Plantation-Based Soil Reclamation of Emerging Contaminants

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Abstract

Soil pollution with emerging contaminants such as human and veterinary pharmaceuticals, antibiotics, steroids, endocrine disruptors, perfluorinated compounds, water disinfection by-products, gasoline, industrial additives, and microplastics is one of the most persistent environmental problems, which poses a serious threat to the humans and the environment. Phytoremediation, one of the innovative strategies for remediating the soil polluted by such emerging contaminants, has been recognized as a powerful in situ approach to soil remediation. The synergistic actions of plants and their associated microorganisms can improve plant growth and enhance the biodegradation of emerging contaminants, thereby accelerating the removal of these pollutants from the soil. In view of the aforementioned discussion, this book chapter is designed to cover the plant species demonstrating higher removal efficiency of emerging contaminants from soil, explain different factors influencing phytoremediation of emerging contaminants in soil, and discuss the different fundamental mechanisms of endophyte-assisted phytoremediation of emerging contaminants. Finally, the advances, challenges, and new directions in the field of phytoremediation technology for the removal of selected emerging contaminants are also discussed.

Keywords

Phytoremediation · Emerging contaminants · Soil contamination · Constructed wetlands · Mechanism · Plant uptake

1.1 Introduction

A large array of emerging contaminants (ECs) are being recognized as a threat to the ecosystem, human health, and the environment, including water, soil, and air (Gomes et al. 2020). Pharmaceuticals and personal care products (PPCPs) such as antiseptics, fragrances, soaps, sunscreens, insect repellents, surfactants, fire retardants, plasticizers, disinfection by-products of urban and industrial origin, pesticides, industrial chemicals, and municipal waste are the primary sources of ECs into the environment (Kumar et al. 2022). Economic growth and consumer-centric lifestyle have largely contributed to the growing concern of ECs, which is likely to worsen in days to come. The use of ECs for health and general life quality is increasing globally, and complete removal from different environmental sources is almost impossible.

Hospitals, industrial-scale animal feeding operations, dairy farms, leaking sewer lines, landfills, and inappropriately disposed wastes are the primary sources of ECs, while wastewater treatment plants (WWTPs) are the main entry point into the aquatic environment in the urban water cycle (Pal et al. 2014). The pharmaceuticals such as analgesics, anti-inflammatory drugs, anti-epileptic drugs, blood lipid regulators, β-blockers, antibiotics, hormones, and cytostatic drugs are frequently encountered in surface water, groundwater, drinking water, and wastewater (Kurade et al. 2021). Different antibiotics, such as tetracycline, quinolones, penicillin, amoxicillin, and gentamicin, are widely used in livestock farming to treat diarrhea and bovine pneumonia. Increased usage of a variety of antibiotics, sulfonamide, and tetracycline group in particular also leads to accumulation of those ECs in environmental matrices, as a part of it excreted out is unaltered in urine and feces by animals. PPCPs and antibiotic traces are commonly found in sewage treatment plants with concentrations ranging from ng/L to μg/L (Chaturvedi et al. 2021). Table 1.1 provides a list of various emerging contaminants with their concentration, class, and sources.

Apart from analytical challenges for quantifying trace amounts (1–100 ng L^{-1}), ECs have gained little recognition in environmental legislative lists. With no regulatory framework, significant ecotoxicological effects of PPCPs on human health are well anticipated. An increased presence of ECs in the environment is likely to cause bioaccumulation in some organisms and biomagnification (propagated through the food chain). Lipophilic compounds or metabolites, with a log $K_{ow} > 3$, tend to accumulate in the environment. Some ionophore veterinary antibiotics, gemfibrozil, ibuprofen, and diclofenac, have been known to bound to sewage sludge (Zenker et al. 2014). Pharmaceuticals can have very different bioconcentration factors depending on the aquatic environment, and relevant species when studied under environmentally relevant concentrations. The transformation product of ECs, though not extensively studied, can have even higher ecotoxicity and bioaccumulation potential (Maculewicz et al. 2022). A significant proportion of pharmaceuticals, possessing bioaccumulation potential, are not biodegradable and have a toxic effect on aquatic organisms. Bioaccumulation in aquatic organisms can have serious implications for top predators such as fish, birds, and humans (Richmond et al. 2018).

The presence of PPCPs in the aquatic ecosystem may exert a significant risk to human health and aquatic life. Though adverse effects of PPCPs on human health are not rigorously assessed, possible human health risks through ingestion of contaminated water (Pai et al. 2020) or food in the long term cannot be ignored. Negative effects of some model PPCPs, such as diclofenac, affecting the kidneys of

Table 1.1 Examples of various emerging contaminants with their concentration, class, and sources

Class	Contaminants and their concentration (ng L^{-1})	Location	References
Analgesics/anti-inflammatory drugs	Acetaminophen, 3610–119,000; ibuprofen, 300–63,000; diclofenac, 73–10,340	Hospital WWTP, South Africa	Kanama et al. (2018)
Antibiotics	Azithromycin, 26–991; carbamazepine, 10–113; estrone, 26–124; bisphenol A, <LOQ–450	Ahar River, India	Williams et al. (2019)
Antioxidants	Nonylphenols, 1519–2773; hexestrol, <LOQ-17; diethylstilbestrol, <LOQ-10; dienestrol, <LOQ-11; estrone, <LOQ-184; β-estradiol, <LOQ-62; 17α-ethynylestradiol, 4–51	WWTP, Guangdong Province, China	Jiang et al. (2020)
Antibacterial agents, disinfectants	N4-acetyl-sulfamethoxazole, 14–31; triclosan, 15–26	Wastewater, Beijing, China	Liu et al. (2020)
Analgesics/anti-inflammatory drugs	Metformin, 4–31; acetaminophen, 3–99; atenolol, <MDL–4; cephalexin, <MDL–3; norfluoxetine, <MDL–10 ng mL^{-1}	Wastewater, Saudi Arabia	Shraim et al. (2017)
Estrogen	17α-Ethinyl estradiol, 1.3–407; bisphenol A, 0.5–450; 17β-estradiol, 27–150; 4-nonylphenol, 0.3–5.4; 4-*tert*-octylphenol, 0.3–7	WWTP, Mexico	López-Velázquez et al. (2021)
Plasticizer	2-Ethylhexyl phthalate, 28–528 ng g^{-1}	Sediments, Jiangsu, China	Fan et al. (2021)

LOQ limit of quantification, *MDL* method detection limit

fish and anti-ovulation potential or antidiabetic drug metformin causing feminization of male fish, have now been established (Ambrosio-Albuquerque et al. 2021). Complications in the reproductive system; reduction in sperm count in humans; egg breakage of fishes, birds, and turtles; and structural and functional impairment of the immune system in marine animals have been attributed to acute and chronic exposure to ECs. Dietary intake of PPCP contaminated with vegetables and fruits can cause a potentially harmful impact on human health. The accumulation of PPCPs in crops irrigated with reclaimed wastewater in the long term poses a risk to human health (Liu et al. 2020). Few PPCPs are known to impact the host immune system, male fertility, and alterations in the gut microbiome, thereby impacting energy metabolism (Kumar et al. 2022). The consumption of antibiotic-contaminated foods and grains has been observed to develop antibiotic-resistant pathogens in the human body and can also aggravate estrogenic activity and immediate systemic hypersensitivity reactions (Keerthanan et al. 2021). The human risk associated with exposure to ECs is determined in terms of risk quotient (RQ), i.e., the ratio between estimated daily intake (EDI) and acceptable daily intake (ADI), and cumulative health hazard index (HI).

The EDI, body weight normalized daily intake of contaminant, is given by Eq. (1.1):

$$\mathrm{EDI} = \frac{\mathrm{CD}}{W}, \tag{1.1}$$

where D is the daily intake rate (g d^{-1}) of contaminated food/drinks containing C ng g^{-1} of EC by an individual with body weight W (kg). Then, the RQ is given as in Eq. (1.2):

$$\mathrm{RQ} = \frac{\mathrm{EDI}\left(\mathrm{ng\ kg}^{-1}\ \mathrm{d}^{-1}\right)}{\mathrm{ADI}\left(\mathrm{ng\ kg}^{-1}\ \mathrm{d}^{-1}\right)}. \tag{1.2}$$

The cumulative health HI is a reflection of the combined risk associated with each contaminant (Eq. 1.3):

$$\mathrm{HI} = \sum_{i=1}^{n} \mathrm{RQ}_i. \tag{1.3}$$

The value of RQ and HI >0.05 is considered to be a distinct human risk (Zhao et al. 2019). A recent study on screening-level risk assessment of 98 PPCPs, detected in the different water environments of India, suggested that a large proportion (47%) of the detected PPCPs possess a possible risk (RQ >1) to either aquatic species or human health. A few PPCPs with very high RQs (>1000) could potentially cause severe health concerns (Sengar and Vijayanandan 2022).

The complete removal of ECs in WWTPs is not possible. Several conventional and advanced treatment processes have been already investigated. However, low octanol/water partition coefficients of ECs make their partitioning out of the aqueous phase a significant challenge. The use of activated carbon and, to an extent, biochar has been effective for the adsorptive removal of some ECs to a moderate extent (Rodriguez-Narvaez et al. 2017). The success of microfiltration and nanofiltration technologies varies depending on the type of membrane and the characteristics of contaminants (Lidén and Persson 2015). Due to toxicity, most of the ECs cannot be utilized as a sole carbon source in the microbiological treatment process and require an additional source of electron acceptor in co-metabolism. Microalgae/fungal based treatments have been effective for PPCPs and endocrine-disrupting chemicals (EDCs) (Matamoros et al. 2015). Biodegradation in the activated sludge process is widely adopted for the removal of EDCs with excellent removal efficiency while being moderately effective against some pharmaceuticals, where adsorption plays the dominant role in the removal. The use of hybrid systems such as ozonation followed by biological activated carbon has been highly efficient in the removal of pesticides and PPCPs (Ahmed et al. 2017).

Environmental engineers have created more effective remediation techniques such as improved oxidation processes, microbial degradation, and enzymatic catalysis in response to the ineffectiveness of standard WWTPs and recalcitrant PPCPs.

However, the cost of these procedures is still debatable, preventing their use in large-scale commercial applications even though these technologies have been demonstrated to be effective and offer several benefits. Plant-based phytoremediation technologies are of immense interest due to their low-cost, eco-friendly biotic approach with low risks. The ubiquitous presence in almost every climatic region and the potential to take up organic and inorganic compounds from the soil-water system make phytoremediation a robust technology. Plants have been successfully utilized for the elimination of heavy metals and polychlorinated biphenyls from the contaminated environment (Passatore et al. 2014). Various removal mechanisms, such as phytostabilization, rhizodegradation, rhizofiltration, phytoextraction, phytoaccumulation, and phytodegradation, may be involved in the process (Wang et al. 2017).

In this chapter, the different plant species and the factors influencing the removal of emerging contaminants have been illustrated. The mechanism of the phytoremediation process and the involvement of the enzymatic system have been discussed. Appropriate modifications to phytoremediation systems have also been discussed.

1.2 Different Plant Species Demonstrating Higher Removal Efficiency of Emerging Contaminants from Soil

The plant-based bioremediation technology enables the plant to accumulate toxic substances in different parts of plants and mobilize them into plant tissues through various metabolism. The studies on molecular and physiological mechanisms of the phytoremediation process have been gaining momentum in recent years through recent engineering and biological strategies related to the optimization and augmentation of metabolic processes. Based on the availability of contaminants in different types, forms, and complexes, plants exploit different mechanisms in combination including degradation (e.g., rhizodegradation), accumulation (e.g., phytoextraction, rhizofiltration), dissipation (e.g., phytovolatilization), and immobilization (e.g., phytostabilization) to degrade, remove, or immobilize the toxic pollutants present in the soil environment. For phytoremediation, plant species are selected based on their adaptation to the regional climate, root depth, and nature and interaction with the contaminants. The ideal depth of different flora is reported as 3 ft., 10 ft., and 20 ft. for remediation using grasses, shrubs, and deep-rooting trees, respectively (Chirakkara and Reddy 2015). An ideal plant species to be employed in the phytoremediation process should possess the following characteristics: hard in nature, high biomass canopy, tolerant to toxic effects of contaminants, easy cultivation, high adsorption capacity, and non-attractive to herbivorous. Besides, the nature of contaminants is a very important factor that determines the different mechanisms and interactions with plant tissues and organs. Based on these interactions, the phytoremediation process can be described as phytoaccumulation (in plant tissues), rhizodegradation (in the root zone), and phytodegradation (metabolism in plant tissues). During metabolic disintegrations, contaminants are either degraded or transformed into other forms and get concentrated in the tissues and organs (Kafle et al. 2022) of hyperaccumulators. The plants have promising characteristics to transfer the contaminants from the root to the shoot and have capabilities of degradation, absorption, accumulation, and transfer to different parts of the plant. In recent years, phytoremediation of radionuclide-contaminated soils using different plant species through improving the soil environment by the addition of fertilizer, organic acids, or chelating agents has been reported extensively (Kafle et al. 2022).

The selection of these plants is based on their ability to survive in a different adverse climate of contaminated sites and the pollutant mobilization potential. The ideal plant used in the phytoremediation process should have the capability of mitigating oxidative stress, which is caused by the activation of the oxidation system by reactive oxygen species (ROS). However, excessive radical scavenger generation can shift the equilibrium between its production and scavenging, leading to damage of plant cells. The important enzymatic antioxidants are superoxide dismutase, catalase, and peroxidases such as ascorbate peroxidase and guaiacol peroxidase (Das and Mazumdar 2016). Besides, superoxide radicals (O_2) play the role of scavengers in the plant by converting it to hydrogen peroxide. These enzymes have the potential to cause severe oxidative stress in plants and can affect their growth and productivity (Rascio and Navari-Izzo 2011). The various physiological responses of plants used in phytoremediation under the influence of different emerging contaminant concentrations are summarized in Table 1.2.

1.3 Factors Influencing Phytoremediation of Emerging Contaminants in Soil

The type of plants and their morphology, environmental conditions, type of pollutants, and soil properties are the major factors that influence the translocation and absorption of emerging contaminants in plants.

1.3.1 Plant Species and Their Morphology

The selection of plant species and their morphological features play a critical role in influencing phytoremediation. The plant species that possess hyperaccumulation properties, high tolerance to onsite conditions, and short life cycles and plants that are easy to handle and harvest are suitable for the phytoremediation of soil. The bioaccumulation factor (BAF) determines whether the plant belongs to the hyperaccumulating species or non-hyperaccumulating species (Chaudhry et al. 2020). The BAF is determined as the ratio of pollutants accumulated in the plant species to the concentration of pollutants present in the soil (Lesmeister et al. 2021). When the calculated BAF is >1.0, it indicates that the plant species possess the ability to hyperaccumulate the pollutants present in the soil (Agarwal et al. 2022). For example, *Helianthus annus* (sunflower), *Zea mays* (corn), *Brassica campestris* (field mustard), and *Pisum sativum* (pea) are some of the hyperaccumulator plants

Table 1.2 The various physiological responses of plants during phytoremediation under the influence of different emerging pollutant concentrations

Common name	Scientific name	Contaminants	Phytoremediation method	Physiological response	References
Ryegrass	*Lolium perenne*	Halogenated flame retardants and Cd	Plant root absorption and bioaccumulation	– The plant assimilated a trace amount of dechlorane plus (DP) and tetrabromobisphenol A (TBBPA) and dissipated in soil with the help of root exudates and rhizosphere microorganisms – Total cadmium in soil was effectively reduced by ryegrass in an optimal bioremediation time of 60 days	Xie et al. (2021)
Water spinach	*I. aquatica*	Sulfamethoxazole	Absorption and accumulation in roots	Sulfamethoxazole is taken up rapidly in the roots of *I. aquatica* with an average accumulation of 18 μg g^{-1} in 24 h	Chen et al. (2017a)
Water spinach and Chinese cabbage	*I. aquatica* *B. rapa chinensis*	Tetracycline	Absorption and accumulation in roots	Tetracycline is taken up rapidly in the roots of *B. rapa chinensis* with an average accumulation of 160 μg g^{-1} in 24 h, and for *I. aquatica*, it is 18 μg g^{-1} in 24 h	Chen et al. (2017b)
Alfalfa	*M. sativa*	Sulfamethazine	Root uptake and translocation	Distribution of sulfamethazine into the root (8.58 μg kg^{-1}), top portion (1.89 μg kg^{-1}), middle portion (1.3 μg kg^{-1}), and sap (0.38 μg kg^{-1}) is done within 72 h of contact time	Kurwadkar et al. (2017)
Horemanii red sword	*E. horemanii*	Atenolol and triclosan	Root uptake and bioaccumulation	The bioconcentration factor of triclosan was 4390 L kg^{-1}, and for atenolol, 2660 L kg^{-1} was observed in 28 days; accumulation in the leaf was higher compared to the root, as leaves were submerged and having direct contact with the pollutant	Pi et al. (2017)
Common water hyacinth	*E. crassipes*		Root uptake and bioaccumulation	17β-Estradiol, 17α-ethinylestradiol, estrone, and bisphenol A accumulated in the roots in	Pi et al. (2017)

		17β-Estradiol, 17α-ethinylestradiol, estrone, and bisphenol A		28 days with average accumulation (2–150 L kg^{-1}) compared to other parts as roots were submerged in direct contact with the pollutants	
Umbrella sedge	*C. alternifolius*	Oxybenzone	Root uptake and accumulation in plant tissues	An antioxidative defense mechanism was adapted to counteract stress and biotransformation of oxybenzone into conjugates of lower toxicity and was observed in tissues after 120 h of study	Chen et al. (2017a)
Lettuce	*L. sativa*	Ibuprofen	Rhizosphere biofilm uptake and biodegradation	90% of ibuprofen was concentrated in the root with a biodegradation mechanism observed in the rhizosphere biofilm endophytic assistance in roots within a contact time of 10 weeks	Hurtado et al. (2016)

with BAF >1.0 (Eapen et al. 2007). The tolerance index (TI) is another factor that defines the ability of a plant to tolerate the pollutant concentration as well as to grow in conditions with longer periods in contaminated soil (Chaudhry et al. 2020). The TI is calculated by comparing the test plant group that is exposed to the pollutant conditions to that of the control (Samreen et al. 2021). When the TI is >1.0, it indicates that the plant can adapt to the pollutant stress conditions. On the other hand, when TI is <1.0, it indicates that the plant is under pollutant stress and cannot adapt to the polluted soil (Belouchrani et al. 2016). Therefore, it is important to select the species with higher BAF and TI values.

The plants absorb the pollutants mostly through roots, and the pollutants get translocated from the roots to the leaves, shoot, and other regions of the plant through transpiration, cohesion, adhesion, and osmosis mechanism (Madikizela et al. 2018). Plant species with a good root system (fibrous root) make more contact with the pollutants present in the soil and accumulate a higher concentration of pollutants as depicted in Fig. 1.1. The root concentration factor (RCF) for *Festuca pratense* (meadow fescue) ranges between 2 and 10 for the removal of metformin (antidiabetic drug) compared to the leaf concentration factor (LCF) due to the presence of a good fibrous root system in the plant (Eggen et al. 2011). Plant species such as *Oryza sativa* L. (rice) and *Glycine max* L. (soybeans) are known to accumulate antibiotics such as norfloxacin, oxytetracycline, and tetracycline via the root region because these species have limited translocation capacity (Bao et al. 2019; Khan et al. 2021). In contrast, certain plant species such as *Echinodorus horemanii* are known to accumulate carbamazepine, ibuprofen, atenolol, and triclosan in its leaf tissue compared to roots due to the fact that this plant belongs to submerged species and it is exposed to these pollutants through direct contact and has good translocation capacity (Bigott et al. 2021).

1.3.2 Type of Pollutants

The molecular weight, size, charge, hydrophobicity, and ratio between octanol-water coefficients (K_{ow}) and octanol air coefficients (K_{oa}), K_{ow}/K_{oa}, of the pollutant determine the translocation of pollutants in the various regions of the plant and its removal method. For pollutants such as PPCPs, the plant cell membrane lacks a specific transport system to accumulate the pollutants; rather, it is driven by the simple diffusion process (Keerthanan et al. 2021). This process mainly depends on the type of pollutants and their chemical properties such as K_{ow} and K_{oa} (Dowdy and Mckone 1997). When log K_{ow} values of the pollutant range between 0.5 and 3.5, these types of pollutants are effectively translocated and transported across the membrane through cell fluids (Rissato et al. 2015). Pollutants with lower K_{oa} values (1–3.5) are effectively absorbed and accumulated in the leaves (Zhu et al. 2020).

Highly hydrophilic pollutants such as caffeine are known to be absorbed and translocated into the roots easily by several plant species, e.g., *Scirpus validus, Elodea canadensis, and Salvinia molesta* (Hu et al. 2021). On the other hand, anionic and hydrophobic pollutants are partitioned into lipid membranes in the

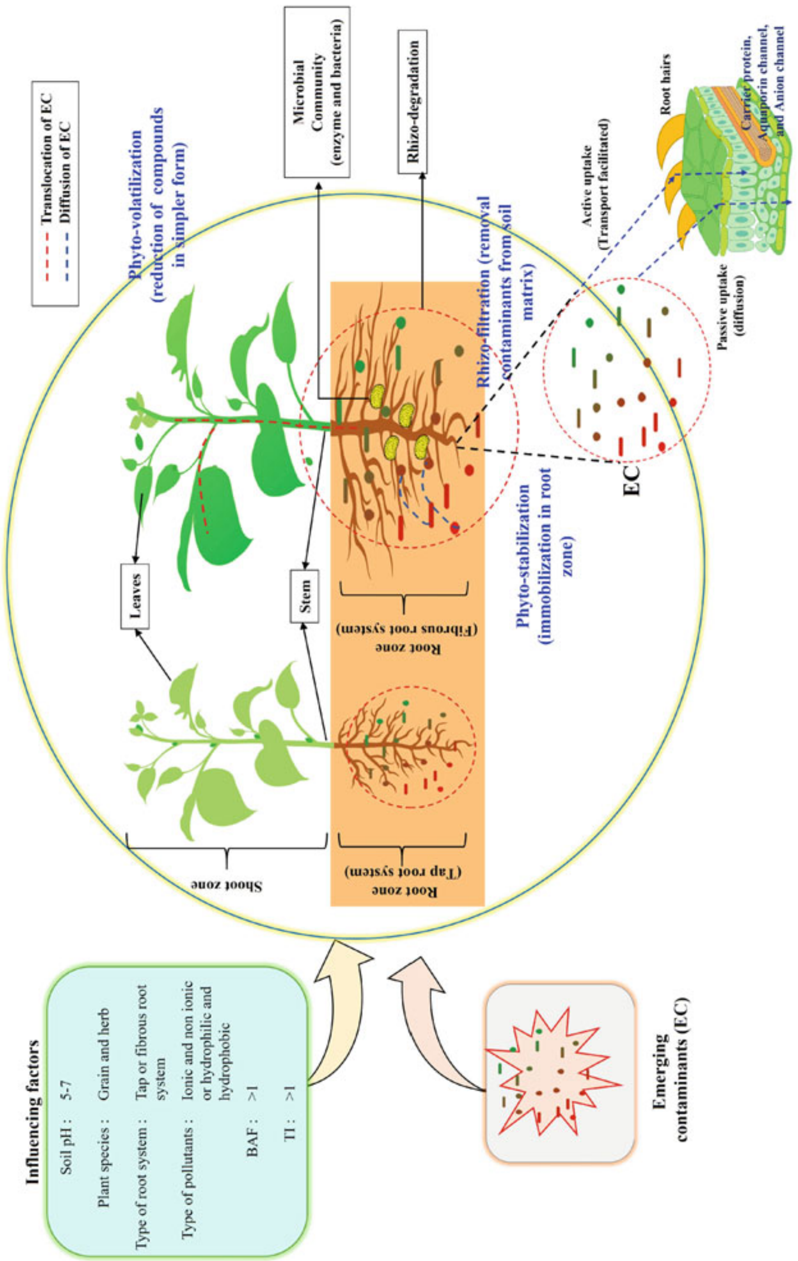

Fig. 1.1 Factors influencing the mechanism of emerging compounds in plants

root zone and are translocated from the roots. Cationic pollutants get accumulated in the leaves as they favor the translocation into other parts (Adeel et al. 2017). Nonionic contaminants are also known to be absorbed through the mechanism of chemical sorption into the membranes and cell walls of the roots (Zheng and Guo 2021). Ionic contaminants such as PPCPs are confined in the phloem and get accumulated in various tissues such as the fruit region of the plant due to the negatively charged cell wall and cytosol of the plant (Goldstein et al. 2014).

1.3.3 Environmental Conditions

Rainfall, sunlight, and temperature play a major role in seed germination and plant growth (Babu et al. 2021). Seasonal climatic variations (warm and cold season) greatly influence phytoremediation especially in tropical and subtropical regions as the conditions facilitate the removal mechanisms in plants (Cristina 2014). A temperate maritime climate zone enhances phytostabilization in plants for phytoremediation (Sherene 2010). The temperature conditions between 25 and 42 °C are known to favor rhizoremediation in the plants as they favor the growth of microorganisms that can enhance the reduction of pollutants. The microorganisms near the rhizosphere reduce the pyrene into phthalic acid in the soil for the phytoremediation to proceed (Gabriele et al. 2021). The microbial community in the roots that forms biofilm around the root zone greatly depends on the temperature conditions. However, with minor deviation from the optimum temperature conditions, the phytoremediation efficiency can significantly decrease, leading to the inhibition of plant growth (Wu et al. 2019).

Optimum rainfall or moisture content in the soil can enhance enzyme activity in the root zone. As a result, the removal of pollutants from the contaminated site becomes higher, and these conditions favor endophytic-assisted phytoremediation (He et al. 2020). In contrast to this, beyond the optimum conditions, water flooding and drought environmental conditions can harm the plant as well as the microbial community. Therefore, it is important to assess the type of plants that are suitable considering the environmental conditions for the better removal of pollutants from the soil.

1.3.4 Soil Physicochemical and Biological Properties

The pollutants can be strongly combined or adsorbed to the soil organic matter (SOM) present in the soil and can potentially reduce the availability of the pollutant for degradation since SOM is known to reduce the solubility of the contaminant (Bartrons and Peñuelas 2017; Nguyen et al. 2019). However, dissolved organic matter (DOM) is a part of SOM that increases the bioavailability of pollutants (Jayampathi et al. 2019). Pyrene bioavailability is greatly increased in the soil matrix when the DOM is present in the soil (Gabriele et al. 2021). Aged soil determines the type of organics present in the soil. Alfalfa phytoremediation studies have shown that an increase in SOM (8.5%) in the soil plays a vital role as a limiting factor for the plant (Wei et al. 2017). Even 6.3% of SOM in the soil can retain the pollutant in the soil and reduce the availability of pollutants in the soil for the plants (Chekol et al. 2002).

The soil pH values determine the availability of contaminants in the soil in neutral or ionic form. At a pH of 6.5–6.7, carbamazepine is known to be available in a neutral form, whereas sulfamethoxazole is present in an ionic form in the soil medium (Holling et al. 2012). Studies have shown that sulfamethoxazole is largely accumulated in the *Brassica campestris* (cabbage) tissue because the ionic form favors the adsorption and translocation of the pollutants from the root to the tissue (Herklotz et al. 2010).

Soil oxygenation is more important for the rhizosphere microbial community as well as for the plant tissues to take up and translocate the pollutants in the aerial parts via the root system (Zhu et al. 2019). Therefore, it is important to mix with porous soil that facilitates soil oxygenation in the soil-contaminated sites for better phytoremediation. Furthermore, the presence of nutrients in the soil can enhance phytoremediation by augmenting the growth of the microbial community as well as the biomass of plant species. These factors not only facilitate phytoremediation but also enhance the endophytic assistance to the plants for the better removal of pollutants in the soil.

1.4 Mechanisms of Endophyte-Assisted Phytoremediation of Emerging Contaminants in Soil

Phytoremediation is an inexpensive and environmentally benign solution that has attracted much attention due to its capacity to remove contaminants through biotic processes with few hazards. Plants use various techniques to eliminate toxins from the contaminated site, including phytostabilization (PS), rhizodegradation, rhizofiltration, phytodegradation, phytoextraction, and phytoaccumulation. Additionally, combinations of plants and microbes, either plant–endophytic or plant–rhizospheric relationships, are also exploited to promote phytoremediation (Kurade et al. 2021).

1.4.1 Mechanisms of PPCP Removal from Soil

PPCPs are a distinct group of contaminants of emerging concern with the innate ability to exert physiological effects on humans, even at low dosages. Most PPCPs are capable of changing biological processes in various organisms because they are unable to create physiological effects at low doses (Kar et al. 2020).

The three main biotic processes to remove organic chemicals are adsorption, bioaccumulation, and biodegradation. Furthermore, the PPCPs can reach plants in many different ways, such as through translocation and diffusion. In addition, PPCPs can diffuse through dissolved organics or enter the roots and aerial tissues in a mass stream. Plants can absorb organic pollutants from the air through their leaves and roots. Still, the roots are the primary pathway for PPCP exposure. Most PPCPs have low volatility. Thus, they are usually exposed to plants through water or soil, either passively or actively. Through either a passive or active transport mechanism, plants can absorb xenobiotic compounds into the plant vacuole along with nutrients. Most organic pollutants are thought to be absorbed via a common mechanism known as passive uptake, controlled by transpiration, except a few hormonelike chemicals (such as phenoxy acid herbicides).

The pollutants are mass-translocated upwards into the shoots, leaves, and fruits across the xylem. This is made possible by the pressure gradient created by transpiration, which is formed in the xylem. Stomata on the leaf surface require a continuous transpiration flow regulated by translocation by constant water evaporation. Water evaporation from plants generates a continuous interaction of water molecules and their adherence to xylem vessels. Osmosis is used to capture and transport water and PPCPs from the roots to the leaves, and a "transpiration–cohesion–adhesion" mechanism follows this process. Compared to xylem sap, the phloem includes a comparatively large number of dissolved organics. These important conduits are in charge of transporting the photosynthesis end products from the leaves to the roots. The contaminants' passing capacity through the endodermis cell membrane is based on the solubility of the contaminants in the aqueous phase (Kurade et al. 2021). The mechanism involved in the uptake of emerging organic contaminants through various phytoremediation processes is shown in Fig. 1.2.

The PPCPs can be potentially absorbed by the plants and have detrimental effects on the physiology and functions of the plant, with the most frequent effects on germination, and growth and development of the plant. Tetracyclines, lincosamides, β-lactams, and macrolides are hazardous to plants and their growth and development. They impair the uptake of phosphorus by numerous plant species, root activity, photosynthesis, chlorophyll content, seed germination, root length, and biomass (Bártíková et al. 2016). Table 1.3 shows the removal efficiency of different plant species for emerging compounds.

1.4.2 Biodegradation of PPCPs Through Enzyme Synthesis

Recent studies have demonstrated that enzymatic degradation is a required method by which plants remove PPCPs from the environment. Monooxygenases, cytochrome P450s, laccase, peroxidase, nitrilase, and other enzymes may be involved in the biodegradation or biotransformation of PPCPs through metabolic pathways. Phase I and II enzymes usually transform the PPCPs in plants. A terminal oxidase called cytochrome P450 (CYP) catalyzes the cleavage of a dioxygen molecule (Hurtado et al. 2016). This is one of the enzymes in the phase I group that integrates into the substrate by using a hydrogen abstraction-oxygen rebound process. These enzymes primarily carry out decarboxylation, hydroxylation, demethylation, dealkylation, epoxidation, and isomerization. On rare occasions, they can work as peroxidases in the presence of H_2O_2 and reductases in the absence of oxygen.

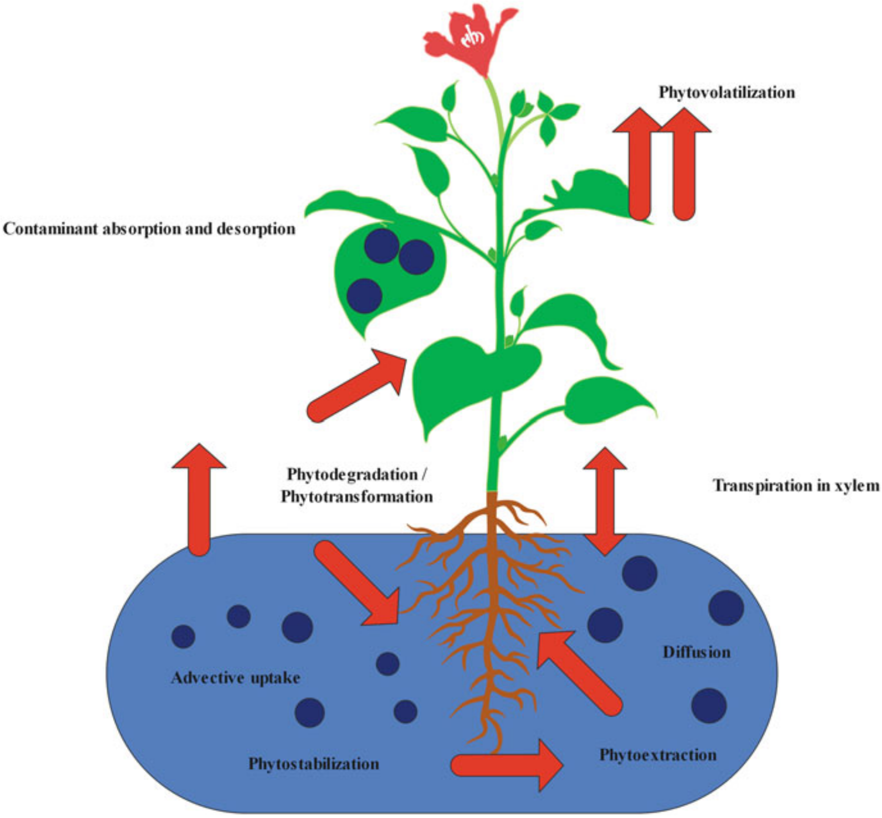

Fig. 1.2 Phytoremediation mechanism

The phase II biotransformation reactions alter PPCPs with hydrophilic functional groups to increase the polarity of the final products in phase I. Phase II metabolism in *A. thaliana* resulted in the acetylation and conjugation of the product of sulfamethoxazole hydrolysis with glutathione, glucuronic acid, and amino acids. These processes subsequently form non-extractable bound residues, which are sequestered most likely by integrating them into the cell walls or other cell components. In phase III, the conjugated metabolites are either deposited into vacuoles or bound to components of the cell wall (Kurade et al. 2021).

1.4.3 Constructed Wetland for the Removal of PPCPs

Constructed wetlands have gained popularity as a technology due to their excellent removal capacity of contaminants including PPCPs, simplicity of usage, low cost, and significant potential for recycling nutrients and water (Wang et al. 2017).

Table 1.3 Removal of emerging compounds (ECs) by plants

S. no.	ECs	EC category	Plant	Concentration (mg L^{-1})	Day	Removal (%)	Mean concentration in plants (μg g^{-1})			References
							Roots	Shoots	Leaves	
1	Sulfamethoxazole	Antibiotic	*I. aquatica*	100	1.5	NA	4.7	4.3	0.03	Chen et al. (2017a)
2	Tetracycline	Antibiotic	*I. aquatica* *B. rapa chinensis*	100 100	1.5 1.5	NA NA	28 640	4 35	9 80	Chen et al. (2017b)
3	Sulfamethazine	Antibiotic	*M. sativa*	10	5	NA	8.58	3.57	NA	Kurwadkar et al. (2017)
4	Atenolol	Beta-blocker drug	*E. horemanii*	0.002	14	NA	0.0026	NA	0.0097	Pi et al. (2017)
5	Oxybenzone	Sunscreen agent	*C. alternifolius*	50 μm	5	74	160	34	4	Chen et al. (2017a)
6	Caffeine	Psychoactive drug	*L. sativa*	0.004	70	43	0.398	NA	0.147	Hurtado et al. (2016)
7	Propranolol	Beta-blocker drug	*L. sativa*	0.004	70	75	0.393	NA	0.119	Hurtado et al. (2016)
8	Tonalide	Aromatic musk	*L. sativa*	0.004	70	61	0.587	NA	0.321	Hurtado et al. (2016)
9	Ibuprofen	Nonsteroidal anti-inflammatory drug	*E. horemanii*	0.002	14	NA	0.0005	NA	0.0025	Pi et al. (2017)
10	Triclosan	Antibacterial and antifungal agent	*E. horemanii*	0.002	18	NA	0.011	NA	0.126	Pi et al. (2017)

The free water surface (FWS) systems, one of the common techniques in tertiary treatment facilities for the removal of different pollutants from water, are composed of shallow basins with water up to 0.4 m in depth and a hydraulic loading rate (HLR) between 0.7 and 5.0 cm d^{-1}. Because vegetation and biofilms work in harmony, organic molecules are degraded aerobically close to the water's surface and anaerobically in deeper waters. It has been noted that the FWS systems have a high removal efficiency for PPCPs, such as naproxen, triclosan, and ketoprofen, as a result of exposure to sunshine (Hijosa-Valsero et al. 2010). Four FWS systems were merged and constructed using a range of vegetation, including *Glyceria maxima, Myriophyllum spicatum, Typha* spp., *Carex* spp., *Phragmites australis, Scirpus sylvaticus, and Schoenoplectus lacustris,* to assess the removal of 65 PPCPs. It showed normal anticipated clearance rates between 42 and 52%, which are lower than those of advanced treatment approaches (Naz et al. 2022). Although less dangerous than those treated with advanced tertiary treatments, PPCPs in water treated by FWS systems were nonetheless present. Therefore, it can be concluded that FWS systems can provide a supplemental treatment option for the treatment of PPCPs and that improved treatment technologies are required for their complete removal from wastewater.

1.4.4 Floating Treatment Wetland

Floating treatment wetlands (FTWs) are currently used to enhance water quality. FTW was first designed to improve the habitat and appearance of ornamental lakes and ponds. The FTW is made by developing emergent macrophytes with roots lying on a floating mat, which, in turn, inhabits deepwater. BOD, NH_4-N, TP, and organic contaminants are all drastically reduced in FTW systems. When roots, rhizomes, and root-bound biofilms are associated with organic pollutants, physical and biological processes transform the pollutants by filtering, entrapping, and biodegrading particulate matter. Several methods have been used to remove different PPCPs, including plant uptake, biofilm-related microbial degradation (salicylic acid, ibuprofen, galaxolide), adsorption onto particulate matter with subsequent sedimentation (tetracycline, triclosan), and photodegradation (triclosan, naproxen, ketoprofen, and diclofenac) (Hurtado et al. 2016).

The subsurface flow (SSF) systems, which are constructed using a porous media like sand, gravel, or small crushed pebbles with a typical bed depth of 0.6 m and an average HLR between 2 and 20 cm d^{-1}, are equal to a wetland of 0.5–5 ha with a flow of 1000 m^3 d^{-1}. The SSF system normally provides two configurations: vertical SSF systems and horizontal SSF systems. These systems have an integrated structure of aerobic, semi-aerobic, and anaerobic zones in the subsurface. The granular medium is traversed by the wastewater either vertically or horizontally. The aerobic zones of the SSF system, which provide oxygen to the substrate through oxidation, are represented by the surrounding region of plant roots and rhizomes. It has been amply demonstrated that SSF systems enhance the removal of BOD, COD, phosphate, and nitrogen and provide optimum denitrification conditions. In addition, by sticking to the organic material in the granular medium, polycyclic musks and other hydrophobic compounds may be successfully eliminated. Eliminating several of the regularly seen PPCPs in three separate rural horizontal SSF systems demonstrated substantial diversity (37–99% for β-blockers, 11–100% for anti-inflammatories, and 18–95% for diuretics) (Zhang et al. 2014).

1.5 Recent Advancements and Challenges in the Field of Phytoremediation Technology for the Removal of Emerging Contaminants

Recent advancements in research and challenges on phytoremediation for the removal of emerging contaminants were analyzed through bibliometric analysis. Bibliometrics is an approach to examining and analyzing the impact of research output through quantitative analysis using various computational and statistical tools. The various analyses such as citation analysis, co-citation analysis, keyword occurrences, and co-authorship analysis can be carried out using suitable software tools (e.g., VOSviewer). This analysis revealed the linkage of different articles published on different domains of phytoremediation and focused on a new dimension of future research on the phytoremediation of emerging pollutants (Narayana Prasad and Kalla 2021).

Literature on recent research on phytoremediation was collected using the Scopus database on 29th of October 2022 using the search terms "*Recent advancements AND challenges AND phytoremediation AND emerging contaminants*." The document type was restricted to research articles, conference proceedings, and review papers published during the last 5 years (2019–2023). A total of 157 articles were found to be relevant to the recent applications in the area of phytoremediation, and screening was done based on relevant information in the search areas. The bibliometric analysis of the exported data was carried out using VOSviewer software (ver. 1.6.18) developed by Leiden University, Netherlands. The keywords mentioned in a research paper provide information on which research work was carried out. Thus, keyword co-occurrence analysis is important in Scientometrics, which can help readers to get a better insight into the current research-focusing area. The collected data comprised 157 research papers including review articles. During the analysis, a total of 5051 keywords was obtained, out of which 351 keywords met the threshold limit (set as a minimum of occurrences of the term to 5). The keywords were further screened to remove the irrelevant occurrences, and a final map was created (Fig. 1.3). The constructed map can be understood in such a way that the size of the circle reflects the weightage of the occurrence, and the nodal color illustrated the different cluster (e.g., red, blue, and green) appearing in the research area. The transition in the cluster color is represented as the evaluation of different research domains of phytoremediation. The red color cluster, having the largest network, showed the major research development on phytoremediation research work in the past 5 years. These research areas included the development of genomics and metabolomics including plant–microbes interaction study, and bioaugmentation.

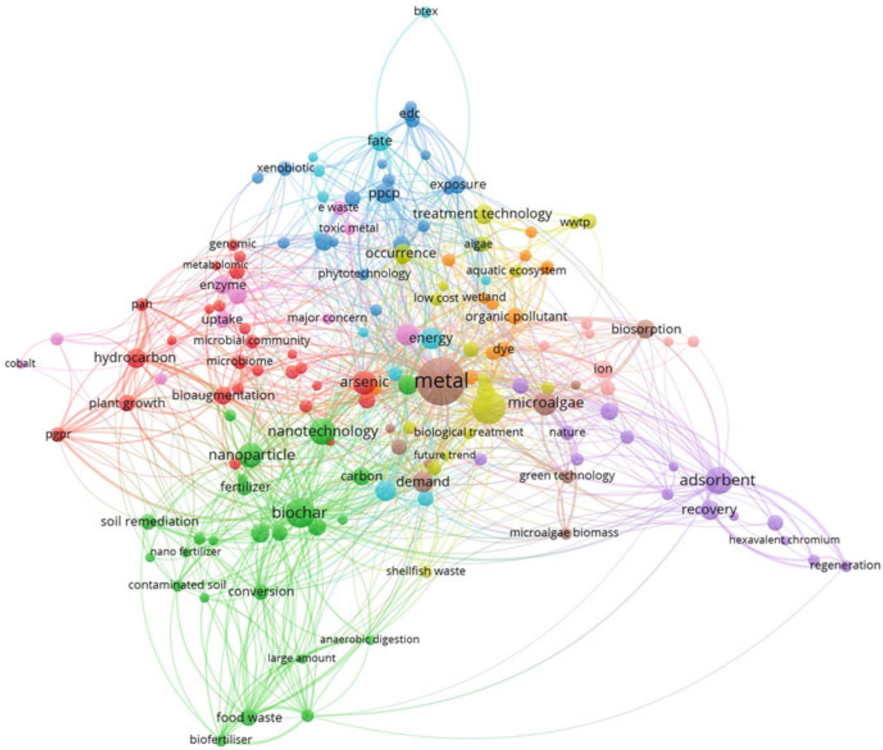

Fig. 1.3 Co-occurrence network visualization map of the key terms appeared during the search of advance research on phytoremediation in ScienceDirect (search terms: Recent advancements AND challenges AND phytoremediation AND emerging contaminants)

The green color cluster represents the research focus on the application of nanotechnology and soil amendments with biochar for enhancement of the phytoremediation process. Besides, the purple color cluster represents the recent application of microalgae in the area of phytoremediation as green technology.

In the recent times, sustainable genetic engineering has been playing an important role in the area of phytoremediation technology to cope up with the situation arising due to the advent of industrial revolution and resulting pollution. The research on phytoremediation techniques is focusing on various aspects of combinatorial genetic engineering tools in which the cluster repeats of spaced palindromic (CRISPR)-Cas9 have showed a greater potential for site-specific expression regulation and provide a new insight on plant functional genomics. The gene editing in plant growth, promoting rhizobacteria (PGPR) using the CRISPR-Cas9 technique, has improved the synthesis of bioactive compounds with simultaneous increase in biomass production, tolerance to pollutants, transportation, accumulation, and detoxification of critical pollutants (Naz et al. 2022). The CRISPR-Cas9 technique is recognized as a modern way to increase the potential of genotypes to perform phytoremediation.

Hyperaccumulator-based phytoremediation technologies have been improved successfully through the application of genetic engineering, which is known as "genoremediation," to overcome the limitation associated with the traditional way of toxin removal from soil. Thus, tremendous efforts have been made in recent years in the area of gene expression-derived transporters/enzymes, and molecular mechanisms have been exploited for augmentation of "genoremediation" of environmental contaminants (Rai et al. 2020). It has also been investigated that the molecular mechanism of phytoremediation and gene manipulations through overexpression of metal chelator and transporter genes resulted in the increase of plant biomass and reduced oxidative stress/phytotoxicity (Rai et al. 2019).

In addition, incorporation of omics tools such as metagenomics, metatranscriptomics, and metabolomics has remarkably revolutionized the potential of phytoremediation in recent years. A remarkable progress has been made using the next-generation sequencing (NGS) tool, as cutting-edge research through expression of alkB gene coding for alkane monooxygenase and CYP153 gene for P450 alkane hydroxylase in *Dietzia* genome, leading to phytoremediation of PHA (Alonso-Gutiérrez et al. 2011). The molecular and genetic prospects of copper accumulation in a hyperaccumulator plant of *Brassica napa* through the expression of ATPase gene system have also been investigated (Zhang et al. 2019).

Several broad-spectrum insecticides such as chlorfenapyr have been classified as hazardous materials and pose substantial risk to the reproductive ability of birds and threat to the environmental stability. Nowadays, integrated green and nanotechnology is focusing on eco-friendly phytoremediation of these toxic recalcitrant compounds and to overcome the challenges associated with the sustainable environmental management of plants used in phytoremediation. Besides, the green synthesis of Fe- and Ag-based nanoparticles is involved in the extraction of toxic compounds both as a stabilizer and as a reducing agent (Romeh et al. 2020). This approach is simple, eco-friendly, nonhazardous, economic, and time efficient and involves coating with natural organic compounds. The fast and efficient removal of chlorfenapyr using a combination of *Plantago major* and green nanoparticles of $F\text{-}Fe^0$, $Ip\text{-}Ag^0$, and $Br\text{-}Ag^0$ supported by activated charcoal has been investigated (Romeh et al. 2020). The effect of solubility-enhancing agents (e.g., SiO_2, argal, and ethanol) has been monitored and found effective for enhanced phytoremediation. Thus, these strategies can also be considered as an eco-friendly and cost-effective alternative approach to traditional remediation technologies for detoxification of contaminated soil.

Anew, biochar preparation is considered as an active research domain under environmental management of phytoremediation plants. Calcium silicate-coated nZVI/biochar composite (BOS) has been prepared using an industrial waste, and phytoremediation technique is employed for As(V) removal (Tan et al. 2022). In this way, the toxicity risk of BOS is greatly reduced compared to the toxicity of raw material. In addition, microalgae-based bioremediation technique has been emerging as a potential alternative in recent years and has been employed for the removal of a variety of toxic chemicals including PPCPs, pesticides, heavy metals, and oil-contaminated sites from water streams (Bhatt et al. 2022).

1.6 Conclusion

In recent years, phytoremediation technology has been proven as an environmentally benign, economically feasible, and sustainable remediation option for the removal of ECs from the soil matrices. Phytoremediation in combination with microbial remediation can be considered an eco-friendly technique as the microorganisms support the plant tolerance that overcomes toxicity in the form of less toxic form. The research on phytoremediation is focusing on plant genomics and proteomics approaches for improvement in the bioremediation potential of plants. The recent challenges, opportunities, and prospects in the area of phytoremediation of ECs lie in the improvement of plant stability and extraction efficiency through genetic engineering, microbial assistance, and chelation support approaches. With the help of molecular tools, adaptive phytoremediation ability can be improved in the current global conditions.

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