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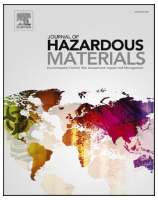

Review

Contaminant containment for sustainable remediation of persistent contaminants in soil and groundwater

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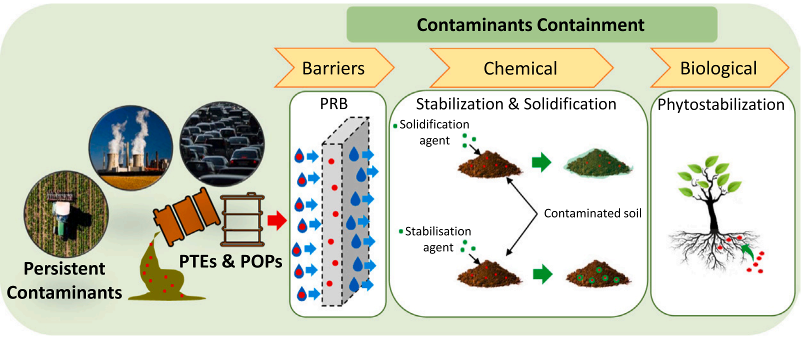
HIGHLIGHTS

- Contaminant containment avoids excavation and removal of contaminated substrates.
- Contaminant containment includes physical, chemical, and biological technologies.
- Contaminant containment measures prevent further migration of contaminant plumes
- Contaminant containment treatment measures require periodic monitoring.
- Includes case studies for successful application of contaminant containment processes.

GRAPHICAL ABSTRACT



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ABSTRACT

Contaminant containment measures are often necessary to prevent or minimize offsite movement of contaminated materials for disposal or other purposes when they can be buried or left in place due to extensive subsurface contamination. These measures can include physical, chemical, and biological technologies such as impermeable and permeable barriers, stabilization and solidification, and phytostabilization. Contaminant containment is advantageous because it can stop contaminant plumes from migrating further and allow for

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Permeable reactive barriers
Stabilization and solidification
Phytostabilization

pollutant reduction at sites where the source is inaccessible or cannot be removed. Moreover, unlike other options, contaminant containment measures do not require the excavation of contaminated substrates. However, contaminant containment measures require regular inspections to monitor for contaminant mobilization and migration. This review critically evaluates the sources of persistent contaminants, the different approaches to contaminant remediation, and the various physical-chemical-biological processes of contaminant containment. Additionally, the review provides case studies of contaminant containment operations under real or simulated field conditions. In summary, contaminant containment measures are essential for preventing further contamination and reducing risks to public health and the environment. While periodic monitoring is necessary, the benefits of contaminant containment make it a valuable remediation option when other methods are not feasible.

1. Introduction

Persistent contaminants include both inorganic potentially toxic elements such as arsenic (As), lead (Pb), cadmium (Cd), mercury (Hg), and selenium (Se), and persistent organic pollutants (POPs) such as polycyclic aromatic hydrocarbons (PAHs) and poly- and perfluoroalkyl substances (PFAS). These persistent contaminants are released into the environment through both natural (geogenic) and anthropogenic sources [1-3]. Some persistent toxic elements (PTEs), such as As and Se, are introduced through weathering of soil parent materials rich in these PTEs [3]. Similarly, some POPs, such as PAHs, are released during natural processes, including bushfires [4,5]. However, most persistent inorganic and organic contaminants are released to the environment through anthropogenic sources, including waste disposal and mining and industrial activities [3].

Various approaches to the remediation of contaminated sites include mobilization and immobilization of contaminants, containment of contaminants, and destruction and degradation of contaminants [6]. An immobilization strategy can be employed to decrease the mobility and availability of persistent pollutants. Conversely, a mobilization approach can be implemented to eliminate these contaminants through soil washing, biodegradation, and phytoremediation techniques [7]. Contaminant containment aims to stop the spread of PTEs and POPs to other locations, while destruction and degradation aim to eliminate POPs completely.

Contaminant containment is a crucial strategy to restrict contaminants' spread in soils and groundwater. When contaminated materials must be left in place at a site, contaminant containment is implemented to prevent offsite contamination. This approach is particularly applicable in situations where extensive subsurface contamination precludes excavation and removal of the contaminated substrates due to potential hazards and exorbitant costs [8,9,6].

There are various technologies for contaminant containment, such as permeable reactive barriers, chemical techniques, such as stabilization and solidification, and biological techniques, such as phytostabilization. One of the main benefits of contaminant containment measures is their ability to prevent contaminant plumes' further migration and reduce contamination at sites where the source is unknown or inaccessible [10]. Unlike ex-situ assisted-treatment options, contaminant containment does not require the excavation of contaminated substrates, thus avoiding increased costs associated with equipment design and material handling. However, it is essential to periodically inspect the containment measures to monitor the mobilization and migration of contaminants [11].

A vast amount of research has been dedicated to investigating various methods for the remediation of contaminated soils, including the mobilization, immobilization, bioremediation, and phytoremediation approaches [12-14]. These studies have indicated that the choice of approach depends on the origin and nature of the contaminants as well as the intended land use of the contaminated site. Although a number of reviews have been conducted on various remediation methods [12,15,5,3], a limited number have specifically focused on the contaminant containment approach and its role in managing the risk associated with contaminated soils [16]. This review aims to examine the literature on contaminant containment strategies critically and evaluate their effectiveness in reducing the risks associated with contaminated soils.

This review aims to consolidate the current understanding and recent advancements in the field of contaminant containment as a risk-management strategy for the remediation of contaminated soils. A comprehensive search was conducted using various reliable databases and sources such as Scopus, Web of Science, Google Scholar, ScienceDirect, and other relevant web sources to achieve this goal. Keywords such as "Contaminant containment," "Immobilization of contaminants," "Stabilization of contaminants," "Solidification of contaminants," "Encapsulation of contaminants," "Phytostabilization of contaminants," "Soil remediation," "Phytoremediation," and "Bioremediation" were utilized to gather the most up-to-date information on the subject. The findings of this review aim to shed light on the various approaches to contaminant containment and highlight their importance in preventing migration and offsite contamination, resulting in a risk-based method of remediation for contaminated soils.

The review summarizes existing knowledge and developments related to contaminant containment as a risk-based approach for soil remediation. The aim is to identify and address current knowledge gaps, particularly concerning the stability of contained contaminants over the long term and their potential dispersion. Furthermore, this review aims to enhance our understanding of contaminant containment, ultimately leading to improved risk-based in-situ remediation methods and reduced costs for contaminated site remediation. The review focuses on the sources of persistent inorganic (PTEs) and organic (POPs) contaminants, different approaches to remediation, the various physicochemical and biological processes involved in contaminant containment, and the potential unintended consequences of these containment operations under field conditions.

2. Sources of persistent contaminants

2.1. Potentially toxic elements (PTEs)

The persistence of inorganic contaminants in the environment has long been a concern, particularly with the presence of PTEs, such as As, Cr, Cd, Se, Pb, V, and Zn, which are non-degradable and remain in the environment for extended periods [12,17]. These elements are considered to be the primary persistent inorganic contaminants in terrestrial and aquatic ecosystems and are known to increase toxicity through processes such as reduction, oxidation, and methylation in soils and aquatic environments [18]. The sources of PTEs in soil include both geogenic and anthropogenic (Fig. 1) sources, with concentrations equal to the sum of inputs from these sources minus losses from factors such as soil erosion, plant uptake, leaching and volatilization of gaseous forms [19].

2.1.1. Geogenic sources

Soil parent material contains many PTEs in a wide range based on the source and type of rocks and minerals and their geochemical composition as well as on soil formation processes [3]. PTEs can be found in rocks (e.g., igneous and sedimentary rocks and coal) and minerals (such as olivine pyroxene amphibolite, feldspars, apatite, and micas) as a result of the isomorphic substitution with other elements. Therefore, PTEs occur in soils through geological weathering and sedimentation processes [3] (Fig. 1). The naturally occurring PTEs in soils are mostly either concentrated in resistant phases or strongly adsorbed by secondary minerals, and thus the mobilization of the geogenically occurring PTEs in soils is lower than the anthropogenically occurring PTEs [19-21]. However, the content, fractionation, and mobilization of the geogenically occurring PTEs in soils widely differ based on the parent rock types. For example, black shales contain significantly elevated concentrations of PTEs compared to the upper crust [19]. Apatite ($Ca_5(F, Cl, OH)(PO_4)_3$) is also rich in several PTEs, particularly Cd and Pb, Cu, and Zn [22,23]. Coal contains large amounts of As (up to 35, 000 mg/kg); thus, about 45,000 tonnes of As is annually released from coal [24]. Pyrites occurring in the black shales underlying geological strata are also considered the geogenic source of As in soils. The igneous rocks contain up to 100 mg/kg As, while the sedimentary rocks contain up to 15,000 mg/kg As in some manganese ores. Therefore, the high As levels in groundwater in some places, such as Bangladesh and West Bengal, mainly come from geological origins. Therefore, bedrock geological composition provides information on PTE background levels and mobility.

The relationships of some elements with minerals, such as Bi, Be, Br, I, Co, In, Nb, Mo, Ta, W, Te, and V, are ambiguous or largely unknown and hence deserve further investigation using integrated approaches [24]. The mechanisms of many element-mineral associations are also unknown. A complete understanding of elementary modes of occurrence requires new technologies for quantitatively analyzing elements associated with particular minerals rather than generic phrases like ‘silicates’, ‘clays’, and ‘carbonates’ [24]. Detailed mineralogical examinations of coal are also justified, as interesting and unusual phases have been discovered [24].

2.1.2. *Anthropogenic sources*

Soil contamination with PTEs can result from a range of anthropogenic activities, including smelting, mining, production of oil and gas, military practices, industrial production, traffic emissions, and agricultural practices (Fig. 1). These activities can lead to elevated soil PTE concentrations [25,3,21]. Coal fly ash can also be a source of PTEs in soils, the content of which depends on its composition [26,27]. Atmospheric deposition, particularly in China and India, can also contribute to soil PTE concentrations [28-30].

Mining and smelting operations are significant contributors to soil PTE contamination, particularly in areas near these activities [31]. In China, mining activities have resulted in millions of hectares of contaminated land, with this area increasing annually [32]. In Europe, large areas of soil have been contaminated by PTEs from mining activities [31]. For instance, high PTE concentrations have accumulated in floodplains along the Elbe and Wupper rivers in Germany due to waste discharge from industrial activities, such as knife manufacturing, textile bleaching, mining, and electroplating.

PTEs can also be introduced to arable soils by applying fertilizers, biosolids, pesticides, and wood preservatives that contain PTEs [19,25, 33,34]. Phosphate fertilizers, for example, are rich in cadmium [35]. Additionally, organic fertilizers like poultry and livestock manures can contain detectable concentrations of PTEs such as copper and zinc [25, 36]. Pesticides, including herbicides and fungicides, and wood preservatives, can also be significant sources of PTEs in soil. For example, inorganic fungicides applied in apple orchards in Virginia, USA, have been found to contain 156, 220, 263, and 1150 mg/kg of copper, zinc, arsenic, and lead, respectively [19]. Moreover, PTEs can be introduced to the soil through military activities and shooting sports [19,37]. The soil at a military shooting range in Korea was found to have lead concentrations ranging from 2000–11,100 mg/kg [38].

Thus, most PTEs occur naturally in soil parent materials, often in

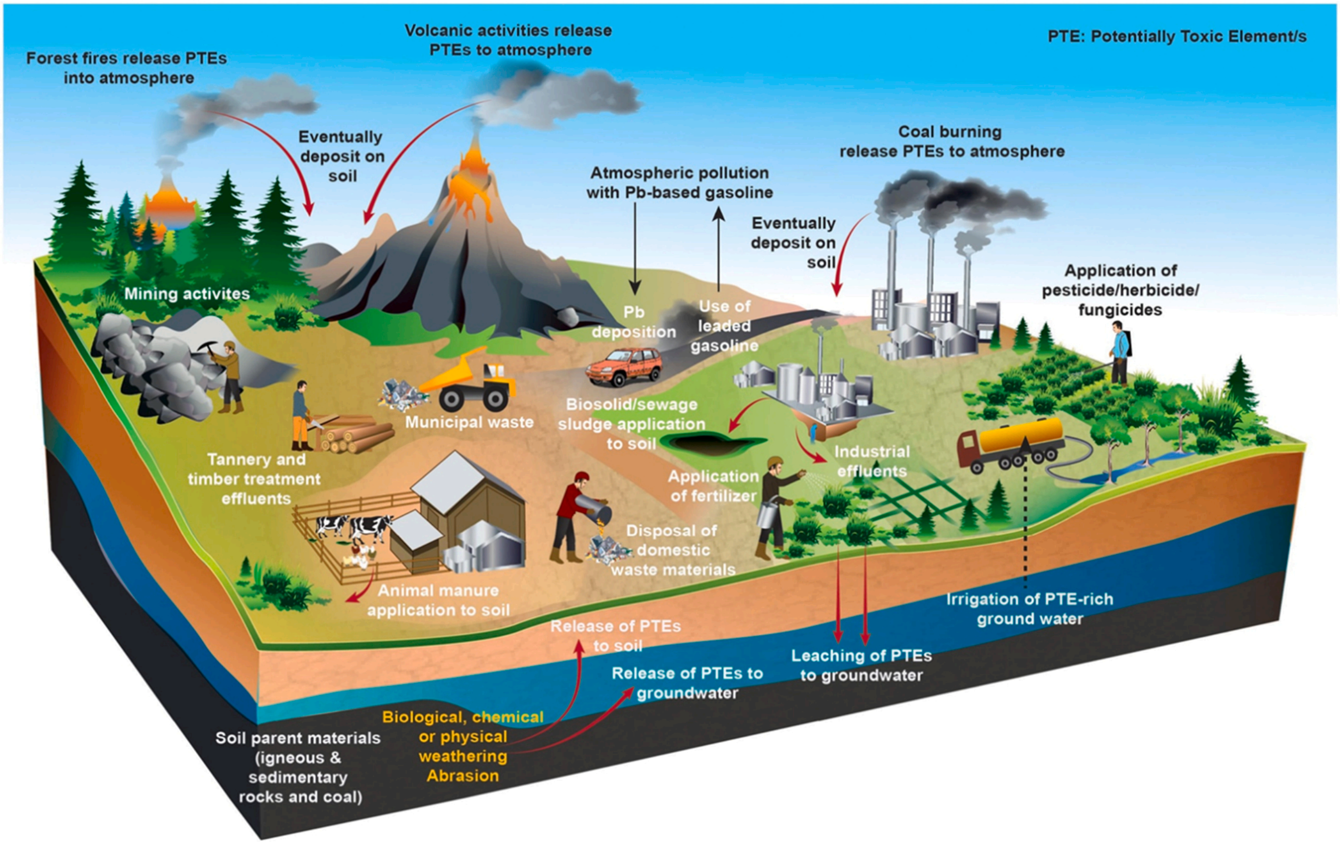

Fig. 1. Sources of toxic elements (TEs) in soil ecosystems [3]. Reproduced with the publisher’s permission.

forms that are not readily available to plants. The concentrations of PTEs from natural pedogenic processes are typically associated with the parent material's origin and nature. However, the bioavailability of PTEs produced by anthropogenic activities is often high.

2.2. Persistent organic contaminants

Persistent organic pollutants (POPs) are a group of man-made organic chemicals that are not only persistent but also bioaccumulative and mobile with a significant transport potential [39]. In 1995, the United Nations Environment Programme Governing Council banned 12 POPs (popularly known as the dirty dozens) due to their environmental threats [40]. Subsequently, additional compounds were added or proposed to be added to this list. The POPs primarily include pesticides and their metabolites and industrial chemicals and their byproducts.

2.2.1. Pesticides and their metabolites

Organochlorine pesticides (OCPs), such as aldrin, chlordane, dichloro-diphenyl-trichloroethane (DDT), dieldrin, endrin, heptachlor, hexachlorobenzene (HCB), mirex, and toxaphene, are widely used for pest control in agriculture and result in widespread environmental contamination. These chemicals are highly toxic and pose a threat to human health and the environment. Due to their harmful effects, their use has been restricted or banned in many countries.

Aldrin is a classic OCP that was widely used to treat seeds and soil, kill insects, and control termites and rootworms. However, it was banned in most countries in the 1990 s due to its toxicity and bioaccumulative nature [41].

Chlordane, a highly toxic insecticide, has widespread residues in soils and is classified as a possible human carcinogen. It is known to cause death in bird species, and its human exposure is primarily through air pollution [42-44].

Chlordecone, another OCP, has similar properties to DDT and mirex and was widely used in agriculture. Its toxicity to aquatic organisms and potential carcinogenicity in humans led to its ban in many countries [45-47].

DDT, once regarded as a remedy for diseases such as typhus and malaria, is banned in most developed countries due to its toxicity and environmental persistence. Despite the ban, its production and use are still allowed in some developing nations to control malaria [48-50,40]. DDT is listed in Annex B of the Stockholm Convention. Chronic exposure to DDT can cause health problems, including cancer, diabetes, reproductive issues, and neurological disorders [51,52]. Major sources of DDT exposure include food contamination.

Dieldrin, a pesticide commonly used for termite and soil insect control, as well as for textile pest management, is formed by the oxidation of aldrin and has a half-life of 5 years [53]. Human exposure occurs primarily through food intake [54], and it can be found in both animal tissue and environmental media. Dieldrin is toxic to aquatic fauna and has been linked to immune and nervous system toxicity, Parkinson's disease, and breast cancer in humans [55].

Endosulfans, another group of pesticides used in agriculture for pest control and wood preservation, were banned in many countries due to their toxicity to humans and fauna and their role as endocrine disruptors and antiandrogens causing nervous system issues and congenital disorders [56]. Some countries implemented the ban gradually [57].

Endrin, a foliar insecticide and rodenticide, causes neurotoxicity in humans with primary exposure through food intake [58,59]. While toxic to fauna, endrin does not accumulate in fatty tissue, as it can be metabolized, but it persists in the environment for a long time, with a half-life in soil of 14 years [60].

Heptachlor is an OCP used as an insecticide in soil and plants and as a mosquito control agent [61]. Human exposure primarily occurs through food consumption [62]. Heptachlor is classified as a possible human carcinogen linked to behavioural and reproductive issues at low concentrations and lethal effects at high concentrations [63].

HCB, a fungicide for food crop seeds, is linked to human exposure through contaminated food and/or treated seed/grain consumption, resulting in skin problems, digestive issues, and potentially lethal metabolic disorders [64]. HCB can also be passed from mothers to infants via the placenta and breast milk and may be lethal to infants [65].

Hexachlorocyclohexane (HCH) is a group of broad-spectrum pesticides with multiple applications in agriculture and parasite control. Its three isomers, including α-HCH and β-HCH, are produced as byproducts during the manufacture of Lindane (γ-HCH) [66]. Lindane is known to accumulate in tissue, causing toxicity to the immune, nervous, and reproductive systems and leading to cancers, kidney and liver ailments [67], and Parkinson's and Alzheimer's disease [68].

Mirex is used as a pesticide for ant and termite control. It is highly persistent, with a half-life of up to 10 years [69], and toxic to plants, aquatic species, and humans, primarily through contaminated food [70,71]. Mirex is also used as a flame retardant in plastics, rubber, and electrical goods [72].

Pentachlorobenzene (PeCB) is an unintentional byproduct and chemical intermediate used as a fungicide and flame retardant [73]. It is toxic to both humans and aquatic fauna [74].

Toxaphene, used primarily in crops and livestock, is a possible human carcinogen and highly toxic to aquatic fauna and humans through dietary exposure [75-78]. It is highly persistent, with a half-life of up to 12 years in soil [79].

2.2.2. Industrial chemicals and byproducts of industrial processes

Polychlorinated biphenyls (PCBs) are a group of chemicals that were widely used in electrical equipment as coolants, lubricants, hydraulic and heat exchange fluids, as well as in paint, carbonless copy paper, and plastics [80,81]. Humans are primarily exposed to PCBs through contaminated food, leading to reproductive failure and immune suppression. Although PCB production was banned decades ago, these chemicals persist in the environment due to the release of old electrical transformers and building materials, which contribute more than the incineration of PCB-containing waste and vehicle emissions [82,83]. Over 90% of PCB accumulation in the human body is through food intake, particularly from meat, fish, and dairy products.

Polybrominated Diphenyl Ethers (PBDEs), similar in structure and properties to PCBs, have been used as flame retardants in electrical appliances, computers, televisions, insulation wires, cables and building materials since the 1960 s [84]. PBDEs are released into the environment via e-waste, resulting in elevated levels in fatty foods, such as meat, fish, and poultry [85]. The four major PBDE compounds are hexabromodiphenyl ether (hexaBDE), heptabromodiphenyl ether (heptaBDE), decabromodiphenyl ether (decaBDE), and octabromodiphenyl ether (octaBDE). The persistent commercial octaBDE degrades via photolytic debromination [86].

Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDF) are POP-derived compounds formed from combustion processes, metal refining, or as impurities in synthesized chlorinated compounds such as pentachlorophenol (PCP) and PCBs, with combustion being the primary source and volatilization being the secondary source for atmospheric emissions [87,88]. The majority of the environmental burden of PCDD/Fs is attributed to industrial activities in the 20th century [89,90], but their presence in the pre-industrial era suggests natural formation [91]. PCDDs are chemically stable and persistent and are found even after over a decade of exposure [92]. PCDDs are toxic and carcinogenic to human health, with 2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD) being evaluated as carcinogenic to humans (IARC group 1 classification), while other PCDDs were evaluated as not classifiable as to their carcinogenicity to humans (group 3) [93]. PCDDs are produced from the incomplete combustion of municipal waste, hospital waste, and hazardous waste, as well as from automobile emissions, coal, peat, and wood [94].

PCDFs, similar in structure, toxic effects, and persistence in the environment to PCDDs, are also produced unintentionally and are released into the environment in trace amounts from various combustion processes and as byproducts in various chlorinated chemical formulations [94]. PCDFs are regarded as possible human carcinogens.

Polycyclic aromatic hydrocarbons (PAHs) are a large class of chemicals consisting of two or more benzene rings [95]. These chemicals are widespread in the environment, with various PAH compounds being found in waste materials, landfill leachates, soils, sediments, groundwater, and the atmosphere [96].

There are three main sources of PAHs in the environment: pyrogenic, petrogenic, and biological. Pyrogenic PAHs are formed from the heating of organic substances at high temperatures in reduced conditions (with low to no oxygen), and are characterized by their more stable six-member ring structure [97]. These PAHs are commonly found near source terms and in urban areas. Petrogenic PAHs are produced from petroleum products during crude oil maturation and processes such as oil spills and leakages and have five-member ring structures [98]. Plants and bacteria form biologically derived PAHs during the degradation of organic matter.

PAHs can be generated through natural processes (e.g. volcanic activity, brushfires, microbial decomposition, and petroleum seepage) or anthropogenic activities (e.g. large point sources such as waste incineration, industrial processes, and coal gasification, as well as small point sources like vehicular fuel combustion, household heating, and cigarette smoke) [99-101,97,102]. Other anthropogenic sources of PAHs include sewage sludge, tar- or creosote-containing waste, and the atmosphere [96].

Both smokers and non-smokers can be exposed to PAHs. Smokers face inhalation risk from cigarette smoke [95], while non-smokers are exposed through their diet, which contributes to over 70% of human PAH exposure (Martorell et al., 2010). Traditional cooking methods, such as roasting, grilling, smoking and frying, can also generate high amounts of PAHs in charcoal-grilled or barbecued foods [103].

The type and concentration of PAHs formed depend on various factors, such as temperature and combustion conditions. For example, PAHs formed at higher temperatures (e.g. power plant stack effluent) generally have fewer alkylated chains than PAHs formed at lower temperatures (e.g., crude oil spill site) [104]. Incomplete combustion, whether natural or anthropogenic, is a primary cause of PAHs emissions to the environment and can produce significant amounts of PAHs [105].

Poly- and perfluoroalkyl substances (PFAS) are a group of major POPs that have received significant attention in recent years. They contaminate terrestrial and aquatic environments through various sources, such as the discharge of aqueous film-forming foam (AFFF) during firefighting or training activities, effluent from wastewater treatment plants (WWTPs), landfills, and the application of contaminated biosolids in agricultural soils [2]. PFAS can also enter the environment via point sources such as storing, handling, using, and cleaning AFFF chemicals. Domestic waste containing hydrophobic and stain-resistant coatings and industrial waste such as fabrics and building materials can also contribute to PFAS contamination when disposed of in landfills [106-109]. Table 1 shows the summary of the sources of persistent contaminants.

3. Approaches to remediation

There are various approaches to the remediation of contaminated sites, which depends on the risk posed by the contaminants to human and ecosystem health and the economic, environmental, and social costs associated with remediation. Risk-based remediation approaches aim to minimize or mitigate the risks posed by the contaminants to the immediate environment, providing economic benefits. The remediation approaches are grouped into mobilization and immobilization of contaminants, containment and control of contaminants, and degradation and destruction of contaminants [5]. The latter approach is aimed at the complete removal of the contaminants.

Pesrsistent contaminants	Sub-category	Example (s)	Source (s)
PTEs	Heavy metals	As, Cr, Cd, Se, Pb, Ba, Hg, Au, V, Zn	*Geogenic:* Rocks, minerals, coal, soil *Anthropogenic:* Smelting, mining, production of oil and gas, military practices, industrial production, pesticides, paint, batteries, traffic emissions, agricultural practices, atmospheric deposition
POPs	Pesticides and their metabolites	Aldrin, chlordane, chlordecone, DDT, HCB, HCH, dieldrin, endrin, heptachlor, mirex, Endosulfans, toxaphene, PeCB	Use of pesticides in agricultural and urban areas
	Industrial chemicals and byproducts of industrial processes	PCBs	Electrical equipment, paint, carbonless copy paper, and plastics
		PBDEs	E-waste
		PCDDs	Combustion processes and volatilization
		PCDFs	Combustion processes and as byproducts in various chlorinated chemical formulations
		PAHs	Pyrogenic, petrogenic, and biological
		PFAS	AFFF, effluent from WWTPs, landfills, application of contaminated biosolids in agricultural soils, domestic and industrial waste

*Source:*Sources of persistent contaminants.

3.1. Mobilization and immobilization

Mobilization and immobilization (also referred as (im)mobilization) approaches are aimed at manipulating the mobility and bioavailability of contaminants [5]. Increasing the mobilization of contaminants in soils promotes their phytoavailability and potential loss to groundwater, thus increasing the potential human health risk. Consequently, developing suitable and adequate remediation approaches to immobilize contaminants, including PTEs in soils, is highly concerning from an agro-environmental point of view to minimize the potential risk to humans and to the environment [3,110,111]. There are recent efforts to remediate contaminated soils effectively. The term "green remediation" has emerged in recent years, aiming to maximize the net environmental benefit of cleanup by considering the environmental impacts of remediation activities at every stage. This includes remedy selection, on-site efficiency, energy requirements, and minimizing impacts on surrounding areas [112-114]. The use of non-edible plants, such as bioenergy crops, and soil amendments for remediating PTEs aligns with the green remediation concept.

Many additives have been examined for their potential to (im) mobilize contaminants in soils. These amendments include organic materials such as biochar, plant- and animal-derived compost, animal wastes, and biosolids. Also, many inorganic amendments such as liming materials, clay minerals, and phosphates have been used to (im)mobilize PTEs (Table 2).

These amendments may increase or decrease the mobilization of contaminants in soils based on the amendment, element, and soil. For example, adding alkaline amendments to acidic soils may increase soil pH and thus enhance the sorption of cationic PTE and thus decrease their mobilization and vice versa with anionic elements. Also, adding amendments rich in clay, Ca, Fe, P, and carbon to contaminated soils may transform the existing bioavailable PTE species in soil into geochemically more stable forms and thus immobilize the PTEs [12, 119]. Different potential mechanisms for PTEs immobilization using soil amendments are included in Fig. 2. For example, the immobilization of cationic PTEs using biochar can be due to the surface complexation with functional groups, precipitation, cation exchange, and electrostatic adsorption and outer-sphere complexation [128,16,129]. The reduction of Cr(VI) to Cr (III) can be a potential mechanism for Cr immobilization [128]. Precipitation of Cd, Cu, and Hg with sulfide can be a reasonable mechanism for their immobilization in soils, particularly under low Eh [128,3,130,131] have summarized the effects of different soil amendments on PTE immobilization and their underlying mechanisms.

However, some soil amendments may increase the mobilization of PTEs in soils. For example, the addition of cow and chicken manure increased the leaching and bioavailability of Cd [132] and Pb [122] in contaminated soils due to the formation of soluble metal–dissolved organic carbon (DOC) complexes. Also, although biochar is a good candidate for the immobilization of cationic PTEs, it may increase the mobilization of anionic PTEs. Biochar may increase the solubility and mobilization of As due to the increase in dissolved organic carbon and

Table 2
Organic and inorganic additives for (im)mobilization of contaminants in soils.

Additives	Soil (source/type)	Findings	Contaminant (s)	Reference
Organic amendments				
Cow Bone-derived biochar	Multi-metal contaminated mining soil	Effective amendment for the metal's immobilization in the soil.	Cd and Zn	[115]
Sheep bone-derived biochar	Mining-contaminated soil	Effective amendment for the metal's immobilization in the soil.	Cd and Zn	[116]
Biochars (iron-modified plant-derived and phosphorus-rich animal-derived)	Paddy soil	Phosphorus-rich biochar was more efficient in Pb immobilization, while Fe-rich and raw biochars were better options for Cd fixation.	Cd and Pb	[111]
Pig carcass-derived biochar	Paddy soil	As immobilization and mobilization occurred under moderately reducing conditions and highly reducing and oxidizing conditions, respectively.	As	[117]
Spent mushroom (SM), pine bark (PB), pruning waste+biosolids (WB) composts	Metal-contaminated soils	The ability to immobilise Cd was higher in SM and WB composts than in PB compost.	Cd	[118]
Mussel shell, cow bone, and biochar	Army firing range soil	- All amendments could immobilize Pb in a small arms range soil. - Mussel shell and cow bone showed a high potential for immobilization of Pb, but they could mobilize Sb.	Pb and Sb	[119]
Biosolid compost, spent mushroom, poultry manure, farmyard manure, fish manure, pig manure, and horse manure	Manawatu sandy mineral soil	Organic amendments addition could increase the reduction rate of Cr(VI) to Cr(III) in the soil.	Cr	[120]
Poultry litter ash	Shooting range soil	The amendment may have the potential for Pb immobilization if the pH of the soil is properly managed.	Pb	[121]
Manure and bone meal	Heavy metal-contaminated soils	The amendments significantly enhanced Pb leaching but decreased metal phytoavailability.	Cd, Zn and Pb	[122]
Activated charcoal, olive oil processing wastes compost, and commercial peat soil material	Polluted agricultural soils	- A mobile fraction of Cu was significantly reduced by amendments application. - The highest decrease in soluble Cu was observed in the presence of the amendments.	Cu	[33]
Biochar, chitosan, activated carbon, organo-clay	Contaminated floodplain soil	Organo-clay increased the solubility of Cd and Pb.	Cd and Pb	[110]
Compost	Sorghum (dry) and barnyard grass (wet) fluvial soil	Mobilization of Cd, particularly in dry soil, and Ni, in dry and wet soils, was decreased.	Cd and Ni	[123]
Inorganic amendments				
Nano-hydroxyapatite, cement kiln dust, bentonite, zeolite, fly ash, sugar beet factory lime, limestone	Contaminated floodplain soil	Liming materials showed high potential for Pb immobilization but could increase the mobility of Cd.	Cd and Pb	[110]
Sulfur	Sorghum (dry) and barnyard grass (wet) fluvial soil	- Cd solubility increased 31% and 49% in dry and wet soil, respectively. - Ni solubility increased 8.7% and 4.6% in dry and wet soil, respectively.	Cd and Ni	[123]
Ca-bentonite (CB) alone and in combination with zeolite (ZL), tobacco biochar (TB), and Ca-hydroxide (CH)	Gold mine-polluted soil	Although CB alone and with TB, CH, and ZL had a high potential for Pb immobilization, its co-application with TB was more effective for Pb immobilization and with ZL was more effective for Cu immobilization.	Cu and Pb	[124]
Phosphate rock	——	Phosphate rock affinity was as follow: Pb> Cu> Zn.	Pb, Cu, and Zn	[23]
Apatite, charcoal and lime	Contaminated soil	The leachability of Cu and Cd was decreased by amendments.	Cu and Cd	[125]
Gypsum (G), monoammonium phosphate (MAP), and elemental sulfur (S)	Previously effluent irrigated soil	G and MAP could increase Cd immobilization, while S reduced Cd immobilization in a dose-additive manner.	Cd	[126]
Al-oxide, zeolite, Mn-oxide, and phosphate rock	Polluted agricultural soils	- Amendments, except Mn-oxide and zeolite, could significantly decrease the mobile fraction of Cu. - Al-oxide revealed the most significant decrease in soluble Cu.	Cu	[33]
$CaCO_3$, iron grit, bentonite, and fly ash	Heavy metal-contaminated soils	- Metal leaching was highly lowered by iron grit, which doubled Pb and Cd phytoavailability. - $CaCO_3$ was the most efficient amendment.	Cd, Zn and Pb	[122]
Various soil amendments and environmental wastes	Sewage effluent irrigated sandy soil	Phosphoric acid, sulfur, and triple superphosphate could immobilize Fe, Al, and Cr.	Al, Zn, Cu, Cr, Fe, Ni, Mn, and Cd	[127]

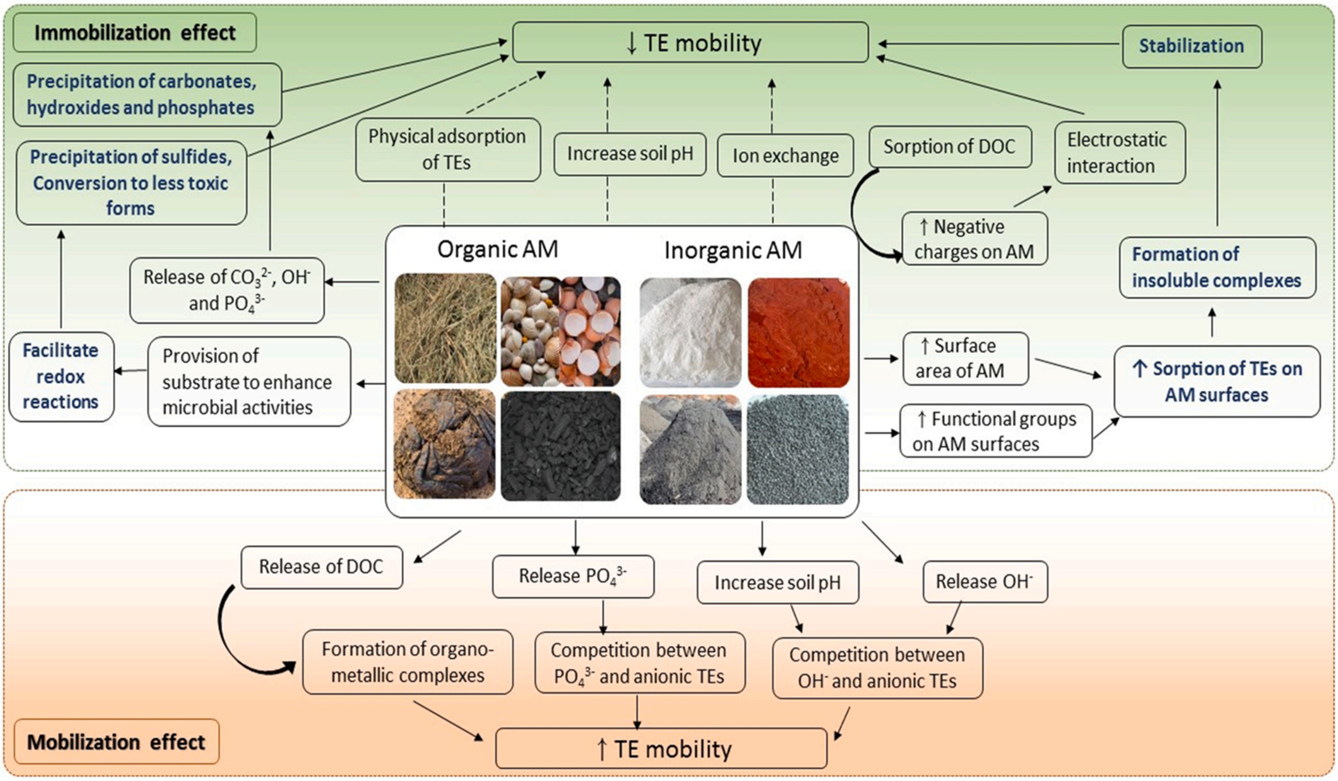

Fig. 2. Mechanisms of PTE immobilization and mobilization from various organic and inorganic soil Amendment Materials (AM).

the soil pH [133]. Biochar may also increase Cu mobilization owing to the increase of dissolved organic carbon [134].

The bioavailability and uptake of PTEs by plants depend on their (im)mobilization in soils. Soil properties, such as soil pH, redox potential (Eh), cation exchange capacity, soil organic carbon (SOC) content, and particle size distribution, highly influence the fractions and species of PTEs in soils, which in turn affects their mobilization [3]. Changes in soil Eh/pH can cause significant alterations in many factors that govern the mobilization of PTEs during flooding/drying conditions. The changes in Eh-pH can affect the reductive/acidic dissolution of PTE carriers, including Fe-Mn oxides, soil organic matter, and sulfur compounds, and consequently affect the release of associated PTEs into the soil solution [135,136]. For example, Shaheen et al. [137] examined the mobilization of As, Co, Cu, Mo, Ni, Se, V, and Zn in the sediments of a fish farm (Fig. 3) and found that flooding the sediments caused a considerable reduction in pH from 8.2 to 5.7. This decrease led to an increase in the dissolved concentrations of Co, As, Se, Ni, and Zn, as well as Fe, Mn, and DOC, under reducing acidic conditions. In contrast, the dissolved concentrations of Mo, Cu, and V increased under oxic conditions.

3.2. *Containment and control*

Contaminant containment and control systems involving in-ground physical barriers or hydraulic pumping systems are designed to block the pathway between contamination source zones and receptors. Ever since the contaminated land remediation industry emerged, installing such systems has remained an ever-present option on the remediation engineer's menu. In England, for example, among all contaminated land sites that have been remediated to date, around 9% involved installing cut-off wall/barrier systems [138]. The fundamentals of this approach and its strategic implications are critically discussed in this section.

3.2.1. *Impermeable and permeable barriers*

The remediation industry first adopted barrier systems to control the subsurface migration of contaminants many decades ago. This approach involves the construction of either active or passive in-ground barriers.

Active barriers are known as permeable reactive barriers (PRBs). They are subsurface structures containing reactive materials that prevent the migration of contaminants while not impeding groundwater movement. These structures are strategically located to intercept plumes of contaminated groundwater. As the groundwater passes through the PRB, a reaction occurs involving degradation, sorption, or precipitation, which either captures contaminants or degrades them to a non-toxic state, with clean groundwater exiting the outer side of the PRB (see Section 4.1).

Historically, passive barriers have been more commonly installed at contaminated sites than active barriers. These are non-reactive impermeable (cut-off) walls designed to impede groundwater flow and isolate contaminated areas [139-141]. There are many types of passive barriers, which are generally categorized based on either the materials they consist of or the construction method employed to install them. In the U. S., barriers consisting of soil mixed with the highly plastic clay bentonite (montmorillonite) are widely used at polluted sites [142]. In the U.K., barriers formed from a mixture of cement and bentonite are common. Both of these types of barriers are usually constructed using a slurry trenching technique and, hence, are sometimes referred to as "slurry walls". In the past few decades, soil mix technology (SMT) has been increasing for barrier construction [143], which involves the use of augers or other mixing devices that apply reagents directly into the ground without the need for excavation. In China, SMT is increasingly used as an approach for contaminant containment at polluted sites [9].

If properly designed with robust quality assurance and quality control (QA/QC) used in their construction, physical barrier systems can be assumed to offer contaminant containment for one decade without malfunction [144]. In the longer term, physical barrier materials may deteriorate under mechanical, chemical, and environmental stresses leading to mechanical and contaminant transport problems and impacting their serviceability and reliability. However, long-term effectiveness is uncertain owing to a lack of field data. It should also be noted that some systems have displayed less than acceptable

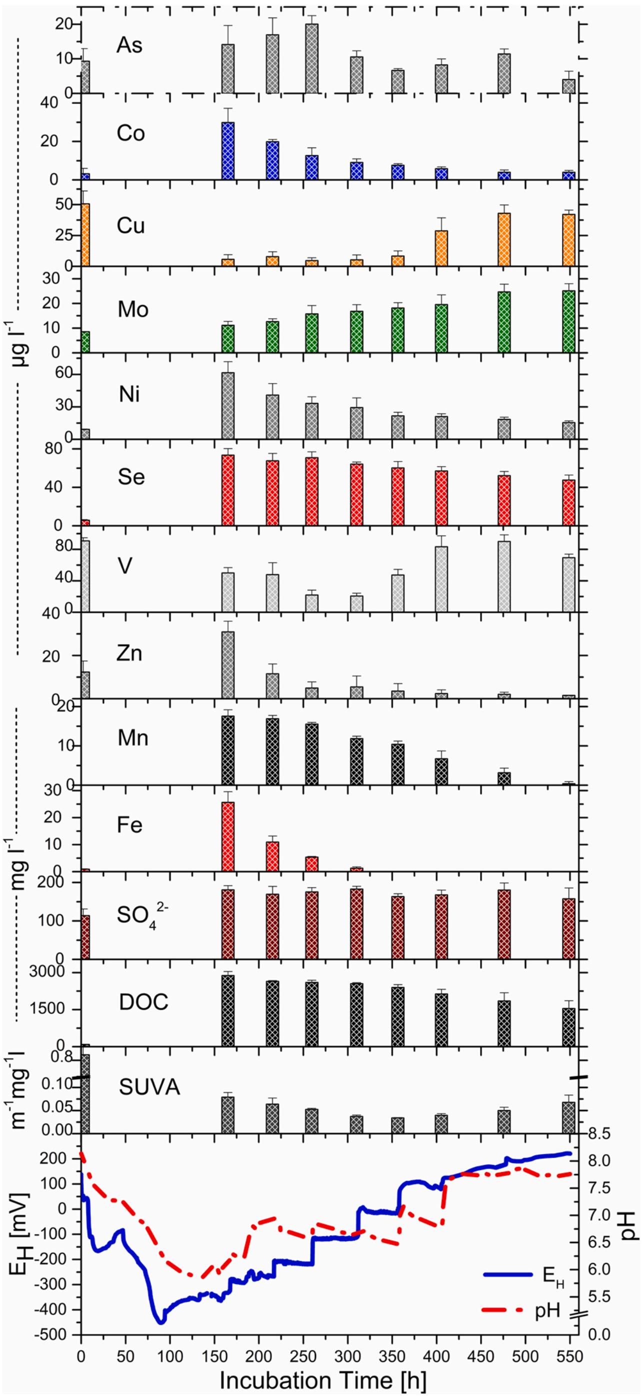

Fig. 3. Development of redox potential and pH in the sediment's slurry and the mean values of different elements and carriers [137]. Reproduced with the publisher's permission.

performance in the short term, with faults discovered at the interface between barrier walls and the low permeability strata that they are keyed into [144]. Such faults ought to be eliminated by QA/QC in construction, and, in any case, faults can often be repaired once detected.

3.2.2. *Hydraulic control by pumping*

Like physical containment, hydraulic control has been widely used as a remedial approach for decades. The process involves groundwater removal by pumping from extraction wells. The purpose of this approach is twofold. First, pumping groundwater creates a cone of depression in the aquifer around the extraction point. Networks of extraction wells can be installed to extend the area of influence. Because contaminated groundwater flow is redirected toward extraction wells under pumping, offsite migration of contaminants is controlled, and the risk to groundwater receptors is mitigated. The second reason is that contaminants are removed with extracted groundwater, reducing the mass remaining in the ground. This process is termed pump-and-treat (P&T). Once contaminant concentrations fall below maximum concentration thresholds, pumping systems can be turned off. However, heterogeneity in the subsurface can substantially affect contaminant removal efficiency and will often lead to issues such as tailing [145] during pumping, back diffusion [146], and rebound [147] after the system is turned off.

Because of such limitations, hydraulic control systems will often need to be continuously operated at contaminated sites for decades, which is associated with high life-cycle costs. Nowadays, remediation engineers are often reluctant to install pumping systems because of the prospect that they will need to be operated for an indefinite period. They can also have low public acceptance [148]. Furthermore, the long-term operation of groundwater pumping systems can result in large energy usage and carbon footprints. For example, one study calculated the emission of 130,000 kg of greenhouse gas per kg of contaminants treated in groundwater [149]. Recognition of the secondary impacts of remediation technologies has led to a shift in the remediation industry toward alternative, more sustainable approaches to minimize potential environmental side effects. When hydraulic control by pumping is selected as a remedial approach, its sustainability may be improved by using renewable energy sources instead of fossil fuel burning. The use of Green & Sustainable Remediation Best Management Practices for handling generated waste can also improve its sustainability. However, compared to conventional P&T systems with vertical wells, horizontal wells have been demonstrated to be more effective. Bortone et al. [150] compared the performance of vertical and horizontal wells for the remediation of groundwater contaminated with Cr (VI). Their results revealed that the optimal P&T configuration using horizontal wells required a single well to completely remove the contaminant plume, compared to 4 wells for vertical wells. The advantages and disadvantages of these treatments are shown in Table 3.

3.2.3. *Strategic factors*

The decision-making process in contaminated site remediation is complex and influenced by various strategic factors. In-situ source depletion is often favoured, as it reduces contamination legacy for future generations, but it can sometimes fail to achieve target concentrations in unfavourable site conditions [151]. As an alternative, contaminant containment and control systems offer increased project certainty and lower costs, as the cost of barriers increases in proportion to the perimeter of the remediated site (length + width), while source-depletion costs increase in proportion to the area of the remediated site [152].

The long-term cost is a critical factor when selecting a remediation strategy and can be underestimated with a high discount rate, which discounts the welfare of future generations [153]. Containment systems can be installed quickly but require post-remediation site management and long-term monitoring to ensure performance [151]. Big data and sensor technology advances offer promising solutions, such as in situ wireless sensors providing real-time data on barrier strength [151].

Still, containment systems may be met with low acceptance due to the perceived environmental injustice of burdening future generations with contamination left in the ground. Combining source-depletion and containment strategies may provide the certainty of containment systems while reducing the source zones and burden on future generations.

3.3. *Degradation and destruction*

The degradation and destruction of contaminants refer to different

Table 3
Advantages and disadvantages of containment barriers and hydraulic control by pumping.

Treatment	Advantages	Disadvantages
Containment Barriers	• Prevent contaminants migration without blocking the groundwater flow in active barriers. • Apply reagents directly into the ground without excavation in SMT as a passive barrier. • Can offer contaminant containment for one decade without malfunction if properly designed. • With QA/QC in their construction, any faults can often be repaired once detected.	• Unclear long-term effectiveness. • Their materials may deteriorate under mechanical, chemical, and environmental stresses over time, impacting the effectiveness and reliability of the barriers. • Some barrier walls have underperformed in the short term due to issues with the interface between the walls and their low-permeability strata.
Hydraulic Control by Pumping	• Control offsite contaminants migration by redirecting contaminated groundwater flow towards extraction wells, mitigating the risk to groundwater receptors. • Remove contaminants with extracted groundwater, reducing their mass remaining in the ground. • Improve the sustainability of the system by using renewable energy sources instead of fossil fuel burning.	• Low public acceptance. • Their removal efficiency can be influenced by heterogeneity in the subsurface, leading to issues such as tailing during pumping, back diffusion, and rebound after the system is turned off. • Require continuous operation at contaminated sites for decades. • Their long-term operation can lead to significant energy consumption and carbon emissions.

processes. Degradation mainly involves the microbial process of biodegradation, while destruction refers to thermal, chemical, and mechanical processes. Organic contaminants, such as pesticides and industrial chemicals, can undergo both biodegradation and destruction, while inorganic contaminants like PTEs are not readily degraded or destroyed.

Microorganisms, including bacteria, fungi, and algae, play a crucial role in biodegrading organic contaminants. There are three main processes of microbial transformation of organic contaminants: biodegradation, co-metabolism, and bioaccumulation [35,154]. Biodegradation occurs when microbes gradually adapt to utilizing the contaminant as a carbon and energy source after a lag phase. Co-metabolism is a form of biodegradation where a contaminant is fortuitously degraded by an enzyme or cofactor produced during the microbial metabolism of another compound [155]. Bioaccumulation occurs when soil microorganisms incorporate and accumulate the contaminant by active uptake processes. For example, some PTEs like Cu and Zn are essential for microorganisms' metabolic functions, and their uptake by microorganisms involves active processes [156].

Thermal, chemical, and mechanical processes are used to destroy contaminants in soils (Table 4). Thermal destruction can be achieved through direct incineration, microwave radiation, plasma gasification, and pyrolysis. Chemical destruction involves hydrolysis, oxidation-reduction, substitution, elimination, dehalogenation, and photolysis [1,16,5]. High-energy ball milling or mechanochemical destruction has recently gained popularity in the remediation of recalcitrant contaminants in soil and solid waste due to the lack of requirements for toxic solvents, extreme temperatures, high pressures, or harmful additives [157,158]. Factors that influence the thermal, chemical, and mechanical destruction of organic contaminants in soil include soil pH, clay content, and organic matter content.

While these technologies have been found to be effective in removing and destroying POPs, they may not be practical for large-scale remediation of soil contaminated with POPs under field conditions because of the need for expensive chemicals and the resulting environmental

Table 4
Destruction methods for treatment of contaminants in soil.

Destruction method	Treatment process	Contaminant	Findings	Reference
Photolysis	Microwave irradiation/persulfate	Ethyl-parathion	Up to ~77% parathion removal with 0.1 mM persulfate/g soil at 60° C	[159]
	Nanometer anatase TiO_2/UV	Pyrene	Efficient for pyrene degradation	[160]
	Nanometer rutile TiO_2/UV	Phenanthrene and pyrene	Efficient for the PAHs degradation	[161]
	Micro-nano TiO_2/sunlight	Pyrene	- Increased degradation due to the synergistic effect of sunlight and TiO_2. - An increase in the degradation rate of transformed pyrene by micro-nano size TiO_2 was observed.	[162]
Chemical treatment	Ozonation and Fenton	PAHs	Effective for the removal of 3–, 4-, 5- and more ring PAHs	[163]
	Ozonation	PCB	- More efficient in freshly spiked soils with the contaminant. - Removal efficiency enhanced by increasing the time.	[164]
	Chlorination + thermal treatment	Heavy metals	Effective for Pb and Cd removal but not for Cu, Zn, Cr and Ni removal.	[96]
	Chlorine dioxide oxidation	PAHs	A higher concentration of the oxidant could enhance the PAHs degradation rate.	[165]
	Magnetite-activated persulfate oxidation	PAHs	Efficient for PAHs removal	[166]
	Electrochemical decomposition with Ti/SnO_2–Sb, Ti/SnO_2–Sb/MnO_2, and Ti/SnO_2–Sb/PbO_2 anodes	PFOA	98.8% PFOA degradation rate	[167]
	Fe^{2+}-EDTA catalyzed persulfate oxidation	PAHs	PAHs were effectively degraded with persulfate oxidation without an iron catalyst	[168]
Thermal treatment	900–1100 °C	PFHxA, PFOA, and PFOS	Complete degradation	[169]
	450 and 550 °C	PFAS	71–99% removal for the field contaminated soil at 550 °C, and > 99% removal from the fortified soils at 450°C	[170]
	Up to 900 °C	Gas oil	- At low heat, insignificant contaminant transformation. - At moderate heat, a high fraction of contaminant can be eliminated. - At high heat, high removal efficiencies can be achieved.	[171]

degradation and disposal issues [172].

4. Processes of contaminant containment

4.1. Impermeable and permeable containment

4.1.1. Impermeable barriers

Physical barriers are conventional containment technologies that play a significant role in managing pollution by preventing the migration of contaminants. Impermeable barriers are often installed to prevent or significantly reduce the movement of contaminants in soils and/or groundwater [9]. Barriers are preferred when widespread subsurface contamination at a site prevents excavation and removal of wastes because of elevated health and safety risks and/or costs [173]. Such containment is also preferred when it is permitted to leave or bury the contaminants at the site [174].

Unlike the pump-and-treat or *ex-situ* treatment approaches, containment does not require pumping contaminated groundwater or excavating contaminated soils. It reduces operational costs and health and safety risks in handling contaminated media. However, physical barriers require regular monitoring and maintenance through periodic inspections for leaks, corrosion, and ponding [9]. For example, groundwater monitoring wells associated with testing the efficacy of physical barriers must be periodically monitored and sampled. Slurry walls, caps, and sheet piles are the most commonly used physical barriers for contaminant containment [175].

In the slurry wall technique, a trench cutter or grab bucket is first used to excavate a trench in the ground to the desired depth. Thereafter, the trench is filled with slurry, for example, cement-bentonite-water, which is solidified into a 0.4–1 m thick wall [176,177]. The slurry mixture has to be compatible with site conditions, geologic strata, groundwater quality, and soil conditions. For instance, a mixture of soil-bentonite slurry should be applied at nearly level sites since it can readily flow. A mixture of concrete-bentonite slurry is suitable for sites with uneven topography since it sets rather quickly [178]. Slurry walls are also called impermeable barriers and are applicable for the containment of a wide class of organic and inorganic contaminants, including metals, pesticides, chlorobenzenes, explosives, chlorinated aliphatic hydrocarbons, monocyclic aromatic hydrocarbons, non-metallic inorganic compounds, phenolic compounds, petroleum hydrocarbons, polycyclic aromatic hydrocarbons, and polychlorinated biphenyls [179].

In-situ capping involves covering contaminated sediments with material layers composed of sand, gravel, or geomembranes to chemically or physically isolate and immobilize contaminants within the sediments. Capping limits surface water infiltration provides a stable surface over polluted sediments and enhances aesthetics at a hazardous site. Cap materials and designs range from basic single layers of compacted clay to complicated multilayer structures. The selection of these materials and designs depends on different factors, including their risk factors, remedial objectives, cleaning goals of the site, the cost and local availability of the materials, climate, physicochemical properties of the contaminants being covered, and the site's predicted future use [178]. The use of physicochemical-based active caps seems promising; however, the pollutants cannot be entirely removed from the environment due to the limited adsorption or reaction capacities of reactive materials of the caps [180]. So, the use of passive caps is still the most prevalent. Capping is mostly used for chlorinated aliphatic hydrocarbons, chlorobenzenes, metals and other inorganics, pesticides, petroleum hydrocarbons, polychlorinated biphenyls, and polycyclic aromatic hydrocarbons. It can also be used for the containment of explosives, monocyclic aromatic hydrocarbons, and phenolic compounds with certain restrictions [179].

Sheet pile walls are built by driving precast concrete, steel, wood, or aluminium piles individually or in groups into the ground. Those can be interlocked to form a continuous barrier. Steel sheets are the most commonly used sheet piles [178,181]. Sheet piling is easier to install than slurry walls; nevertheless, it is more difficult to construct in rocky soils and areas where the bedrock is shallow. In addition, sheet piling may allow leakage of the contaminated groundwater if the interlocking joints are not sealed correctly. Considering the above factors, the use of sheet piling is mostly restricted to temporary dewatering of the site [178].

4.1.2. Permeable reactive barrier (PRB)

Permeable Reactive Barrier (PRB) approach for the containment of contaminants was introduced as an alternative to conventional remediation techniques, such as pump-and-treat, which were found to be either impractical or costly in the long-term restoration of contaminated groundwater [182-184]. High efficiency, low maintenance, low operation costs, and low ongoing energy requirements are some of the advantages of PRBs over conventional remediation techniques [185,186].

PRB technique, as a passive form of the treatment, has been proven to be one of the most promising *in-situ* treatments of groundwater contaminants [183]. In this technique, the polluted groundwater travels by natural hydraulic gradient through the permeable reactive zone, where the contaminants are immobilized or removed [182]. Different factors, such as groundwater velocity, soil properties, and barrier characteristics, should be considered for designing the PRBs [182,187]. Higher hydraulic conductivity of the reactive materials than that of the surrounding soils ensures the spontaneous flow of groundwater through the PRBs without any extra source of energy [182].

PRBs have been shown to be efficient for both organic and inorganic contaminations [188]. Recently, Bortone et al. [189] proposed an innovative *in-situ* DRAINage technique, a combination of advanced drainage systems and adsorption processes, for Cr (VI)-contaminated groundwater. Using a natural gradient of groundwater, the system collects contaminated water through a drainage system and treats it directly in an active cell downstream without requiring external energy inputs. Initial findings showed the high efficiency of the system compared to PRBs. Table 5 shows selected studies on PRBs techniques used for the protection of groundwater from organic and inorganic contaminants. As can be seen from Table 5, the focus of the studies on the PRBs was mostly on the permeable adsorbing barrier (PAB), using an adsorbent as the reactive material for contaminants' remediation. Several researchers have reviewed this technique for the remediation of groundwater [183,190,191,184].

4.1.3. Case study: Permeable reactive barriers for the protection of groundwater from cadmium contamination

In a study by Di Natale et al. [182], a PRB technique using activated carbon was used to protect a river from inflowing cadmium-contaminated groundwater (Fig. 4). The leachate of cadmium to the groundwater was from polluted topsoil due to an extreme rainfall event resulting in 100 mm infiltration height during 24 h. In this study, the adsorption isotherms of activated carbon (Aquacarb 207EA™) were first experimentally determined, and then a theoretical model was proposed by interpretation of experimental results. The experimental results revealed an increase in adsorption capacity with concentrations of cadmium, which strongly depended on working conditions [182]. The experimental analysis showed a low efficiency of PRB at lower and higher pHs. An increase in adsorption capacity was observed by increasing pH, with the maximum value observed at a pH of ~7.5. Moreover, the adsorption capacity decreased by increasing the salinity of the solution using NaCl or $NaNO_3$.

In this study, two design requirements of PRBs were addressed. First, it was shown that the width of the barrier should be adequate for the adsorption of the contaminants. Second, the desorption phenomena after saturation of the barrier may occur due to the mobilization of stored contaminants into the soil by rainfall infiltration, causing a contaminated plume at the barrier's exit. However, the overall results indicated that the PRB technique could ensure long-term efficiency by

Table 5
Selected studies on PRBs used as groundwater protection from organic and inorganic contamination.

Contaminant (s)	Scale	Reactive material	PRB technique	Observations	Reference
Inorganic					
Ammonium, lead, and copper	Batch and column	Clinoptilolite (01–29B)	PRB	- $>$ 80% removal efficiencies of the contaminants with 1 g clinoptilolite were observed except for high concentrations of NH_4^+ and Cu.	[186]
Copper, cadmium, cobalt, nickel, and Zinc	Pilot	Compost and sulfate-reducing bacteria	Sulfate-reducing PRB	- Significant removal of metals during 21 months was observed within the barrier. - The concentrations of metals in the influent declined within the barrier from 3630 μg/L to 10.5 μg/L for copper, from 2410 μg/L to 136 μg/L for zinc, from 15.3 μg/L to 0.2 μg/L for cadmium, from 5.3 μg/L to 1.1 μg/L for cobalt, and from 131 μg/L to 33 μg/L for nickel.	[192]
Chromium	Full	Zero-valent Iron (ZVI)	PRB	- After 8 years working period, the PRB remained effective in reducing chromium levels from $>$ 1500 μg/L in groundwater hydraulically upgradient to $<$ 1 μg/L in groundwater hydraulically downgradient.	[193]
Sulphate and cadmium	Batch	A mixture of organic sources for bacterial growth, a porous medium, a neutralising agent, and ZVI	Biological PRB	- The processes were bio-reduction by sulphate-reducing bacteria and sorption by organic matter. - The best mixture was 30% perlite, 30% silica sand, 22% limestone, 9% compost, 6% leaves, and 3% ZVI, which presented the optimal conditions for the growth of sulphate-reducing bacteria and 83% removal of sulphate in 22 days. - This combination, with a major contribution of sorption over bioprecipitation could completely remove cadmium.	[194]
Nickel and copper	Column	ZVI/pumice	PRB	- The mixture of iron and pumice granular performed well for both heavy metals removal and in maintaining long-term hydraulic conductivity. - The weight ratio of 30:70 ZVI: granular pumice mixture showed the best performance.	[188]
Lead	Batch and column	Granular dead anaerobic sludge	PRB	- 97% removal of 50 mg/L lead occurred at 2 h, pH 5, with 0.5 g/100 mL reactive material under 250 rpm. - The thicker PRB was found to be better than the thinner ones.	[195]
Cadmium	Batch and column	Zeolite	PRB	- Maximum removal efficiency of 50 mg/L cadmium was observed after 1 h contact time at pH 6.5, in the presence of 0.25 g/100 mL resin and 270 rpm speed. - The PRB started to saturate after ~120 h, indicating a reduction in zeolite functionality percentage.	[187]
Lead, Cadmium, and Zinc	Batch	Gravel, limestone, and soda-lime glass beads with cementitious material (Portland cement with and without fly ash)	Permeable Reactive Concrete (PRC)	- At 1 mM concentration of the metals, the highest removal for all tested metals was as follows: Concrete containing gravel aggregate$>$ concrete containing limestone aggregate$>$ concrete containing glass beads. - Removal mechanisms: absorption, adsorption, internal diffusion, precipitation, and co-precipitation	[196]
Lead, Cadmium, and Zinc	Column	Cementitious material (Portland cement with and without fly ash)	PRC	- Removal mechanisms: hydroxide metals precipitation, complexation, and metals sorption into the hydrated cement paste or metal precipitates.	[197]
Lead and cadmium	Batch and column	mixed materials (fly ash, corn straw, zeolite synthesised from iron–manganese nodule and fly ash)	PRB	- Higher removal efficiency of 7 mg/L lead and 0.7 mg/L cadmium in a weak acidic solution at 25 °C was observed. - The functional groups of –OH and $C=C$ played a significant role in metals removal.	[185]
Copper	Batch	Olive seeds	PRB	- 99% removal of 10 mg/L copper occurred at 70 min under pH 5.5 with 250 rpm speed in the presence of 0.8 g/50 mL sorbent.	[198]
Copper and cadmium	Batch and column	Humic acid extracted from sewage sludge coated sand	PRB	- $>$ 98% removal efficiency of 10 mg/L of metals was observed at one h contact time and pH 7 in the presence of 0.25 g/50 mL sorbent with 200 rpm agitation speed. - Maximum sorption capacity for cadmium and copper was 18.9 and 87.5 mg/g, respectively. - Main adsorption mechanism: physisorption	[199]
Cesium	Batch and column	Granular activated carbon	PRB coupled with microwave	- The dielectric properties of activated carbon improved the efficiency of microwave regeneration. - Maximum removal efficiency of caesium from 61% to 80% was achieved for regeneration times from 5 to 15 min	[200]
Organic					
Tetrachloroethylene	Case study	Activated carbon	PRB	- Good efficiency of the barrier - After 60 years of operation, in which adsorption and	[201]

(*continued on next page*)

Table 5 (*continued*)

Contaminant (s)	Scale	Reactive material	PRB technique	Observations	Reference
				then desorption occurred, the out-flowing level was always lower than the regulatory limits.	
Ciprofloxacin	Batch and column	Sodium alginate/graphene oxide hydrogel beads	PRB	- Maximum adsorption capacity: 100 mg/g at pH 7 - Main adsorption mechanisms: electrostatic interaction, hydrophobic interaction, ion exchange, pore filling, and H-bonding	[202]
Trichloroethylene	Column, pilot, and field	-	Coupling of large-diameter PRB wells	- Significant reduction in trichloroethylene concentration was observed. - Reinjection and extraction wells of treated groundwater at the plume fringe could promote a positive hydraulic gradient, improve groundwater transport through the reactive media and control the plume.	[203]
Polycyclic aromatic hydrocarbons (PAHs)	Batch and column	Wheat straw and coconut shell biochar	Permeable reactive biobarrier	- Almost complete removal of phenanthrene was observed by both adsorbents. - Coconut shell biochar was more promising to treat PAHs than wheat straw biochar. - Bacterial communities of both columns contained Pseudomonas, Sphingomonas, and Mycobacterium genera. - In the column with coconut shell biochar, Pseudomonas and Sphingomonas were 7 times more abundant than in the column with wheat straw biochar.	[204]
Agrotoxic compounds carried by agricultural runoffs	Column	A porous material supporting an enriched microbial biofilm	Permeable reactive surface-biobarriers	- The biobarrier was economically adequate to remove the pollutants due to an insignificant difference in the removal efficiency in the presence of GAC as an adsorbent. - The microalgae Micractinium sp., one of the most prevalent microorganisms isolated in the microbial biofilms, showed the ability to accumulate permethrin and cypermethrin insecticides.	[205]
Dieldrin, endrin, DDT and lindane	Batch and column	Iron turning waste	PRB	- In the batch system, 86–91% degradation of dieldrin, endrin, and DDT was observed, while only 41% degradation of lindane occurred after 10 min reaction using 1 g of the reactive material in 200 mL of 20 μg/L pesticides. - Favourable pH: Acidic (pH = 4) - In the column system, the removal efficiency of dieldrin, lindane, and endrin with iron turning waste alone was 83–88%, which was stable during 60 min. DDT removal was 58%. - $\geq$ 94% of all pesticides (2 μg/L) were removed by 150 g iron turning waste at 1.6 h hydraulic retention time.	[206]
Tetracycline hydrochloride	Column	Heterogeneous electrocatalyst (TiO_2/graphite composite)	Permeable electrochemical reactive barrier (PERB)	- Tetracycline was degraded under a wide range of pH and a low applied potential. - 60% degradation of 50 mg/L tetracycline was observed under 1.2 V interelectrode potential difference and the anode 10 cm above cathode at pH 3.	[207]
Tetracycline	Batch and column	Hydroxyapatite nanoparticles prepared from sewage sludge waste and cement kiln dust	PRB	- 90% removal efficiency of 50 mg/L tetracycline at pH 5 with 0.4 g/50 mL adsorbent during 2 h at 200 rpm speed was observed. - Adsorption process: chemisorption - Maximum adsorption capacity in batch and column studies was 43.5 and 41.5 mg/g, respectively. - Main adsorption mechanisms: electrostatic attraction, surface complexation, and intra-particle diffusion	[208]
Levofloxacin	Column	Three porous shapeable three-component hydrogen-bonded covalent-organic aerogels	PRB	- The reactive material revealed satisfactory performance in the adsorption of levofloxacin with high adsorption capacity, excellent recyclability, wide pH tolerance, and good anti-ion interference. - Adsorption mechanisms: synergistic effect of electrostatic force, pore preservation, H-bonding, hydrophobic-hydrophobic interactions, π-π electron-donor-acceptor, and dipole-dipole interactions.	[209]

preventing river contamination for as long as seven months.

This case study indicated the effectiveness of the use of activated carbon in the PRB technique for cadmium removal from a contaminated shallow aquifer. However, there was a possibility for the reversibility of the adsorption process and the progressive release of cadmium from the barrier into the clean groundwater. Proper design of the barrier is critical to keep the cadmium concentrations below their critical limit values. This study demonstrates that PRBs can be a reliable strategy for assuring compliance with environmental safety guidelines and reducing contaminant risks, provided the above concerns are addressed.

Similar case studies using the PRB system as a remediation technique have been published recently [210,211].

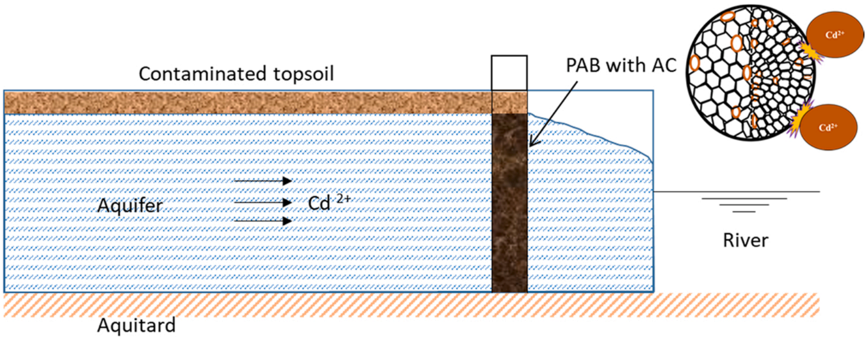

Fig. 4. Example of the PAB application in the case study from Di Natale et al. [182].

4.2. Chemical containment

4.2.1. Solidification/Stabilization

The most widely used chemical containment method is Solidification/Stabilization (S/S). Solidification refers to contaminated soils, sediments, or other hazardous wastes being trapped by the solid material formed via chemical reactions (e.g., the Portland cement-based Solidification). Stabilization focuses more on immobilizing the persistent inorganic or organic contaminants due to precipitation, complexation, physical adsorption, hydrogen bonding, and other potential pathways [212,213]. Research on S/S is booming (Fig. 5). In particular, materials and agents used during this process, such as biochar, slag, or metal oxides, have been widely explored in the last ten years [214]. As a well-established remediation technology, the commercialization of S/S has taken off since the 1980 s [213]. In recent years, its potential has been further promoted due to new research on green and sustainable stabilization materials [215,153,131], as well as lower life cycle environmental footprints [216]. Numerous successful attempts from the U.S. Superfund Programs have confirmed its practical applicability. For instance, 9 out of 35 superfund remedy decision documents during 2015–2017 selected *in situ* S/S as the remediation method [217]. The popularity of S/S stemmed from its ability to remediate contaminated environmental compartments rapidly and cost-effectively. It is also a process that can be applied either *in-situ* or *ex-situ* and remediate both persistent inorganic and organic contaminants.

Numerous attempts have been made regarding the S/S of toxic metals and metalloids (hereinafter referred to as heavy metals). The hydration of cementitious materials, including Portland cement, pulverized fly ash, silica fume and ground granulated blast-furnace slag, result in the formation of the calcium silicate hydrate (C-S-H) gel with a layered structure, encapsulating metals within the solid structure [218,219]. Furthermore, the hydration of reactive MgO would form the brucite ($Mg(OH)_2$) with a lamellar structure, favouring the encapsulation and simultaneous precipitation of heavy metals as well [220,221]. Compared with the metal solidification process with a focus on mechanical strength as well as chemical encapsulation, the stabilization aspect of S/S involves various processes, including ion exchange, electrostatic interactions, complexation and precipitation that change the speciation of heavy metals from labile ones to less labile ones with low mobility [128,3,222].

Various stabilization agents, especially green remediation materials, have been widely used in laboratory tests, greenhouse studies and field demonstrations of chemical stabilization. Biochar, a biomass waste-derived material with well-developed pores and multiple functional groups for metal stabilization, has recently attracted much attention [223-225]. Tea Stalk biochar supported nanoscale ZVI showed higher than 65% Cr (VI) removal efficiency for remediation of simulated groundwater in batch scale [226]. The oxygen-containing functional

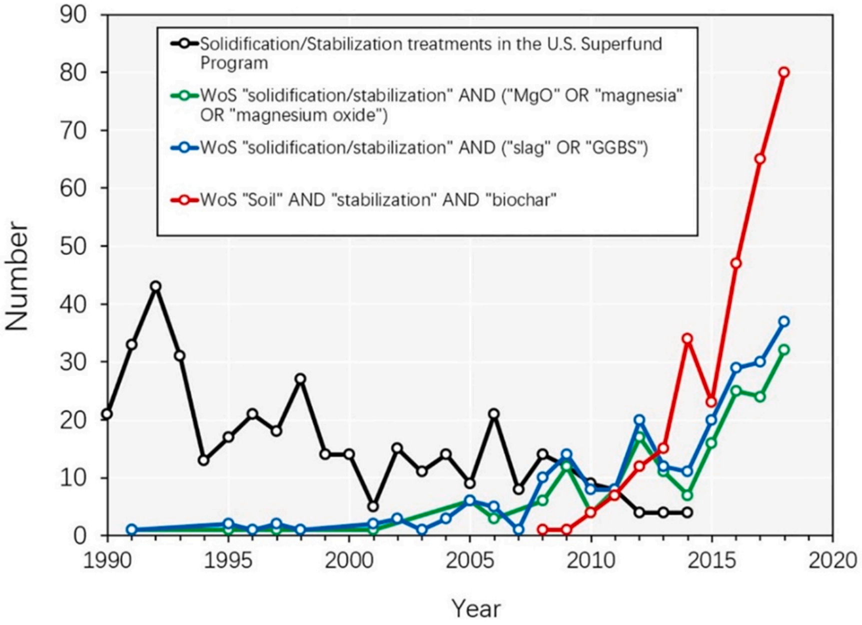

Fig. 5. Number of Solidification/Stabilization (S/S) treatments in the U.S. Superfund program (CERLA) and relevant research articles [214]. Reproduced with the publisher's permission.

groups favour surface complexation, while the ash compositions assist in metal stabilization via precipitation (Fig. 6) [128,227,117]. Biochar can also achieve co-benefits of soil health improvement, crop yield increase, and climate change mitigation [228,229]b; [230]). Natural minerals, such as montmorillonite, palygorskite and sepiolite, immobilize heavy metals via ion exchange and surface complexation with the hydroxyl groups [231,232]. Industrial wastes, including steel slag, red mud, and coal fly ash, stabilizes metals due to an elevation in soil pH (i.e., the liming effect), as well as the surface complexation and precipitation [233-235]. Green-synthesized nanomaterials also immobilize heavy metals effectively [236,237]. Apart from heavy metals, limited evidence has shown that other persistent inorganic contaminants, including fluoride [238,239] and cyanide [240], can also be remediated by S/S.

It has long been established that conventional Portland cement-based S/S processes often fail to immobilize organic contaminants due to the prevention of hydration [241-243]. Recent observations suggest that organic amendments can immobilize organic contaminants via chemical stabilization. For instance, organochlorine pesticides, including DDT, DDE and dieldrin, can be stabilized by dairy manure compost, yet the underlying mechanisms were poorly understood [244]. Biochar effectively immobilizes a variety of persistent organic contaminants, including PCBs [245,246], pesticides [247,248], and dioxins [249]. Organic contaminant retention mechanisms may include pore-filling, hydrogen bonding, electrostatic interactions, and hydrophobic interactions (Fig. 6) [125,246].

It should not be neglected that too much focus has been put on short-term S/S performances while long-term effectiveness is often overlooked. Various natural forces, including temperature variations (i.e., the freeze-thaw cycling), rainfall events (i.e., the wet-dry cycling), carbon dioxides (i.e., carbonization), and microbial activities (i.e., biological degradation), result in the deterioration of an S/S system in the long run [250] (Fig. 7). Several attempts have been made to seek novel materials with long-term stability. For instance, Shen et al. [221] observed that MgO-based solidification agents successfully immobilized Cd and Pb in a soil-washing residue under wet-dry cycling. A significant reduction (>96%) in the amount of dissolved Cd and Pb from the soil washing residue was observed after treating the leachates with the amendments. In another study, Liu et al. [251] used novel iron carbide loaded on *N*-doped nanotubes with high efficiency (>82%) for the adsorption and reduction of Cr (VI) in groundwater in batch experiments. Hou et al., [151] noticed that the joint application of organic fertilizer and biochar in lab-scale experiments assures long-term effectiveness under freeze-thaw cycling, suggesting that this stabilization method can be applied for the sustainable risk management of agricultural lands in seasonally-frozen areas. Wang et al. [252] found that humic acid-modified montmorillonite served as a long-term stabilization agent towards Cd and Hg, possibly due to the strong surface complexation between heavy metals and the humic acid layer. Apart from emerging materials with excellent stability, novel long-term performance prediction methods are also needed. Most studies have adopted a qualitative artificial aging method [250,253]. Limited studies have adopted quantitative aging methods on the basis of rainfall quantification [221,254,252]. Other factors causing the deterioration (aging), including microbial activities, chemical oxidation and photochemical transformation, should also be taken into account in a "quantitative" manner in future studies.

4.2.2. Case study

In a recent study conducted by Yang et al., [256]c), the effects of aging on metal(loid)-contaminated soil remediation using standard biochars were investigated. The study involved 2304 observations across six different biochar feedstocks, two pyrolysis temperatures, eight metal(loid)s, four aging methods, and six sampling intervals. Results showed that sewage sludge biochars had the highest resistance to both natural and artificial aging, likely due to the abundance of oxygen-containing functional groups favouring metal complexation and poorly developed pore structures limiting access to natural aging forces.

A correlation was also observed between ash content and pyrolysis temperature, with high-ash biochars showing less resistance to aging at higher pyrolysis temperatures, while low-ash biochars were more resistant. Furthermore, Cu and Sb exhibited similar aging behaviours, with both highly susceptible to chemical oxidation-induced dissolved organic carbon release.

The cluster analysis revealed that aging patterns from wet-dry and freeze-thaw cycling were similar to those of naturally aged soils. The comparison of lab aging data with existing biochar field aging results also highlighted contrasting long-term immobilization performances attributed to a variety of factors related to biochar properties and climate.

The study demonstrated that biochar could effectively immobilize metal(loid)s in soil. However, the suitability of biochars for metal(loid) immobilization varies depending on the geographic context. Therefore, the study's findings have significant implications for developing sustainable strategies for the remediation of metal-contaminated soil.

4.3. Biological containment

Biological contaminant containment involves modifying the residence time within a given area or space. For example, in the use of vegetation to stabilize contaminants, various processes are known to help retard offsite migration towards more sensitive environments. One process is the incorporation of contaminants, mostly inorganic contaminants, within the tissue of plant species. The residence time can be potentially very large in long-lived plant species. However, plant system residence times depend on plant species and chemical characteristics. Carbon residence times, for example, are believed to be relatively short, on the time scale of days rather than years [257]. There are several biological containment approaches.

Microbial processes are essential in biological containment, both passively and with engineered systems. Microbial designed system can be used to transform the speciation of contaminants to more benign forms [258,259] or to precipitate and recover metals [260-262]. For *in-situ* stabilization, microbial matter and processes can similarly provide substantial benefits to containing contaminant movement by forming microbial networks, biological crusts [263] and extracellular polymeric substances (EPS). Increased production of EPS and biochemical compounds can be increased exponentially through the growth of revegetation and phytostabilisation techniques [264-266].

4.3.1. Phytostabilization

Phytostabilization of contaminated soil is the most frequently applied biological containment used in practice. Phytostablization involves using plant growth and characteristics to reduce the offsite movement of contaminants [10]. Phytostabilization has been reported for numerous contaminants, including, As [267], Ag [268], Cu and other metals [269,270], pyritic materials [271], and PAHs [272]. Phytostabilization has also been reported for emerging contaminants, including PFAS [273], pharmaceuticals [274] and potentially microplastics [275]. The simplicity, limited upfront deployment of the technology, and low-cost drive the widespread application.

Phytostabilization may reduce offsite movement primarily through reduced erosion from rainfall, wind erosion, runoff, and accumulation of contaminants in plant tissue. Vegetative growth also reduces soil erosion from sub-surface processes within the rhizosphere [10]. Phytostabilization approaches may also assist in the management of contaminated sites via enhancing biological removal processes [276-279]. Rhizospheric degradation of organic contaminants is well known to occur and has been reviewed and researched extensively (see, for example [280, 281]. Phytoremediation may also occur within plant vascular systems [282,283] predominantly via hosting bacteria and phyto-volatilization [279,284]. Limmer and Burken [284] outlined two major processes of organic contaminant volatilization. Direct volatilization occurs

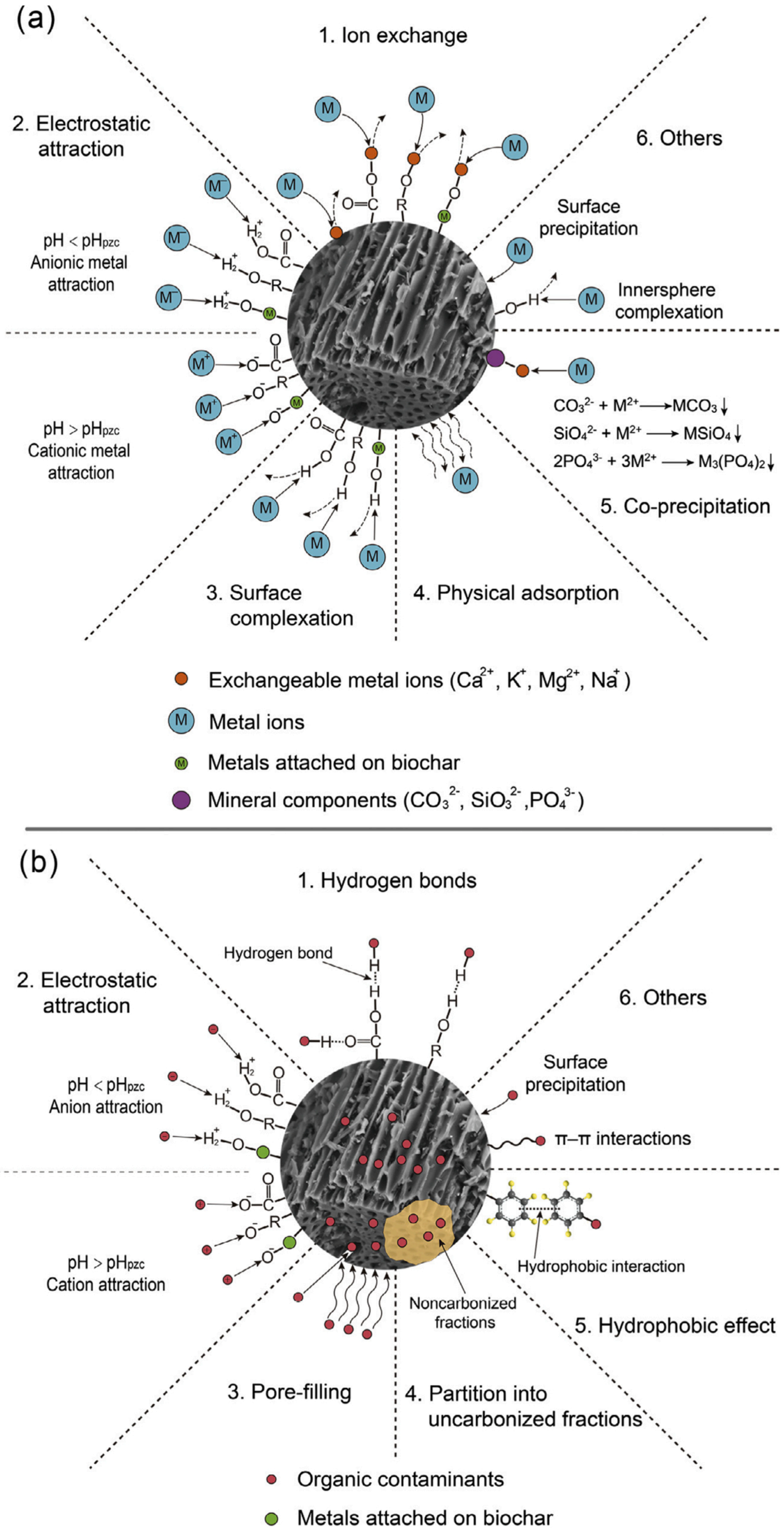

Fig. 6. Mechanisms dominating the biochar-induced adsorption and stabilization of (a) metals and (b) organic contaminants [227]. Reproduced with the publisher's permission.

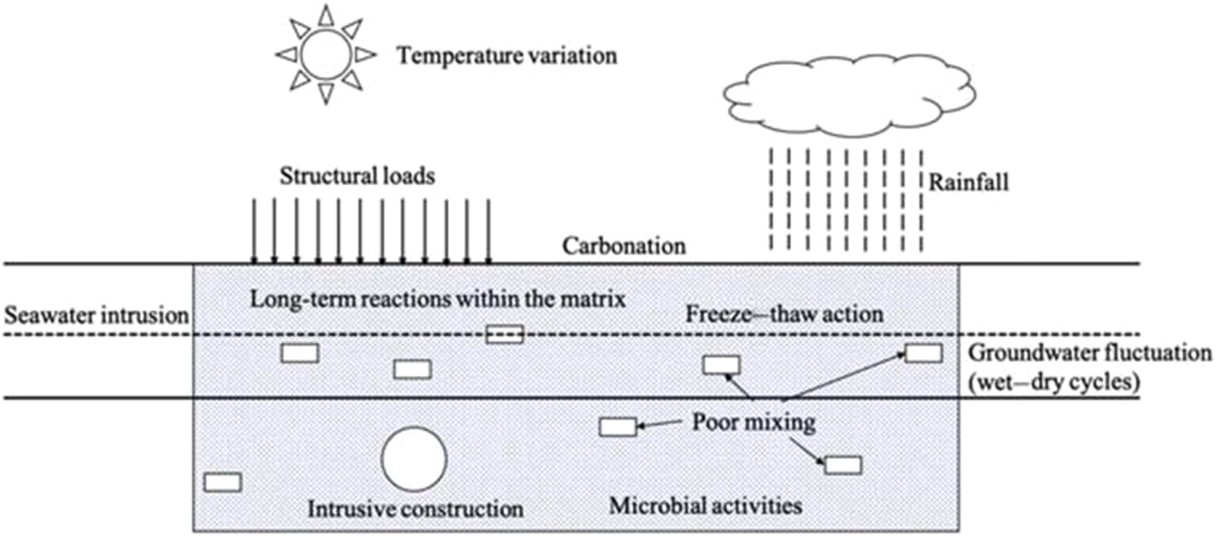

Fig. 7. Factors affecting the long-term effectiveness of S/S [255]. Reproduced with the publisher's permission.

primarily through gas exchange between aerial shoots and the atmosphere and is believed to occur mostly through stomata. However, due to physical spaces between cells and tissue of leaves and trunks, a gas loss may also occur through cuticles and woody tissue [284,285]. Indirect phytovolatilization occurs via subsurface processes through changes in contaminant and water fluxes. Given that phytovolatilization occurs via the water stream, it is largely restricted to organic compounds with low octantal-water partition coefficients, including compounds such as methyl tert-butyl ether (MTBE), trichloroethylene (TCE), and tetrachloroethylene (PCE) [276]. Phytovolatilization also occurs with some metalloids, though the processes depend on the properties of the element.

Phytovolatilization of metal(loid)s is mostly restricted to metalloids, such as As, Sb and Se [286,278,287], due to their ability to be reduced, oxidized and methylated within the environment [288,289]. Whether direct phytovolatilization of metalloids occurs via plant metabolism is controversial. Their methylation may pre-empt volatilization in the environment in the rhizosphere, which typically includes either a reduction or oxidation step [288,290]. For some time, it was believed that As methylation via *in-vivo* plant metabolism was possible, with considerable reports of methylated As in plants [291]. However, more recent evidence has indicated, in the case of As, that methylation occurs within the root zone, soil or water system by microbial communities rather than plants themselves [292]. Thus, phytovolatilization of As from plants most likely derives from microbial systems' indirect processes in the soil environment, transported into the xylem system, and transpired into the atmosphere. However, whether this contributes noticeably to the loss of As, Sb or Se from contaminated sites is unlikely [293,294]. Volatile methylated species tend to be unstable in the atmosphere during daylight but may be more stable during the night [295]. Whilst recent evidence indicates that volatile methylated As species potentially have longer half-lives [278,296], they are unlikely to represent sufficient losses to reduce As levels at phytostabilized sites, with most atmospheric As being sourced from natural sources, such as volcanic activity [297].

Introducing phytostabilization techniques into contaminated sites provides significant benefits but also entails substantial changes to the biogeochemistry of the site [298,299]. Plants are well equipped to modify the soil conditions via several strategies to cope with low nutrient supply, high contaminant load, or other stressors [266,300,301]. Phytostabilization also necessitates fertilizers with inorganic and organic products, further promoting changes in contaminant dynamics [302]. The introduction of living plant biomass and organic matter has the potential to mobilize Fe^{III} phases hosting As [303]. Quinone moieties, which are known functional groups of humic substances (e.g., Humic Acid), can act as electron shuttles in soils systems [304-306] and modify local geochemical conditions [307], promoting the transformation of critical mineral phases. At landscape scales, dissolved organic matter fluxes have been linked to plant communities and associated with Fe fluxes [299]. Indeed, changes at the local scale can have significant impacts downstream in aquatic and ecological systems. For example, with a contaminated catchment area, bushfires have been directly linked with large shifts in dissolved inorganic loads within local river systems [308], which may potentially be associated with changes in season and long-term climate trends [309]. Changes to conditions at contaminant sites must be assessed and designed with care to ensure shifts in contaminant dynamics are not deleteriously modified.

4.3.2. *Phytocapping*

Contaminated sites differ greatly in regard to spatial scale, location (e.g., remote regions versus high-density urban settings), contaminant composition, and concentration. The ability to remediate a site using degradation approaches, removal or fixation depends critically on these factors. For example, highly metal-contaminated sites, frequently observed in mining or post-mining environments, may have levels of 5000 mg/kg up to > 100,000 mg/kg. At these extreme levels, remediation options become limited. Remediation approaches may become limited due to existing solid-phase species or impracticalities of removal by other approaches. Using containment with engineered capping works in such scenarios becomes a likely site management strategy.

The integrity of conventional covers used in municipal covers and contaminated materials are globally acknowledged to progressively decline with time [310,311]. Phytocapping is a sub-discipline of phytoremediation, which refers to the use of green plants to remove, contain, or neutralize environmental contaminants [312]. In contaminated landfill soils, phytocapping may be necessary to prevent the percolation of contaminants and stabilize the migration of soil, water, or gas-borne pollutants [310]. Phytocapping is also known as evapotranspiration covers in the U.S. [310].

The primary goal of phytocapping is to limit water entry into the waste containment system by using plants and soil. The system's design depends on the intended end-use, and most phytocapping applications have been for municipal waste containment facilities, which pose different risks than high-profile contaminant containment cells [313]. The design considerations include the level of accepted risk, legislation, suitability of plant species, and local climate [313]. The typical landfill cover design involves adding a low permeability clay lining with hydraulic conductivity in the range of 10^{-7} to 10^{-9} cm s^{-1} or lower, which is then topped with additional soil material [314,315]. However, the design specifications may vary by jurisdiction. The cover materials' high clay and low nutrient content limit the post-closure options unless specifically designed for phytocapping [313].

Maintaining a healthy plant system is essential for any given climate and phytocap construction. Local materials are commonly used to construct the water and root storage layers to minimize costs and aid local plant species in accessing nutrients. Active plant growth is crucial to ensure effective transpiration during and following rainfall periods. Local water sources are generally required to maintain water deficits in the phytocap; however, they may pose challenges due to contamination of groundwater or surface water sources, high salt content, inaccessibility of water, or unavailability for irrigation [316-319]. Conversely, local waters may also contain significant nutrients or be used to facilitate nutrient provisions in the soil cap.

Nutrients from traditional agrochemical sources can be an expensive addition to support plant growth on caps. Alternative materials which provide co-benefits generally aid plant function. Rapidly promoting good soil structure in caps and nutrient supply can be achieved using organic waste products, such as composts, biosolids etc. This can be critical since phytocapping with tree species will result in limited soil volume to acquire nutrients and moisture. Organic materials in the form of organic waste byproducts are potentially cost-effective in providing carbon and nutrients concurrently, thus providing several benefits [280, 302].

A growing number of organic products can be used for improving phytocap conditions, including biosolids, pulp-mill byproducts, green waste, and compost blends tailored to a given soil [320,321]. Biochar is an increasingly popular research material for improving agricultural and human-engineered soil conditions. Biochar can broadly be considered a carbon-rich product produced by biomass combustion (pyrolysis) under high temperatures and low oxygen conditions [322]. Biochar may enhance plant growth by supplying and retaining nutrients and by improving the physical, chemical, and biological properties of the soil, but also by tailoring properties for contaminant behavior and nutrient provisions [323,324], though this has rarely been applied to phytocapping systems in the literature. However, especially in the construction of phytocapping systems in contaminated land environments, there is potential in the use of biochar products to (1) improve the growth conditions of plants, (2) modify the ecohydrological profile of the cap, (3) deliver nutrients to the cap, and (4) immobilize or mobilize contaminants which may exist in the capping system. Multiple materials may be required to engineer a suitable soil capping material, which will be suitable to ameliorate site contamination, acidity, sodicity etc., and the use of multiple blended materials is often required [112]. Thus, purposely-designed blended waste byproducts surface capping layers are likely to be beneficial in the long-term and cost-effective, though poorly documented to date.

4.3.3. Case study

Nguyen et al. (2017) conducted a pot experiment to examine the impact of various herbaceous and woody plant species on the labile pool of six metals, including Ag, Cu, Pb, Zn, Se, and Ni, present in their rhizosphere. The researchers evaluated the concentrations of trace elements in above and below-ground biomass of each species, the labile and bioavailable fraction of trace elements in the rhizosphere, and key soil parameters such as percent organic matter, electrical conductivity (E. C.), pH, and dissolved organic carbon (DOC).

The study results showed that the levels of trace elements in plant tissues differed among species, with roots having higher concentrations than above-ground tissues. The presence of plants significantly affected the labile pool of many trace elements in the rhizosphere, including Cu, Ni, and Ag. Interestingly, the rhizosphere of all tested plants had more DOC than the soil of control pots without plants.

The research revealed that the root systems of various plant species had varying effects on soil DOC, leading to changes in the labile pools of Cu and Ni in the rhizosphere. The findings indicated that specific plants might increase metal solubility in the rhizosphere through root exudation, resulting in increased metal uptake by plants. This phenomenon can occur through the development of metal-organic ligand complexes or root exudates disturbing metal bounds in soil organic matter.

The study has significant implications for phytostabilization, where plant selection is critical to achieving the desired outcomes. The findings suggest that certain plant species can increase the solubility of trace elements in the rhizosphere through root exudation, which could increase metal uptake by plants. This information can help optimize the use of phytostabilization in contaminated sites.

Overall, the study provides insights into the impact of different plant species on the bioavailability of trace elements in soil and emphasizes the importance of selecting appropriate plant species in phytostabilization to achieve successful remediation of contaminated sites.

5. Conclusions

The implementation of contaminant containment as a risk-based approach is crucial in the remediation of contaminated soil at a site where excavation and removal of the contaminated substrate are not feasible due to potential hazards and costs. The measures employed in contaminant containment encompass physical, chemical, and biological technologies, such as impermeable and permeable barriers, stabilization and solidification, and phytostabilization. Although these measures effectively prevent further contaminants' migration and reduce remediation costs, ongoing monitoring of the sites is required to assess the remobilization and migration of contaminants.

To advance non-invasive approaches for risk-based remediation of contaminated sites, the following research areas should be pursued:

- Development of innovative adsorbents from natural resources for the removal of both inorganic and organic contaminants in permeable reactive barriers.
- Utilization of industrial, agricultural and mining byproducts as part of the engineered adsorbents and stabilizing and solidifying substrates, with pre-treatment for the immobilization or removal of existing contaminants in these byproducts.
- Implementation of low-cost technologies for the recovery of contaminants from spent adsorbents used in reactive barriers.
- Examination of the stability and remobilization of solidified and buried contaminants under anaerobic conditions over the long term.
- Investigation of groundwater contamination through the release and movement of stabilized and solidified contaminants over the long term.
- Assessment of the life cycle and risk of recycling and reusing spent adsorbents used in reactive barriers.
- Selection of vegetation based on phytostabilization potential, tolerance to extreme weather conditions, indigenous availability, and long-term sustainability, as plant density and species diversity can influence contaminant containment effectiveness.
- Engineering of microbial consortia to enhance the functionality of bioremediation in contaminant containment, including the isolation and application of functional microorganisms from natural or engineered environments.

Environmental implications

Effective contaminant containment is crucial for minimizing the environmental impact of hazardous materials and pollutants. Failure to contain the contaminants from polluted sites can lead to serious environmental consequences, including soil, water, and air pollution, which can adversely affect human health and ecosystems. Contaminated water sources can harm aquatic life and pollute the sources of drinking water, while contaminated soil can reduce the productivity of agricultural land and pose a risk to human and ecological health through exposure to toxic substances. Implementing robust contaminant containment measures prevents offsite contamination and reduces risks to public health and the environment.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

No data was used for the research described in the article.

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