Chapter 13.
Actions to tackle soil pollution

Technologies for remediating polluted soils

This section includes an overview of each of the main remediation technologies. The overviews are intentionally brief to allow readers to gain a quick understanding of the basis of each technology, their application, and their strengths and weaknesses. This overview does not endorse any one remedial approach over another. With scientific research and development, the capabilities of technologies are improving and new ones are coming to the fore. There are many resources that can assist in the assessment and selection of remediation and risk reduction strategies for polluted soils. These include FAO's Environmental Management Toolkit volume 5 (FAO, 2020a) and volume 6 (FAO, 2020b), the GSP's Online Database on Best Management and Remediation Techniques for Polluted Soils (FAO, forthcoming) and the State of Knowledge of Soil Biodiversity (FAO *et al.*, forthcoming). In addition to these documents, there are a number of useful websites, studies and scientific publications that provide detailed information about soil remediation technologies, their applicability, and strengths and weaknesses. These include: the United States Environmental Protection Agency website for Remediation Technologies for Cleaning Up Contaminated Sites (US EPA, 2019a) which has links to Superfund Remedy Reports, the Federal Remediation Technologies Roundtable Remediation Technologies Screening Matrix, and Clean-up Information (Clu-In) Technology Focus Area,[6] the Interstate Technology and Regulatory Council,[7] and Contaminated Land: Applications in Real Environments (CL:AIRE) which is a not-for-profit organization that stimulates the regeneration of contaminated land in the United Kingdom of Great retain and Northern Ireland by promoting practical and sustainable remediation technologies.[8]

Technologies reviewed in this section address both point source and diffuse pollution (see Glossary). The technologies are categorized in two levels: first as either biological or physical/chemical treatments, and second as either *in situ* or as *ex situ*. Nature-based (biological) solutions are grouped separately because of their likelihood to provide a more sustainable solution in terms of both environmental impact (maintaining soil biodiversity and soil functions) and economic feasibility.

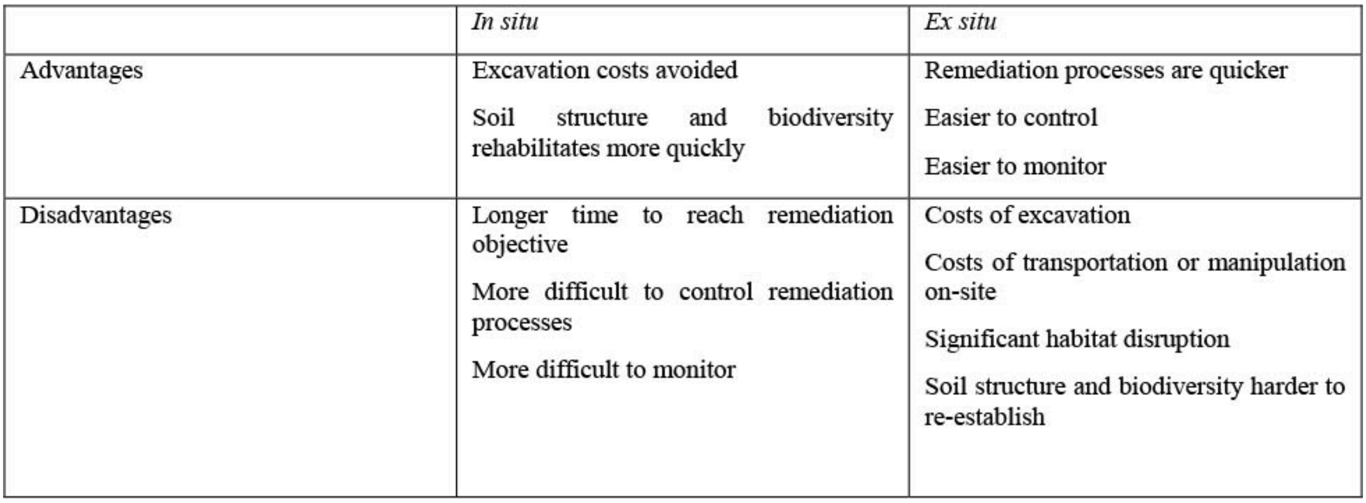
In situ technologies are those where the soil remains in the ground during the treatment. *In situ* techniques may involve some manipulation of the soil to introduce substances to stimulate the remediation. Some of the technologies separate or concentrate the contaminants such that the polluted fraction can be extracted, and treated on-site or disposed of elsewhere. The main advantage of *in situ* treatment is that it allows soil to be treated without being excavated and transported, resulting in potentially significant cost savings and fewer environmental changes. *In situ* treatment can also often difficult to restore after more invasive treatments. However, *in situ* treatment can require longer time periods as variability in the environmental conditions of the site and soils can affect its efficiency. There is also less certainty about the uniformity of treatment and its efficacy is more difficult to verify.

Ex situ technologies require the soil to be excavated. The excavated soils maybe treated on-site (and the cleaned soil replaced) or transported for treatment elsewhere. *Ex situ* technologies tend to be more controllable and require less time, however they have the additional expense of excavation and transportation. As *ex situ* treatments tend to degrade the structure and organic matter in the soil, its rehabilitation can be more complex, costly and time-consuming (Kuppusamy *et al.*, 2016).

The advantages and disadvantages of *in situ* and *ex situ* technologies are summarized in

Table 1. Case studies are included as practical examples of the use of the technologies.

Table 1. Summary of advantages and disadvantages of *in situ* and *ex situ* technologies



	In situ	*Ex situ*
Advantages	Excavation costs avoided Soil structure and biodiversity rehabilitates more quickly	Remediation processes are quicker Easier to control Easier to monitor
Disadvantages	Longer time to reach remediation objective More difficult to control remediation processes More difficult to monitor	Costs of excavation Costs of transportation or manipulation on-site Significant habitat disruption Soil structure and biodiversity harder to re-establish

13.4.1. *In situ* nature-based technologies

Nature-based soil remediation technologies use soil-dwelling organisms to biodegrade, stabilize or separate the contaminants. The techniques use microorganisms (bacteria, fungi, and archaea), soil macroorganisms, and plants. Often a nature-based remediation strategy will include more than one technique, for example the symbiosis between microorganisms and plant roots can enhance biodegradation. Nature-based technologies are continually improving in terms of the concentration and range of organic and inorganic contaminants that are treatable. Nature-based technologies have been used successfully to treat soils polluted with petroleum hydrocarbons, chlorinated solvents, polycyclic aromatic hydrocarbons, pesticides, as well as trace elements. The times required to reach the remediation objective can vary significantly depending on the technique and concentration and type of pollution. Some *ex situ* bioremediation can take as little as 12 weeks while phytoremediation of wetlands can take years. Remediation strategies can be expedited by optimizing the conditions in the soil, and through the application of multiple techniques, to stimulate the biological processes (Song *et* to the remediation. Examples include enhanced bioleaching and biovolatilization of arsenic (Šimonovičová *et al.*, 2016).

13.4.1.1. Bioremediation

Bioremediation refers to an *in situ* biological treatment that uses soil microorganisms for remediation, and is primarily aimed at degrading organic contaminants, including petroleum hydrocarbons, solvents, and pesticides and transform species of trace elements to reduce their availability. These biological treatments can be conducted either aerobically or anaerobically. The treatment methods are different in terms of the contaminants that can be degraded and their operating conditions. Aerobic biological treatment uses atmospheric oxygen, sometimes aspirated through the soil to stimulate aerobic microorganisms. Whereas anaerobic biological treatment excludes oxygen and is often stimulated by the addition of reducing agents. While some contaminants can be degraded by both techniques, aerobic biological treatment tends to be used to degrade non-chlorinated or slightly chlorinated hydrocarbons while anaerobic biological treatment is used for highly chlorinated hydrocarbons. The CLU-IN website (US EPA, 2020) includes information on both techniques, the contaminants that they can treat and case studies.

The capacity of a microbial population to degrade organic contaminants within soil can be enhanced either by stimulation of the indigenous microorganisms (biostimulation) or by the introduction of specific microorganisms to the local population (bioaugmentation). This is also termed enhanced bioremediation. Organic contaminant degradation can be enhanced by optimising conditions for the microorganisms with aeration, addition of nutrients, alteration of pH and temperature control (Margesin, Zimmerbauer and Schinner, 2000). Materials with high concentrations of nutrients, labile carbon and microorganisms, such as manure or sewage sludge, may be added to increase the rate of biodegradation. Care should be taken with sewage sludge and some manure as they could also contain significant organic and inorganic contaminants that would exacerbate the pollution (see Chapter 3 - section 3.2.3 on organic fertilizer). Sometimes, microorganisms that have adapted to degrade the specific organic contaminants at another site can be applied to enhance the process (Federal Remediation Technology Roundtable (FRTR), 2007). However, exotic microorganisms may not perform as expected when introduced to a different soil biome, sometimes leading to disruption of ecosystem functions and autochthones biodiversity after application. Genetic methods have been used successfully to identify, propagate and reintroduce indigenous microorganisms that effectively degrade the organic contaminants (Di Gregorio *et al.*, 2016). The speed and efficiency of *in situ* biological treatment also depends on the type of soil and its characteristics as well as other environmental conditions of the site.

Some contaminants such as the explosives RDX and HMX, highly chlorinated organics and hexavalent chrome that may not be amenable to biodegradation under aerobic conditions can be effectively treated anaerobically. To exclude oxygen, the soils are generally wetted and organic and inorganic amendments added to stimulate the anaerobic microorganisms. Electron donors can be added to the soil to create reducing conditions that stimulate the reductive dechlorination of chlorinated organic

The principal mechanism of microbiological remediation of soil polluted with trace elements is to immobilize them and reduce their bioavailability. Trace elements cannot be degraded by microorganisms, but they can be converted to another form with less hazardous physical and chemical properties. For example, aerobic and anaerobic microorganisms can reduce hexavalent chrome to its trivalent state which is less toxic and less mobile (Sumikura and Shiiba, 2016; Thatoi *et al.*, 2014).

Biodegradation may be enhanced by combining both phytoremediation and microbial bioremediation techniques (Lucas García *et al.*, 2013).

13.4.1.2. Bioventing and biosparging

Bioventing and biosparging are similar techniques that stimulate the biodegradation of any aerobically degradable compounds by the direct injection of air into the soil. Bioventing is undertaken in the soil vadose zone (the unsaturated strata above the water table), and biosparging in the saturated zone below the water table. Air is pumped at low rates sufficient to stimulate and sustain existing soil microorganisms to biodegrade the organic contaminants. The low rate of air flow aims to minimize the volatilization and release to atmosphere of organics and is often used to treat soil polluted with less volatile hydrocarbons. In the case that there are volatile contaminants present it could be necessary to install vapour extraction and treatment such as active carbon filtration or catalytic oxidation. The techniques are often used to treat soil that is polluted with less volatile petroleum hydrocarbons where there are fewer emissions of volatile vapours. Many national agencies provide guidance on remediation technologies. The Government of Canada’s guidance on biosparging is available on their website (Government of Canada, 2017a). Bioventing was an element in the remediation strategy used for the clean-up of the 18 de Marzo Petroleum refinery in Mexico as described in the case study below.

Case study 1. Integrated remediation strategy for 55 ha petroleum refinery site. Mexico City.

The 18 de Marzo Refinery in Azcapotzalco, northwest of Mexico City, operated from 1933 until it closed in 1991. It left a 55 ha site polluted with total petroleum hydrocarbons (TPH). As the city expanded, there was a need to remediate the site. A group of national and international experts were brought together to characterize the pollution across the site, assess risks to human health and the environment, and to develop the remediation strategy.

The site was divided into seven zones based on the nature of the contaminants and the polluted media (soil or groundwater). Each zone had a specific remediation strategy that was phased into the overarching strategy for the whole site.

Soil polluted with medium and heavy fraction hydrocarbons was screened to remove large rocks and gravel and then treated in biocells (subsurface biopiles). The indigenous microorganisms were stimulated with nutrients and aeration.

Bioventing was undertaken in zones where the contaminants (light fraction hydrocarbons, benzene, ethylbenzene, toluene and xylene) were above the groundwater. Extraction/bioventing wells with magnetic valves were sunk into the soil. Air was blown into the soil and extracted along with the volatilized hydrocarbons which were destroyed in a catalytic oxidation unit.

In situ air and steam sparging was used to treat polluted soils below the surface of the groundwater. This increased the evaporation and degradation of the volatile contaminants from the soil and groundwater.

Groundwater was also extracted into long trenches where it was treated to increase the dissolved oxygen, extract contaminants and capture volatiles through active carbon filters.

The soil from the zones that were polluted with organo-lead compounds was excavated and disposed of at a landfill.

Case study 2. Bioremediation of an abandoned industrial site. Turin, Italy.

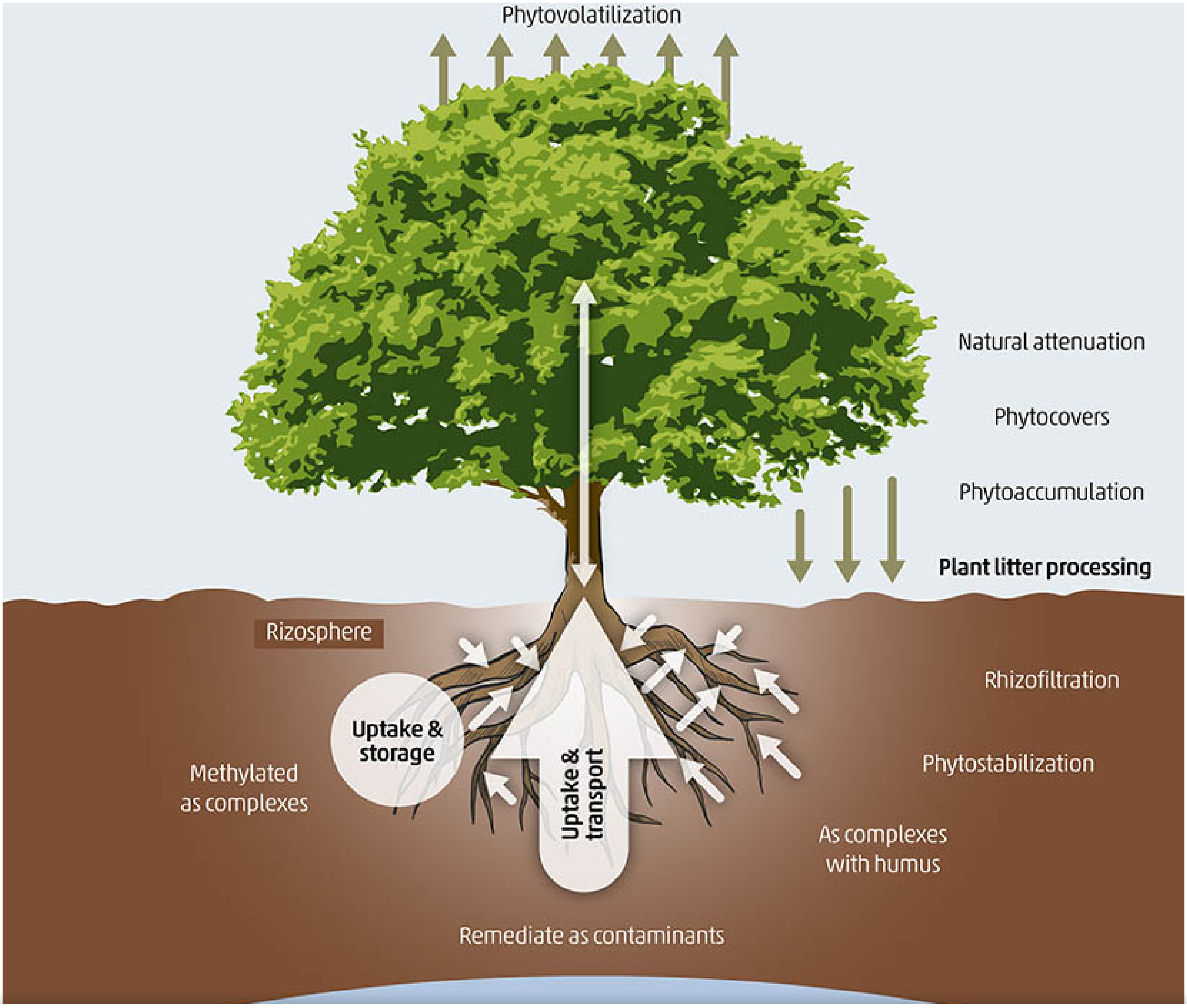
The industrial site, comprising approximately 20 000 m^2, had operated from 1960 until its closure in the late 1990s. The site had been used for the storage of mineral oil and processing industrial waste and still contained the industrial plant including underground storage tanks (Figure 3). Leaks and spillage had caused the site to be polluted with a range of organic contaminants including petroleum hydrocarbons, BTEX (benzene, toluene, ethylbenzene and xylene), aliphatic and aromatic hydrocarbons and trace elements (iron and manganese). Site characterization identified that the polluted area extended for 4 000 m^2 and up to 7 m deep where the contaminants had also spread into the saturated zone. The concentration of contaminants ranged to several mg/l. Italian law stipulates the maximum level of each contaminant in soil and groundwater, which for total hydrocarbons is 350 µg/l. The remediation was undertaken by B&A Consultancy in three phases, commencing with the dismantling, cleaning and removal of the industrial plant and underground storage tanks. The second phase involved removing the polluted soil from the vadose (unsaturated) zone which was bioremediated in a biopile and subsequently backfilled on the site. The third phase was the bioremediation of the saturated zone by air sparging, bioventing and soil vapour extraction. The site was set up with 50 air injection wells and 97 extraction wells (Figure 4). The vapours that had not biodegraded were extracted and filtered through activated carbon filters before release to the atmosphere. The whole operation took seven years and cost USD 1.4 million, the equivalent of approximately USD 50 /m^3. The site will continue to be monitored for a period of three years following completion of the remediation activities to ensure that contaminant levels remain below the regulatory limits. The photographs below show the preparation of the site and the modular air sparging and soil vapour extraction equipment.

13.4.1.3. Phytoremediation

Phytoremediation refers to *in situ* technologies that use plants for treating polluted soils. Phytoremediation plays two principal roles in remediating polluted soils: stabilizing the contaminants so that they are less mobile and less available to cause harm; and removing them by facilitating their degradation or transferring them to other media (Salt *et al.*, 1995). Depending on the plant mechanism in the remediation process and contaminant type, the phytoremediation can be divided in several techniques: phytostabilization, phytoextraction, phytodegradation, rhizodegradation, and phytovolatilization, which are described in detail below.

Phytoremediation has been used extensively for remediating soils that have been polluted with trace elements, but can also be effective in facilitating the removal and biodegradation of organic contaminants (Huang *et al.*, 2005). Figure 5 below shows the different processes that plants support for the remediation of soils polluted with arsenic.

Figure 5. The phytoremediation functions of a plant source for remediating arsenic (As) contaminated soil.



Source: adapted from Vithanage *et al.*, 2012.

The effectiveness of phytoremediation techniques is strongly influenced by the characteristics of the contaminants and soil, as well as the selected plant species (Figure 6). It also depends on the interactions of the plants' root systems with the microorganisms in the soil (Ma *et al.*, 2016). Its effectiveness can be enhanced by adding amendments to the soil, for example chelating agents can be applied to increase trace element mobility. Amendments that adjust the soil pH can increase or decrease the mobility of trace elements. Electokinetics have also been used to enhance the mobility and uptake of trace elements by plants as is demonstrated in the Case study 9. Improving soil fertility can also assist phytoremediation.

The success of phytoremediation can be improved by using indigenous plant communities that are tolerant of the specific environmental conditions of the site, such as level and type of contamination and climatic conditions. However, the germination and development of vegetation directly on polluted soils, even using tolerant plant species, can be difficult due to other extreme characteristics of the polluted soils. In general, the establishment of vegetation cover leads to a diminution of soil pollution, reduced soil erosion and runoff, and an improvement of landscape and soil functions.

Phytoremediation processes may be enhanced by modifying plant growth characteristics and growing conditions by improving soil conditioning and management practices. Depending on the phytoremediation process and contaminants involved, enhancement of plant properties can focus on modification of the above-ground biomass, for example increasing it for phytoextraction. The enhancements can also focus on modifying the characteristics of the root system (for example the morphology, surface area, microbial associations and root exudates).

Phytostabilization

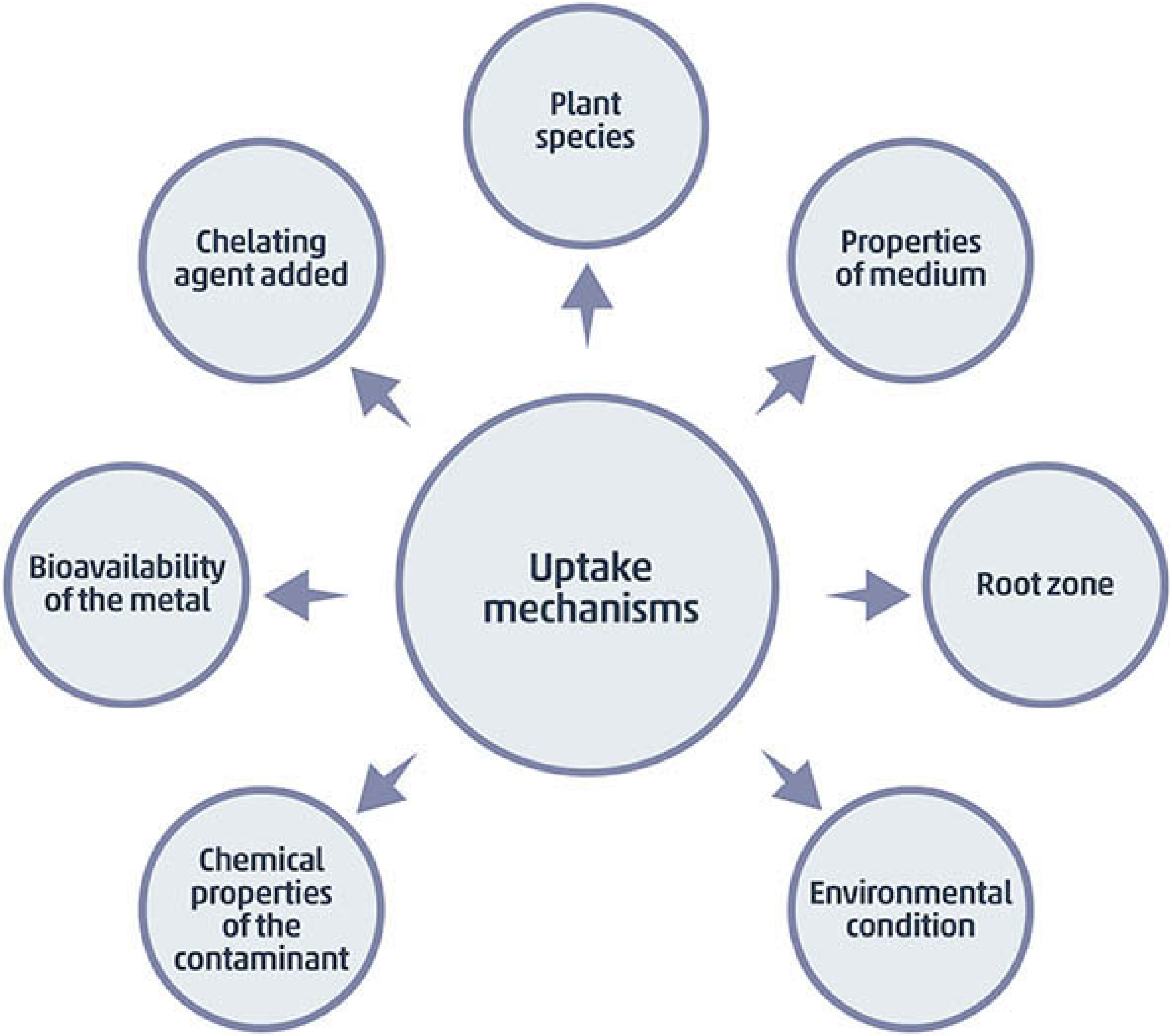
Phytostabilization uses contaminant-tolerant plants to consolidate and immobilize polluted soils to prevent the spreading of the contaminants by wind and water erosion. The evapotranspiration of the plants reduces the moisture content in the soil and the flow of leachate, thus preventing dispersal of the contaminants further into the ground and protecting groundwater.

The main objective of this phytotechnology is to decrease the availability and mobility of contaminants in the soil. The immobilization of trace elements in the soil depends on the plant species and site conditions. It can involve the formation of compounds with low solubility, chelation, adsorption onto the surface of roots, and absorption by the roots. Plants roots can change the rhizosphere conditions, in particular pH levels, and exudate compounds which can have an important role in modifying the availability of trace elements (Abreu *et al.*, 2014). Phytostabilization was used in the remediation of a polluted military site in Ukraine as illustrated in the case study below.

Case study 3. *In situ* phytostabilization of military training area: Dolyna, Ivano- Frankivsk

Adverse health effects in the local population in Dolyna led to the identification of risks from a 5 hectare military site that had closed in 1992. Soil and groundwater were polluted with trace elements and unknown organic compounds. The site remained abandoned until the early 2010s when a programme was developed to mitigate the risks to public health and the environment. While efforts were being made to find a long-term solution, the local authorities, in conjunction with NATO, developed an interim phytostabilization strategy that aimed to stabilize the trace elements in the ground while producing a safe biofuel crop. *Miscanthus x giganteus* was selected for its properties of concentrating trace elements in its rhizomes with minimal transfer to the foliage (Pidlisnyuk *et al.*, 2019). A trial area of 0.6 ha was planted with *Miscanthus x giganteus* and monitored over three years. A variety of soil amendments were tested. The addition of lime and organic manure proved the best cultivation technique to stimulate biofuel growth, while minimising the uptake of trace elements by the foliage. During the three years, the concentration of carbon, nitrogen, and phosphorus in the soil increased, the soil was stabilized, and soil erosion reduced. The whole project cost USD 8 000, the equivalent of USD 1.3/m^2, 70 percent of which was for planting materials and cultivation.

Figure 6. Factors that affect uptake mechanisms of trace elements.



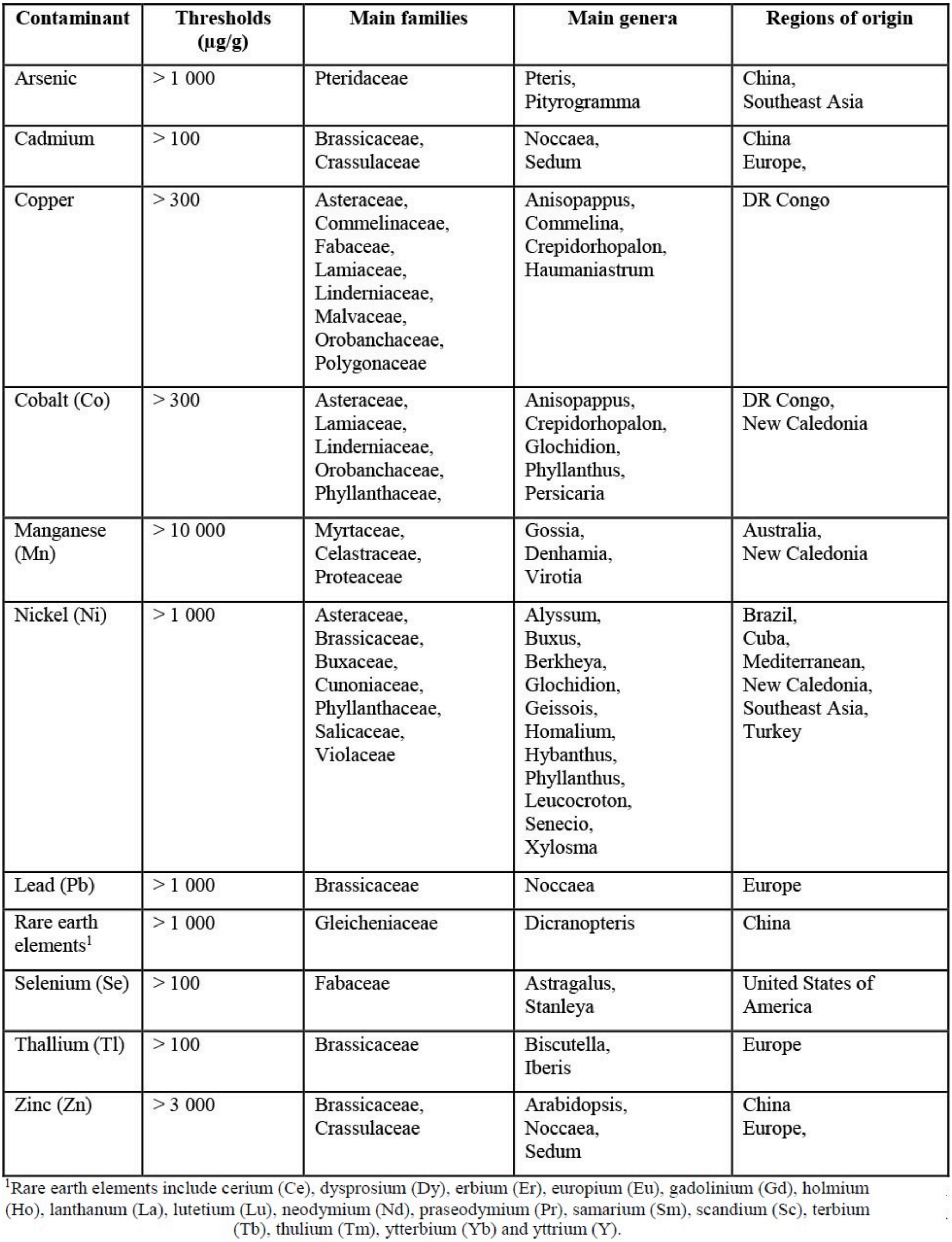
Source: adapted from Tangahu *et al.*, 2011.

Phytoextraction

Phytoextraction processes extract both inorganic and organic contaminants from soil by direct uptake into plants. The rate and proportion of the contaminants that are transferred from the roots to the shoot system is dependent on the contaminant and the plant species.

Unlike organic contaminants, which can serve as a source of carbon and energy for soil microorganisms, trace elements are not biodegradable and cannot be chemically eliminated. Instead, they have the ability to enter living tissues, accumulate (bioaccumulation) and concentrate (biomagnification) in the food chain (Wu *et al.*, 2010). Several trace elements have an essential role in plant growth and metabolism (iron, manganese, zinc, copper, magnesium, molybdenum, and nickel), while others do not have a known function (cadmium, chromium, cobalt, lead, or mercury). Certain plant species are demonstrated hyperaccumulators of these non-essential trace elements, absorbing trace elements through their roots and translocating them to their shoots, contributing to the animals and humans. Reeves et al. (2018) developed a global database of hyperaccumulator plants, useful not only for research purposes but also for designing phytoremediation programs as well as for risk assessment (Table 2).

Table 2. Examples of families, genera and regions of occurrence of hyperaccumulators and the threshold concentrations of contaminants in dry weight foliar tissues to be considered hyperaccumulator.



Contaminant	Thresholds (µg/g)	Main families	Main genera	Regions of origin
Arsenic	> 1 000	Pteridaceae	Pteris, Pityrogramma	China, Southeast Asia
Cadmium	> 100	Brassicaceae, Crassulaceae	Noccaea, Sedum	China Europe,
Copper	> 300	Asteraceae, Commelinaceae, Fabaceae, Lamiaceae, Linderniaceae, Malvaceae, Orobanchaceae, Polygonaceae	Anisopappus, Commelina, Crepidorhopalon, Haumaniastrum	DR Congo
Cobalt (Co)	> 300	Asteraceae, Lamiaceae, Linderniaceae, Orobanchaceae, Phyllanthaceae,	Anisopappus, Crepidorhopalon, Glochidion, Phyllanthus, Persicaria	DR Congo, New Caledonia
Manganese (Mn)	> 10 000	Myrtaceae, Celastraceae, Proteaceae	Gossia, Denhamia, Virotia	Australia, New Caledonia
Nickel (Ni)	> 1 000	Asteraceae, Brassicaceae, Buxaceae, Cunoniaceae, Phyllanthaceae, Salicaceae, Violaceae	Alyssum, Buxus, Berkheya, Glochidion, Geissois, Homalium, Hybanthus, Phyllanthus, Leucocroton, Senecio, Xylosma	Brazil, Cuba, Mediterranean, New Caledonia, Southeast Asia, Turkey
Lead (Pb)	> 1 000	Brassicaceae	Noccaea	Europe
Rare earth elements[1]	> 1 000	Gleicheniaceae	Dicranopteris	China
Selenium (Se)	> 100	Fabaceae	Astragalus, Stanleya	United States of America
Thallium (Tl)	> 100	Brassicaceae	Biscutella, Iberis	Europe
Zinc (Zn)	> 3 000	Brassicaceae, Crassulaceae	Arabidopsis, Noccaea, Sedum	China Europe,

[1] Rare earth elements include cerium (Ce), dysprosium (Dy), erbium (Er), europium (Eu), gadolinium (Gd), holmium (Ho), lanthanum (La), lutetium (Lu), neodymium (Nd), praseodymium (Pr), samarium (Sm), scandium (Sc), terbium (Tb), thulium (Tm), ytterbium (Yb) and yttrium (Y).

Source: Reeves et al., 2018

Careful risk assessments should be undertaken to select the appropriate hyperaccumulating plant species and determine safe and acceptable use of the above ground plant growth. As the above-ground harvest management options for a crop including energy generation, biofuel production, gasification, composting and phytomining. Phytomining or agromining refers to the full agronomic process using hyperaccumulator plants as ‘metal crops’. The process involves the farming of ‘metal crops’ on sub-economic deposits or industrial or mineral wastes to obtain valuable element(s) from their harvested biomass via the production of a ‘bio-ore’ (Van der Ent *et al.*, 2018). In selecting this management option, consideration should be given to the ultimate fate of the contaminants that have been concentrated (Mohanty, 2016).

Phytoextraction has also been demonstrated to be an effective technique to reduce salinity of agricultural soils, thus allowing a wider range of crops to be grown and improving yields. The technique relies on cultivating suitable plant species (e.g., halophytes), that can tolerate saline soils. These plants can remove sodium from the soil cation exchange complex and enhance levels of calcium in the soil solution (Ashraf *et al.*, 2010).

Case study 4. Phytoremediation of dissolved Fe and Mn from acid mine drainage. Tuscany, Italy.

The mountain stream Ritonto flows for 2 km through the historic Fontacinaldo pyrite mine and is polluted by acid mine drainage (Figure 7). The unfiltered water in the stream had a pH of 4.1 with average concentrations of iron and manganese of 56 mg/l and 11.9 mg/l respectively. The stream fed into the river systems that eventually drain into the Mediterranean Sea on the west coast of Italy. In order to protect soil and water resources lower in the river system, a passive biofiltration, neutralization and phytoremediation system of wetlands was constructed as a bypass in the stream. As the site was isolated and would be required to function permanently, it was important to choose a remediation strategy requiring low levels of operation and maintenance. The system comprised:

water intake screen, pump and settling tank;

sedimentation wetland;

three passive system wetlands with the aim of reduction of iron through anaerobic treatment;

four passive system wetlands with the aim of reduction of manganese through aerobic treatment; and

one terminal wetland, prior to the reintroduction of the water in the Ritorto creek.

Figure 7. Acid mine drainage in the site before remediation. ©Ambiente S.P.A.

Source: reproduced with permission from Bocini, Cozzani and Falconi, 2017.

The intake pump was specified up to 60 l/minute which was calculated on the basis of the variability of the streams flow rates throughout the year. The wetlands were constructed by excavating a series of basins on the northern bank of the stream and lining them with a high density polyethylene impermeable membrane.

The anaerobic lagoons were filled with a treatment medium consisting of a thin, permeable layer of organic material placed above a bed of limestone (Figure 8). The combination of organic and limestone substrate allows for simultaneous removal of metals and providing alkalinity in the water and thus reducing the initial acidity. The anaerobic lagoons have depths of about 100 cm, comprising 30 cm - 60 cm of organic substrate (spent mushroom compost) and 15 cm – 30 cm of limestone, inside which the water flows horizontally with a hydraulic head of five cm. Anaerobic lagoons are then completed by the planting of plant species such as *Typha* sp. and *Juncus* sp. that stimulate microbial processes. The organic substrate may require replacement after 15 years.

Figure 8. Site during preparation of the limestone layer for remediation. ©Ambiente S.P.A.

Source: reproduced with permission from Bocini, Cozzani and Falconi, 2017.

The aerobic lagoons were filled with a treatment medium consisting of a layer of 60 cm of compost within which water flows with a hydraulic head not exceeding 8 cm. Aerobic lagoons are usually completed by the planting of extensive flora root systems (e.g., *Phragmites* sp.) that can stimulate the microbial processes and facilitate the transfer of oxygen to the deeper layers. The surface area of the lagoons were sized on the basis that the daily treatment rate of manganese is 0.5 g/m^2.

The effluent, before its re-introduction into the Ritorto creek, passes through a sedimentation lagoon to allow completion of the precipitation of heavy metals. It consists of a lagoon where the water surface is exposed to the atmosphere and to the action of floating plants such as macrophytes such as duckweed and water hyacinth.

The system achieved the remediation target for both elements which is 2 mg/l and native plant species began to recolonize the banks of the stream (Figure 9) (Bocini, Cozzani and Falconi, 2017). The system was initiated in 2004 and completed in 2015 with a total cost of USD 5 million.

Figure 9. Site after remediation. ©Ambiente S.P.A.

Source: reproduced with permission from Bocini, Cozzani and Falconi, 2017.

Case study 5. Biomass refining. India

With the global need to reduce reliance on fossil fuels and to move to renewable energy, and carbon neutral economies, there has been a drive to exploit biomass more efficiently. Biomass has been used as an energy source in thermal power generation. Biorefining takes the concept further to convert the cellulose, hemicellulose and lignin from non-food biomass such as bamboo, corn stalks, straw and bagasse into valuable raw materials for further manufacture. The cellulose can be converted to glucose and ethanol, and fibres including those for paper manufacture. With the concern over the release of microplastics from clothing made from synthetic fibres, the demand for natural fibres is likely to increase. The hemicellulose can be converted to sugars, ethanol and other basic organic chemical compounds such as acetic acid, formic acid and furfural. Solid biofuels can be manufactured from lignin (Holm-Nielsen and Ehimen, 2014).

A Finnish Indian-joint venture is constructing a biorefinery in Assam, India for processing 5 million tonnes of bamboo per year into ethanol and basic organic chemicals. The expected cost of the refinery is USD 190 million (Chempolis, 2019) and is expected commence operations in 2021. The biorefinery is also expected to be able to process harvested biomass from phytoextraction remediation. The trace elements that have been accumulated in the biomass are expected to be captured in the fractionation residues which will subsequently be used for power generation for the refinery (Rehman, 2020).

Phytovolatilization

Phytovolatilization processes involve specialized plant enzymes that can transform and volatilize inorganic and organic contaminants in the plant – microorganism – soil system. In essence, the contaminant is transferred from the soil into the plant, where is transformed and released to the atmosphere. This technique has been used for soils polluted with inorganic and organic mercury, where the plants are able to reduce Hg^{2+} to elemental mercury, which is less toxic and is ultimately volatilized from the plant (Heaton *et al.*, 1998; Kumar, Smita and Cumbal Flores, 2017). As the contaminants are transferred from one medium to another, careful risk assessments need to be undertaken to ensure the appropriateness of the approach.

Rhizodegradation

Rhizodegradation is the breakdown of organic contaminants in soils by fungal and microorganism activity associated with the root zone (Singh and Ward, 2004). This plant-assisted biodegradation is sustained by root exudates that can enhance microorganism activity and biodiversity, and support biotransformation of organic contaminants through co-metabolism. Cultivation of *Phragmites australis* in dredged sediments was demonstrated as an exploitable biostimulation approach to accelerate the depletion of PAHs. *Phragmites australis* accelerated the oxidation of the PAHs by rhizodegradation (Di Gregorio *et al.*, 2014).

13.4.1.4. Vermiremediation

Although many contaminants are toxic to earthworms, and they are often use as bio-indicators for polluted soils, under suitable conditions they can be used in remediation strategies. Earthworms can be tolerant to many chemical contaminants including trace elements and organic contaminants in soil and can bio-accumulate them in their tissues. Earthworm species have been found to remove trace elements, pesticides and lipophilic organic contaminants, including polycyclic aromatic hydrocarbons (PAH), from the soil. They absorb the chemicals from the soluble soil fraction in the interstitial water through their moist body wall and also ingest them. As the soil passes through the earthworm gut contaminants are either bio-transformed or biodegraded rendering them non-toxic. Meanwhile the quality of the soil is improved significantly in terms of physical, chemical and biological properties as the worms thoroughly upturn and disperse the soil, ingest large volumes of soil and excrete nutritive materials (nitrogen, phosphorus, potassium and micronutrients) in the form of vermicasts along with millions of beneficial soil microorganisms including nitrogen fixers (Sinha, Bharambe and Ryan, 2008). It was demonstrated that in soil polluted with 20 g/kg - 60 g/kg of petroleum, the content of hydrocarbons decreased by 99 percent after 22 weeks in the presence of worms and a proprietary mix of nitrogen fixing bacteria, yeasts and fungi (Chachina, Voronkova and Baklanova, 2016).

13.4.2. *Ex situ* biological treatment

Ex situ biological treatment requires the soil to be excavated and treated on site or at a specialist soil treatment facility. The bioremediation processes are similar to those used *in situ* techniques. However, *ex situ* techniques tend to allow greater control of the bioremediation processes through easier processes tend to be faster and more predictable but more expensive than their *in situ* equivalent. *Ex situ* processes tend to be more disruptive to the soil structure and its biological communities, and post-remediation rehabilitation can take longer.

13.4.2.1. Biopiles

Biopiling is a bioremediation technology, extensively used for *ex situ* remediation of polluted soils by a wide range of petrochemical and other organic chemical contaminants. The technique involves the excavated soil being homogenized and amended to enhance the conditions for biodegradation by microorganisms. The piles are often constructed and manipulated in the same way as a compost windrow. Biopiles are sometimes referred to as biocells. The activity of microorganism populations, growing near optimum conditions, can be stimulated aerobically or by the addition of nutrients, minerals, moisture or pH adjustments to maintain optimum biodegradation (Germaine *et al.*, 2015; Pavel and Gavrilescu, 2008). Enhanced bioremediation in a biopile is demonstrated in the Case study 6 of Penrice Soda, South Australia below and that of the 18 de Marzo refinery in Mexico Case study 1.

Case study 6. Biopile: enhanced bioremediation of soil polluted with fuel oil. South Australia

During the early 1970s fuel oil spilt from a 500 m^3 above ground storage tank at Penrice Soda factory, Osborne, South Australia. On investigation in the 2000s, approximately 3 000 m^3 of soil was still polluted with the oil. The remediation strategy was based on a biopile with negatively forced aeration and leachate capture. A biocell was excavated and hermetically sealed with a high density polyethylene (HDPE) liner. A system of pipes was installed to capture leachate and condensate, and to provide the negative pressure for the biopile's aeration (Figure 10). The pipes were linked to a carbon filtered air extraction and filtering unit. The polluted soil was excavated and mixed with green waste to increase the natural microbial metabolic activity, as well as the porosity, and placed into the biocell. Once constructed, a network of water dripper lines was installed on top of the biopile. The biopile was covered in a further HDPE liner. The increased porosity allowed the vacuum pump to draw air down through the pile, while a proprietary formulation was fed through the water drippers to stimulate the enhanced bioremediation. The formulation contained microorganisms and nutrients and was diluted before inoculating the biopile. The negative forced air prevented smells and volatile contaminants from escaping from the biopile (Figure 11).

Figure 10. Construction of the leachate control and forced aeration pipes. © McMahon Services.

Source: reproduced with permission from Zero Waste South Australia, 2013.

Figure 11. Biocell and pipe setup for remediation.

Source: adapted from McMahon Services, undated; Zero Waste South Australia, 2013.

The process had the advantage that the soil could be treated on-site, avoiding transport costs and was quicker and more controllable than *in situ* remediation. The soil required to be well mixed to ensure an even rate of bioremediation throughout the pile.

The enhanced biopile remediation successfully reduced TPH concentrations to acceptable levels. The remediated soil was backfilled into the original excavations. The total cost was USD 900 000,

Case study 7. Biopile remediation of soil polluted with PCBs using spent mushroom compost. Brescia, Italy

The Caffaro company had previously manufactured chemicals on an 11 000 m^2 site in Brescia, Italy since 1906. From 1938 until 1984 the company manufactured polychlorinated biphenyls (PCB), a chemical that is now listed under the Stockholm Convention as a persistent organic pollutant (POP). During this period the site became polluted with PCB. The site is no longer used for industrial production and has been classified by the Italian authorities as a Site of National Interest for Reclamation. Waste disposal and remediation activities have been undertaken to remove the gross quantities and areas with high levels of PCB pollution. There remain areas of the site with PCB contamination levels below 50 parts per million, the lower limit for designation as POPs under the Stockholm Convention. Nevertheless these levels polluted soils potentially limit the use of the land.

A project was undertaken by Teseco to demonstrate the effectiveness of using spent mushroom substrate (SMS) from cultivation of *Pleurotus ostreatus* for the remediation of these soils. The decontamination capacity was verified at a mesocosm scale and validated at pilot scale in a dynamic biopile pilot plant treating ten tonnes of a historically polluted soil with PCB concentrations of 9.28 ± 0.08 mg/kg soil dry weight. Mixing of the SMS with the soil was required for the depletion of the contaminants. At the pilot scale, after eight months of incubation, 94.1 percent depletion was recorded. Positive correlations between actinobacteria and firmicutes active metabolism, soil laccase activity and PCB removal were observed. The SMS was found to be exploitable as a versatile low-cost organic substrate capable of activating processes for the oxidation of highly chlorinated PCBs. Moreover, its exploitation as bulking agent in biopiles is a valuable management strategy for the re-utilization of an organic waste deriving from the industrial cultivation of edible mushrooms (Siracusa *et al.*, 2017).

13.4.2.2. Bioleaching

Bioleaching is an extractive technology that uses a solution inoculated with microorganisms to leach trace elements from polluted soils. It is also a process that is used in the mining industry as an alternative to cyanide to extract metals from low-grade ores or mine wastes (Liu *et al.*, 2007). It is considered as an efficient and cost-effective alternative to physicochemical treatment technologies for soil remediation (Chen and Lin, 2010). The inoculated liquid is trickled over an *ex situ* pile of polluted soil. As the liquid percolates through the soil, the microorganisms act on the metal contaminants, which dissolve into the leachate and collect at the bottom of the pile. The leachate is further processed to recover or safely dispose of the metals. A potential weakness of the technology is the potential for flow channels to develop, with the bypassed soil remaining untreated.

13.4.2.3. Composting

provide the optimum levels of air and moisture to microorganisms. Generally, the mixture contains 75 percent of polluted soil and 25 percent of organic fraction, but may be varied to suit the type of soil, contaminants and their concentration (Kumar *et al.*, 2011; Pavel and Gavrilescu, 2008). To stimulate the composting process, the pile may be mechanically churned to homogenize the mixture, maintain aeration, and ensure even biological activity throughout the pile (Figure 12).

Figure 12. Windrow turning machines in Texas, United States of America. ©Saqib Mukhtar.

13.4.2.4. Landfarming

Landfarming is an *ex situ* bioremediation technique, where excavated polluted soil is transported to the landfarming site and spread in a thin layer onto biologically active land or an impermeable surface. The polluted soil is ploughed into the soil surface, sometimes with the addition of organic amendments (e.g. manure or sewage sludge). This process stimulates biodegradation by the inherent microorganisms, aerobically stimulated by the ploughing, which may be repeated, and by adding nutrients for growth promotion of microorganisms (Kumar *et al.*, 2011; Pavel and Gavrilescu, 2008). Landfarming was used to remediate soil polluted with creosote as is explained in the following case study.

Case study 8. Landfarming of soil polluted with creosote. KwaZulu-Natal province, South Africa.

Approximately 450 m^3 of soil had become polluted with creosote at a timber treatment company in KwaZulu-Natal. The pollution resulted from creosote dripping from timber directly onto the soil while it was stacked for drying. A laboratory study (Atagana, Haynes and Wallis, 2003), undertaken in 2003, that demonstrated that the soil with creosote at >250 000 mg/kg could effectively be bioremediated by increasing the carbon to nitrogen ratio and neutralising the acidity.

The polluted area 25 m by 40 m by 0.45 m deep was excavated to remove the soil and the top of the underlying shale layer that was also polluted. The clean shale surface was made impermeable with a layer of clay and the polluted soil placed on top. The site was relatively flat so the risk of run off was low. Analysis of composite soil samples indicated concentrations of 310 000 mg/kg creosote. The remediation objective was to reduce the creosote concentration to below 2 000 mg/kg. The soil was amended with dolomitic agricultural lime to increase the soil pH to neutral and monoammonium phosphate to alter the carbon to nitrogen ratio which facilitated oxidation. The soil was ploughed every 14 days to aid aeration. Sewage sludge from a waste-water treatment plant was mixed into the soil after approximately 60 days and again at 150 days after commencement. Soil moisture was monitored and maintained at approximately 70 percent of field capacity by watering the area manually during the drier months.

The initial amendments of lime and monoammonium phosphate stimulated biodegradation compared to the control. However, it was the application of sewage sludge that significantly increased the biodegradation. The lower molecular weight organics rapidly degraded in the first five months but the higher molecular weight PAHs showed the slowest rates of biodegradation, for example with chrysene ($C_{18}H_{12}$) only reducing to 25 percent of its original concentration by the tenth month. The remediation objective was reached within ten months (Atagana, 2004).

13.4.2.5. Bioreactors

Bioreactors are open or closed installations that agitate the soil while adding nutrients to stimulate microorganisms to degrade the contaminants. They may be operated aerobically or anaerobically depending on the contaminant and the microorganisms best suited for the biodegradation. Typically, the time required for remediation is significantly shorter than static remediation strategies. There are two main types, solid phase and liquid phase. A solid phase bioreactor is generally a batch process undertaken in an enclosed reaction chamber with internal stirrers. The process proved effective in treating tropical soil polluted with up to 35 percent total petroleum hydrocarbons, over the course of 42 days (Rizzo *et al.*, 2010). In a liquid phase bioreactor, polluted soil is sprinkled with water and agitated with mixers. It is also a batch process. When the desired level of contamination has been reached, the soil solids can be filtered and returned to the site and the water retained for the next batch. The biodegradation process in both solid and liquid phase bioreactors is highly controllable and generally rapid due to the homogeneity of the materials and the effective contact of the microorganisms with the contaminants (Kumar *et al.*, 2011; Pavel and Gavrilescu, 2008).

13.4.3. *In situ* physical/chemical treatment technologies

Physical and chemical treatment techniques tend to be more aggressive than nature-based processes but are capable of treating soils with more persistent contaminants or those containing higher contaminant concentrations. The processes tend to achieve the remediation objectives more rapidly than nature-based equivalents. However, they tend to be more costly, resource intensive and, following treatment, it is often more difficult to re-establish biodiversity and soil quality in the treated soils.

13.4.3.1. *In situ* physical treatment

Electrokinetic separation

Electrokinetic remediation uses electrical fields and electrochemical processes to enhance the migration of polar inorganic and organic molecules out of soil. It is useful to increase the extraction rates for contaminants in low permeability soils. It has been used in conjunction with *in situ* phytoextraction in Guiyu China as shown in the case study below. The technique was also used to remove trace elements from polluted soil in the Janghang smelter case study from the Republic of Korea.

Case study 9. *In situ* phytoextraction enhanced with electrokinetics. Guiyu, Guangdong, China.

Leachate from e-waste recycling operations was polluting soil and groundwater with trace elements, including cadmium, copper, chromium, lead, mercury and zinc. The recycling operations were moved to a more appropriate location and in 2016 a research programme was undertaken to evaluate remediation strategies based on phytostabilization/phytoextraction enhanced with electrokinetics (Figure 13). Eight plots were prepared by ploughing to homogenize the levels of contaminants between the plots and to remove large pieces of e-waste. Baseline sampling and analysis showed that the plots had similar concentrations of trace elements with only cadmium, copper and lead exceeding the national environmental standards by 173 percent, 78 percent and 16 percent respectively. *Eucalyptus globulus* was chosen for metal extraction due to its tolerance to metal toxicity and unpalatable nature. The eight plots comprised one control and seven planted with *E. globulus*. Of the seven planted plots, six had a network of electrodes around the plants to test the effectiveness of electrokinetics to increase *E. globulus* uptake of the trace elements. The trial plots tested alternating current (AC) and direct current (DC) at 3 low voltages (2 V, 6 V and 10 V).

Figure 13. Design of the phytoextraction enhanced with electrokinetics remediation approach.

Source: adapted from Luo *et al.*, 2018.

The results showed that growth rates were less than would be expected in background soil conditions but the plants were effective in significantly reducing moisture down to 1 metre below ground level and thus reducing the risk of leachate penetration. Growth rates and trace element uptake were enhanced by electrokinetics (apart from plot 10 V DC). Overall, DC at moderate voltage was determined to the most effective for remediation. Phytoextraction with electrokinetics required half the time of phytoextraction alone to reach the remediation objective.

Soil vapour extraction and air sparging

Soil vapour extraction and air sparging are similar processes to their biological equivalents, bioventing and biosparging described in *section 13.4.1.1*, but rely solely on the air (which may be heated) passing through the polluted soil to volatilize the volatile and semi-volatile contaminants. These processes are most effective in soils with high porosity. They are not effective in clay soils.

Soil vapour extraction is the term for the process operated in the unsaturated vadose layer. Unlike bioventing, it relies on extraction pumps to provide a vacuum that draws air through the soil. Passive sparging, the air is injected below groundwater level. The contaminants transfer from the soil and groundwater to the air bubbles, which migrate upwards into the vadose zone. As the objective of both these processes is to volatilize the contaminants, the air flow rates tend to be high. Although the focus is on extraction, the high air flows can facilitate aerobic biodegradation of the contaminants. In both processes the air and volatilized contaminants are captured by the vacuum extraction system followed by a treatment process for the volatile contaminants (Brusseau, Pepper and Gerba, 2019). The treatment system would be specific for the flow rate of the extracted air and the type and concentration of the contaminants. For solvents and petroleum hydrocarbons, typical treatments include recovery, catalytic oxidation and active carbon filters.

Figure 14. Air sparging with soil vapour extraction process.

Source: adapted from Khan, Husain and Hejazi, 2004.

Multiphase extraction is a variation of the process where the vacuum extracts air, vapours, liquid contaminants and polluted groundwater. The level of ground water around the extraction well drops, exposing further soil for vapour removal. The above ground treatment is more complex and typically requires phase separation prior to specific treatment for each medium. The United States EPA through its CLU-IN website provides guidance on soil vapour extraction,[9] air-sparging[10] and multiphase extraction.[11]

Case study 10. *In situ* remediation of soil polluted with chloroform and tetrachloromethane

Leakage from an old underground storage tank at a chemical manufacturing site in northern Italy had polluted the vadose and saturated soil layers with tetrachloromethane (CCl_4) at > 10 mg/l, chloroform at > 10 mg/l and hexavalent chromium (Cr(VI)) at > 2 mg/l and to a lesser extent perchloroethene (PCE) and trichloroethene (TCE). The pollution was below the current chemical manufacturing infrastructure and extended over 2 000 m^2 and up to 17 m deep. The risk assessment and conceptual site model indicated that the saturated zone had high concentrations of both chloroform and CCl_4, while the vadose zone was only affected by chloroform.

The remediation strategy included the installation of a hydraulic containment barrier using pump and treat techniques for the saturated zone and soil vapour extraction for the chloroform in the vadose zone (Figure 15). In September 2017, after a year of operations the concentrations of contaminants in the saturated zone had decreased significantly but had not reached the remediation targets that had been agreed to with the company, namely 66 µg/l for CCl_4 and 65 µg/l for chloroform. In addition, there was some evidence of degradation of anaerobic catabolites, dichloromethane and chloromethane along with concentrations of TCE and Cr(VI) present in the groundwater. The groundwater velocity was 284 m per year.

Source: reproduced with permission from Leombruni *et al.*, 2019.

The remediation strategy was revised to include *in situ* chemical reduction and stimulation of anaerobic biodegradation. In December 2017, 10 tonnes of a proprietary reagent comprising a microemulsion of zerovalent iron and a controlled release organic carbon substrate was pumped into the 28 wells used pump and treat. The operation took 15 days. In the saturated zone the reagent established enhanced reducing conditions for biotic and abiotic dechlorination of the organic compounds. After 15 months contamination levels of CCl4 and chloroform were below the remediation targets in all the main control piezometers (Figure 16). This represents more than 98 percent reduction in contamination levels in 15 months (Leombruni *et al.*, 2019).

Figure 16. Contaminant concentrations during and after completion.

Source: adapted from Leombruni *et al.*, 2019.

The costs of the revised remediation strategy is claimed to be an order of magnitude lower than pump and treat and dig and dump methods.

13.4.3.2. *In situ* chemical treatment

The purpose of chemical treatment is to eliminate or destroy the contaminants, or change their redox status and to make them more amenable for elimination or stabilization.

Solidification/stabilization

Contaminants are physically bound or enclosed within a stabilized mass (solidification), or chemical reactions are induced between the stabilising agent and contaminants to reduce their mobility (stabilization). The mobility of organic and inorganic compounds can be reduced through various precipitation, complexation, and adsorption reactions. Commonly applied inorganic stabilization agents include soluble silicates, zeolites, lime, phosphates, and sulphur-based binders. Organo-clays have been used to stabilize organic chemicals that are poorly addressed by precipitation and complexation reactions (US EPA, 2015). Cementitious processes with the use of lime or cement can be used to bind high concentration inorganic contaminants. In both cases, the soil is unlikely to be suitable for agricultural use and the site will require some long-term monitoring to ensure that the contaminants remain immobile.

Activated carbon and biochar can also be used to reduce the bioavailability of trace elements and organic contaminants and can assist in returning polluted soil to agricultural use (Denyes, Rutter and Zeeb, 2013; O'Connor *et al.*, 2018). O'Connor et al. (2018) reviewed the field-scale use of biochar in eight factors including application time period, climate, dosage, mixing depth, biochar feedstock type and biochar properties. Biochar applications significantly reduced uptake of cadmium in rice crops. It also helped to increase yields from polluted soils. However, it was noted that its effectiveness decreased with time due to aging factors such as the leaching of biochar alkalinity. The mechanisms involved in biochar-induced immobilization of trace metals are acid neutralization in soil and increase in soil cation exchange capacity (Younis et al., 2015 and references therein). The carbon can be incorporated directly into the soil by ploughing. As well as stabilising contaminants, the addition of carbon to the soil contributes to carbon sequestering as a mitigation measure against climate change and improves soil fertility (FAO, 2019). This technology is presented in the case study below.

Case study 11. Stabilization of trace elements with biochar as a soil amendment. Pakistan.

Sewage sludge and sewage water can be used to irrigate and add nutrients to the soil. However, care has to be taken to ensure that the materials are not polluted with trace elements. In this case in Pakistan, soil was treated with sewage water that contained cadmium and nickel contaminants, which impacted agricultural production. The soil was amended by incorporating biochar at a ratio of 3 to 5 percent of wet soil weight. The biochar captured the trace elements making them less available for interference with and uptake by the crops. The biochar had been produced from post-harvest cotton biomass. The amended soil was used to cultivate spinach and fenugreek which showed a 30 percent increase in growth and a 50 percent decrease of uptake of trace elements, compared to the unamended soil control (Younis *et al.*, 2015).

Where groundwater is polluted, the contaminants can be absorbed onto fine particles of carbon suspended in water that is injected into the saturated zone to form reactive barriers. The technique has been used at full scale for the *in situ* treatment of groundwater polluted with petroleum hydrocarbons. As highlighted in Chapter 3, poly- and perfluoroalkyl substances (PFASs), which are commonly used in firefighting, have become a contaminant of concern in groundwater, and are now listed under the Stockholm Convention. The injection of a reactive barrier of colloidal activated carbon is one of the technologies that has been demonstrated to be effective in preventing the dispersal of PFAS. The technique brought contamination levels of perfluorooctanoate down from 3 260 ng/l to below 30 ng/l in shallow anaerobic aquifers slightly contaminated with PFAS (McGregor, 2018).

Case study 12. Colloidal active carbon reactive barrier to PFAS migration Camp Grayling. Michigan, United States of America.

Camp Grayling in Crawford County, Michigan is a year-round training centre for the Michigan Army National Guard (MIARNG). The Michigan Department of Military and Veteran Affairs (DMVA) has been remediating chlorinated solvent impacts in the site groundwater from historical operations at the facility since the late 1980s. In 2016, the DMVA became aware of the potential contamination of per- and polyfluoroalkyl substances (PFAS) from historical operations such as on-site firefighting training and began testing groundwater at the Grayling Army Airfield (GAAF). PFAS was found commingled with a chlorinated solvent plume that was migrating towards the property boundary. The DMVA reviewed potential remedial options to test in the field such as pump and treat, but ultimately decided to test an in-situ reactive barrier application of colloidal activated carbon.

Colloidal activated carbon (CAC) was selected because of the expected rapid reductions of PFAS through its removal from the dissolved mobile phase. Colloidal activated carbon effectively increases the retardation factor of PFAS migration by several orders of magnitude and thereby eliminates down-gradient receptor exposure (Figure 17). In addition, CAC was selected due to its expected lower total project costs when compared to operating a mechanical system over a similar timeframe. The CAC barrier application was performed in the autumn of 2018 (Figure 18) and PFAS levels remained at non-detectable levels for more than a year of monitoring.

Figure 17. PFAS analysis in up and downstream wells following application.

Source: adapted from Regenesis Inc., 2019.

Figure 18. Cores showing the dispersal of the active carbon following injection. ©Regenesis Inc.

Source: Regenesis Inc., 2019.

PFAS contamination is particularly challenging because of its recent discovery, which means that few *in situ* treatments are available. The department’s environmental task force conducted an evaluation of the groundwater remedial technology and became aware of a new approach to eliminate risk using the liquid activated carbon *in situ*. This technology has been proven at other sites where PFAS has been found and has quickly and effectively eliminated the down gradient risk of PFAS. The technology vendors claim that these active carbon barriers should remain effective for decades.

Oxidation

Solutions of chemical oxidising agents are injected directly into the polluted soil or placed as a

Roundtable (FRTR), 2007; Tsitonaki *et al.*, 2010). These oxidising agents have been able to cause the rapid and complete chemical degradation of many organic contaminants; more stable organic contaminants are still amenable to partial degradation which aids subsequent bioremediation. *In situ* chemical oxidation is capable of achieving high treatment efficiencies (greater than 90 percent) for unsaturated aliphatic (e.g., trichloroethylene) and aromatic compounds (e.g., benzene), with very fast reaction rates (90 percent destruction in minutes). The long-term efficacy of the technology depends on many factors including the selection of the oxidizing agent and the mechanism for introducing it to the polluted soil; however the most important factor is morphology and geology of the site. Where the site comprises different zones with high and low permeability, the contaminants may be quickly eliminated from the zones of high permeability. With time contaminants migrate back from the zones of low permeability that the oxidants did not reach. This effect is termed "rebound" and can severely limit the long-term effectiveness of the technology and may require multiple treatments. Careful consideration of the conceptual site model will assist in identifying the potential risks of rebound. This process is capable of addressing high concentrations of organic point source pollution. As the technology involves the risk and safety of the use of potentially harmful oxidizing agents will be another important consideration. Further information on *in situ* chemical oxidation is available on the United States EPA CLU-IN website.[12]

Reduction

Reduction covers a range of reactions including dechlorination of organochlorine compounds and conversion of trace elements to a different (less toxic and/or mobile) valent state.

As with *in situ* chemical oxidation, the reducing agents are injected directly into the polluted soil or as a permeable or semi-permeable reactive barrier. The injectable reducing agents can include nanoscale materials such as zerovalent iron that because of their minute size can permeate through the soil matrix. Other reducing agents include iron minerals, polysulphides, dithionite, and bimetallic materials. The reduction process can dechlorinate organic compounds (e.g., organochlorine pesticides), polycyclic aromatics, and chlorinated solvents (e.g., trichloroethylene), and convert hexavalent chromium to the less toxic and less mobile trivalent state. The reactions are complex and involve the reducing element moving up through its oxidation states releasing electrons that react directly with the contaminant or generate hydrogen that is catalysed to substitute the chlorine in the contaminant. (Gavaskar, Tatar and Condit, 2005; Tratnyek and Johnson, 2006). The United States CLU-IN website also includes guidance on *in situ* chemical reduction.[13]

13.4.3.3. *In situ* thermal treatment

Five technologies are considered under the *in situ* thermal treatment classification: electrical resistance heating, steam injection and extraction, conductive heating, radio-frequency heating, and vitrification. With the exception of vitrification, the main objective of these technologies to increase the removal efficiency of volatile and semi-volatile contaminants by heating the soil. The increased temperatures can stimulate the chemical and biological degradation of some contaminants. Vapour extraction and ex integral part of these technologies. The surface of the soil is covered to ensure all released vapours are captured by the extraction system and to provide thermal insulation. *In situ* vitrification uses much higher temperatures to convert the soil into a glass. The non-volatile contaminants such as trace elements and radioactive materials are incorporated into the glass which, when cooled, immobilizes them. (US EPA, 2015). The very high temperatures can cause thermal degradation of organic components that also require sound environmental management to minimize the risk of the release of toxic emissions such as polychlorinated dibenzodioxins and furans. The United States EPA's CLU-IN website has extensive guidance on all the *in situ* thermal remediation technologies.[14] Vidonish et al. (2016) reviewed *in situ* and *ex situ* thermal treatment techniques and provide useful descriptions of their relative advantages with cost comparisons.

The same techniques can also be employed in *ex situ* in the form of in pile thermal desorption (see section 13.4.8). In pile thermal desorption involves the construction of a sealed treatment area on a location close to the polluted soil. The polluted soil is excavated and placed in the pile along with the heating and extraction network.

The high temperatures used in *in situ* and *ex situ* thermal treatment degrade the soil structure, chemical composition and biological community such that it is difficult to return it to agricultural production.

Electrical Resistance Heating

Electrical resistance heating involves setting up a network of electrodes in order to pass a current through the polluted soil. As the current flows through moisture in the soil pores, the resistance of the soil produces heat. The electrodes are sunk into the soil and can be designed to deliver electric power at selected depths. Volatilization and steam stripping are the usual removal mechanisms for most contaminants and require extraction and treatment for the off-gases. The wells for the electrodes can used also as part of the extraction system.

Steam Enhanced Extraction

In steam enhanced extraction a network of injection and extraction wells are set up in the polluted soil that facilitate steam to be injected into the saturated zone. The steam mobilizes the contaminants into the groundwater and as vapour. The groundwater together with liquid and gaseous contaminants are removed from the extraction wells for further *ex situ* separation and treatment.

Case study 13. Steam enhanced extraction at Beede Waste Oil superfund site – Terrathem. New Hampshire, United States

The Beede Waste Oil superfund site occupies a total of approximately 17 hectares within a predominantly residential area. Between 1920 and 1994 the site was the location of several oil-related operations, including waste oil processing and re-sale, fuel oil sale, contaminated soil processing into cold-mix asphalt, anti-freeze recycling, and other related industries. The soil, which consisted of silty to gravelly sands, was heavily contaminated with oil and other chemicals.

Between 2000 and 2005 a vacuum-enhanced recovery system recovered 340 000 litres of the light non-aqueous phase liquid (LNAPL) oil. However, pooled and residual LNAPL, consisting of a mixture of oil types remained over much of the treatment area across a smear zone created by water table depression and fluctuation. In the early 2010s it was determined to remediate the site to remove this residual pollution. A strategy of steam enhanced extraction (SEE) was agreed for the target treatment zone which comprised an area of 10 650 m^2, volume of 10 150 m^3, with an average depth of 5 m to 8 m below ground surface (Figure 19). The steam extraction system comprised 88 steam injection wells, 31 multiphase extraction wells and 38 multi-depth temperature monitoring strings.

Figure 19. SEE wellfield and treatment equipment. ©Terratherm Inc., undated.

The remediation objective was to reduce VOC levels in subsurface soils deeper than three metres to below the soil leachability clean-up goals specified by regional authority’s Ambient Groundwater Quality Standards (AGQS). However, it was anticipated that the chemical properties of naphthalene may have prevented short-term attainment of the low clean-up goal of 4 mg/kg.

The contaminants of concern (COCs) were trichloroethene (TCE), cis-1,2- dichlorothene (cis-1,2-DCE), benzene, ethylbenzene, tetrachloroethene, 1,1,1-trichloroethane, total alkylbenzenes and naphthalene.

The first phase of the SEE operation was undertaken between May 2015 and February 2016. The steam mobilized in the oil in the smear zone and the contaminants of concern that, together with polluted groundwater, were extracted to a treatment plant. The treatment separated the oil from the other contaminants and cleaned the groundwater, which then was returned to the aquifer. The SEE system removed approximately 65 400 litres of LNAPL oil and over 68 000 kg of COC mass from the site. Post-treatment sampling revealed that the SEE remediation met the clean-up standards for the target VOCs as well as for naphthalene.

Conductive Heating

Conductive heating uses a network of vertical heater and extraction wells or, when the polluted area is close to the ground surface, heater blankets spread over the surface. The vertical radiant heaters are surrounded by a sealed steel housing to protect them from the surrounding soil and groundwater.

Some swells are designed to combine both soil heating and extraction. Heating is usually powered by electricity and the heat penetrates the surrounding soils by thermal conductance.

Case study 14. *In situ* thermal desorption of Teterboro Landing Brownfield Redevelopment. New Jersey, United States.

For 70 years, the 25 ha Teterboro Landing site in New Jersey was operated by Bendix Aviation Corporation with activities at the site including manufacturing aerospace technology. In March 2007, a developer purchased the property with plans to redevelop the site into a transit-oriented development with connections throughout the Meadowlands Region. Through all the years of industrial activity, the soil had become heavily polluted with oil and chlorinated organic compounds. The conceptual site model indicated that *in situ* thermal desorption and multiphase extraction and treatment was the preferred option due to its likely speed of remediation.

The site was set up with 907 electrically heated thermal wells, 80 temperature monitoring points, 25 pressure monitoring points and 35 multi-phase extraction points (Figure 20). The maximum depth of the site was 12 m. The treatment included a thermal oxidizer for the treatment of volatile off-gases which was rated for 4 250 Nm^3/h.

Figure 20. *In situ* thermal desorption and treatment equipment. ©Terratherm Inc., undated.

Hot soil sampling protocols were used to monitor the progress of the remediation and to demonstrate compliance attainment. The ISTD system operated for eight months, at which time interim soil sampling showed that all but one sampling location had met the remedial goal of 1 mg/kg (Figure 21). A small area with high starting concentrations proved to be recalcitrant, with soil concentrations plateauing at levels between 5 mg/kg and 20 mg/kg. Four additional heater wells were installed, and 10 days later the remedial goals were achieved in this location. The total energy used for heating was 23 million kWh, equivalent to 290 kWh/m^3 of treated soil. An estimated contaminant mass of 15 000 kg was recovered and destroyed on-site through the thermal oxidizer treatment system. Remediation at the Teterboro Landing site was completed in 2013. The site is noteworthy because, at the time, it was the largest *in situ* thermal desorption project to have been completed in the Unites States of America, covering an area of 1.3 ha, with a treatment volume of 93 300 m^3.

Figure 21. Initial and final concentrations of the contaminants of concern.

Source: adapted from Terratherm Inc., undated.

Radio-Frequency Heating

Radio-frequency heating (RFH) uses a high frequency alternating electric field for *in situ* heating of soils. The technique depends on the presence of dielectric materials with unevenly distributed electrical charges. The application of an electric field produces movement of the “polar” molecules, and this vibration creates mechanical heat. This technique generally relies on the presence of water in the soil. As the soil dries, the effectiveness of RFH drops and so it may be necessary to add water to maintain a stable moisture content.

13.4.3.4. *In Situ* vitrification

In situ vitrification is a thermal treatment process that converts polluted soil to stable glass and crystalline solids. There are two methods for producing heat for melting the polluted soil: using electrodes and electrical resistance or plasma arc technology. Due to the energy requirements, the process is expensive and has generally only been used for radioactive wastes. The technology was demonstrated in 2000 at the Los Alamos National laboratory (Figure 22) for the *in situ* vitrification of an old radioactive effluent disposal trench where the polluted soil and underlying strata were melted to a depth of seven metres (Veolia Nuclear Solutions, 2017).

Figure 22. *In situ* vitrification operations at Los Alamos National Laboratory. ©Veolia

Source: Veolia Nuclear Solutions, 2017.

Vitrification is also used as an *ex situ* treatment for stabilizing radioactive wastes including polluted soil into glass blocks that are suitable for long-term storage. The process reaches 1 600 °C to melt the soils and radioactive wastes, which cool to from a vitrified block. The technology can operate at permanent facilities or on site with a mobile plant. The vitrification can take place either in cells excavated in the ground or in an above ground module. All systems use electrodes to provide the electrical heating (Kurion Veolia, 2016).

13.4.4. Nanotechnologies

Nanoremediation methods entail the application of reactive nanomaterials for transformation and detoxification of contaminants. These nanomaterials have properties that enable both chemical reduction and catalysis to mitigate the target contaminants. For nanoremediation *in situ*, no groundwater is pumped out for above-ground treatment, and no soil is transported to other places for treatment and disposal (Otto, Floyd and Bajpai, 2008).

Nanomaterials have highly desired properties for *in situ* applications. Because of their minute size and innovative surface coatings, nanoparticles may be able to pervade very small spaces in the subsurface and remain suspended in groundwater, in theory allowing the particles to travel farther than larger, macro-sized particles and achieve wider distribution. However, in practice, current nanomaterials used

Many different nanoscale materials have been explored for remediation, such as nanoscale zeolites, metal oxides, carbon nanotubes and fibres, enzymes, various noble metals, mainly as bimetallic nanoparticles (BNPs), and titanium dioxide. Of these, nanoscale zerovalent iron (nZVI) is currently the most widely used as was discussed under *in situ* chemical reduction in *Section 13.4.3.2*. Karn, Kuiken and Otto (2009) reviewed 45 polluted sites that had been remediated using nanomaterials to identify the types of nanomaterials used, and the media that was remediated (Figure 23).

Figure 23. Nanomaterials and the media treated.

Source: adapted from Karn, Kuiken and Otto, 2009.

13.4.5. *Ex situ* physical treatment

13.4.5.1. Separation

The use of soil particle size separation is based on the finding that most organic and inorganic contaminants tend to bind, either chemically or physically, to clay, silt, and organic soil particles. The silt and clay, in turn, are attached to sand and gravel particles by physical processes, primarily compaction and adhesion. Size separation is generally undertaken as an initial step in washing processes, to remove the coarse sand and gravel fractions from the fine clay and silt particles, concentrating the contaminants into a smaller volume of soil that can be further treated or disposed of using other *ex situ* methods. The cleaned coarse fraction, sand and gravel can be returned to the site. There are three main separation techniques:

Gravity separation

Gravity Separation is a solid/liquid separation process that relies on a density difference between the phases. Effectiveness of gravity separation depends on the solids' settling velocity, which is a function of particle size, density difference, fluid viscosity, and concentration (e.g. too many particles hinder settling). Gravity separation is also used for removing immiscible oil phases, and for grading soils into different fractions according to particle size. It is often preceded by coagulation and flocculation of fine particles to increase their size, thereby allowing more easy removal by settling.

Magnetic separation

Magnetic Separation is used to extract slightly magnetic particles from host materials such as water, soil, or air. It may be used for separating uranium and plutonium compounds, which are slightly magnetic while most host materials are nonmagnetic. The process operates by passing contaminated fluid or slurry through a magnetized volume. The magnetized volume contains a magnetic matrix material such as steel wool that extracts the slightly magnetic contamination particles from the slurry.

Sieving/physical separation

Sieving/Physical Separation processes use different size sieves and screens to effectively concentrate contaminants into smaller volumes.

The United Kingdom's Contaminated Land: Applications in Real Environments (CL:AIRE) have published a series of guidance on contaminated land remediation, including Technical Bulletin 13 "Understanding Soil Washing" that also describes physical separation techniques (Pearl, 2007). The commercially available process equipment is summarized in Table 3.

Table 3. Commercially available physical separation equipment.

Source: Pearl, 2007.

13.4.5.2. Soil washing

Soil washing is a water-based process for scrubbing soils *ex situ* to remove organic and inorganic contaminants. The process removes contaminants from soils either by physical or by chemical means.

With chemical soil washing, soil particles are cleaned by selectively transferring the contaminants on the soil into solution. This is achieved by mixing the soil with aqueous solutions of acids, alkalis, complexing agents, other solvents and surfactants. The resulting cleaned particles are then separated from the resulting aqueous solution. This solution is further treated to remove the contaminants.

With physical soil washing, differences between particle grain size, settling velocity, specific gravity, surface chemical behaviour and rarely magnetic properties are used to separate those particles which contain the majority of the contamination from the bulk that are contaminant-depleted. The equipment used is often standard mineral processing equipment that was developed in the mining industry.

Attrition scrubbing removes adherent contaminant films from coarser particles. However, attrition washing can increase the fines in the processed soils.

Soil washing systems incorporating most of the removal and separation techniques are often included as the first step in an *ex situ* treatment train to address to soils polluted with a wide variety of trace elements, radionuclides, and organic contaminants. Soil washing was one of the main technologies that was used to remediate soil polluted with trace elements from the Janghang smelter case study.

Case study 15. Soil washing and chemical extraction with trace elements. Janghang, the Republic of Korea.

Over 50 years until its closure in 1989, the Janghang Smelter refined non-ferrous metals including copper, tin, gold and silver. The smelter was situated on a promontory on the west coast at the mouth of the Geum river. The area is a mix of industrial, urban, agricultural and forested landscapes. Emissions of fly ash and raw materials from the smelter's chimney polluted the surrounding areas with arsenic, cadmium, copper, lead, nickel and zinc. The schematic in Figure 24 below shows the dispersal of contaminants from the chimney with the heavier particles of fly ash and minerals falling closer to the chimney with small particles of arsenic travelling further. This pollution was impairing the health of the local population and the quality of agricultural production.

Figure 24. Schematic of the dispersal of contaminants.

Source: adapted from Ministry of Environment and Korea Environment Corporation, undated.

The plant had been state owned until its privatization in 1971. The "Polluter Pays" principle was adopted to fund the remediation strategy, with costs apportioned between the government and the private companies according to the duration of their respective ownership. In 2011, the Korea Environmental Corporation undertook an environmental assessment to identify the extent and distribution of the pollution. The pollution covered an area up to four kilometres from the chimney with the highest concentrations within the first one and a half kilometres. The satellite image in Figure 25 below shows the distribution of the pollution. For the remediation strategy it was divided into two zones:

Zone A: within 1.5 km from the chimney, an area of approximately 1 million m^2 with arsenic, lead, cadmium, copper, zinc, and nickel at high concentrations

Zone B: 1.5 km to 4 km from the chimney, which contained localized polluted areas of totalling approximately 234 000 m^2 with principally arsenic at lower concentrations

Figure 25. Trace element pollution around the Janghang smelter.

Source: Ministry of Environment and Korea Environment Corporation, undated.

The remediation strategy involved the purchase of the most polluted land closest to the chimney (indicated by the purple line in Figure 25). The residents in Zone A were relocated to mitigate their risk of exposure. The remediation of Zone B was the next priority as farmers were still living and working there.

The remediation of Zone B initiated in 2012 and took three years to complete. As it was such a large area, it was divided into three sectors and separate contracts were awarded for their remediation. All three companies adopted soil washing/chemical extraction as their prime technique. The soils were excavated and screened to remove the clean gravel and rocks. Two of the companies washed the fine fraction with either sulphuric or phosphoric acid. Although phosphoric acid was found to be more efficient, its higher cost meant that sulphuric acid was eventually the preferred eluent of both companies. The third company used a reductive dissolution process using sodium hydrogen sulphite. The soil washing capacity of each company was 20 m^3/hour, operating 8 hours per day.

Two of the companies also operated *ex situ* electrokinetic remediation units with capacities of 2 040 m^3 and 900 m^3 per batch (Figure 26). Each batch required up to five months to complete.

Figure 26. Electrokinetic process.

Source: adapted from Soil Environment Center (www.sec.re.kr/info/tech_01/board/view.do?brdno=70)

The farmers received compensation from the government for the periods when the remediation activities prevented them from farming their land.

Remediation in Zone A was initiated in 2016 and is expected to finish in 2020. The Zone was divided between three companies to undertake the remediation. They operated similar processes of pre-screening and soil washing/chemical extraction with two companies using sulphuric acid and the third using oxalic acid. Most of the cleaned soil was able to be returned to the excavation sites, however approximately 15 percent had to be disposed of at a containment landfill. Clean soil was imported to replace lost soil where necessary.

Zone A also included historic forested areas that were an important amenity with nature trails. A risk reduction strategy was developed to minimize the exposure of visitors while protecting the trails. The trails and car parks were repaved to cover any contamination. Around the trees, iron oxide was used to stabilize the trace metal contaminants. In other areas the soil surface was covered with organic mulching membranes and plants to minimize the risk of dispersal of polluted soil by wind and rain. Access was also controlled to exclude the public from areas that remained untreated.

Throughout the whole project there was a communication programme to inform stakeholders of the progress of the project and to divulge safety information. There was also an environmental

The remediation objective of project was achieved with all soils cleaned to below threshold levels for each contaminant. The total cost of the land purchase and subsequent remediation was USD 360 million.

Unless otherwise stated, all information was provided by Korea Environment Corporation and Korea Environmental Industry and Technology Institute

13.4.5.3. Solidification/stabilization

As in the *in situ* process, the contaminants in *ex situ* solidification/stabilization are physically bound or enclosed within a stabilized mass (solidification), or chemical reactions are induced between the stabilizing agent and contaminants to reduce their mobility (stabilization). *Ex situ* processes, however, typically require disposal of the resultant materials at a licenced disposal facility. In some regulatory environments, the material can be replaced on site.

Depending on the nature of the contaminants, solidification/stabilization processes use a range of materials to bind the polluted soils including cement and bitumen. Radioactive materials are often vitrified into a solid glassy block for long term storage.

13.4.6. *Ex situ* chemical treatment

13.4.6.1. Chemical extraction

Chemical extraction is a means of separating hazardous contaminants from soils, thereby reducing the volume of the hazardous waste that must be treated. The technology is similar to soil washing but uses an extracting chemical rather than water and wash-improving additives, such as surfactants. They vary with regard to the chemical employed, type of equipment used and mode of operation. Chemical extraction is often used to further separate contaminants following their concentration by physical separation. The extraction methods include dissolution in strong inorganic acids as in the Janghang smelter case study, forming complexes with chelating agents, and dissolution in organic solvents (Dermont *et al.*, 2008).

13.4.6.2. Chemical reduction/oxidation

The *ex situ* chemical reduction and oxidation processes are identical to those discussed under the *in situ* processes above. The advantage of the *ex situ* processes is that through mechanical mixing and easy monitoring, the reactions can be completed more rapidly, effectively and controllably.

13.4.6.3. Dehalogenation

Polluted soil is screened, processed with a crusher and pug mill, and mixed with reagents. The mixture is heated in a reactor. The dehalogenation process is achieved by either the replacement of the halogen molecules or the decomposition and partial volatilization of the contaminants (Government of Canada

Base-catalysed decomposition technology has been used for the treatment of the off-gas and condensate from thermal desorption plants. The combination of technologies has been used to treat soils polluted with intractable chlorinated organic compounds including hexachlorobenzene, polychlorinated biphenyls and polychlorinated dibenzo dioxins and furans. The process operates between 180ºC and 300ºC and uses a strong base and polyethylene glycol to catalytically dehalogenate the contaminant. This technology was used for the remediation of soil polluted with hexachlorocyclohexane and polychlorinated dibenzo dioxins at the Spolana site in Neratovice, Czech Republic (Bozek *et al.*, 2010; Kubal *et al.*, 2004)

13.4.7. Mechanical-chemical treatment

Ball mills have been used as a mechanical-chemical destruction method for treating polluted soil with organochlorine contaminants and other POPs. The surfaces of the polluted soil matrix are fractured by mechanical chemical processing creating highly reactive sites. These reactive sites can interact with contaminant molecules forming contaminant radicals, which fragment into smaller 'daughter' ions and ultimately neutral species. The process has been used in conjunction with nanoscale bimetallic compounds to remediate soils polluted with trace elements (Shin *et al.*, 2015).

The technology was operated at full-scale for 30 months from 2004 to remediate polluted soil at a pesticide manufacturing site at Mapua in New Zealand. The soils were polluted with DDT, aldrin, dieldrin and lindane. The process involves physical separation of the coarse fraction (diameter greater than 10 mm) that required no further treatment. The polluted fraction was dried and again separated into two size bands. The size band from 2 mm to 10 mm also met the New Zealand standards for industrial soils and required no further treatment. The fine fraction less than 2 mm diameter and the dust from the drier's cyclone had a mean total pesticide concentration of 790 mg/kg. This fraction was mixed with metal salts and a hydrogen donor in the proportion 97 percent soil to 3 percent reagents. The mixture was treated in a vibratory mill with two horizontally mounted cylinders containing a grinding medium. The grinding medium provided the mechanical impact energy required to drive the chemical reaction. The required residence time within the reactor was on average 15 minutes. The treated soil was analysed to confirm compliance with clean-up standards and then deposited in a clean backfill area. The mean total pesticides concentration of the treated soil was 85 mg/kg. Over the two and a half years operation, a total of 55 250 m^3 of soil was excavated, of which 5 500 m^3 were treated using mechanical chemical dechlorination. The total cost of the project, including construction and operations was USD 8 million (United States Environmental Protection Agency, 2010).

In 2012, mechanical-chemical dechlorination was tested as a potential technology for the remediation of 495 000 m^3 of soil and sediment polluted with polychlorinated dibenzodioxins (PCDD) at the Bien Hoa Airbase, Viet Nam (Figure 27). During the trial one hundred tonnes of this soil were successfully treated in a 6 tonne per hour in a continuous process using a cascade of four ball mills. Subsequently, further tests were undertaken to confirm the capability of the technology to reduce PCDD concentrations in soil from 70 000 ng/kg TEQ to 914 ng/kg TEQ (Cooke, 2015; Environmental

Figure 27. Continuous mechanical chemical dechlorination plant in Bien Hoa, Viet Nam. ©Environmental Decontamination Ltd.

Source: Environmental Decontamination Ltd, 2020.

13.4.8. *Ex situ* thermal treatment

Thermal treatment has a long history of commercialization as proven technology in the destruction of hazardous chemicals and remediation of highly polluted soils. The soils that result from the process will generally be sterile but, provided that residual levels of contamination are acceptable, may be mixed with clean soil for use in agriculture.

13.4.8.1. Thermal desorption

Thermal desorption is a commercially proven physical separation process for soil remediation. As with the *in situ* thermal desorption, the process uses heat to drive off volatile contaminants such as petroleum hydrocarbons, chlorinated organics and trace elements such as mercury. *Ex situ* thermal desorption is generally undertaken using two principle methodologies: in pile and continuously fed rotary processing plants. In pile thermal desorption involves the construction of a sealed treatment area on a location close to the polluted soil. The polluted soil is excavated and placed in the treatment area along with the heating and extraction network. The pile is sealed with an extraction cover with the extracted contaminants recovered, filtered or destroyed in a catalytic oxidizer.

Thermal desorption plants are rotary heaters that are continuously fed with polluted soil (Figure 28). As the soil travels through the rotary heater, the volatile contaminants are driven off. The process is operated anaerobically under a vacuum or with a carrier gas to ensure that the volatilized gases do not combust in the desorption unit. Depending on the nature of the off-gases, they can be condensed and collected, or destroyed in a secondary combustion chamber or by catalytic oxidation. Whether condensing or destroying the off-gases, the emissions to air would have to be treated to remove particulates and acid gases. Most thermal desorption units are heated indirectly to avoid the risk of combustion. The temperature of the operation will depend on the nature of the contaminants. At high temperatures, it is possible that some of the organic contaminants will be pyrolysed into lower molecular weight compounds.

Figure 28. On site rotary thermal desorption.

Source: adapted from Vander Linden and McCreery, 2013.

Thermal desorption plants can be operated on the site of the contaminated soil or as a pre-treatment process at the disposal facility, such as high temperature incinerator or cement kiln. Operating the rotary thermal desorption plant on the site has the advantage that the excavated soil does not need to

Case study 16. On-site rotary thermal desorption of hydrocarbon polluted soil at former Zastava industrial site. Kragujevac, Serbia.

In the late 2010s, the FIAT automobile manufacture acquired the former Zastava industrial site in order to construct a new manufacturing facility (Figure 29). The conceptual site model identified 134 000 m^3 of soil that was heavily polluted with hydrocarbons at concentrations that ranged from 5 000 mg/kg to 70 000 mg/kg. The remediation target agreed with FIAT and the regulatory authorities was to achieve concentrations less than 750 mg/kg. Given the urgency to redevelop the site, a remediation technology was needed that would process the soil rapidly and guarantee the achievement of the remediation target. Given the large volumes to be treated, excavation and on site rotary thermal desorption and thermal oxidation of the volatilized hydrocarbons was chosen as the most suitable technology. The modular plant was shipped and assembled on the site. The soils were excavated and screened to 50 mm. The oversized fraction did not require further treatment. The fraction below 50 mm was fed to the indirectly heated rotary thermal desorption unit (Figure 30), where the hydrocarbons were volatilized and destroyed in the thermal oxidizer. Throughout the operation there was a programme of environmental monitoring for air emissions, stack emissions and noise level, as well as quality control of the treated soil. The treated soils were backfilled on the site. The treatment rate was 7 500 m^3/month and the whole operation took 18 months to treat the 134 000 m^3.

Figure 29. The modular plant and contamination site. ©GRS Valtech, undated.

Figure 30. Soil post treatment thermal desorption using the modular plant. ©GRS Valtech, undated.

13.4.8.2. *In pile* thermal desorption

In pile thermal desorption technologies function very similarly to the *in situ* thermal desorption that is described in *section 13.4.3.3*. In pile thermal desorption involves the construction of a sealed treatment area on a location close to the polluted soil. The polluted soil is excavated and placed in the pile along with the heating and extraction network. The advantage of in pile thermal desorption is that the soil can be homogenized and, if necessary, reagents added. With the installation of the insulated and impermeable linings, the extraction system and the heating wells during the construction of the pile, the process can be more efficient and more easily controlled.

Case study 17. In pile thermal desorption and thermal oxidation of vapours at industrial site. Harnes, France.

Soil at this 34 ha former industrial site was mainly polluted with oil and legionella bacteria, with smaller areas with high concentrations of asbestos and trace elements. The conceptual site model identified the heterogeneity of the pollution with a number of areas of localized pollution dispersed over the whole site. *In situ* thermal desorption was ruled out because the spatial dispersion of the pollution hot spots. *In situ* technologies that involved the injection of air or water were also excluded because of the risks of fugitive emissions of legionella. A remediation strategy based around excavation and on site *ex situ* in pile thermal desorption was selected (Figure 31). The temperatures in the piles would be sufficient to destroy the legionella bacteria. A treatment zone measuring 7 566 m^2 was constructed with three piles and the vapour treatment plant. Soil was excavated and transported to the treatment area where the piles were constructed. Each pile contained 2 000 m^3 of polluted soil. The overall process time for each pile was 3 to 4 months which was made up of 30 days for excavation and construction, 50 days treatment, 15 days cooling and 20 days dismantling and back-filling the remediated soil. A total of 12 000 m^3 polluted soil were remediated over 1.5 years (information provided by Haemers Technologies).

Figure 31. Side view of one of the piles with heaters and part of the extraction and treatment system. ©Haemers Technologies.

13.4.8.3. Cement kilns

Increasingly the cement industry is seeking to improve the sustainability of its manufacturing processes by substituting virgin raw materials with secondary materials or by-products from other industries. The high temperatures and residence time of modern pre-calcining cement kilns potentially make them suitable for being adapted to process polluted soils. The organic contaminants are oxidized and the non-volatile trace elements and soil minerals are incorporated in the cement. Maintaining the quality of the final cement product is crucial, so it is necessary to analyse both the mineral composition of the soil and the concentration of the contaminants, such that the materials can be pre-processed and introduced into the kiln at appropriate points and feed rates. Soil is generally ground and homogenized in a pre-processing unit. In some kilns it is also dried, with any volatile emissions being combusted in the kiln. There are two main points where soils with organic contaminants may be fed into the kiln, the main burner and the pre-calciner. Commonly, pre-processed soils with high concentrations of hazardous organic contaminants are mixed with the fuel (liquid or powdered coal) or water and injected alongside the main burner at the hot end of the rotary kiln. In the last ten years Chinese cement companies have developed pre-processing technology to dry and grind the soil. The dried soil and the off gases from the drier, which will contain contaminants volatilized during the drying process, are fed directly into the pre-calciner. The advantages and disadvantages of each method are summarised in Table 4.

Table 4. Comparison of feeding points

Cement has strict quality standards on the concentration of halogen salts and trace elements, so heavily polluted soils may not be suitable. The soil minerals are absorbed into the clinker along with the other raw materials that have been fed through the pre-heater section. The exhaust gases from kiln pass through a series of cyclones and filters to remove and recycle particulate or gaseous emissions. Soils with volatile trace elements such as mercury are not suitable for use in a cement kiln. Soils polluted with DDT have been successfully used as secondary raw materials in Viet Nam and China (Li *et al.*, 2015; Yan *et al.*, 2014).

Case study 18. Huaxin Cement, remediation of 400 000 tonnes of soil polluted with DDT and hexachlorocyclohexane (HCH). Hubei, People's Republic of China.

Due to the expansion of the city, there was a need to rapidly remediate an old production site of DDT and lindane pesticides. Soils with POPs concentration below 50 mg/kg were bioremediated. It was decided to thermally oxidize soils having higher concentrations of DDT (243 mg/kg to 429 mg/kg) and HCH (37.9 mg/kg to 60.6 mg/kg) by using the soil as an alternative raw material in the Huaxin Cement kiln. The plant was specifically modified for the purpose. A pre-processing unit (CSP) that ground and dried the soil was constructed (Figure 32). Hot gases (300 ºC to 350 ºC) from the clinker cooler passed through the CSP to partially volatilize the DDT and HCH contaminants and dry the soil. The exhaust gases from the CSP were combusted in the pre-calciner. The ball mill in the CSP ground the soil to less than 200 µm which was stored in a silo before being fed pneumatically into the pre-calciner (1 000 ºC) where the remaining DDT and HCH contaminates were combusted. The soil passed through the rotary kiln with the other raw materials and was converted to cement clinker.

Figure 32. Schematic of Huaxin Cement polluted soil processing.

Source: adapted from Li *et al.*, 2015.

Trial burns demonstrated the effectiveness of the process with destruction and removal efficiency of greater than 99.9 percent and PCDD and PCDF emissions from the stack less than the 0.1 ng/Nm^3 TEQ which conforms to Chinese and European Union regulations. During operations quarterly monitoring confirmed that the emissions standards were maintained. The plant successfully co-processed 400 000 tonnes of soil polluted with DDT and HCH within two years (Li *et*

13.4.8.4. Incineration

High temperature incineration is a well-proven commercially available destruction technology for a wide range of hazardous waste. These facilities tend to be large and complex operations located to serve the needs of major centres of chemical and manufacturing industries. They are regulated under national environmental legislation and have operating permits that set limits for the types and characteristics of wastes that can be treated and for the emissions to air and water. As a dedicated hazardous waste destruction technology, high temperature incineration can treat the soils with extremely high levels of pollution of the most persistent contaminants including high concentrations of POPs.

The typical design includes a rotary kiln primary combustion chamber with feed systems for solid and liquid wastes (Figure 33). The solids form a glassy slag that is quenched in a water bath and extracted for recycling or disposal. To ensure complete combustion, the hot gases pass through a secondary combustion chamber where they remain at a temperature of at least 1 100 ºC in an oxidising atmosphere for a minimum of two seconds. The gases are quenched to avoid the potential for reformation of polychlorinated dibenzo dioxins and furans, and then pass through scrubbers and particulate filters before being released to atmosphere.

Figure 33. Design of a typical high temperature incinerator. ©Veolia.

Polluted soil can be treated directly in the rotary kiln. However, it is likely to be more efficient to pre-treat the soil with physical separation followed by thermal desorption such that only the contaminants are destroyed in the incinerator.

Case study 19. Remediation of former chemical manufacturing site. Mantova, Italy.

The polluted site is being remediated by ENI Rewind and extends 90 ha within the 614 ha Chemical Complex at Mantova, one of Italy’s largest petrochemical industrial sites, which has been designated a Site of National Interest for reclamation and environmental clean-up. The site consists of two zones that require remediation, known as Collina and Cratere (Figure 34). The pollution in the two zones has the same origin, wastes from the chloralkali process and the manufacture of chlorinated organics. Collina is characterized as contaminated soil, while Cratere has higher concentration of contaminants and is sludgy. The details of each zone and concentration of the contaminants are shown in Table 5 below.

Table 5. Quantities and Concentration of contaminants in each zone.

Source: information provided by Veolia.

Figure 34. Aerial view of Cratere (foreground) and Collina (background). ©Veolia.

The remediation strategy was agreed with the regulatory authorities. For the polluted materials in both zones, due to the high concentration of highly stable chlorinated organic contaminants and mercury, the only option was to excavate the materials and transport them for destruction in a high temperature incinerator. As Italy does not have sufficient incineration capacity that is licensed to accept such materials, they are being transported to high temperature incinerators of the SARP Industries – Veolia Group in France. These facilities were able to thermally oxidize the chlorinated organics and capture the mercury contaminates in the gas cleaning system prior to emissions to atmosphere. The less polluted soils are being treated in GRS Valtech's direct-fired thermal desorption treatment facility also in France.

The excavation operations were planned to commence first in the Collina zone and must be carefully managed to avoid fugitive emissions. A steel framed roof was constructed over the site and sealed such that the air and vapours in the working area could be extracted and treated before emission to atmosphere (Figure 35). The excavation vehicles were designed to be intrinsically safe to work in a potentially flammable atmosphere.

Figure 35. Sliding roof over excavation zone of Collina. ©Veolia.

The remediation strategy for Collina anticipates a total of 100 000 tonnes of polluted soil of which 50 percent is classified as hazardous and requires thermal treatment, with the remainder suitable for landfill in Italy. It is expected that 30 000 tonnes will be treated by thermal desorption and 17 000 tonnes by high temperature incineration.

It is anticipated that 78 000 tonnes of contaminated soil and wastes from Cratere will be sent for destruction by high temperature incineration.

The project started in July 2017 and is expected to complete in 2025. The total cost of the project is expected to be USD 300 billion, which includes USD 70 million for disposal by high temperature incineration and thermal desorption.

13.4.9. Sequestration

Sequestering aims to reduce the public health and environmental risks associated with the polluted soil by interrupting the pathway for the hazardous contaminants to reach a receptor.

Where there is an urgency to eliminate the polluted soil, for example to redevelop the site, or where insufficient funds are available for any of the treatment techniques discussed above, excavation and off-site disposal in an engineered landfill is an option. For soils with contaminants that cannot easily be treated, such as radioactive isotopes, engineered landfill can be a potential option. This is sometimes referred to as “dig-and-dump”. The polluted soil will be considered a waste. The transport and disposal will need to comply with any national hazardous waste regulations. To avoid the contaminants leaching from the soil during its repository in the landfill, it may be appropriate to stabilize them in the soil before disposal (Stablex Canada Inc., 2020). The landfill should guarantee the encapsulation of the polluted material with an impermeable lining and a leachate collection and treatment system. The landfill surface should be capped to avoid water ingress and minimize leachate generation, and to avoid the escape of gases and vapours which should also have a dedicated extraction and treatment system. There should be a long-term programme of monitoring and maintenance of the landfill even after it has been completed and closed. As capacity at landfill sites is often limited and viewed as a strategic resource, many landowners and regulatory regimes are attempting to minimize “dig and dump” solutions. As landfill is at the bottom of the waste management hierarchy many regulatory regimes are promoting the circular economy and imposing tax on landfills to encourage more sustainable management of polluted soil and other wastes (European Commission, 2019).

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[6] https://www.epa.gov/remedytech/remediation-technologies-cleaning-contaminated-sites

[7] https://www.itrcweb.org/

[8] https://www.claire.co.uk/

[9] https://clu-in.org/techfocus/default.focus/sec/Soil_Vapor_Extraction/cat/Overview/

[10] https://clu-in.org/techfocus/default.focus/sec/Air_Sparging/cat/Overview/

[11] https://clu-in.org/techfocus/default.focus/sec/Multi-Phase_Extraction/cat/Overview/

[12] https://clu-in.org/techfocus/default.focus/sec/In_Situ_Oxidation/cat/Overview/

[13] https://clu-in.org/techfocus/default.focus/sec/In_Situ_Chemical_Reduction/cat/Overview/

[14] https://clu-in.org/techfocus/default.focus/sec/Thermal_Treatment%3A_In_Situ/cat/Overview/