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Chapter

Persistant Organic Pollutants in Soil and Its Phytoremediation

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Abstract

Persistent organic pollutants (POPs) of soil mainly exhibit toxic characteristics that posses hazard to whole mankind. These toxic pollutants includes several group of compound *viz*., polychlorinated biphenyls, polybrominated biphenyls, polychlorinated dibenzofurans, polycyclic aromatic hydrocarbons, organophosphorus and carbamate insecticides, herbicides and organic fuels, especially gasoline and diesel. They can also be complex mixture of organic chemicals, heavy metals and microbes from septic systems, animal wastes and other sources of organic inputs. Phytoremediation is an emerging technology which can be used for remediation of soil from organic pollutants. In this chapter an attempt has been made to discuss about the sources of organic pollutants, factors that influenced the uptake of organic pollutants by plants, the different mechanism responsible for organic pollutants, phytoremediation of organic pollutants and their advantages and limitation.

Keywords: Persistent organic pollutants (POPs), Phytoremediation, Soil beneficial microbes

1. Introduction

Land and water are the two crucial pillars of natural resources on which the sustainability of agriculture and the continued existence of civilization rely. Unfortunately, both have been drastically degraded due to various natural (leaching, mineralization, volcanic eruption, etc.) as well as anthropogenic (industrial waste, chemical agriculture, smelting, mining) activities.

Out of different component of soil degradation, the organic pollutant (OP) in soil is considered as an important cause that poses serious environmental damage as well as several health hazards to mankind. Generally, organic pollutants persist in the soil in very low concentrations and keep accruing over long period of time. Though steadily increasing, these low concentrations of organic pollutant in the affected soil, makes a times constrained toxicological study difficult. These organic pollutants are both lipophilic and hydrophobic in nature [1] and these organic pollutant may be deposited in the soil in every geographical area of earth [2] through spontaneous processes of nature like forest fires, volcanic eruptions *etc*, or by some anthropogenic practices. These organic pollutants entered into plant system

Biodegradation

through different plants mechanism. However, some of the organic component of the wastes is biodegradable, but heavy metals and metalloids are an emerging threat due to their long-term persistence in the environment. By adopting some phytoremediation process the effect of organic pollutants to the environments could be alleviated to some extent [3].

2. Organic pollutants in soil: sources and its effect on environment

The natural sources of organic pollutants are those that occur spontaneously without human involvement. Apart from the erosion of materials from the soil, organic pollutants in the soil may be sourced from spontaneous atmospheric sedimentation after forest fires. The forest fires which occur in high vegetation areas are a major source of organic pollutants in soil. Polycyclic aromatic hydrocarbons, anubiquitous organic pollutant, are considered to be carcinogenic in nature and hazardous to humans [4]. They are released by the burning of vegetation/biomass [5–7] and remain either absorbed in the surface soil or are mobilized due to rain water percolating through the soil [8, 9]. Several other organo-halogen compounds may be formed in the soil due to the burning of flora and fauna due to similar spontaneous sources like volcanic eruption and other geogenic causes [10, 11].

The anthropogenic sources of organic pollutants can be developed through several ways. Agricultural practices may be an anthropogenic source of organic pollutants due to contamination by several point source pollutants or diffused source pollutants. Fertilizers or pesticides which are the direct inputs in an agricultural field are the source of point source organic pollutants. Atmospheric deposition and flooding form an indirect means of pollution to the soil and are referred to as diffused organic pollutants. Ever since the advent of conscious agriculture, fertilizers and pesticides have existed to reduce and prevent any loss to the crop as well as to increase the productivity [12]. With the growth in global population, demand for food is increasing but due to the limited availability of new agricultural land, intensification of agricultural production will be required [13].

Organic fertilizers have revamped the agricultural production system, especially as people are becoming more health and nutrition conscious. These organic fertilizers are a great means for producing organic products while improving the overall health of the soil by enriching it with organic carbon and slow release of nutrients. Organic fertilizers can be prepared from compost, animal waste, municipal wastes, sewage and waste water [14]. These materials appear to have a more environment friendly disposal and recycling option [15, 16]. However, in the long run, we may find that there are certain loopholes associated with the management of organic fertilizers as well.

Organic manures prepared from animal waste may contain increased levels of copper and zinc which are added as a part of animal feed and are in turn reflected in their fecal material [17, 18]. These excess of these elements in the soil acts as pollutants and associated with risks to the agricultural production [19, 20]. Concerns over organic pollutants from organic manures rise when the manures are the sources of antimicrobials in the soil after incomplete metabolism in the animal/human body [21, 22]. Due to the increased concentration of the antimicrobials in the soil after treatment with organic manures, several resistant strains may develop and accumulate in the soils which are again recycled to the human/animal body posing a great health risk worldwide [23–25].

Biological wastes, such as waste water, municipal solid waste compost, green waste and food waste from households can be manufactured into organic fertilizers

by fermentation and composting. However, recent studies have found that such fertilizer can be a source of bio-solids and micro-plastic particles that are very challenging to remove [26]. Bio-solids contain high concentrations of organic matter and biogenic compounds, especially nitrogen and phosphorus, necessary for plant growth and have been tested to be appropriate for use as fertilizer [27]. However, bio-solids contaminated with lipophilic trace elements when applied to land are one of the most important soil contributors of trace elements in soils [28–30]. Bio-solids are also a source of nano- and micro-plastics. It is estimated that of all the microplastics that go through the wastewater treatment plant, 95 percent is contained in the bio-solids [31]. Besides trace elements, wastewater sludge and bio-solids can be contaminated with POPs including polychlorinated dibenzo-p-dioxins and dibenzo furans (PCDD/F), poly chlorinated biphenyls (PCBs), chlorinated paraffin (CPs) and perfluorinated alkylated substances (PFASs) likeperfluoro octane sulfonate (PFOS) or perfluorooctanoic acid (PFOA), which has resulted in the pollution of agricultural soils [32–34].

The first pesticides were based on inorganic chemicals such as nitrogen, sulfur, copper, mercury and arsenic compounds [35–37]. However, midway toward the 20th century, when the world evidenced a major shift in agriculture with the beginning of green revolution, the inorganic pesticides were replaced by the organic compounds. These organic pesticides, since then, have been used continuously in agriculture with commercialized in the global market [12].

Organic pesticides are washed off the sprayed plants or seeds by rainfall or irrigation and deposited in the soil [38]. Agricultural soils are also frequently affected by accidental releases of pesticides from leaking [39]. The inappropriate disposal of unwanted or out of date pesticides, pesticide packaging and the cleaning of application equipment can also cause pollution. Most of the pesticides, though organic in nature, are not degraded and persist in the soil owing to their long half-lives. These organic pesticides and their residues may accrue in soils [40–43] and may cause detrimental effects on the animals and humans over a long period of time [44, 45]. Some volatile compounds may be transported over distances and deposit in a nonnative soil as well [46].

3. Factors affecting uptake of organic pollutants by plants

Contamination of soil environment with heavy metal accumulation has become a rife across the globe. Phytoremediation has emerged out to be quite effective in this aspect. It involves growing of plants to purge contaminants from soil without hampering its regular growth and development. Literature reported by several scholars states that the mechanism of phytostabilization, rhizodegradation, rhizofiltration, phytodegradation and phytovolatilization [47] are effectual for eliminating organic contaminants from the lithosphere. The uptake of organic pollutants by plants is determined by various components. An understanding of these factors is beneficial to upgrade the uptake capabilities of the crop physiology.

3.1 Plant species

The absorption of organic contaminant by plants includes a series of complex reactions. The absorption of a compound is influenced by different attributes of the plant as well as properties of the element. The plant species should have vigorous growth rate, high biomass, substantial root system and resistance to excessive concentration of polluting metals [48]. The identification of plant species acceptable for heavy metal accretion into their system along with effective growth and

development with the conventional management practices is an important pre requisite for the uptake of organic compound from a highly degraded environment. The burning of the crop after harvest gains energy and recycles the metal from the ash, as a result of which it gets removed from the soil system. In a green house experiment conducted by Ampiah-Bonney *et al*. [49], it was observed that *Leersiaoryzoides*, a type of terrestrial plant could maintain the high arsenic uptake up to 6 weeks of study in its system in addition to producing good yield. Cho-Ruk and his co-workers [50] studied the test crop (*Alternantheraphyloxeroides*) for uptake of lead into its physiology and found that the characteristic stolons and huge fibrous root system provided larger surface area for better assimilation of the metal. The efficacy of the process was noted to be around 30–80%. The Brassica species also have excellent mechanism for uptake of cadmium and lead from the soil solution by releasing root exudates that forms complexes with these metals, thereby reducing their mobility in the environment [51].

3.2 Properties of medium

The absorption of pollutants by crops also depends on the medium. The contaminants exist in adynamic state between soil particles, in between air and water [52] of the media. It has been reported that pH and redox potential of the medium as well as presence of electrolytes hold utmost importance in the bioavailability of organic compounds into the soil solution which facilitate its uptake by the plant root system. The content of organic matter in soil is again a vital environmental factor affecting the absorption of non-ionic organic compounds by the roots from soil. The package and practices of the crops are developed accordingly to escalate the phyto-extraction and phyto-stabilization processes. In an investigation carried out by Marques et al. [53], it was found that heavy metal availability in the medium reduced by 80% after treatment of polluted soils with compost. The amount of lead taken up by the plant was highly reduced after application of lime which increased the soil pH to 6.5–7.0 as observed by Traunfeld and Clement [54].

3.3 Rhizosphere chemistry

The rhizosphere chemistry regulates the concentration of soluble cations within the region of the soil influenced by root secretions and microorganisms. It is also affected by the concentration of ions present for possible absorption by plants [55]. The root ecology can assimilate pollutants and reserve or mobilize them inside the plant tissue. The organic molecules enter the root cell either through apoplastic pathway or symplastic pathway. This process of rhizo filtration prevents leaching of heavy metals to freshwater bodies and groundwater table. The diverse microbial community present in the rhizosphere further enhances the breakdown of complex organic compounds into simpler substances by releasing certain enzymes. These along with the root exudates liberated by the plant system helps in rhizo-degradation of the contaminants. Sunflower and Indian mustard have been found to have massive fibrous root habitat which makes them favorable terrestrial candidates for metal removal through rhizo filtration [56].

3.4 Incorporation of amendments

There is also a great possibility of improving the rapid absorption of heavy metals by plants through the use of chelating agents, natural zeolites, lime and other amendments. They make the contaminants available in the solution which in turn

increases their absorption by the crop. The compounds often remain sorbed onto the clay mineral lattice which makes it unavailable for absorption. Consequently, sudden change in soil environmental quality leads to groundwater contamination. The ligand group of the chelating compounds undergo ion exchange and form complexes at the exchange sites of the soil minerals liberating the organic pollutants into the system for uptake by plants. A laboratory study performed by Roy *et al*. [57] reported that exposing plants to EDTA for an extended period of time strengthen the metal translocation in plant anatomy altogether improving the phyto-extraction process.

3.5 Properties of the contaminants

The pathway through which the organic compounds penetrate the plant body is related to the physicochemical property of each element such as lack of affinity for water, dissolution in water and vapor pressure [52]. The solubility of the pollutants in the water is highly dependent on the time to which the metals can be retained in the medium as well as the interactivity with other elements and substancesin the medium [47]. Most of the contaminants are hydrophobic in nature which allow them to accumulate in aerial plants of the plant. The phytovolatilization occurs at relatively low concentration keeping the air pollution free *B. juncea* and *Brassica napus*have provided excellent results for phytovolatilization of soils tainted with selenium [58].

3.6 Environmental conditions

Abiotic factors like temperature, humidity, stress condition, rainfall also affect the uptake mechanism of organic pollutants by plants. For instance, Merkl *et al*. [59] observed an increase in the diameter of the rootand reduction in root length due to its impermeability in dry soil under drought stress condition. This limits the absorption of heavy metals by plants making them prone to run-off and soil erosion.

4. Mechanisms of organic pollutants uptake by plants

Plant absorbed the organic pollutants such as hormones, polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs) and antibiotics, herbicides and bisphenol A (BPA) *etc*. Most of the organic pollutants are manmade xenobiotic released to environment as spills, wood treatment, explosives, pesticides, herbicides, industrial chemical, petrochemical *etc.* [60]. These organic pollutants are absorbed by higher plants through root and (or) leaves. Plant roots can absorb PCBs, PCDD/Fs, herbicides, antibiotics and BPA; whereas above ground plant parts especially leaves can absorb PCBs, PCDD/Fs and herbicides if these organic pollutants come in direct contact as liquid or in vapor form from the atmosphere [61].

Leaves absorbed different kind of organic contaminants from atmosphere *via* stomata and cuticle. The stomata of leaf are abundant on abaxial side of a leaf and are mainly involved in absorption the organic substances than the thicker cuticular layer of the adaxial side. Stomata of leaf allow easy passage of gases and liquid form of organic pollutant. The degree of opening of aperture of stomata and its number on leaf determine the permeability of gaseous from of organic pollutants. However, moisture on the leaf surface, surface tension of the liquid contaminants (eg. pesticides, herbicides, liquid aerosol *etc.*) and morphology of stomata

determine the permeability of liquid organic pollutant through stomata [62]. After entry of gas molecules through the aperture, these are transported to other plant parts*via* the phloem [63].

Although uptake of organic pollutants is absorbed by plants either from air or soil, but roots play the major role in the absorption of organic pollutants from soil. Generally, organic pollutants are of low volatility, so root tissues is the first site of contact between plant and the organic pollutants in contaminated soil or water [61]. Some lipophillic organic pollutants are passively adsorbed to the lignin of cell wall of plant surface or root that come in contact with the contaminant [64] and thus phytostabilize the pollutants and prevent their entry to groundwater through leaching or to air by volatilization or into the food chain. Again these contaminates are easily passed through the cuticle free non-suberized cell walls of root hairs from the surrounding environment unlike cuticular layer of leaf. Plant roots absorb organic pollutant inside in two phases *viz.* uptake of the substances from surrounding soil and water into root (first phase) and are subsequently distributed and accumulated in different parts of the plant (second phase) [62]. In the first phase organic pollutants are taken up by plant root across the cell membrane by passive process of diffusion [63, 65]. The root concentration factor *i.e.* the ratio of a pollutant concentration in plant root as compared to external solution determines the movement of pollutant to the root [52, 60]. The hydrophobicity of the organic pollutant is one of the factors affecting its uptake. After uptake organic pollutants are translocated to different plant parts [66]. There are two kinds of transport pathways in higher plants *i.e.* short distance transport (intracellular and intercellular transport) and long distance transport (conducting tissue transport). In studies of mechanism of organic pollutant uptake, different researchers have revealed that these pollutants after uptake by root penetrate through free intercellular space (apoplast) or cell to cell movement *via* plasma desmata (symplastic way) along with water and enter the root xylem transport tissues [52, 67]. In case of compounds that move in the apoplast of the root cortex need active transportation through plasma membranes of endodermal cells *i.e.* symplast to move to the xylem where subsequent translocation of compounds occurs [52, 68]. For long distance transport to other parts of the plant *i.e.* to leaves translocation of organic pollutants is necessary. The organic pollutants that move in symplastic way (cell to cell) in the root enter into the root xylem from root symplast by simple diffusion similar to the uptake process [60]. The ratio of a compound concentration in the xylem sap to the external solution known as transpiration stream concentration factor determines the translocation of organic compound [52, 60, 68]. Flow of compound along with water from root to shoot is influenced by transpiration pull which is more at high atmospheric temperature, low relative humidity with moderate wind flow and good amount of light.

Generally, organic pollutants are less toxic to the plant as get conjugated and stored or degraded enzymatically after entry to the cell and are less reactive. Depending on the properties of organic pollutants, these may be degraded in the plant root zone or uptake by plant followed by different processes like degradation, sequestration and volatilization. According to "green liver concept" organic pollutants or xenobioticsare metabolized by plants similarly as mammalian live function. Organic pollutants are gone through three phases; chemical modification, conjugation and compartmentation [60, 69, 70]. The detoxification process involves enzyme catalyzing reactions (oxidation, reduction, hydrolysis, conjugation *etc.*). Chemical modification includes functionalization (initial transformation) *i.e.* by enzymatic oxidation, reduction, hydrolysis *etc*. ahydrophobic organic pollutant receives a hydrophilic functional group like carboxyl, amino, hydroxyl *etc.* to attain polarity which boosts toxicant molecules' reactivity and affinity to enzyme for further transformation and conjugation.

Generally, a huge part of organic toxicant undergo conjugation, aprocess of coupling of the toxicants with intracellular endogenous compounds such as amino acids, proteins, organic acids, different carbohydrate molecules, lignin *etc.* [62]*.* Intermediates of initial transformation or original pollutants containing function group are liable to conjugation with different cellular compounds [60, 62]. For example, oxidative transformation of organic herbicide such as atrazine by creating a hydroxyl side group and this transformation is catalyzed by cytochrome P450 monooxygenasesenzyme [71]. Creation of such side group support the process of conjugation and these conjugates are very less toxic as compared to parent compounds. Immediate temporary detoxification of organic pollutants encompasses conjugation followed by compartmentation of conjugates in the vacuole (soluble conjugates that couple with sugar, amino acids, peptides *etc*.) and by sequestration on cell wall (insoluble conjugates that couple with lignin, cellulose, pectin, starch *etc.*) where these can cause least harm to vital cellular activity [60, 62, 69, 70, 72].

Plants do not possess any special excretion mechanism to keep away contaminants conjugate from vital cell constituents and activities, therefore depend on active transport of these conjugate complexes to vacuole and cell wall using ATP dependent glutathione pump [73]. Glutathione plays an important role conjugation and sequestration of organic toxicants [74]. One example of functionalization followed by conjugation and compartmentalization is vacuole deposition of 2,4-D after hydroxylation and conjugation with glucose and malonyl residues [62]. Organic compounds move by simple diffusion from xylem to symplast of shoot and then to leaf. In the leaf cell compartmentation of pollutant occurs similarly as in root cell [69, 72]. Epidermis and trichomes are the part if these compounds or conjugates of pollutants are stored or accumulated at tissue levels in leaves [75, 76].

Degradation or decomposition of organic pollutants both in root and (or) shoot tissue is one of the important step of organic pollutant transformation and phytoremediation. Degradation process is enzyme catalyzed process. It results either into complete mineralization of organic pollutant to $CO₂$, water and other simple molecules or partial degradation to more stable intermediate (for conjugation and sequestration) that can be further stored in the plant [64]. Enzymes directly involve in the degradation of organic pollutants are dehalogenases, peroxidases, phenoloxidases, ascorbatoxidase, catalase, carboxylesterases, peroxygenases, nitrilases, Esterases, phosphatases, mono- and dioxygenases, nitroreductases*etc.* Enzymes catalyze conjugation arecytochrome P450-containing monooxygenases, Glutathione-S-transferases, malonyl-O-transferase, glucosyl-O-transferaseetc.

5. Phytoremediation technology: advantages and limitations

Phytoremediation is an *in-situ* approach in which standing green plants extract, stabilize and degrade contaminants from polluted sites. It is an emerging technology that exploits the plant's natural absorption capacity and subsequent detoxification of heavy metals and other pollutants. Some of the plants used in phytoremediation of contamination like heavy metals and other organic pollutants are listed in **Table 1**.

The phytoremediation processes includes phytoextraction**, phytostabilisation, phytovolatilization,** phytodegradation, phytoaccumulation, rhizofiltration and rhizodegradation. Among these, phytostabilisation also provides the additional benefits like waste stabilization, minimal soil erosion, and hydraulic control [83].

Phytoremdiation works best in shallow contaminated soils. Vegetation with rhizosphere depth of less than 10 feets are more efficient. Good results are obtained in places with low levels of existing pollution. A wide range of contaminants like hydro-tolerant heavy metals (nickel, zinc, arsenic, selenium, copper, cadmium etc.),

Table 1.

List of plants suitable for phytoremediation along with their bioenergy approach.

radioactive nuclides, petroleum products, pesticide residues and radioactive nuclides are targeted [84]. The efficiency is also determined by the pollutant's hydrophobicity nature. If the pollutant strongly prefers organic material, then it becomes very difficult to separate the pollutants from the compounds. Extreme hydrophilic contaminants remain in the solution and pass through plant tissues without significant accumulation.

6. Steps in phytoremediation

6.1 Selection of plants and plant density

Plant is selected on the basis of the nature of contaminant, soil characteristics and local climatic parameters. Generally, plants with heavy biomass (> 3 tons/ acre) are chosen. When targeted area of remediation is groundwater, deep rooted trees like willow, cotton woods and poplar are planted in rows perpendicular to the flow of water. Some monitoring wells are placed in the surrounding areas.

6.2 Irrigation and soil amendment practices

Flooding encourages the dissolution of contaminants and increases net evapotranspiration. Simultaneously, pH of the soil may alter which require additional adjustments. Efficiency of phytoextraction can be increased by using chelating agents. Ethylenediaminetetraacetic acid (EDTA) forms chelate complexes with heavy metals and radionuclides that keep them in the solution. This helps is easy absorption by vegetation.

6.3 Agronomic practices

It includes the following processes.

6.3.1 Inorganic amendments

In a trial conducted by Vamerali and his co-workers expected that cement acted by capping pollutants, lime by raising pH, and iron sulphate by immobilizing As [85]. Lime and cement at small rates (1%) did reduce the mobility of Pb, Cu and Zn, but not of Cd [86]. Due to their relatively small active rate, they concluded that cement and lime can be applied cheaply on a large scale, with some attention to lime, which raises pH and As mobilization [87]. The response of fertilizers toward phytoextraction of heavy metals was found to be plant specific [88].

6.3.2 Organic amendments

The removals of some metals were enhanced by manure, a fact suggesting that organic matter plays an active role in soil pore-water metal mobility. This response was probably caused by increases in metal influx [89] and the chelating ability of humic acids.

6.3.3 Plowing

Plowing has shown to reduce the impact of metal pollution in plants. Plowing has shown to reduce the impact of metal pollution in plants [88].

Intercropping.

Intercropping with *C. crepidioides*, *Galinsogaparviflora*, *Solanum nigrum* and *Solanum orientalis* significantly decreased Cd contents in shoots of grape seedlings by 78.7%, 12.7%, 29.8% and 26.5%, respectively [90].

6.3.4 Monitoring

Sampling of soil/ water is practised at definite intervals. A differential contaminant concentration ensures the efficacy of the process. Subsequent modifications are made if the process is too slow. This is a 'feedback loop' that may necessitate the alteration or modification of the previous steps.

6.3.5 Harvesting

After harvesting, the hazardous biomass may be composted or incinerated which provide heat and electricity.

6.4 Advantages of phytoremediation

- i. The pollutants are phytostabilized in the rhizosphere which prevent runoff into nearby water bodies and agricultural lands.
- ii. Phytoremediation uses green plants and natural resources which makes it less expensive than other industrial methods. It is a passive technology that saves a lot input and maintenance costs and suitable for remediation of large areas. Zadrow [91] performed a comparative study between the costs of remediating 500 ppm lead polluted soil through conventional means

Table 2.

Estimated savings using phytoremediation over other conventional methods [92].

(excavation, disposal) and phytoremediation. He stated that costs of excavation and disposal were \$300,000 per acre, while phytormediation costs \$110,000 per acre (approx.). Thus phyto-remediation is estimated to cost effective (**Table 2**).

- iii. Phytoremediation sites are esthetically more pleasing that other system.
- iv. Most of the hyper accumulators' plants have shallow root zones and remediate the soils within the depth of agricultural importance. Hence, it is ideal for restoring agricultural soils contaminated by dispersed contaminants from industrial waste outlets [93].
- v. Ash (incinerated biomass) containing higher metal content can be processed to separate the metal from it. For example, 'A. murale' can be processed to separate nickel if its content is above 20% [94].

It has certain limitation such as phytoremediation technology requires more onfield results to be embraced as a mainstream technology for remediation of polluted soils by government agencies so that the benefits of this emerging technology are utilized and also it is a slow process and takes a long time (3–4 years) to meet the clean-up goals. The waste biomass is a biohazard and must be handled carefully. Sometimes improper handling and elevated post-harvest handling costs are notable setbacks of this technology [84].

Phytoremediation can be enhanced by the assistance of chelating agents like EDTA and EDGA. However, significant results had been seen only when larger quantities of chelating substances were applied and a potential threat of chelate enhanced metal leaching and groundwater contamination is a serious concern. The addition of EDTA has been shown to increase metal shoot: root ratio with the cost of lower net root and shoot biomass production [95]. Alternatively, a biodegradable chelating agent like EDDS in hot solution (90°C) can be used in substitution to chemical enhanced phytoremediation to reduce chemical leaching [96].

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