Soil Reclamation Through Phytoextraction and Phytovolatilization

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Abstract

Environmental pollution becomes most severe due to anthropologic actions including domestic waste generation and excessive utilization of fertilizers and pesticides to get better yield. Although the phenomenon of hyperaccumulation of metal ions in shoots of certain plants is known since long, the contemporary environmental concerns have prompted broad-based studies on hyperaccumulator plants that can phytoremediate contaminated soils. Phytoremediation is considered as an eco-friendly technology which is deployed to alleviate pollutants from environment components. The present chapter discusses phytoextraction and phytovolatilization mechanisms that are involved in the decontamination of the soil.

Keywords

Phytoremediation • Salinity • Hyperaccumulator • Pollutants

3.1 Introduction

Phytoremediation (phyto, plant, and *remedium*, restoring balance) is visualized as benign technology that depends upon the remarkable ability of some plants to remove or neutralize various chemicals (organics and metal ions) from the soil,

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water, and air (Sarma 2011). It is very eco-friendly, cost-effective, aesthetically pleasing, and noninvasive to redress the alleviation of environmental hazards (Elizabeth 2005). Phytoremediation is brought about by plants having the ability to extract and accumulate the toxic metals or ions in the aboveground shoots (phytoaccumulation), or removing or decomposing various organic chemicals from the soil (phytodegradation), or acting as "filter" to remove toxic matter from an aqueous environment (rhizofilteration).

To complete the increasing demand of world population, there is excessive utilization of fertilizers and pesticides to get better yield. So, today environmental pollution becomes most severe also due to anthropologic actions including domestic waste generation (Kabata-Pendias and Pendias 1989). When excessive heavy metals/ions are present in the environment, a large amount absorbed by plant roots translocated to upright direction leading to reduced growth and metabolic disorder (Bingham et al. 1986). Buildup of soil salinity is one of the world's oldest and most serious agricultural problems in arid and semiarid regions (Tanji 1990). About 7.0 million hectares of agricultural land is infested with salinity worldwide, and these domains are expanding further. The chlorides and sulfates of sodium, calcium, and magnesium are the dominating soluble salts in them (Dahiya and Laura 1988). The existing technologies on farm salinity management that work well include surface and subsurface drainage. These are basically civil engineering technologies and are costly to install, are difficult to maintain, and have the problem of saline effluent management. Apart from that, under Indian conditions with fragmented landholdings, a wide application of such technology seems utopian. Phytoextraction is the natural ability of certain plants to accumulate unusually high amount of metal ions particularly in their leaves (Elizabeth 2005; Angrish and Devi 2014).

Phytoextraction and phytovolatilization occur simultaneously. Phytovolatilization is a diffusion process in which volatile organic compounds (VOCs) are absorbed by the plants and are released into the atmosphere. In recent years considerable research efforts have been made in the use of plants to remove inorganic or organic contaminants from the soil by the technique of phytoremediation (Devi et al. 2016). To improve the previous phytoremediation processes that are based on biological and engineering strategies, there is a need to know the physiological and molecular mechanism of different plants. This chapter represents the summarized work of the eminent scientists on phytoextraction and phytovolatilization processes that can be used in higher education teaching.

3.2 Origin

The US Environmental Protection Agency proposed the term phytoremediation in 1991 which was firstly reported by Raskin et al. But in open technical literature, the term phytoremediation was firstly used by Cunningham and Berti (1993). A German botanist works on the leaves of different plant species that are grown naturally on the soil which contained extraordinary high levels of zinc (Baumann 1885). It has been observed that 1% and 1.7% zinc accumulate in dry leaves of violet (*Viola* *calaminaria*) and the mustard (*Thlaspi calaminare*) species, respectively, whereas the plants growing in controlled condition accumulated zinc from 0.001% to 0.02% in their dry leaves. Half a century after, a word "alkali disease" was noted in animals in South Dakota. The cause of this disease was traced to the accumulation of selenium up to 0.6% in dry shoot/leaf mass (Byers 1935, 1936) of *Astragalus*. Shortly thereafter, two Italian botanists (Minguzzi and Vergnano 1948) reported 1% nickel in leaves of *Alyssum bertolonii* growing on nickel-enriched serpentine soils near Florence, Italy. The quest for using this unique hyperaccumulation ability of some plants was thus initiated.

3.2.1 Overview of Phytoremediation

Phytoremediation is also low cost over conventional methods for hazardous waste management (McCutchen and Schnoor 2003). Phytoremediation is a nondestructive cleanup method in which plants can be used as a tool to decontaminate the soil and water (Fig. 3.1).

There are five kinds of phytoremediation sub-techniques which exist (Salt et al. 1998):

- Phytoextraction: wherein plants accumulate pollutants (metals) in order to decontaminate soils
- Phytodegradation: wherein plants degrade organic pollutants directly via their own metabolic activities
- Phytostabilization: wherein plants stabilize pollutant in soil
- Phytovolatilization: deployment of plants to remove pollutants from air
- Rhizofilteration: deployment of plant roots or whole plant for filtration

3.3 Phytoextraction

Plants have been used to remove contaminants from soil, water, and air into harvestable plant biomass. Excessive amount of the contaminants are absorbed by the plants from the soil that are called as hyperaccumulators. The hyperaccumulator plants of Brassicaceae family (Kumar et al. 1995) have been deployed for phytoextraction. McCutchen and Schnoor (2003) observed that phytoextraction is becoming a more widely used remediation technology where field-level results have been shown (Brown et al. 1995). It includes the extent of contamination, metal bioavailability, and the plants' ability to intercept, absorb, and accumulate metals from soil which is becoming a challenge for researchers and managers of phytoextraction enterprises (Thangavel and Subbhuraam 2004). Salt et al. (1998) highlighted the remarkable ability of certain plants to hyperaccumulate metal ions (Cd, Ar, Pb, Ni, Co, etc.) in their harvestable parts (Salt et al. 1995; Cunningham and Ow 1996; Suresh and Ravisanker 2004). Hyperaccumulation of metal ions in plants takes place against concentration gradient at the expenditure of metabolic energy which

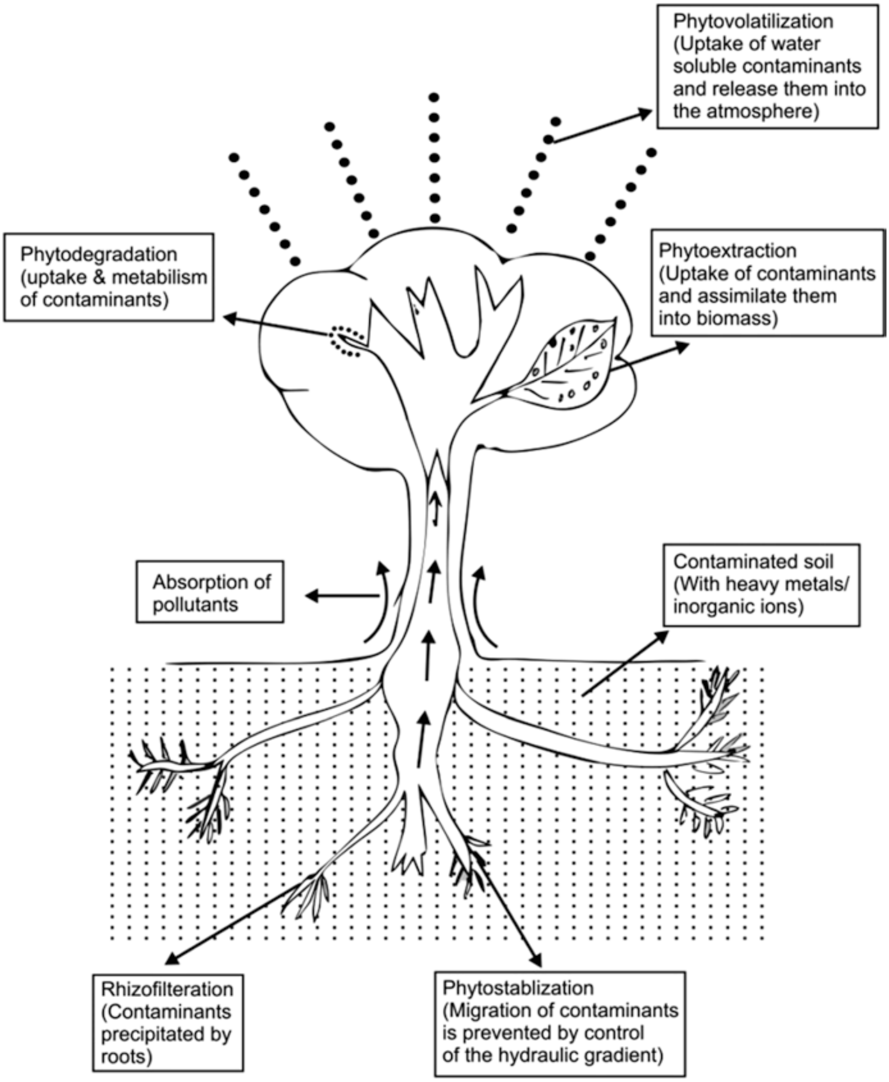
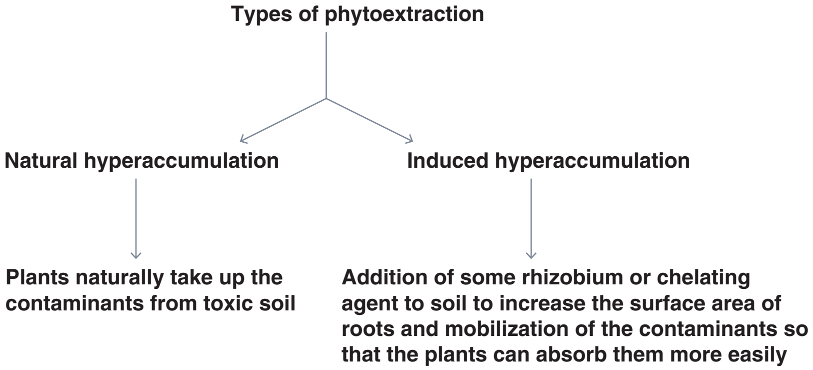


Fig. 3.1 Overview of phytoremediation

is obviously derived from the sun. Ion hyperaccumulation in harvestable parts is therefore acknowledgeably a "green" technology that is environmentally benign.

In contrast to heavy metal ions, phytoremediation of the component ions of salinity, i.e., Na^+, Ca^{2+}, Mg^{2+}, Cl^-, and SO_4^{2-}, has not received desired attention. There are scanty reports in literature (Yeo 1974; Williams 1960; Sairam and Tyagi 2004; Devi et al. 2016) where attempts to alleviate salinity using salt hyperaccumulating plants have been made. It is a matter of common knowledge that halophytes, which constitute the bulk of native flora of the saline soils, not only survive but also thrive on the saline milieu. This requires repeated cropping until the contaminated soil has reached acceptable levels for the farmers to cultivate their regular crops.



3.4 Mechanism of Hyperaccumulator Plants

Based on the availability of contaminants present in soil ecosystem, the hyperaccumulator plants can absorb. This capacity for accumulation is the result of the plants to that environment (Fig. 3.2). Sen et al. (1982) observed that despite aridity, the habitats of halophytes in arid regions are mostly wet. Dry and saline habitats do not have any vegetation. Halophytic roots are able to absorb water only from somewhat dilute soil solutions. As water is transpired, accumulation of salt takes place in shoot, particularly leaves. Under physiological drought conditions, the leaves of saline plants play an important role and develop a combination of xeromorphic and halophytic characteristics, viz., hair cover, salt excretory glands, and salt storage glands. Two of these features, i.e., salt glands and succulence vis-à-vis ion storage in cells, are important.

3.4.1 Salt Excretion

Salt excretion takes place through certain specialized glandular cells. Salt excretory glands have been reported in some of the non-succulent halophytes of the Indian arid zone, viz., *Aeluropus lagopoides*, *Sporobolus helvolus*, *Chloris virgata*, *Cressa cretica*, *Tamarix dioica*, *T. ericoides*, *and T. troupii.* As early as 1935, Frey-Wissling noted that important structures in the salt economy of some halophytes are salt glands. This fascinating trait has evolved convergently in many different families of angiosperms such as Plumbaginaceae, Tamaricaceae, Primulaceae, etc. including bladder trichomes of some Chenopodiaceae, e.g., *Atriplex* species. Excess salt may well be secreted by salt glands in some halophytes, e.g., *Spartina townsendii* (Skelding and Wintebotham 1939) and *Limonium* (Ziegler and Luttge 1967). Salt crystals secreted by glands are likely to fall again on the soil below due to gravity,

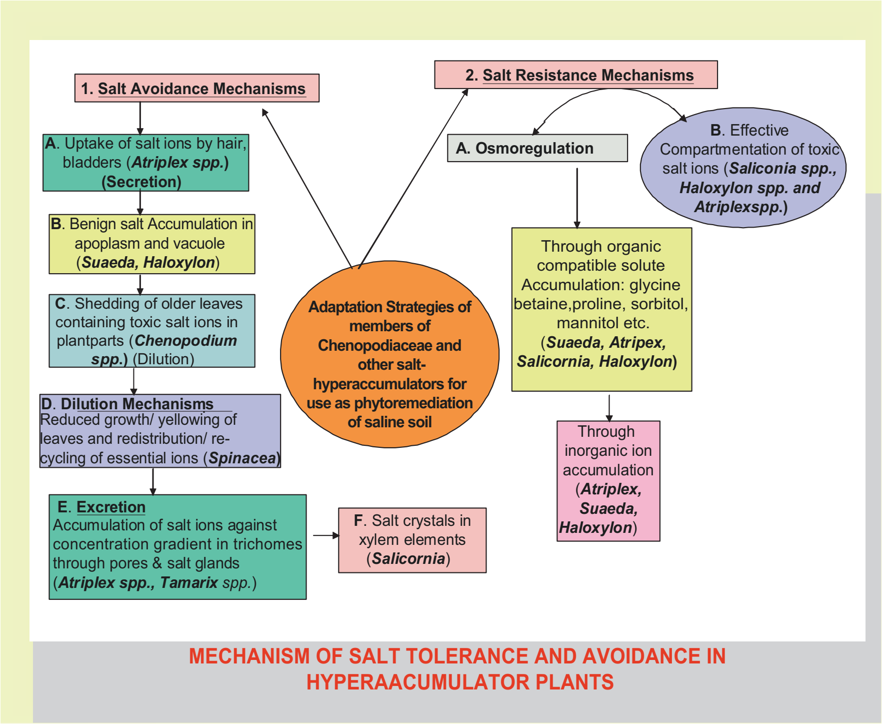


Fig. 3.2 A flowchart of some important salt tolerance strategies adopted by hyperaccumulator plants

dewdrops, or rainfall. The use of salt-excreter plants in saline soil remediation must, therefore, be critically assessed taking in account all these factors.

3.4.2 Succulence Mechanism

Ion accumulation in succulent halophytes, like *Haloxylon recurvum*, *H. salicornicum*, *Portulaca oleracea*, *Salsola baryosma*, *Sesuvium sesuvioides*, *Suaeda fruticosa*, *Trianthema triquetra*, *Zygophyllum simplex*, *Suaeda fruticosa*, *Salsola baryosma*, *Trianthema triquetra*, etc. where these are sequestered in high concentration in vacuolar sap is therefore an important mechanism of interest for salt hyperaccumulation from phytoremediation point of view (Sen et al. 1982).

3.5 Function

Because of several drawbacks, the older and traditional methods are not suitable for practical applications, and hence, the deployment of phytoremediation strategies to make soil heavy metal contamination-free is necessary (Lasat 2002). Potential for phytoremediation depends upon the interactions among soils, heavy metals, bacteria, and plants. Potential for phytoremediation depends upon the interactions among soils, heavy metals, bacteria, plants and their interactions are affected by a variety of factors, such as characteristics, activity of plants and rhizobacteria, climatic conditions, soil properties, fixation, mineralization, synthesis, and release of organic and inorganic compounds, root system etc.

1. *Role of mycorrhizae in phytoremediation*

Remediation of heavy metal contamination in soils is difficult as these cannot be destroyed biologically but are only transformed from one more toxic to less toxic form (Garbisu and Alkorta 2001). Phytoextraction is the use of plants to extract, sequester, and/or detoxify pollutants through physical, chemical, and biological processes (Wenzel et al. 1999). The process of metal uptake and accumulation in plants after mycorrhizal application increases the surface of the root (Fig. 3.3). Contaminants present in the soil are sorbed at root surface and enter into the root cells by crossing cellular membrane. Some of the contaminants absorbed are stored in the vacuole, and the rest of them enters into the root vascular tissue (xylem). Finally contaminants are translocated from root to shoot portion of the plant and dumped at a point sink for their incineration (Huang et al. 2005).

2. *Role of plant growth-promoting rhizobacteria (PGPR)*

Inoculation of PGPR in spermosphere and seed microbiolization with hyperaccumulator plants (Glick et al. 1999; Glick 2003) help in mitigating toxic effects of heavy metals on the plants (Belimov et al. 2004) and the release of chelating agents, acidification and phosphate solubilization (Abou-Shanab et al. 2003a). The use of PGPR with PGP ability in combination with plants is expected to provide high efficiency for phytoremediation (Whiting et al. 2001; Abou-Shanab et al. 2003a).

For example:

1. Size of Indian mustard increased by 50–100% upon inoculation with *K. ascorbata* SUD165/26 in Ni-contaminated soil (Burd et al. 1998).
2. In the presence of PGPR, toxicity level of nickel was significantly reduced in canola or tomato seeds (Burd et al. 1998).
3. PGPR enhanced accumulation of Se and Hg in wetland plant tissues (de Souza et al. 1999b).

3. *Plant-bacteria interactions*

During the process of symbiosis (plant and bacteria), the adaptation capabilities of both partners should be more in helping in alleviation of high level of heavy metals. Herein, bacteria help in augmentation of the contaminated soil and ameliorate functionality with improved soil and plan health (Elsgaard et al. 2001; Filip 2002).

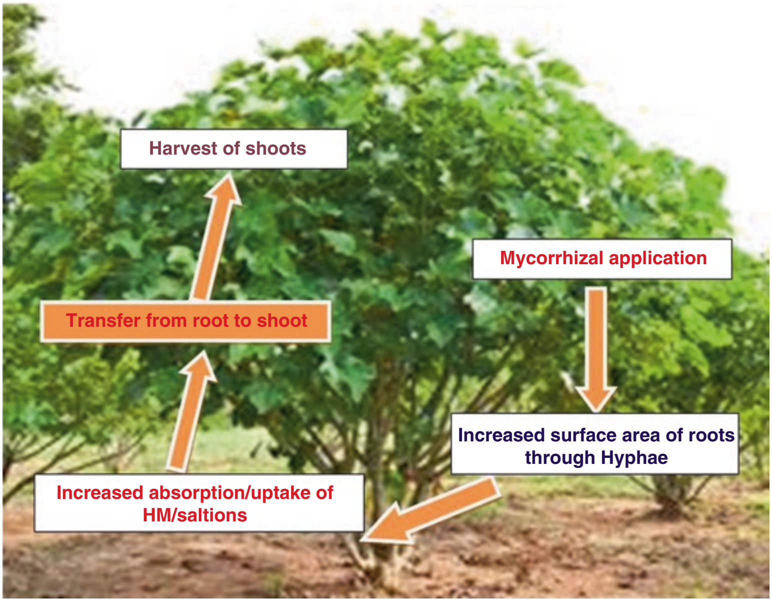


Fig. 3.3 Increased uptake of contaminants on application of mycorrhiza

3.6 Phytovolatilization

Phytoextraction and phytovolatilization occur simultaneously. Phytovolatilization is one of the important processes of uptake and transpiration of water-soluble contaminants by the plants. Contaminants which are present in plants in soluble form undergo several processes and finally volatilize into the atmosphere along the stream of transpiration. Phytovolatilization has been widely used to remove mercury by converting its more toxic mercuric ion into less toxic elemental mercury. In the presence of VOCs, plants may help in alleviation and transportation of different types of organic compounds and thereby affect the fate of contaminants (Fig. 3.4) (Limmer and Burken 2016).

Direct Phytovolatilization In this process plant-mediated uptake and translocation of contaminants to the shoot portion to diffuse across hydrophobic barriers such as cutin in the epidermis or suberin in woody dermal tissues.

Indirect Phytovolatilization By deploying ample amount of soil plants, take vast quantities of water whereby activities of plant roots may increase the flux of volatile contaminants (Jasechko et al. 2013) from the subsurface through the following ways:

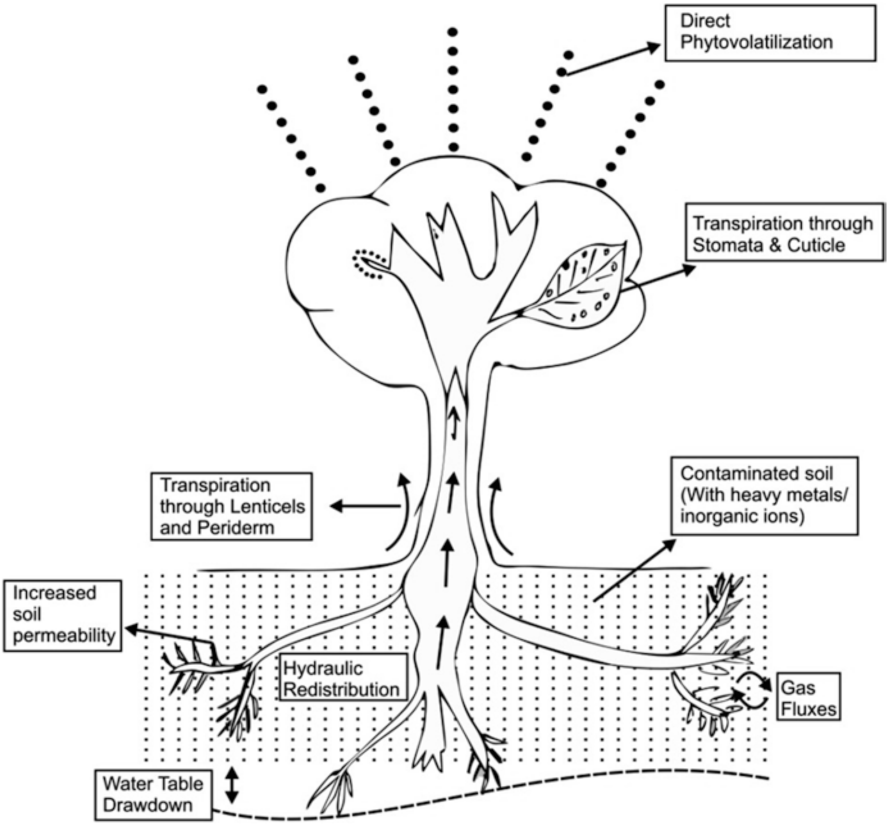


Fig. 3.4 Phytovolatilization processes: direct and indirect

- Lowering the water table.
- Water table fluctuations cause gas fluxes.
- Increased soil permeability.
- Hydraulic redistribution.
- Interception of rainfall that would otherwise infiltrate to dilute and advert VOCs away from the surface.

According to Negri et al. (2003), plant roots redistribute water throughout the subsurface by employing two types of hydraulic lift (Figs. 3.5 and 3.6) (Neumann and Cardon 2012). It is a pace of transportation stream wherein organic contaminants cross the cellular membrane of root passively and whereby volatilize (Dettenmaier et al. 2009).

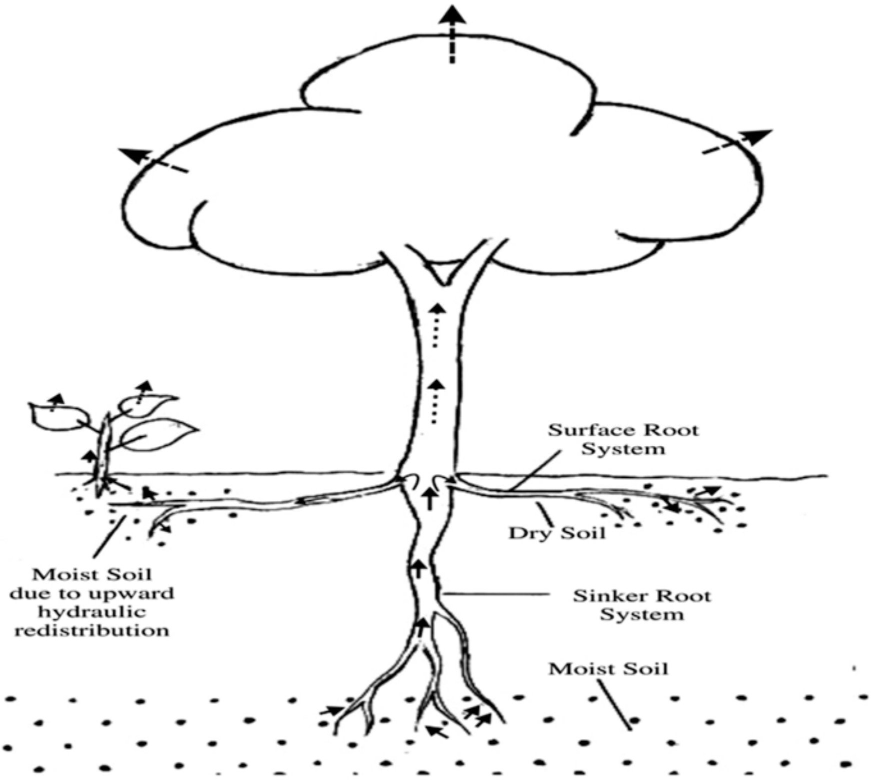


Fig. 3.5 Upward hydraulic redistribution in trees

3.7 Functions of Plant Volatiles

There are a number of functions implied through plant VOCs wherein several of them are:

1. *Plant Reproduction*: Floral scent is a signal for pollinators that can be used to pollinate wherein a diverse blend of plant VOCs attract pollinators and to ensure reproduction (Knudsen and Tollsten 1993). There is a large diversity of volatiles that may contain from 1 to 100 volatiles wherein amount varies from the low picogram range to more than 30 μg/h (Knudsen and Gershenzon 2006).
2. *Plant Defense*: To succumb the adverse effect, a blend of VOCs are produced upon attack of biotic stress (Vancanneyt et al. 2001; Dicke and van Loon 2000).

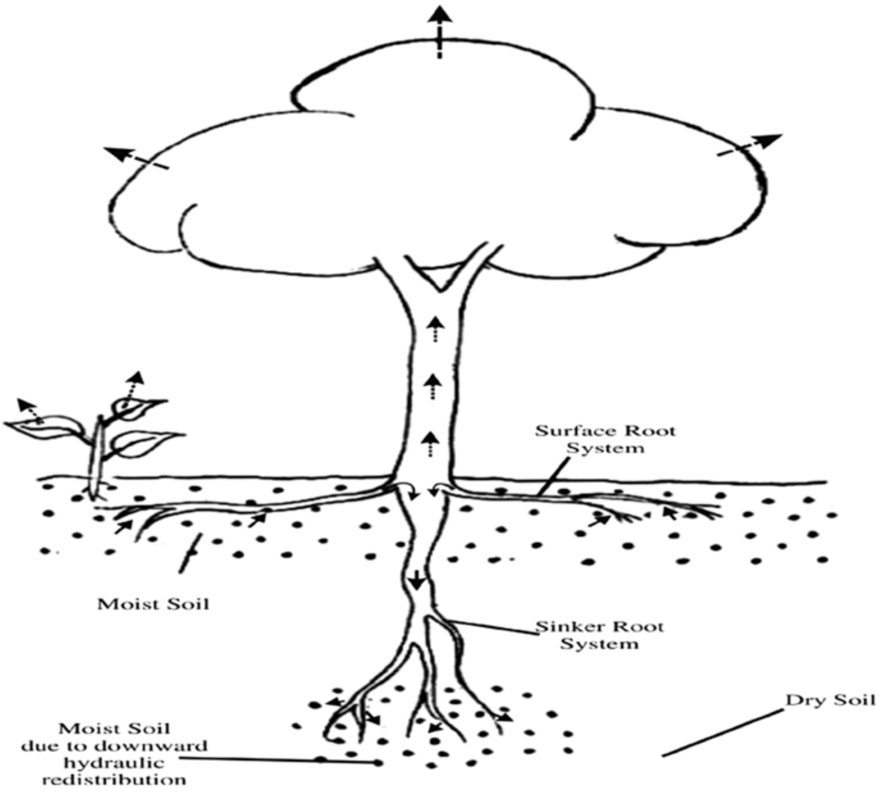


Fig. 3.6 Downward hydraulic redistribution in trees

The produced VOCs help in sustainability of plants in direct/indirect way by deploying lipoxygenase (LOX) pathway, the shikimic acid pathway, and products of the terpenoid pathway (Kessler and Baldwin 2001; Pichersky and Gershenzon 2002; Horiuchi et al. 2003; Gols et al. 2003; Heil 2004).

3. *Plant-Herbivore-Carnivore Interactions*: This type of tritrophic interaction induced by VOCs includes interactions between lima bean plants (*Phaseolus lunatus*), herbivorous spider mites (*Tetranychus urticae*), and carnivorous mites (*Phytoseiulus persimilis*) (Takabayashi and Dicke 1996). Merely lying of egg on plants produces VOCs which attract egg parasitoids (Hilker and Meiners 2002). Similarly, herbivore- and wound-induced VOCs attract predators/parasitoids in plant-caterpillar-parasitoid (Dicke and van Loon 2000) and plant-caterpillar-predatory bug interactions (Kessler and Baldwin 2001).
4. *Plant-Plant Interactions*: Herbivore-infested plants produce VOCs that also mediate plant-plant interactions and may induce the expression of defense genes

(Dicke et al. 1990; Arimura et al. 2002, 2004b). Release of herbivore-induced volatiles occurs both locally from damaged tissues and systemically from undamaged tissues and displays distinct temporal patterns (Arimura et al. 2004b). *Nicotiana tabacum*, for example, releases several herbivore-induced volatiles exclusively at night. These nocturnally emitted compounds repel female moths (*Heliothis virescens*), which search for oviposition sites during the night (De Moraes et al. 2001).

5. *Role of Plant Volatiles in Belowground Defense*: The emission of VOCs is not limited to aerial parts of the plants; rather it involves rhizosphere VOCs that help in plant defense against root-feeding enemies.

For example:

1. A bacterial (*Pseudomonas syringae* strain DC 3000) or fungal (*Alternaria brassicicola*) pathogen or rootfeeding insect (*Diuraphis noxia*) triggers the rapid emission of 1,8-cineole upon infection with *Arabidopsis* roots (Hammer et al. 2003; Chen et al. 2004; Ro et al. 2006) which enhances plant defense.
2. Upon attack by weevil larvae *Otiorhynchus sulcatus*, emission of VOCs by roots of *Thuja occidentalis* was shown to attract the entomopathogenic nematode *Heterohabditis megidis* (Boff et al. 2001). Similarly, root-feeding larvae (*Delia radicum*) emit VOCs by turnip roots that attract the parasitoid *Trybliographa rapae* (Neveu et al. 2002).
3. By deploying GC-MS, the emitted VOC was identified as the sesquiterpene (*E*)-*β*-caryophyllene that produced belowground upon root-insect-induced plant signal that strongly attracts an entomopathogenic nematode *Heterorhabditis megidis* (Rasmann et al. 2005).

6. *Abiotic Stresses*: Under abiotic stress it has been reported that plant VOCs maintained photosynthetic rate at elevated temperatures (Copolovici et al. 2005; Penuelas et al. 2005). Besides, fumigation with exogenous isoprene of fosmidomycin-fed leaves of red oak (*Quercus rubra*) and kudzu (*Pueraria lobata* [Willd.] Ohwi.) increased the ability of photosynthetic apparatus to recover from a brief high-temperature exposure (Sharkey et al. 2001). In addition, isoprenoids served as antioxidants to protect plants against a range of stresses including ozone-induced oxidative stress (Loreto et al. 2001, 2004) and singlet oxygen accumulation (Affek and Yakir 2002).

Some relevant reports regarding phytoextraction and phytovolatilization are tabulated (Table 3.1.).

Table 3.1. Some case studies involving different plants/halophytes in organic/inorganic ion remediation through phytoextraction and phytovolatilization

Sr. No	Hyperaccumulator plant(s) used and nature of studies	Quantification of remediation	Reference
1.	In a closed system with hybrid poplars after 7 days of exposure	Fraction of trichloroethylene (TCE) to the TCE taken up by the plant was 70–90%	Gordon et al. (1998)
2.	Phytovolatilization by alfalfa (*Medicago sativa*) treated with TCE and 1,1,1-trichloroethane (TCA) in soil mesocosms	Similar and notable fractions of TCE and TCA were volatilized	Narayanan et al. (1995)
3.	Poplar cuttings dosed with C-MTBE for 7 days	Volatilized 54% of the total MTBE	Rubin and Ramaswami (2001)
4.	In closed system with poplar and willow cuttings dosed with C-PCE or C-TCE	75% of the contaminant taken up by the plant was phytovolatilized	Jasechko et al. (2013)
5.	Hydroponic hybrid poplars dosed with C-MTBE for 10 days	Directly phytovolatilize 17% of the total (96%) MTBE	Jasechko et al. (2013)
6.	*Salicornia europaea* collected from the vicinity of Maharloo salt lake near Shiraz, Fars Province, Iran	High (30%) Na^+ accumulation corresponding to 31,500 μg g^{-1} dry weight. Amounts of Ni, Cr, Cd, Pb, and Hg were also found to be high in this plant	
7.	*Apocynum lancifolium, Chenopodium album*; Girlan, Khirezm region, northwest Uzbekistan	*Chenopodium album* produced 3.25 t ha^{-1} $year^{-1}$ dry biomass removing 569.6 kg ha^{-1} salt ions from 0.3 m of the soil profile amounting to 1.47% of the soil salts	Hamidov et al. (2007)
8.	*Suaeda fruticosa, Suaeda nudiflora, Salsola baryosma, Haloxylon recurvum*, and *Atriplex lentiformis* grown in salinity microplots at CCS Haryana Agricultural University, Hisar	These plants were found to be best salt hyperaccumulators and also had high biomass. These plants had the potential of desalinization of saline soils from 16 dSm^{-1} to 2 dSm^{-1} in 4.9–6.1 years	Datta and Angrish (2006) and Devi et al. (2008, 2016)
9.	Wild-growing *Tecticornia indica* and *Suaeda nudiflora*; Soliman sublake, northeast Tunisia	Both perennial plants exhibited high productivities and Na+accumulation, i.e., *T. indica* 7.4 t dry weight ha^{-1} and Na^+ 0.7 t ha^{-1} and *S. nudiflora* 0.75 t ha^{-1} and 0.22 t ha^{-1}, respectively. Soil salinity was lowered and microbial biomass was more in the remediated soil	Ouni et al. (2013)

3.8 Application

Phytoremediation processes may be applied near the industries or where the effluent has been reached. Worldwide phytoremediation projects have been carried out to mitigate the organic and inorganic contaminants that are released from different sources and excessive utilization of fertilizers and pesticides for agricultural purposes. Members of Chenopodiaceae and alpine pennycress, hemp, pigweed, etc. have proven to be successful for hyperaccumulating contaminants at toxic waste sites, i.e., abandoned metal mine workings and ongoing coal-mine discharges. This technology has become increasingly popular and employed at sites with soils contaminated with lead, uranium, and arsenic. Phytoremediation is a natural process which depends upon the rooting system and plants' ability to accumulate maximum contaminants in their aboveground biomass. These hyperaccumulator plants are also exposed to the herbivore animals, so it enters into the food web. Phytoremediation processes also have some advantages and disadvantages as follows:

Advantages

- Phytoremediation is less costly and easy to install both in situ and ex situ.
- Physiology of plants can be easily studied.
- It is very eco-friendly, aesthetically pleasing, and publicly acceptable.
- The process of phytomining increases the possibility of the reuse of valuable metals.
- It is more economically viable using the same tools and supplies as agriculture.
- It is less disruptive to the environment.
- It reduces the risk of spreading the contaminants by avoiding excavation.

Disadvantages

- Phytoremediation is limited up to the spreading of the roots.
- It requires a long-term commitment.
- It also requires the screening of hyperaccumulator plants.
- Toxicity of the contaminants leads to the death of the plant.
- There is recycling of the contaminants by entering into the food chain or released into the environment during autumn season.
- Environmental damage may be increased due to greater solubility or leaching of the contaminants.

3.9 Conclusion and Future Projections

On the basis of the literature reports, it is inferred conclusively beyond doubt that hyperaccumulator plants were able to phytoremediate the contaminated soils very efficiently and effectively (Fig. 3.7). These could provide proficient, sustainable, and low-cost plant-based technology for greening of contaminated wastelands and amelioration of physical and chemical nature of top layer of soil especially in arid

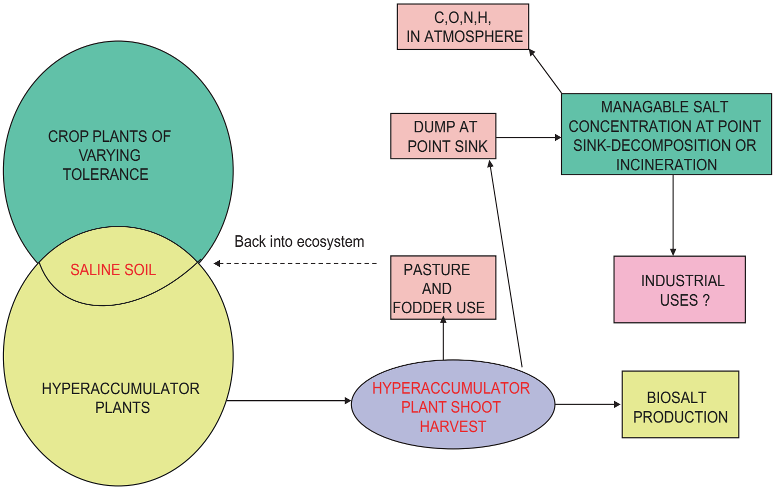


Fig. 3.7 Complementary use of hyperaccumulator plants and crop systems

and semiarid tracts of India. These hyperaccumulator plants also provide fodder, substituted vegetables, grain, fire (fuel) wood, and oil and hence are economically viable plants as well for livestock and rural people (Abbad et al. 2004). Another feasibility in the near future is the production of bio-salt or vegetable salt (CSMRI) from these hyperaccumulator plants.

In fact these plants use sun's energy to remove contaminants from soil. So transpiration-/translocation-mediated and active uptake and sequestration of contaminants are the core of hyperaccumulation technology. This phytoremediation technology involves the repeated cropping (harvestings) of these hyperaccumulator shoots until the soil contaminants have reached acceptable levels for the farmers to cultivate their regular crops. Further, these hyperaccumulator plants should always be harvested and dumped at a point sink or incinerated for further industrial uses as well.

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