven to have a holistic approach which can help in restoration of contaminated sites with production timber, essential oils, energy, and employment to the rural peoples and with several other ecosystem services.

Keywords

Bioenergy • Electrokinesis • Heavy metals • Phytoremediation • Pollution • Transgenic plants

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1.1 Introduction

The world population has exceeded seven billion and is rapidly approaching eight billion. This ever-increasing population has exerted tremendous chaos on the existing natural resources and has created immeasurable amount of wastes across the globe. When pollution is in manageable amount, the terrestrial, aquatic and atmospheric ecosystems can dilute, degrade or absorb the contaminants naturally. The rising burden of pollutants requires additional measures to curb the detrimental effects of pollution (Glick 2003; Glick 2010). Contaminants pose a threat to the environment because of their abundance and recalcitrant nature. Rampant industrialization and urbanization are the main culprits for the gradual degradation in environmental quality. The release of natural and anthropogenic contaminants is a major concern in the last few decades. There are numerous contaminants that continuously cause problems, some of which are easily curable but many are not. Plants act as Green Livers for the ecosystem clarifying any ill effects caused by contaminants and toxicants in the ambient environment (Sanderman 1994).

1.1.1 Contaminants: Sources, Types and Effects

A pollutant is anything that is present in the environment in excess to its original concentration. Waste generation by anthropogenic activities is so diverse in nature that it is difficult to categorize them effectively. Contaminants that create nuisance in soil and water are usually industrial wastes, municipal solid wastes, agricultural runoffs and leachates (organic pollutants) and radioactive wastes. The organic pollutants, heavy metals and radioactive wastes are dealt here as they are potentially the most problematic pollutants in terms of soil and water. They cause adverse effects directly to the plants as well as animals including human beings and sometimes indirectly by changing the natural composition of ecosystems (Fig. 1.1).

1.1.2 Heavy Metals

Heavy metals have been reported as one of the major nemeses for the environment. Apart from natural processes, maximum number of anthropogenic activities releases heavy metals (Tangahu et al. 2011). The problem lies when contaminants migrate to pristine areas in the form of metal dust or leachates as in the case of soil and also as sewage sludge (Gaur and Adholeya 2004). Heavy metals are those elements which have an atomic number more than 20. Metals are also present naturally in soil. Many of them are essential for growth and sustenance of soil flora and fauna. Zinc, copper, manganese, nickel and cobalt are imperative for survival of the plants. The importance of some metals such as cadmium, lead and mercury is unknown in respect to plants (Lasat 2000; Gaur and Adholeya 2004). Heavy metals are non-biodegradable, therefore creating problems in the overall biological systems. Heavy metals such as lead, cobalt and cadmium are more deleterious in nature because of their high bioaccumulation rate even at lower concentration

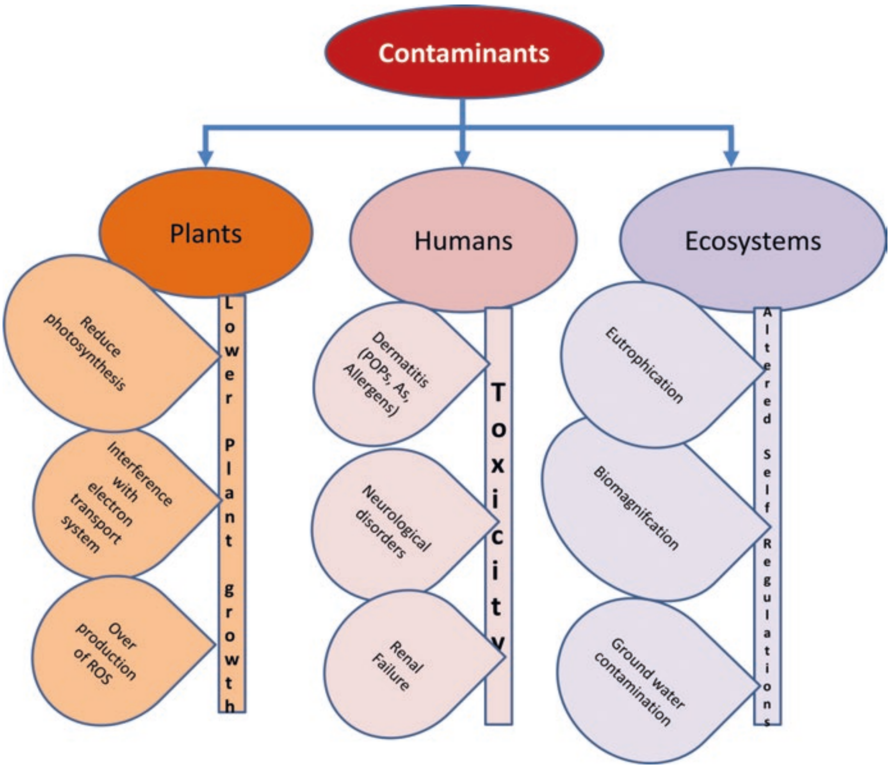


Fig. 1.1 Adverse impacts of contaminants on the environment

(Pehlivan et al. 2009; Tangahu et al. 2011). Heavy metals may cause negative impact on plant growth and soil microflora (Roy et al. 2005). Arsenic is one major environmental pollutant which falls under the category of heavy metal having atomic number 33. Arsenic is found in the environment as organic arsenic species, inorganic arsenic compounds and arsine gas. Arsenic is a very toxic element, and its toxicity is usually dependents on the species. The inorganic compounds of arsenic are usually more toxic than its organic counterparts. Arsenites are more toxic in nature than arsenates as they are more prone to cause DNA breakdown (Ampiah-Bonney et al. 2007; Vaclavikova et al. 2008). Arsenates are found to be more stable thermodynamically than arsenites; therefore, they cause groundwater contamination (Chutia et al. 2009). Arsenic compounds are carcinogenic in nature and cause dermatitis where the groundwater is contaminated. Lead with atomic number 82 is a highly toxic element which is non-biodegradable and remains in the environment for a very long time and accumulates in the first 8 in. of the soil and remains immobile. Sources of lead include natural sources, industrial sites, leaded fuels and orchards where the use of lead arsenate takes place (Traunfeld and Clement 2001; Tangahu et al. 2011). The harmful effects of lead are spread across a wide range of organisms such as humans, animals, plants and microbes. In terms of human health, lead causes major adverse impacts such as mental retardation and brain damage (Cho-Ruk et al. 2006). Mercury is another heavy metal that is notoriously toxic and is available in soil in three soluble forms. It is a toxic element with a high bioaccumulation potential in living organisms such as human beings, fish and other animals. Mercury is found in naturally as well as by anthropogenic activities in the environment. Mercury pollution in the environment is caused by mining, petrochemical, painting industries, also from fertilizers, medical instruments, etc. (Resaee et al. 2005). Usually terrestrial plants are not very sensitive to the adverse impacts of mercury, but it has been found that mercury interferes with electron transport in mitochondria and chloroplasts and adversely affects oxidative metabolism and photosynthesis. Mercury acts as an inhibitor of aquaporin activities and causes reduction in water uptake in plant. In human beings, the toxic impacts of mercury include neurological and renal disorders (Resaee et al. 2005). As toxic metallic species cannot be degraded, there is a requirement of physical removal or transformation to lesser toxic or non-toxic compounds.

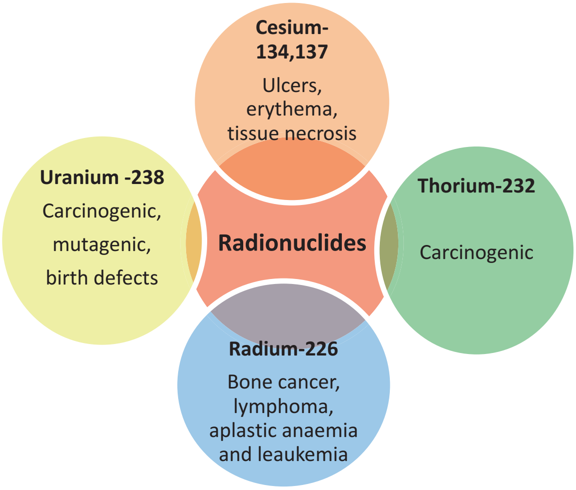
1.1.3 Organic Pollutants

Organic pollutants are synthetic and recalcitrant in nature. These organic xenobiotics are persistent in the environment and are highly toxic. They are known as persistent organic pollutants (POPs) as they are not easily degradable. Pesticides, petroleum products, pharmaceuticals, polyaromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) are some of the existing organic pollutants (Abhilash and Singh 2009). Twelve major POPs are known as the 'dirty dozen' which have been called for elimination and phasing out by the United Nations Environmental Program (US EPA 2005). Aldrin, dieldrin, chlordane, DDT, endrin, heptachlor, mirex, toxaphene, PCBs, HCBs, dibenzodioxins and dibenzofurans are the twelve most dangerous pollutants in respect to organic contaminants. Organic pollutants are a real menace for the ecosystem because of their persistence in the environment, lipophilic nature and high bioconcentration potential. These pollutants tend to get deposited in the adipose tissues of organisms (POPs, WHO Report 2008). Over a period of time, the pollutants reach a high level of toxicity because of their high bioconcentration potential, even though the exposure is limited. The pollutants move up the food chain as a result of biomagnification. Therefore, it is reported that the apex consumers reveal the maximum amount of organic pollutant concentration in their tissues. Marine mammals are known to have the highest concentration of these pollutants which caused reproductive disorders and higher susceptibility to infections resulting from microbes. The soil that is contaminated by organic pollutants causes death of soil microflora and reduction in plant growth and yield. Leaching of these pollutants causes groundwater contamination. Fertilizers when reaching the surface water bodies cause eutrophication by nutrient enrichment. The algal bloom caused by this nutrient enrichment reduces the dissolved oxygen level of the water bodies culminating in the death of aquatic flora and fauna. These are just few of the impacts of organic pollutants; there can be numerous direct and indirect effects of these contaminants. It is essential to remove these harmful toxicants from the environment to continue the balanced functioning of the ecosystems.

1.1.4 Radioactive Contaminants

Radioactive contaminants are introduced into the environment mostly by anthropogenic activities. Although radioactive elements are present in the environment naturally, they are not as harmful as contamination caused by anthropogenic causes because in nature, they are in a very low concentration. The environment is contaminated by radionuclides by nuclear weapon testing, disposal of nuclear wastes, emissions from nuclear power plants and also from spillage from plant operations such as nuclear fuel mining, milling and nuclear testing fallout, etc. In the process of oil drilling, sometimes radionuclides that occur naturally are brought up to the surface of the Earth (Fulekar et al. 2010). Chernobyl disaster in 1986 was one of the first nuclear power plant disasters which exposed the devastating effects of nuclear accidents to the world. The most recent nuclear accident occurred at Fukushima, Japan, during an earthquake at 2011; at Fukushima, an explosion was caused by failure of emergency cooling. Radionuclides are highly unstable nuclei possessing additional energy. There is a constant radioactive decay experienced by the radionuclides which forms alpha, beta and gamma particles as a result (Ghosh and Singh 2005; Fulekar et al. 2010). Consumption of food crops and water contaminated by radionuclides is one of the major causes of exposures to humans. The persistence of radiation in the environment can be over billions of years; therefore, it can cause irreparable damage to organisms as well as the ecosystem (Fig. 1.2) (Malhotra et al. 2014). Generally, the radiation released by the radionuclides can be carcinogenic and mutagenic in nature and is also known to cause birth defects and abnormalities in humans over a long period of exposure. Uranium-238 the most common natural isotope of uranium has a half-life of 4.46 billion years that is used in nuclear weapons and nuclear fuel. It is known to cause birth defects, cancer and mutations in the genes of humans (Jadia and Fulekar 2008). Thorium-232 is the most stable isotope with a half-life of 14 billion years, is used in nuclear fuel and alloying agent and is found to be carcinogenic in nature. Spinks and Woods (1990) state that radium-226 has a half-life of 1600 years and is used in an abundant fashion in our daily lives in the form of luminous paints and in dials of watches. An exposure for a long duration may cause fatal diseases like bone cancer, lymphoma, aplastic anaemia and leukaemia. During the Chernobyl accident, several radionuclides were released into the atmosphere; among them were isotopes of caesium-134 and caesium-137. These isotopes are retained by the soil and not washed away even by the heaviest rainfall. Isotopes of caesium are taken up by the plants, and they easily enter the food chain; also adverse effects are caused when there is an exposure to the contaminated soil surface (Westhoff 1999). The beta and gamma radiations of the radionuclides are highly dangerous and can cause ulcers, erythema or tissue necrosis in humans.

Fig. 1.2 Adverse impacts of radionuclides on humans



1.2 Contaminant Remediation Techniques

The above-mentioned problems are just the tip of the iceberg, and there are several underlying issues related to these contaminants that can cause direct or indirect impact on the environment. It is highly imperative to remediate the contaminated spheres of the environment. There are several conventional methods and techniques applied for the remediation of the contaminated areas. Some of the traditional methods to combat the problem of contaminated soil include:

1. *Soil excavation*: Treatment or removal of contaminants in the case of soil is done by onsite management or by excavation of the contaminated soil and by its disposal at a landfill site. This method of disposal is not a real solution of the problem as it merely dislocates the contaminants from one area to another (Tangahu et al. 2011).
2. *Soil washing*: As an alternative to the dislocation of contamination from the source to a landfill area, an onsite management method is applied. Soil washing is carried out by two processes: first of them is by dissolution or suspension of contaminated soil in a wash solution which is chemical in nature and the second process concentrates the contaminants into a smaller volume of soil by techniques such as gravity separation, particle size separation and attrition scrubbing. Heavy metals, organic xenobiotics and radionuclides can be removed by this process. This method is not cost-effective, and residues rich in contaminants require additional treatment. Therefore, this process is not extensively used (Tangahu et al. 2011).
3. *Stabilization/solidification*: In this process, the contaminants present in the soil are stabilized or solidified either by physical or chemical interactions between the contaminant and a stabilizing agent (Gomes 2012).

4. *Vitrification*: In the process of vitrification, heat is used for melting and subsequently solidifying the contaminants in a solid material which is glasslike in nature. Vitrification can be carried out onsite (in situ vitrification) and also aboveground in a separate treatment unit (ex situ vitrification).
5. *Electrokinetic treatment*: The electrokinetic remediation technique is solely in situ-based where direct electric potential is applied using cathodes and anodes. According to Cameselle et al. (2013), various reactions take place in the contaminated soil due to the electric potential; as a result, the contaminants move towards the cathode or anode. The mobilization or transport mechanisms in electrokinetic treatment are of two types, electro-osmosis and electromigration. When there is a combined effect of electric charge and electric field on soil particle surface, it results in an electro-osmotic flux which causes the movement of negatively charged particles towards the cathode. In the electromigration mechanism, movement of ionic species takes place in the electric field towards the oppositely charged electrode (Cameselle and Reddy 2012).

   Some other methods such as incineration and chemical oxidation/reduction are also used for the remediation of contaminated soil, but most of these traditional methods are not feasible because of high cost and problems regarding disposal of contamination-rich residues. Some of these techniques also destroy the soil biota causing the area to become devoid of life. Hence, it is essential for the sake of the environment to find alternative technologies that are environment-friendly and green in approach. These technologies must be cost-effective and reduce the pollutant load in the environment, and at the same time, the technique should have features which help them to resolve other major concerns like fuel crisis, emission of greenhouse gases, etc.

1.3 Phytoremediation: A Successful and Environment-Friendly Approach

Everyday new technologies are being developed by humans to vanquish the evil effects of pollution created by humans themselves. The solution lies in the hands of nature itself; plants are the nature's best defence against all man-made pollution. The word phytoremediation originates by combining two words *Phyto* (Greek) meaning plants and *remedium* (Latin) meaning removal or correction of evil. In general words, phytoremediation means removal, degradation or stabilization of pollutants using plants. At current time, plants have regained their former status of importance because of their multifaceted applications. The contaminants are removed from soil, water and sediments using plants. Certain plant root systems have special uptake capabilities, and also the shoot systems are capable in translocation, accumulation and degradation of the contaminants. These features allow efficient uptake and removal of harmful toxicants from the environment. Phytoremediation is a solar energy-driven process and does not require external energy, so it is cost-effective and less (zero) polluting in comparison with traditional methods. There are several definitions of phytoremediation given by various researchers; few have been compiled in Table 1.1.

Table 1.1 Definitions of phytoremediation

No.	Definition	Reference
1	Phytoremediation is a set of techniques or processes where plants are used for extracting, containing, degrading/destroying or immobilizing contaminants from the medium (soil, water or sediments)	EPA (2000)
2	The usage of plants for remediation of toxicants found in groundwater, contaminated soil, sludge, wastewater, surface water and sediments	Rodriguez et al. (2005)
3	Phytoremediation is a technology that makes use of plants to purify contamination from water, sediments or soil	Tangahu et al. (2011)
4	The application of plants for extraction and sequestration followed by detoxification of the contaminants	Ismail (2012)
5	A sustainable and green process in which live plants are used for removing or degrading contaminants from the environment	Cameselle et al. (2013)

1.3.1 Types of Phytoremediation

1.3.1.1 Phytoextraction

In terms of economic opportunities, phytoextraction presents the largest benefits (Raskin et al. 1997; Ismail 2012). Phytoextraction is considered as the most efficient method for removal of an isolation of contaminants from the polluted medium that is the soil where the fertility and structure of the soil is retained (EPA 2000). In the process of phytoextraction, the plant absorbs contaminants from the soil/water through roots and transfers or translocates them to the aerial parts of the plants. The aerial parts can be burnt to gain energy, and the metal can be recycled from the ash (Liu et al. 2000; Prasad and Freitas 2003 Erakhrumen and Agbontalor 2007; Moreno et al. 2008). Phytoextraction is most effective in large areas which have a contamination level of low to medium range, and the depth is also shallow (Kumar et al. 1995a, b; Blaylock and Huang 2000). The plant must possess some special characteristics to be efficient in the process of phytoextraction. These characteristics include tolerance towards the specific contaminant, efficient translocation of contaminants to aerial and harvestable parts of the plant and ability of plant to survive in stress conditions like soil pH, salinity, soil structure, water content and resistance to pests (Brooks 1994; Ismail 2012).

1.3.1.2 Phytostabilization

There are certain plant species that specialize in immobilizing contaminants in the soil or groundwater itself. These plants absorb and accumulate the contaminants in plant tissues, adsorb on the root surface or precipitate them within the root zone thereby preventing migration of contaminants in the soil and their movement by erosion (Liu et al. 2000; Prasad and Freitas 2003; Erakhrumen and Agbontalor 2007; Moreno et al. 2008). This method of phytoremediation is also known as phytorestoration. The plants used for phytostabilization must be weak in translocating the contaminants from the root to the aerial parts; must grow fast, having developed root systems and canopies, and must be tolerant towards abiotic and biotic stresses (Ismail 2012).

1.3.1.3 Phytofiltration

The process of phytofiltration can be of two types, one through the roots that is known as rhizofiltration and another one by seedlings that is known as blastofiltration. The roots or seedlings of the plant accumulate the contaminants from the effluents when grown in water that is aerated (Raskin et al. 1997). In this technique, plants are grown hydroponically; then they are transplanted in polluted water where they accumulate the contaminants (Dushenkov et al. 1995; Salt et al. 1995; Flathman and Hannza 1998). The phytoremediation of effluent or domestic wastewater is carried out using rhizofiltration. The contaminants are adsorbed or precipitated onto the plant roots and also in some cases absorbed and sequestered in the roots of plants present in constructed wetland for purification of effluent and wastewater (Liu et al. 2000; Prasad and Freitas 2003 Erakhrumen and Agbontalor 2007; Moreno et al. 2008). Ideally for rhizofiltration, plants must have roots that are fast growing and have higher efficiency in accumulation of contaminants over a longer time period. The toxic contaminants form a precipitate over the root surface which is then harvested and disposed (Flathman and Hannza 1998). The process of blastofiltration belongs to the second generation of water treatment technology which is plant based. After germination as there is an immense increase in the surface and volume ratio, the seedlings more effectively absorb or adsorb larger amounts of contaminants in ionic form making it more efficient than rhizofiltration (Raskin et al. 1997).

1.3.1.4 Phytovolatilization

In the process the contaminant is taken up by the plant and released by the process of transpiration either in the same form or in a modified form. In the process of phytovolatilization, the plant uptakes water which includes the contaminants, and the contaminants when reaching the aerial parts of the plants move out by transpiration (Liu et al. 2000; Prasad and Freitas 2003 Erakhrumen and Agbontalor 2007; Moreno et al. 2008). Some toxic contaminants exist in the atmosphere in gaseous form, for example, metallic species-like arsenic, mercury and selenium. In case of heavy metals, the plants adsorb metals in their elemental form, and then they are biologically converted into gaseous species which is known as biomethylation to create volatile molecules that are released into the atmosphere. There is a major disadvantage of this process in that volatile gaseous species may return to the ecosystem by precipitation thus creating havoc by spreading the toxic metals to a wider range of area (Henry 2000).

1.3.2 Mechanism of Phytoremediation

The basic steps involved in metal detoxification include metal ion binding on the cell wall of roots, metal ion transportation to the shoots and chelation of contaminants in cytosol (Fig. 1.5). The first step of mechanism of contaminant accumulation is the adsorption of metals on the root surface of the plants. Numerous metal transporters are located in the cell wall which allows metal ions to move inside the cell. Metal transporters can be grouped into ZIP family, NRAMP family and CTR family. IRT1 was found in *Arabidopsis thaliana* that belongs to the ZIP family expressed to accumulate higher amount of Fe at the time of Fe deficiency (Eide et al. 1996; Zaal et al. 1999; Guerinot 2000; Vert et al. 2002). This element has also been found to be characterized in *A. thaliana* and responsible for the accumulation and transport of Mn, Zn and Cd (Cohen et al. 1998; Korshunova et al. 1999; Zaal et al. 1999). Nishida et al. (2011) reported that expression of AtIRT1 enhances Ni accumulation in *Saccharomyces cerevisiae*. NRAMP is another metal transporter family which helps the plants to transport a number of metals like Cd, Ni, Zn, Fe, Cu, etc. (Nevo and Nelson 2006; Krämer et al. 2007).

In metal accumulator and hyperaccumulator plants, there are several defence mechanisms involved like (1) production of antioxidative components, e.g. ascorbate peroxidase (ASP), catalase (CAT), superoxide dismutase (SOD), glutathione S-transferase (GST), glutathione reductase (GR), proline, etc. (Ni et al. 2013; **Shanmugaraj et al.** 2013**; Yu et al.** 2013**;** Bauddh and Singh 2012a, b, 2015a, b), (2) production of phytochelatins (Cobbett 2000; Lee et al. 2003; Manara 2012), (3) production of metallothioneins (Nordberg 2004; Zimeri et al. 2005; Zhigang et al. 2006), (4) production of ferritins (Ravet et al. 2009; Liu et al. 2010; Yin et al. 2008; Rastgoo and Alemzadeh 2011), etc. These systems make a plant tolerant and enhance the metal-accumulating ability of plants at an even higher contamination level.

The production of metallothioneins in metal accumulator plants has been reported, and it is found that this component has the ability to detoxify the metal ion (Cobbett and Goldsbrough 2002; Papoyan and Kochian 2004; Zhigang et al. 2006; Mijovilovich et al. 2009). Many studies showed a substantial role of MTs in detoxification of Cu in many plants like *Nicotiana tobacum*, *N. caerulescens*, *Thlaspi caerulescens*, etc. (Kägi 1991; Maiti et al. 1991; Roosens et al. 2004; Papoyan and Kochian 2004; Mijovilovich et al. 2009; Leitenmaier and Küpper 2013).

It has been observed that during exposure to a biotic stresses like heavy metals, drought, salinity, etc. plants experience the overproduction of reactive oxygen species (ROS), e.g. superoxide radical (O_2^-), hydroxyl radical ($OH^•$), hydrogen peroxide (H_2O_2), singlet oxygen ($^1O_2$), etc. (Fig. 1.3) which can lead to a number of abnormalities like peroxidation of lipids and damage of proteins, enzymes, cell wall, etc. (Mittler 2002; Sharma and Dubey 2005; Asada 2006; Vanderauwera et al. 2011; Sharma et al. 2012; Noctor et al. 2014; Arora et al. 2016).

To overcome these adverse changes caused by ROS, plants produce antioxidative defence system which comprises of both enzymatic components like superoxide dismutase (SOD), catalase (CAT), peroxidase, ascorbate peroxidase (APX), glutathione reductase (GR), guaiacol peroxidase (GPX), etc. and several non-enzymatic components like ascorbate, carotenoids, glutathione (GSH), phenolics, tocopherols, etc. (Fig. 1.4) (Asada 2006; Slater et al. 2008; Sharma et al. 2012; Sewelam et al. 2016).

Phytochelatins are low molecular weight cysteine-rich proteins synthesized from glutathione by an enzyme phytochelatin synthase during prolonged exposure of

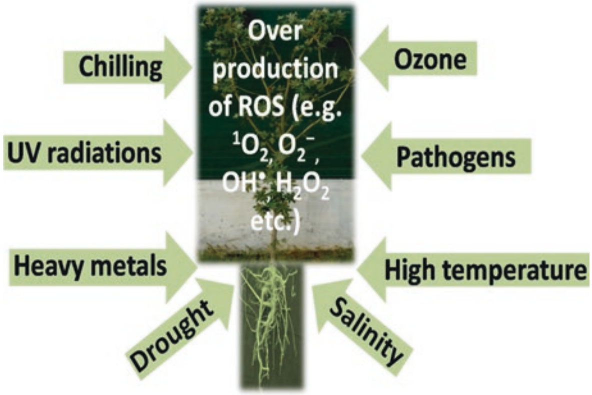


Fig. 1.3 Overproduction of reactive oxygen species (ROS) under biotic and abiotic stresses (Ashry and Mohamed 2012; Sharma et al. 2012; Noctor et al. 2014)

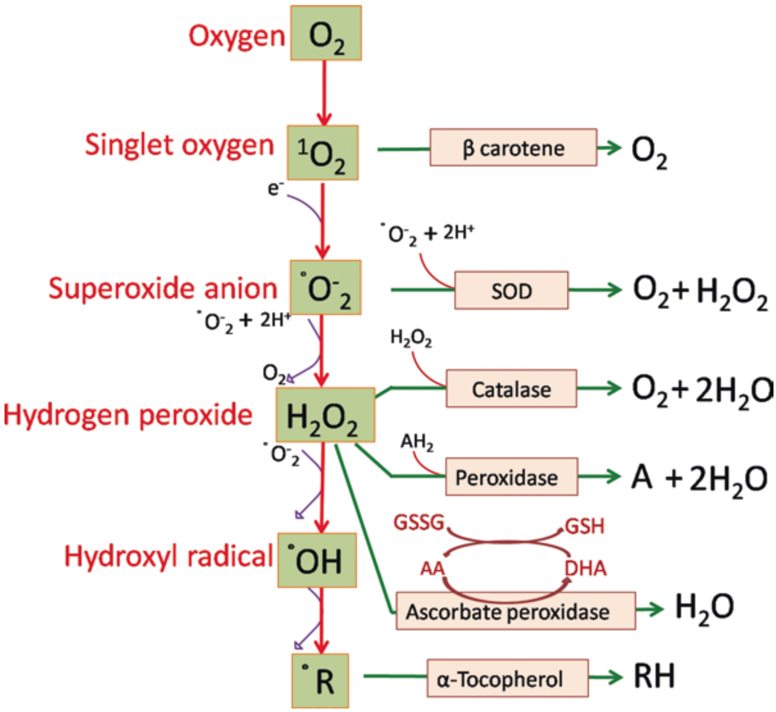


Fig. 1.4 The mechanism of formation of reactive oxygen species and their removal by antioxidants and antioxidative enzymes. *AA* ascorbic acid, *DHA* dehydroascorbic acid, *GHS* glutathione, *GSSG* oxidized glutathione, *SOD* superoxide dismutase (Adopted from Slater et al. 2008; Page No. 230)

heavy metals (Tommasini et al. 1998; Cobbett 2000; Clemens 2001; Schützendübel and Polle 2002; Harada et al. 2002; Gao et al. 2013). Phytochelatins contain gamma glutamylcystein and glycine in its structure $(\gamma\text{-Glu-Cys})_n\text{-Gly}$ (Kondo et al. 1984;

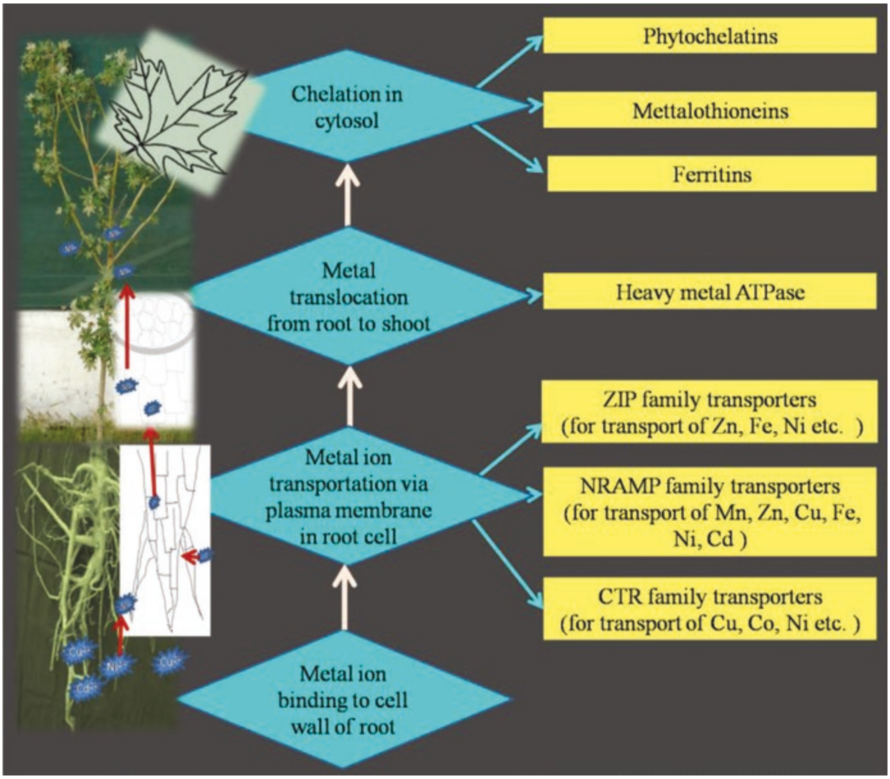


Fig. 1.5 The properties which make a plant metal accumulator/hyperaccumulator (Harada et al. 2002; Vert et al. 2002; Manara 2012; Gao et al. 2013)

Grill et al. 1986). An enhanced transcription of genes which synthesizes the precursor (glutathione reductase) of PCs was reported by Xiang and Oliver (1998) which confirmed the role of PCs as metal detoxifier (Hartley-Whitaker et al. 2001; Andresen et al. 2013). Further, Gao et al. (2013) demonstrated that the synthesis of PCs in plant *Phytolacca americana* is Cd dose dependent.

Ferritins are the proteins which have the ability to bind excess content of Fe in plants (Briat 1996; Fabisiak et al. 1999; Briat et al. 2006; Ravet et al. 2009; Briat et al. 2010). Phytoferritins are basically found in the mitochondria (Zancani et al. 2004, 2007) and non-photosynthetic plastids such as chromoplasts, proplastids, etioplasts, etc. (Seckback 1982; Ragland et al. 1990). Deák et al. (1999) proposed that ferritin can protect the plant from oxidative damage persuaded by a number of abiotic as well as biotic stresses (Fig. 1.5).

On the other hand, many plants secrete exudates from their roots which can chelate the metals and in soil only and prevent metal uptake inside the cell (Fig. 1.6) (Marschner 1995; Salt et al. 2000; Jung et al. 2003; Liao and Xie 2004, Schwab et al. 2005; Bais et al. 2006; Dong et al. 2007). The production of several organic acids as root secretion like malate, citrate, succinic, malonic, oxalate, etc. have been

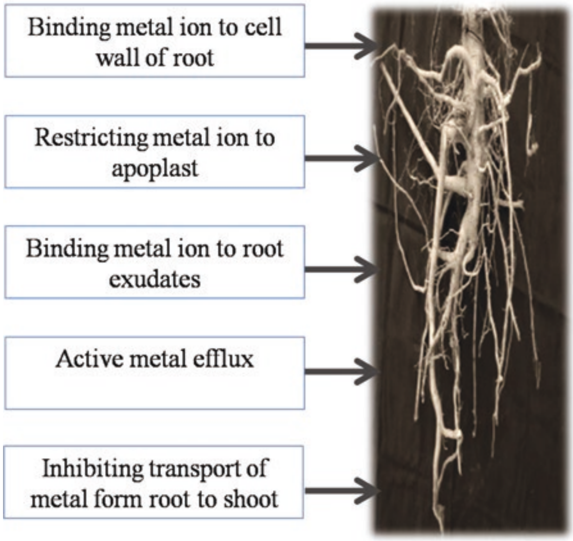


Fig. 1.6 Mechanism of metal excluder plants (Marschner 1995; Salt et al. 2000; Jung et al. 2003, Liao and Xie 2004, Schwab et al. 2005; Bais et al. 2006; Dong et al. 2007)

also reported to serve as a line of defence against toxic metals (Bidwell et al. 2002; Hall 2002; Pittman 2005; Hinsinger et al. 2006; Sun et al. 2006; Verbruggen et al. 2009; Gao et al. 2013). Verbruggen et al. (2009) suggested that these organic acids help in vacuolar transportation of heavy metals especially for Cd. Phytosiderophores have been reported by many authors that they produced specially by roots of leguminous crops during exposure of several heavy metals like Cu, Zn, Cd, etc. and play an important role in restricting the entry of metal ions inside the cell (Awad and Römheld, 2000; Shenker et al. 2001 Chaignon et al. 2002; Xu et al. 2005; Phytotechnology Mechanism 2005). Active metal efflux system in metal excluder plants also helps to restrict the entry of toxic metals (Baker 1981; van Hoof et al. 2001; Tong et al. 2004; Yang et al. 2005; Kushwaha et al. 2016).

1.3.2.1 Factors That Affect Uptake Mechanisms

The uptake mechanisms of plants used in phytoremediation are affected by several factors. The knowledge of these factors can be used to increase the efficiency of the phytoremediation potential of the plants.

1.3.2.1.1 Plant Species

Certain species of plants have superior remediation properties than other species; therefore, more efficient species must be selected for phytoremediation of contaminants. The plants that are most suitable must be hyperaccumulators and must produce more amounts of biomass (Rodriguez et al. 2005).

1.3.2.1.2 Properties of Growing Medium

Development of agronomical practices is carried out for enhancement of phytoremediation; factors such as pH, chelators and fertilizers are adjusted to increase the phytoremediation efficiency (Prasad and Freitas 2003).

1.3.2.1.3 Root Zone

Root zone is the main site for extraction, accumulation and stabilization of the contaminants. Therefore, the root zone must be well developed with high extraction, accumulation and stabilization efficiency. Sometimes, the degradation of contaminants takes place by enzymes that are exuded by the plant roots (Merkl et al. 2005).

1.3.2.1.4 Uptake Mechanism by Vegetative Parts

The environmental factors play a critical role in the uptake mechanism by vegetative parts. The growth enzymes are affected by the temperature which in turn affects the root length. The fate of metabolic activities of the contaminants inside the plants is very important in deciding the phytoremediation potential and efficacy (Mwegoha 2008).

1.3.2.1.5 Chelating Agents

The addition of chelating agents can enhance the capacity of the plants to extract and accumulate contaminants from the soil. Even micronutrients can be added along with the chelators to increase uptake. Chelating agents like EDTA are added in case of heavy metal contaminants. There is a chance of leaching in case of addition of chelators which are synthetic in nature (Van Ginneken et al. 2007; Tangahu 2011).

1.3.3 Indices Used for Assessment of Phytoremediation Potential

The suitability of plant for the purpose of phytoremediation depends on several factors: some of them are intrinsic plant characteristics; others are dependent on the environment or the contaminants. It is of utmost importance for the plants to accumulate a large amount of contaminants from the site. Also the ability of the plant to translocate the contaminants from the roots to shoots is of concern. Enrichment coefficient and translocation factor are two methods to measure the amount of contaminant accumulated and translocated by the plant. The amount or degree of heavy metal concentration/accumulation in the plants which are grown on contaminated sites is determined by enrichment coefficient (Kisku et al. 2000).

$$EC = \frac{\text{Metal concentration in roots or shoots}}{\text{Metal concentration } \textit{at} \text{ the site}} \quad (1.1)$$

Translocation factor (TF) is the ratio which defines the movement or mobilization of metal from roots to shoots of any plant. Equation 1.2 gives the formula for calculation of TF (Barman et al. 2000; Gupta et al. 2008; Shi et al. 2011).

$$TF = \frac{\text{Metal concentration in plant shoots}}{\text{Metal concentration in plant roots}} \quad (1.2)$$

Tolerance index is another major index which determines the suitability of any plant for the purpose of phytoremediation. It is imperative for a plant to exhibit healthy growth for its own survival and for extraction and accumulation of toxicants. The TI of any plant is based on the biomass produced by the plant. Equation 1.3 states the formula for the calculation of tolerance index (de Souza et al. 2012).

$$TI = \frac{\text{Biomass of plants cultivated in contaminanted soil}}{\text{Biomass of plants cultivated in control conditions}} \tag{1.3}$$

These indices are used by the researchers to test the potential of the desired plants for phytoremediation.

1.3.4 Different Aspects of Phytoremediation

1.3.4.1 Application of Edible Crops

In the present world, the availability of land as a resource is a major cause of concern due to the exponential population rise. It is imperative that land usage should be judicious and serve multidimensional benefits. Therefore, researchers have tried hitting two birds with one stone and have developed phytoremediation techniques using edible crops. Application of edible crops for remediation will serve several benefits such as decontamination of the land, food production, and efficient land usage. The edible crops studied for phytoremediation potential by various researchers include wheat (Khan et al. 2011), maize (Mojiri 2011), sunflower (Liphadzi et al. 2003), Indian mustard (Sainger et al. 2014), *Amaranthus* (Shevyakova et al. (2011), tobacco (Chitra et al. 2011), tomato (Uera et al. 2007), *Trapa* (Sweta et al. 2015), etc. Tabulation of these examples has been done in Table 1.2. These are just few examples of the edible crop plants utilized for phytoremediation; there are plenty of literatures available on many other plants as well. Albeit, numerous studies have been carried out testing the phytoremediation potential of edible crops; there are some major demerits associated with them. According to Bauddh et al. (2015a, b), the first obvious demerit is the bioaccumulation of toxicants in the edible plant which can further lead to biomagnification and move up the food chain causing toxicity to animals and humans. Other negative traits of edible crops regarding phytoremediation include short life span, low biomass production and high palatability. For efficient remediation of contaminants, the plants ideally must have a long life span, should be unpalatable and must produce larger amount of biomass for higher accumulation of contaminants (Pandey and Singh 2011). The above-mentioned problems of edible crops reduce the overall feasibility of phytoremediation by using these crops. If these problems can be solved like containing the contaminants in the unpalatable portions of the plant and increasing the biomass by technological interventions (biotechnological), only then edible crops may also be effectively used for the remediation purposes.

Table 1.2 Edible crops used in phytoremediation

Plant species	Family	Contaminants	Remarks	References
Triticum aestivum (wheat)	Poaceae	Cu, Cr, Zn, Fe, Ni, Cd, Pb and Mn	Soil used as substrate, maximum accumulation of iron succeeded by manganese and zinc	Chandra et al. (2009)
Triticum vulgare	Poaceae	Methyl parathion, *p*-nitrophenol and hydroquinone	Experiments were carried out using wheat plants to remediate soil contaminated with methyl parathion which after hydrolysis forms *p*-nitrophenol which in turn forms hydroquinone with release of nitrate after metabolism. The uptake and degradation of methyl parathion, *p*-nitrophenol and hydroquinone were increased by 64.85 %, 94.7 % and 55.8 % when wheat plants were used in unsterilized soil	Khan et al. (2011)
Oryza sativa (rice)	Poaceae	As, Hg, Pb, Cr and Cd	Maximum amount stored in roots and least in grains; translocation of As lowest and Hg highest from roots to other parts of the plant	Liu et al. (2007)
Hordeum vulgare (barley)	Poaceae	Hg	In the field experiment carried on for 3 years, mercury was phytoextracted by the barley plant up to 719 mg/ha in a soil where Hg concentration was 29.17 μg/g at 0–10 cm soil depth. The concentration of Hg in the plants was equivalent or higher than Hg present in the soil	Rodriguez et al. (2005)
Solanum tuberosum (potato)	Solanaceae	Ni, Zn, Cu, Cr, Cd, Pb and Mo	Potato plants were planted in sewage sludge and yard manure compost, and it was found that concentration of heavy metals Zn, Cu and Mo were significantly high in the tubers, whereas Ni, Cd, Cr and Pb did not exhibit significant accumulation in the plants	Antonious and Snyder (2007)
Zea mays (maize)	Poaceae	Cd and Pb	Roots of maize were more efficient in phytoextraction and accumulation of lead and cadmium than the shoots. Phytoremediation potential of the plant decreased when the levels of dosage of Cd were increased from 8 to 16 ppm	Mojiri (2011)
Helianthus annuus (sunflower)	Asteraceae	Cd, Pb and Ni	EDTA $Na_4.H_2O$ added 1 g/kg to the soil for enhancing the phytoremediation potential of the sunflower plant. It was observed in the field experiment that leaves of the plants grown in the soil with the chelating agent accumulated more Cd, Ni and Pb than the soil without the chelator	Liphadzi et al. (2003)

Brassica juncea (*cv. T-59*) (Indian mustard)	Brassicaceae	Ni	Out of four cultivars, cv. T-59 variety of mustard plant exhibited high-tolerance index accumulation potential for nickel. The plants accumulated (roots and shoots) 6–6.51 μg Ni g^{-1} from the soil dosed with 8 mM of Ni	Sainger et al. (2014)
Amaranthus spp.	Amaranthaceae	Ni and Fe	Three hybrids of the *Amaranthus* plants were experimented on with varying concentration of $Nicl_2$ and 2 μM Fe^{3+}; EDTA was also added. It was observed that *Amaranthus paniculatus* f. *cruentus* that is red *Amaranthus* (Vishneviy dzhem) accumulated maximum amount of Ni in the shoots and caused Fe reduction in the roots. Ni and Fe exhibit antagonistic behaviour towards each other. Accumulation of Ni in the shoots inhibited Fe accumulation	Shevyakova et al. (2011)
Nicotiana tabacum (tobacco)	Solanaceae	Cd	The author cultivated tobacco, corn and wheat plants in a pot experiment to their study of phytoremediation potential against Cd at varied concentrations. It was found that the tobacco plants recorded maximum accumulation of Cd in their roots and shoots in comparison with corn and wheat. Thus, tobacco was considered as the hyperaccumulator species among the three	Chitra et al. (2011)
Solanum lycopersicum (tomato)	Solanaceae	Ethidium bromide	The study found that tropical plants have a high uptake potential for EtBr. 1.0±0.23 μg $^{kg-1}$ EtBr was taken up by the tomato plants in this experiment	Uera et al. (2007)

1.3.4.2 Application of Weeds

Phytoremediation can effectively curb the toxic impacts of the environmental contaminants. Researchers have tried developing methods of phytoremediation using weeds. Terrestrial as well as aquatic weeds have been experimented with, and encouraging results have been recorded. If aquatic weeds efficiently remove contaminants from effluents, it will prove to be a boon as they are fast growing, and surface water can be easily treated by using them. Several researchers have used aquatic weeds such as alligator weed, duckweed, water lettuce, water hyacinth and *Azolla spp*. for the remediation of several toxicants from water (Cho-Ruk et al. 2006; Skinner et al. 2007; Zhang et al. 2008; Rahman et al. 2008). Terrestrial weeds such as *Parthenium hysterophorus*, *Tridax procumbens*, *Cyperus procera*, *Euphorbia hirta* and *Datura stramonium* are just few of the examples which have been studied for their phytoremediation potential against heavy metals (Kumar et al. 2013). Table 1.3 describes some of the successful experiments on remediation of contaminants by terrestrial as well as aquatic weeds.

In the studies conducted by Kumar et al. (2012 and 2013), emphasis has been given on EC and TF of the contaminants in the plant bodies. Enrichment coefficient gives an accurate estimation of the total contaminant (heavy metal accumulated by the plants from a contaminated site). If the EC is high, the plant is considered to be suitable for phytoremediation. *Eichhornia crassipes* showed high values of EC and TF when tested with heavy metals such as Cr, Pb, Ni and Cd making this aquatic weed most suitable among other weeds for phytoremediation of heavy metals (Kumar et al. 2012). Among the terrestrial weeds, *Tridax procumbens*, *Cyperus procera*, *Euphorbia hirta*, *Parthenium hysterophorus and Datura stramonium* exhibited higher EC in that order and were found suitable for phytoremediation purpose by Kumar et al. (2013). According to Baker (1981) if the translocation factor is more than one, then the plant is termed as metal accumulator, and if it is below one, the plant is known as metal excluder. Kumar et al. (2013) in their study found that TF of the terrestrial weeds ranged between 0.119 for Cd in *T. procumbens* and 3.86 for lead in *S. oleracea* (described in Fig. 1.7). *P. hysterophorus* and *S. oleracea* exhibited TF more than one for all the heavy metals studied (Cu, Pb, Cd and Ni) which made them ideal metal accumulators. The *Cyprus spp.* (*C. procera and C. rotundus*) recorded all the TF values less than one making the weeds unsuitable for phytoremediation.

The aquatic weeds studied by Kumar et al. (2012) presented impressive results regarding TF. It was found that most of the aquatic weeds had TF above one. The study of the average TF (Fig. 1.8) for all these aquatic weeds disclosed the fact that *Marsilea minuta* (2.82), *Bacopa monnieri* (1.84) and *Hydrilla verticillata* (1.69) were most efficient in translocation of heavy metals from the roots to shoots and thus can be used for remediation of heavy metal-contaminated sites.

1.3.4.3 Application of Trees

Trees are considered as one of the most important entities in terms of phytoremediation. Trees have higher biomass and extensive root system which enable them to accumulate more contaminants from the surrounding soil. Many authors have

Table 1.3 Terrestrial and aquatic weeds used in phytoremediation

Plant species	Family	Contaminant	Remarks	References
Alternanthera philoxeroides (Alligator weed)	Amaranthaceae	Pb	The uptake of Pb in the plant was by phytoextraction, and accumulation efficiency was about 30–80%. High accumulation efficiency was attributed to very long stolons and largely spread fibrous roots.	Cho-Ruk et al. (2006)
Pistia stratiotes (water lettuce)	Araceae	Hg	Different concentration of mercury in the form of $HgSO_4$ was tested for extraction in the laboratory experiment. It was observed that the highest concentration of Hg used showed maximum accumulation by the plant	Skinner et al. (2007)
Azolla spp.	Azollaceae	As	Two species of Azolla, namely, *A. caroliniana* and *A. filiculoides* were treated in the Arsenic nutrient solution. It was found that *A. caroliniana* released more arsenate and arsenite in the form of efflux than *A. filiculoides*. The efflux in the form of arsenate was released nine times higher than arsenite	Zhang et al. (2008)
Spirodela polyrhiza (duckweed)	Araceae	Arsenate and Dimethylarsinic acid (DMAA)	In the hydroponic media, arsenic was absorbed as well as adsorbed by the plant. In the plant by phosphate uptake, pathway arsenic was taken up; also by physiochemical adsorption on Fe plaques on the plant surfaces, arsenic was adsorbed in the form of arsenate	Rahman et al. (2008)
Eichhornia crassipes (water hyacinth)	Pontederiaceae	Cr, Cu, Ni and Pb	*Eichhornia* was found to be a very good accumulator of Cu, Ni and Pb. Other macrophytes were more efficient in accumulating Cr. It was also observed that translocation factor (TF) and enrichment coefficient (EC) of Eichhornia were also high making it suitable for phytoremediation	Kumar et al. (2012)
Cyperus procera	Cyperaceae	Cr, Cu, Ni, Pb and Cd	The enrichment coefficient in the roots and shoots was studied along with translocation factor. It was observed that for the heavy metals Cr and Pb, the EC was highest 318.960 and 318.876 in the roots, and similar values were found for shoots also. In case of Cu and Cd, the ECs in roots were 7.305 and 6.665; shoots were 5.062 and 5.445, respectively	Kumar et al. (2013)

(continued)

Table 1.3 (continued)

Plant species	Family	Contaminant	Remarks	References
Euphorbia hirta	Euphorbiaceae	Cr, Cu, Ni, Pb and Cd	The EC in the roots and shoots of *E. hirta* was highest for Cr and Pb. Lowest values were obtained in case of Ni and Cu	Kumar et al. (2013)
Datura stramonium	Solanaceae	Cr, Cu, Ni, Pb and Cd	For Cr the EC in shoot was recorded as 133.418 and 68.840 in roots. For Pb EC was 135.905 in shoots and 161.031 in roots. The values of EC for Cu were as low as 2.885 and 2.254 in roots and shoots. Similarly low values were recorded for Ni which was 6.690 in roots and 12.147 in shoots	Kumar et al. (2013)
Parthenium hysterophorus (congress grass)	Asteraceae	Cr, Cu, Ni, Pb and Cd	The highest EC was found for Pb, i.e. 227.606 in roots and 242.394 in shoots followed by Cr for which EC was 174.567 in roots and 206.153 in shoots; for the other heavy metals, EC was below 20	Kumar et al. (2013)
Tridax procumbens (coat buttons)	Asteraceae	Cr, Cu, Ni, Pb and Cd	For Cr the ECs in roots and shoots were very high, i.e. 609.157 and 1130.372, respectively. For the rest of the heavy metals, the EC varied. Among them for Pb higher, EC was observed than Ni and Cd	Kumar et al. (2013)

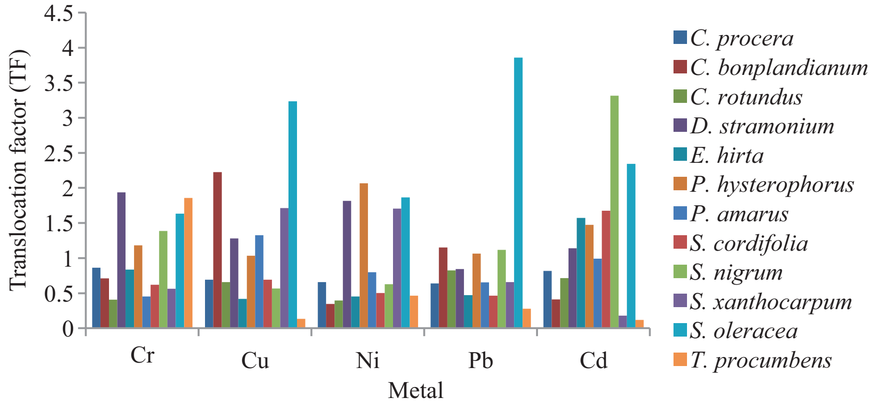


Fig. 1.7 Translocation factor (TF) of the terrestrial weeds grown naturally in the metal-contaminated sites (Kumar et al. 2013)

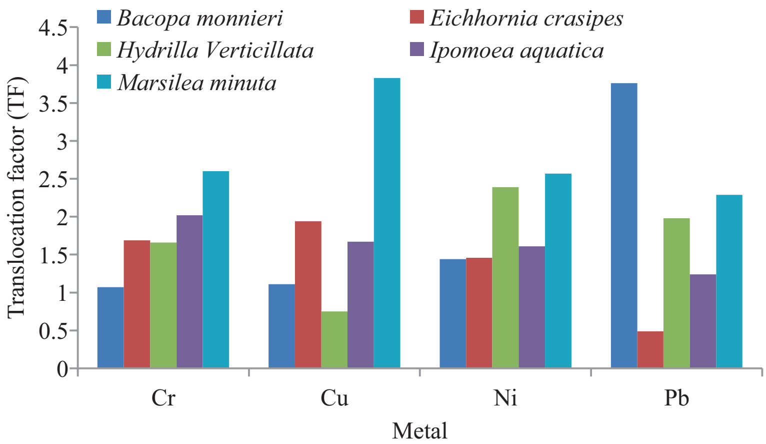


Fig. 1.8 Translocation factor (TF) of the aquatic weeds (macrophytes) naturally growing in the drain receiving tannery effluent (Kumar et al. 2012)

studied the phytoremediation potential of the trees extensively, and few of the studies have been compiled in Table 1.4. The species of trees from the Salicaceae family (willow, poplar) were found to be most appropriate for the phytoremediation purpose of contaminants. More research needs to be carried out using multipurpose trees that would help in remediation of contaminants in addition to carbon sequestration and employment generation.

De Souza et al. (2012) studied three species of leguminous plants *Erythrina speciosa*, *Schizolobium parahyba* and *Mimosa caesalpiniaefolia* for their lead tolerance at seedling stage. The indices studied by the author were TF, BCF and TI. The tolerance index is calculated on the basis of the biomass yield of the plant (Shi et al.

Table 1.4 Trees used for phytoremediation

Plant species	Family	Contaminants	Remarks	References
Salix viminalis (willow)	Salicaceae	Cd and Zn	The field study was conducted in two different contaminated sites one with calcareous soil and another with acidic soil. The phytoextraction of Cd and Zn was found to be more efficient in the acidic soil. There was larger biomass production and more metal accumulation in shoots in the acidic soil; this attributed to more extraction of Cd and Zn	Hammer et al. (2003)
Populus spp. (hybrid poplar)	Salicaceae	Zinc	Different concentrations of Zn were applied as $ZnSo_4$ solution. The root tissues accumulated more amounts of heavy metal than other parts of the plants	Hamon et al. (1999)
Populus spp. (poplar)	Salicaceae	As, Co, Cu, Pb and Zn	Three species *P. alba*, *P. nigra* and *P. tremula* were studied in a pot and field experiment. The uptake mechanisms by the plants were phytoextraction and phytostabilization. The fine roots accumulated the highest amount of trace metals than other aerial parts. *P. nigra* reported the highest accumulation of the contaminants	Vamerali et al. (2009)
Salix spp. (willow)	Salicaceae	Cd	Two clone species of willow used for the study and uptake mechanism by the plants were phytoextraction and phytostabilization. High levels of accumulation were found in the aerial parts of the plant	Vandecasteele et al. (2005)
Schizolobium parahyba (Brazilian fire tree)	Fabaceae	Lead	Different concentrations of lead were added to the soil (250, 500 and 1000 mg Kg^{-1}), and seedlings of *S. parahyba* were tested with tolerance factor, bioconcentration factor and tolerance index indices. It was found that there is maximum lead accumulated in the roots followed by leaves and stem. The accumulation of Pb in the leaves reached toxic levels	de Souza et al. (2012)

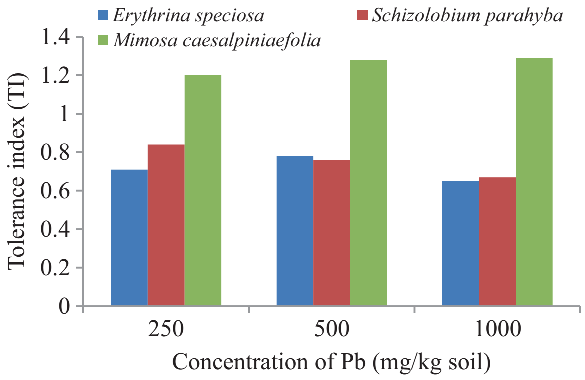


Fig. 1.9 Tolerance index (TI) of some tree species growing in lead-contaminated soil (Source: de Souza et al. 2012)

2011). The biomass yield of the controlled plant and plants grown in a contaminated site are compared. The author found that the tolerance index of *Mimosa caesalpiniaefolia* recorded the highest readings of 1.20, 1.28 and 1.29 for 250, 500 and 1000 mg Kg^{-1} of lead; *Erythrina speciosa* recorded 0.71, 0.78 and 0.65 for 250, 500 and 1000 mg Kg^{-1} of lead; and *Schizolobium parahyba* recorded 0.84, 0.76and 0.67 for the similar Pb concentrations. Therefore, it can be concluded that *Mimosa caesalpiniaefolia* was the most tolerant species followed by *Schizolobium parahyba* and *Erythrina speciosa.* The TI of the three species is represented in Fig. 1.9.

1.3.4.4 Application of Bioenergy Crops

Holistic approach should be applied for remediation of toxicants from the environment. It is of utmost importance to detoxify the contaminants using sustainable means. Amalgamation of phytoremediation techniques with sustainable approach would provide multidimensional benefits for the entire Earth. Using bioenergy crops or trees is one such measure that is sustainable in approach and can be effectively tapped for phytoremediation. Several bioenergy crops have been tested for phytoremediation potential by the researchers in the recent past. If bioenergy crops are used for phytoremediation, it would save contaminated sites from being discarded; also it would generate employment and increase the interest of the people in plantation of such crops. Both edible and nonedible energy crops have been tested for their phytoremediation potential by researchers with encouraging results (Rowe et al. 2009; Shi and Cai 2009; Meers et al. 2010; Bauddh and Singh 2012a, b, 2015a, b; Bauddh et al. 2015a, b, 2016a, b). The use of edible crops for phytoremediation poses a bit of a concern because it is assumed that toxicants might enter the food chain. The study conducted by Meers et al. (2010) showed that the grains, the edible part of maize, accumulated the lowest amount of heavy metals. The researcher attributed this result to the defence mechanism of the plant to restrict toxicity from reaching the reproductive parts and seeds and constraining them within the vegetative parts of the plants. More research needs to be carried out to test the phytoremediation potential of the bioenergy crops as it would help in detoxifying the environment along with the generation of clean fuel and lower the carbon emission into the atmosphere. Using bioenergy crops would provide the most wholesome results in comparison with all other plants combined (Table 1.5).

1.3.4.5 Aromatic Plants Used in Phytoremediation

It is of preference to use nonedible crops for the purpose of phytoremediation because of the obvious reasons of avoiding bioaccumulation and biomagnifications of toxicants. Very recently few aromatic plants have been tested for their potential to remediate contaminants. This will serve the dual purpose of providing essential oils derived from the plant along with cleansing the environment. The plants such as *Ocimum basilicum* (basil), *Cymbopogon martinii* (palmarosa), *Vetiveria zizanioides* (vetiver), *Cymbopogon flexuosus* (lemon grass), *Mentha sp.* (geranium mint) (citronella) and *Cymbopogon winterianus* have been considered for their phytoremediation potential. Gupta et al. (2013) suggest that the likes of basil are viable and feasible for phytoremediation, and other aromatic grasses (lemon grass, citronella,

Table 1.5 Bioenergy crops used for phytoremediation

Plant species	Family	Contaminants	Remarks	References
Ricinus communis (castor)	Euphorbiaceae	Cadmium and nickel	*Ricinus communis* extracted large amounts of Ni from the soil because of its high above- and belowground biomass.	Bauddh and Singh (2015b)
			In a comparative study between two plants, *Ricinus communis* and *Brassica juncea* for Cd, drought and salinity tolerance, it was found that *Ricinus communis* was more tolerant to the stresses applied singly or in a combination than *Brassica juncea*	Bauddh and Singh (2012b)
Linum usitatissimum	Linaceae	Cadmium	The plant showed high bioconcentration factor values and highest values for translocation factor of 54–66% and was overall tolerant in Cd-contaminated soil. Flax accumulated a high amount of Cd from soil; the values were >100 mg/kg	Shi and Cai (2009)

(continued)

Table 1.5 (continued)

Plant species	Family	Contaminants	Remarks	References
Cannabis sativa (hemp)	Cannabaceae	Cadmium	In the study, BCF was found to be highest for hemp roots and low in shoots. Due to higher biomass, Cd accumulation was high in hemp. TI was moderate for hemp	Shi and Cai (2009)
Zea mays (maize)	Poaceae	Zinc, cadmium and lead	Overall accumulation and tolerance for heavy metals by the plants showed promising results. The accumulation of heavy metals in the grains was found to be the lowest that was attributed to the defence mechanism of the plant. If energy was produced at the site from maize, renewable energy of 33,000–46,000 kW h ha^{-1} y^{-1} could be generated	Meers et al. (2010)
Arachis hypogaea (peanut)	Fabaceae	Cadmium	Maximum amount of Cd was accumulated by peanut plant in the shoots making it efficient for phytoremediation of Cd. The highest values for Cd uptake were recorded in peanut; the values were 56.0–68.9 μg/ plant	Shi and Cai (2009)
Salix calodendron (willow)	Salicaceae	Cadmium and zinc	The Zn and Cd present in the contaminated soil could be reduced at the rate of 96 and 5.6 mg Kg^{-1}, respectively, over the period of 20 years	Rowe et al. (2009)

palmarosa and vetiver) are perennial in nature as well as stress tolerant. These qualities make them appropriate for removal of toxicants from the environment. These perennial herbs can be planted at the contaminated sites, and they can accumulate contaminants in the biomass. The plants can be harvested, and their essential oil can be extracted by steam distillation. In this process, the essential oil forms a separate layer on the top, and the water containing the contaminants is left in the lower layer; the essential oil can be separated and used after its quality assessment (Pandey et al. 2015).

1.3.4.6 Plants as Hyperaccumulators

Certain plants have the tendency to accumulate larger amount of contaminants from the environment without showing adverse effects. These plants can be considered to be most ideal in terms of suitability for removal of toxicants. Different researchers have put forth several definitions for hyperaccumulator plant species; the plant species that can accumulate contaminants (metals, metalloids, etc.) at levels 50–500 times higher than their concentrations in soil are considered as hyperaccumulators (Clemens 2006, Kotrba et al. 2009). Another variation is mentioned by Brooks et al. (1998) who state that hyperaccumulators are those plant species which accumulate any element from the substrate at concentration 100 times higher than the substrate or medium. There are certain standards set for considering any plant as a hyperaccumulator; specifically for metals the concentration must be 0.1 weight % as dry weight; for Cd it is variable up to 0.01 weight % and 1 % for Zn (Reeves and Baker 2000). More than 45 families of plants are known to belong to hyperaccumulating species and over 450 plants. The number of hyperaccumulating plants is less in context to the problem of pollution because of their biomass which is low, their slower growth rate and being specific in contaminant accumulation (Chaney et al. 2005). Few examples of hyperaccumulating plant species have been tabulated in Table 1.5. It is seen that the plant family Brassicaceae is dominant in producing hyperaccumulators; other families such as Fabaceae and Crassulaceae also contain hyperaccumulators. Certain plants that are hyperaccumulators can be made more efficient with genetic engineering and with biological amendments (Table 1.6).

1.3.5 Application of Chemical and Biological Amendments to Enhance Phytoremediation

Although phytoremediation is an excellent option for the effective removal of contaminants from the environment, there are few drawbacks of this technique too. One of the major drawbacks is the time taken for complete remediation of a particular site which could be as long as 15–20 years, even if hyperaccumulating species are used. At the recent past, certain amendments in the process of phytoremediation are applied to make it more effective in terms of time and efficiency. Even highly efficient plants exhibit deleterious effects of heavy dosage of contaminants. There is usually a reduction in growth and yield of plants due to over accumulation of the contaminants. The phytoremediation potential of plant species as well as other organisms is being thoroughly studied to find methods to eliminate the risk of

Table 1.6 Example of hyperaccumulator plants used for phytoremediation

Plant species	Family	Contaminants	Reference
Brassica juncea	Brassicaceae	Ni, Cd, Pb and Zn	Sainger et al. (2014)
Astragalus racemosus	Fabaceae	Heavy metals and metalloids	Reeves and Baker (2000)
Sedum alfredii	Crassulaceae	Zn^{2+}	Yang et al. (2006)
Thlaspi caerulescens	Brassicaceae	Zn^{2+}, Ni^{2+} and Cd^{2+}	Milner and Kochian (2008)
Alyssum sp.	Brassicaceae	Heavy metals and metalloids	Reeves and Baker (2000)

ever-increasing contaminant load. Algae, fungi and bacteria are few organisms which have the ability to speed up the process of phytoremediation. Since the past few years, researchers are working on making biological amendments to plant species to increase their efficiency in remediation of toxicants. The importance of bacteria and fungi in increasing plant efficiency for phytoremediation has been dealt in this chapter.

1.3.6 Role of Bacteria in Enhancement of Phytoremediation Potential of Plants

According to Glick (2010), there are rich population of bacteria near the rhizosphere because of the release of nutrient-rich exudates; these bacteria can degrade organic contaminants by phytostimulation or rhizodegradation (Kuiper et al. 2004). In context to phytoremediation, the biodegradative bacteria and bacteria that promote plant growth are very useful. Bacterial species such as *Pseudomonas* spp. are capable of degrading organic xenobiotics with the help of several enzymes produced on its plasmids (Cork and Krueger 1991; Glick 2010). The bacteria that are degradative in nature are capable of converting nonhalogenated compounds in easily metabolizable compounds catechol or protocatechuate. Halogen-based aromatic compounds which are the main constituents of biocides are very slowly degraded by plasmid-encoded enzymes (Glick 2010). Growth-promoting bacterial species releases phytohormones such as auxin which have a direct effect on the plant (Brown 1974; Patten and Glick 1996). A higher concentration of the heavy metals in the plant body causes synthesis of stress ethylene and deficiency in iron content (Glick 2010). A few bacteria release an enzyme ACC deaminase that is capable of lowering the phytohormone ethylene in a plant that is subjected to stress (Glick 2010). Another such enzyme IAA is released by IAA bacteria which helps in adventitious and lateral root elongation and prevent environmental stress-related adverse effects (Lindberg et al. 1985; Frankenberger and Arshad 1995). Table 1.5 represents few examples of bacteria and associated plants used for phytoremediation (Table 1.7).

Table 1.7 Bacteria and plant combination for enhanced phytoremediation

Plant species	Family	Bacteria	Contaminants	Remarks	References
Brassica juncea	Brassicaceae	*Azotobacter chroococcum* HKN-5 + *B. mucilaginosus* HKK-1 + *B. megaterium* HKP-1	Zn, Pb, Cu and Cd	There was a distinct increase in metal bioavailability and biomass of the plant when the bacterial strains were incorporated with the mustard plant	Wu et al. (2006)
Sedum alfredii	Crassulaceae	*Burkholderia cepacia*	Zn and Cd	The results of the study indicated increased metal uptake by the plant; also there was an increase in translocation of metals from root to shoot. The plant also exhibited increased biomass.	Li et al. (2007)
Brassica juncea	Brassicaceae	*Bacillus sp*. 32, *Pseudomonas* sp. A4	Cr	The presence of IAA enzyme, siderophores and phosphate solubilization caused increase in length of roots and shoots	Rajkumar et al. (2006)
Thlaspi caerulescens	Brassicaceae	Rhizosphere bacteria	Zn	The uptake efficiency of the plant for the metal zinc increased in presence of rhizosphere bacteria	Whiting et al. (2001)
Vigna radiata (green gram)	Fabaceae	*Bradyrhizobium* sp. RM8	Zn and Ni	Due to the presence of IAA and siderophores, there was a positive addition in nodules and plant nutrition	Wani et al. (2007)
Ricinus communis	Euphorbiaceae	*Pseudomonas* sp. M6, *Pseudomonas jessenii* M15	Ni, Cu and Zn	Biomass increase was observed due to IAA, ACC enzyme increase and phosphate solubilization	Rajkumar and Freitas (2008)
Solanum lycopersicum	Solanaceae	*Pseudomonas* sp. RJ10, *Bacillus* sp. RJ16	Cd and Pb	There was a distinct increase in aboveground biomass, length of the roots and metal uptake capacity of the plant	He et al. (2009)
Helianthus annuus	Asteraceae	*Streptomyces tendae* F4	Cd	Decreased metal uptake and increased iron content exhibited due to siderophores	Dimpa et al. (2009)
Cajanus cajan (pigeon pea)	Fabaceae	*Glomus mosseae*	Cd and Pb	There was an enhancement of biomass, nodules, nitrogenase activity and leghemoglobin content when the microbes were incorporated with the metal-stressed plant. The process of biosorption was the mechanism of contaminant removal adapted by the plants	Garg and Aggarwal (2011)

1.3.7 Role of Fungi in Enhancement of Phytoremediation Potential of Plants

According to Glick (2010) almost 90 % of plants that are terrestrial have mycorrhizal association. Therefore it is prudently suggested that the beneficial impacts of fungi in regard to phytoremediation must also be taken into account to increase the efficiency of the plants for the remediation of harmful toxicants. The species of fungi that form mycorrhizal association with the plants have proven to increase the accumulation and tolerance of contaminants from the soil or water. Few examples of fungi and plant association that remediates contaminants have been listed in Tables 1.7 and 1.8.

1.3.8 Technological Interventions in Plants Used for Phytoremediation

It is said that plants have intrinsic qualities that enable them to detoxify contaminants, but there is a lacuna in terms of catabolic pathway which they lack, inhibiting complete degradation of the contaminants. Microbes are efficient in this matter and can completely degrade xenobiotics (Abhilash et al. 2009). Genetic engineering plays a pivotal role in enhancement of the plants' ability to accumulate and detoxify contaminants. Transgenic plants as well as electrokinetic techniques have been employed to enhance the phytoremediation potential, and it has been successfully implemented. The role of transgenic crops and electrokinetic process in enhancement of phytoremediation potential has been briefly described in this section. For the enhancement of phytoremediation potential, another approach has been followed by Bauddh and Singh (2015a). The authors have used inorganic fertilizers, biofertilizers (*Bacillus subtilis* and *Azotobacter chrocoocum*), slow-release fertilizers and vermicompost to study their effects on accumulation and partitioning capacity of *Brassica juncea* and *Ricinus communis* for cadmium. It was found that protein content that decreased due to Cd stress was recovered by using biofertilizers. The use of biofertilizers increased metal accumulation, whereas vermicompost decreased bioaccumulation by the plants. The biofertilizers and vermicompost increased the overall health of the plants. *Ricinus communis* was found to be more tolerant and accumulated more Cd than *Brassica juncea*.

1.3.8.1 Transgenic Plants and Phytoremediation

Earlier applied only for inorganic pollutants; gradually, transgenic plants have progressed towards remediation of organic pollutants such as explosives, chlorinated solvents and hydrocarbons (Salt et al. 1998; Pilon-Smits 2005). Heavy metals were the first contaminants to be remediated by transgenic plants using tobacco plant which expressed a metallothionein gene to create higher tolerance for cadmium and *Arabidopsis thaliana* plant which overexpressed a reductase gene mercuric ion for creating more tolerance to Hg (Misra and Gedamu 1989; Rugh et al. 1996). The plants that have been developed with transgenes are used in two ways for

Table 1.8 Mycorrhizal fungi used for enhancement of phytoremediation

Plant species	Family	Fungi	Contaminants	Remarks	References
Apium graveolens (celery)	Apiaceae	*Glomus macrocarpum*	Cd	The Cd^{2+} accumulation increased in the roots, but it was found that the translocation of the metal to shoots was diminished	Kapoor and Bhatnagar (2007)
Oryza sativa	Poaceae	*Glomus versiforme*, *G. mosseae* and *G. diaphanum*	Zn, Pb, Cu and Cd	The root and shoot biomass increased when the plants were inoculated with the arbuscular mycorrhizal fungi, and the accumulation of the heavy metals in the roots was found to be high, but lower translocation was found in the aerial parts	Zhang et al. (2005)
Zea mays	Poaceae	*Glomus mosseae*	Cd	The Cd uptake by the plants increased by inoculation of *G. mosseae*	Malekzadeh et al. (2011)
Pteris vittata	Pteridaceae	*Glomus intraradices*, *G. geosporum* and *G. mosseae*	As	The study found that plant growth increased, and nitrogen, phosphorus and chlorophyll contents also were found to be significantly higher	Leung et al. (2010)
Calopogonium mucunoides	Fabaceae	*Glomus etunicatum*	Pb	The inoculated plants showed higher concentration of metals in the roots but lower concentration in the shoots	de Souza et al. (2012)

phytoremediation purpose: first is the use of transgenes for metabolizing the contaminants and second is the use of transgenes to increase the resistance of the plants towards the toxicants (Abhilash et al. 2009). Some examples of transgenic plants used for remediation of contaminants have been listed below in Tables 1.7 and 1.9.

1.3.8.2 Role of Electrokinesis for Enhanced Phytoremediation

In situ treatment of contaminated sites can be done by the techniques associated with electrokinetic remediation (Reddy and Cameselle 2009). In this technique the contaminated soil is subjected to electric potential directly by inserting electrodes into the ground. Various transport processes and reactions are induced by the electric potential; this causes the movement of contaminants towards the oppositely charged electrodes. The mobilization of the toxicants occurs by two processes: (a) electromigration is a process in which the contaminants move towards the electrodes of opposite charge and (b) electro-osmosis is a process in which the net flux of water is induced by electric field through structure of soil that is porous in nature. Usually, the particles of soil are charged negatively; thus they move towards the cathode (Cameselle and Reddy 2012). Phytoremediation coupled with electrokinetic techniques have a promising future and need to be researched further for contaminants like heavy metals and others as well. Several researchers imply electrokinetics during cultivation of plants in contaminated sites and have been found that the application of electrokinetics enhanced the bioaccumulation of contaminants (Tables 1.8 and 1.10).

1.3.9 Multitasking Approach of Phytoremediation

It is known that all plants provide innumerable benefits to the ecosystem. We are aware of only a small fraction of ecosystem services that is provided by the plants. Hence, the preference of plants over traditional techniques for remediation of contaminants is understandable. The traditional methods would only address the problem of the contaminants, but when plants are applied for the same purpose, several added advantages would be achieved (Fig. 1.10). The first and the foremost advantage of phytoremediation is the release of oxygen by the plant which would be a major boon. The second merit would be the carbon sequestration by the plants. It is well known that plants are the major storehouses of carbon. If trees are used for phytoremediation, a large amount of CO_2 can be fixed by the plants which would help in curbing the greenhouse effect. The use of bioenergy crops for phytoremediation would remove the contaminant along with energy generation; this would be a very major advantage for the people as well as the environment. As phytoremediation is a solar energy-driven process, using plants, the energy may be used up in application of the traditional methods. If the plants used for the remediation of contaminants are cash crops, they would provide employment for the masses. This is the most important merit for the humans especially the ones living in the developing countries. Employment generation would boost the application of plants for

Table 1.9 Transgenic crops used in phytoremediation

Plant species	Family	Gene	Contaminants	Remarks	References
Nicotiana tabacum	Solanaceae	Nfsl	Trinitrotoluene	The gene released the nitroreductase enzyme which removed a large amount of TNT from the solution and reduced TNT to form 4-hydroxylamino-2, 6-dinitrotoluene	Hannink et al. (2001), (2007)
Oryza sativa	Poaceae	CYP1A1	Simazine and atrazine	Cytochrome P450 monooxygenase enzyme was successfully incorporated to remediate xenobiotics simazine and atrazine	Kawahigashi et al. (2005)
Solanum tuberosum	Solanaceae	CYP1A1, CYP2B6 and CYP2C19	Herbicides and sulphonylurea	The enzyme cytochrome P450 monooxygenase increased resistance of the plants towards sulphonylurea and other herbicides	Inui and Ohkawa (2005)
Brassica juncea	Brassicaceae	γ-ECS, GS γ-	1-chloro-2,4-dinitrobenzen, phenanthrene, metolachlor and atrazine	The two enzymes glutamylcysteine synthetase and glutathione synthetase derived from the gene sourced by the plant itself resulted in increased tolerance towards 1-chloro-2,4-dinitrobenzene, phenanthrene, metolachlor and atrazine	Flocco et al. (2004)
Nicotiana tabacum	Solanaceae	LAC	Bisphenol A and PCP	The enzyme laccase was secreted into the rhizosphere, and this helped in removal of the pollutants bisphenol A and PCP	Sonoki et al. (2005)

Adapted and modified from Abhilash et al. (2009)

Table 1.10 Plants used in phytoremediation treated with electric current

Plant species	Family	Contaminants	Remarks	References
Lactuca sativa (lettuce)	Asteraceae	Cd	In the hydroponic culture, the nutrient solution and Cd were added; the plant was subjected to 1 V cm $^{-1}$ AC current for 60 days for remediation of Cd	Bi et al. (2010)
Lolium sp. (ryegrass)	Poaceae	Cu, Cd and As	The DC of 30 V was applied after 5 days of germination for 90 days or remediation of As, Cu and Cd	O'Connor et al. (2003)
Solanum tuberosum	Solanaceae	Zn, Pb, Cd and Cu	For remediation of the heavy metals, AC or DC 500 mA for 90 days after 30 days of plantation was applied	Aboughalma et al. (2008)
Brassica juncea	Brassicaceae	Zn, Pb, Cd and Cu	For a period of 16 days,8 h a day each direct current was applied for remediation of the heavy metals	Lim et al. (2004)
Poa pratensis (Kentucky bluegrass)	Poaceae	Pb	Remediation of Pb was done after adding urea to the plants and applying DC continuously for 15 days at 500 mA intensity	Putra et al. (2013)

Adapted and modified from Cameselle et al. (2013)

phytoremediation as the plants can be harvested for their parts, and the pollutants can be removed at the same time. It would help in the overall societal development and improve the ambient environment.

1.3.10 Economic Feasibility of Phytoremediation Over Conventional Methods

Any technology or process needs to be economically feasible to be practically applied. It is same in the case of the phytoremediation also as the process needs to be beneficial in terms of monetary gains as well. It has been found that using plants for remediating pollutants has indeed been superior to traditional techniques in

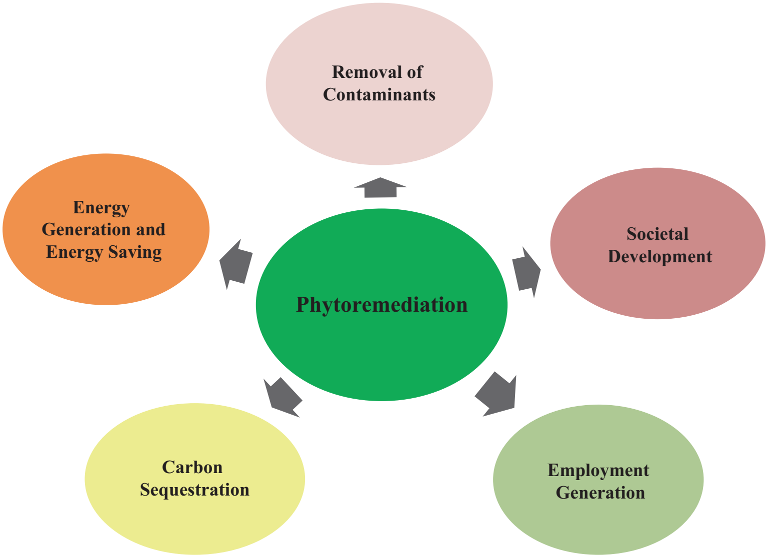


Fig. 1.10 Additional merits of phytoremediation

Table 1.11 Cost comparison between phytoremediation and traditional methods for contaminant removal

Contaminants	Estimated cost of traditional techniques	Estimated cost of phytoremediation	Reference
Petroleum hydrocarbons	$850,000	$70,000	Jipson (1996)
Heavy metals	$250 per cubic yard	$80 per cubic yard	Black (1995)
Lead (10 acres)	$12 million	$500,000	Plummer (1997)
Nitrogen and phosphorous (present in water causing eutrophication and algal bloom)	–	121.1 Yuan/ton of water hyacinth (shadow price) 1,332,581 Yuan (annual cost)	Wang and Wan (2013)

monetary terms. Table 1.9 is a compilation of comparison of the cost between phytoremediation and traditional techniques of studies conducted by several authors like Black (1995), Jipson (1996), Plummer (1997), Wang and Wan (2013), etc. Traditional techniques have cost more than the phytoremediation processes making phytoremediation feasible for implementation. Phytoremediation is more economically beneficial than traditional techniques because of the additional merits such as energy generation, food production, essential oil production, timber production and several other ecosystem and societal services (Table 1.11).

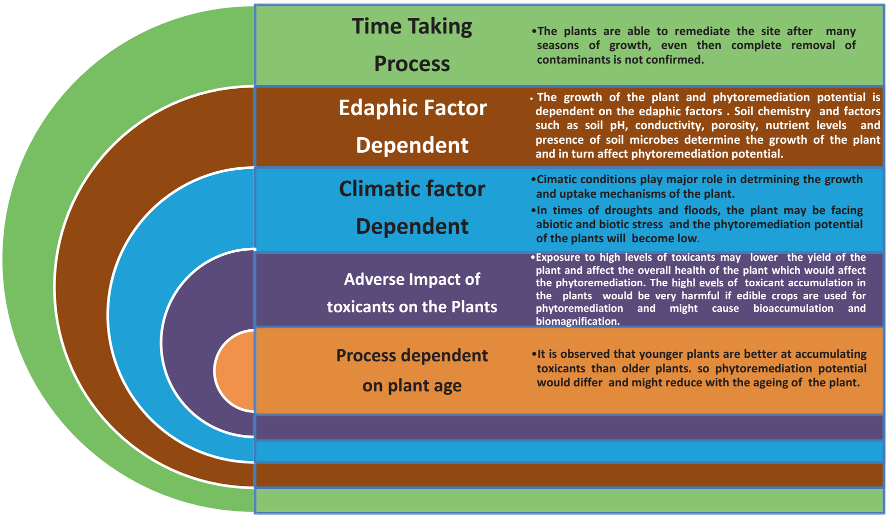


Fig. 1.11 Constraints of phytoremediation (Tu et al. 2004; Mwegoha 2008)

1.3.11 Constraints of Phytoremediation

All technologies and processes comprise of some pros and cons, and this is also applicable in the case of phytoremediation. Phytoremediation is a time-taking process as a long time taken for maximum removal of contaminants from the site; even then complete removal of the contaminants is not guaranteed. After excavation, incineration or disposal might take maximum time in months to accomplish the task, whereas phytodegradation or phytoextraction might take several years (Mwegoha 2008). The phytoremediation process is dependent on edaphic factors and soil chemistry where the soil pH, conductivity, porosity, nutrient levels and presence of soil microbes are instrumental in deciding the uptake mechanisms of the plants. Climatic factors are also very essential in determining the uptake mechanisms, and climatic stress can cause lower phytoremediation potential of the plants. Toxicants are known to have detrimental effects on the plant bodies; even hyperaccumulators exhibit negative impacts after prolonged exposure to the toxicants. Therefore, over a period of time, the efficiency of the plants for phytoremediation reduces making the process unfeasible. Another factor that might hamper the phytoremediation potential of the plant is the age of the plant. Younger plants are said to accumulate more contaminants that the older plants. Some studies suggest that older plant having more biomass accumulates more toxicants in total which can compensate for their lower physiological activities (Tu et al. 2004). Overall despite several constraints, phytoremediation proves to be an environment-friendly and sustainable approach which can be implemented effectively.

1.4 Conclusions

At present era, phytoremediation provides a solution to the most disastrous problem of pollution that is faced by mankind. Phytoremediation not only addresses the problem of pollution but also provides several ecosystem services along with making it a viable and feasible approach. Especially the use of bioenergy crops, aromatic plants and tree species can result in a holistic development of the ecosystem and its population. Being economically feasible, it can be encouraged to be adapted by the masses for decontamination of the sites. A wide range of contaminants can be remediated by plants at a lower cost which is a commendable feat. Technological and biological amendments can be made to increase the efficiency of the plants for the remediation of the contaminants. It is of immense importance for the sake of our environment to promote phytoremediation.

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