In-Situ Remediation Approaches for the Management of Contaminated Sites: A Comprehensive Overview

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Abbreviations

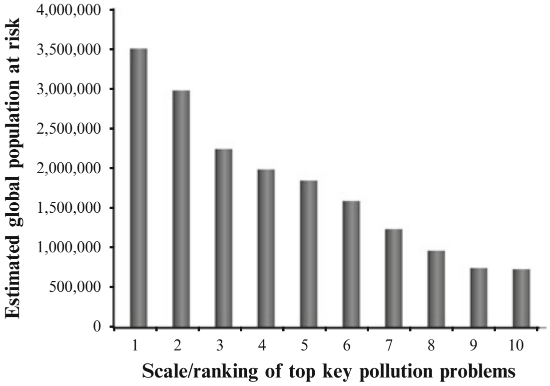
$	Dollar
<	Less than
>	Greater than
2,4-D	2,4-Dichlorophenoxyacetic acid
Ag	Silver
Al	Aluminium
AM	Arbuscular mycorrhiza
As	Arsenic
B	Boron
Be	Beryllium
BTEX	Benzene toluene, ethylbenzene and xylenes
C	Carbon
CCA	Chromated copper arsenate
Cd	Cadmium
CEC	Contaminants of emerging concern
CFU	Colony forming units
CN	Cyanide
Co	Cobalt
Cr	Chromium
Cs	Cesium
Cu	Copper
DC	Direct current
DCA	Dichloroaniline
DCE	Dichloroethane
DDT	Dichlorodiphenyltrichloroethane
DNA	Deoxyribonucleic acid
DNAPL	Dense non-aqueous phase liquid
DPE	Dual-phase extraction
DUS/HPO	Dynamic underground steam stripping with hydrous oxidation
EDTA	Ethylenediaminetetraacetic acid
EPH	Extractable petroleum hydrocarbons

EZVI	Emulsified zero-valent iron
FCC	Federal Communications Commission
Fe	Iron
Fe_2O_3	Iron oxide
FRTR	Federal Remediation Technologies Roundtable
g	Gram
GAC	Granular activated carbon
GHz	Gigahertz
h	Hour
HCB	Hexachlorobenzene
Hg	Mercury
HMW	High molecular weight
HPCD	Hydroxypropyl cyclodextrine
HTTD	High temperature thermal desorption
IAA	Indole-3-acetic acid
ISTD	In-situ thermal desorption
ISV	In-situ vitrification
J	Joule
K	Potassium
kg	Kilogram
kW	Kilo-watt
L	Litre
LNAPL	Light non-aqueous phase liquid
LTTD	Low temperature thermal desorption
m	Metre
M	Molar
MFCs	Microbial fuel cells
mg	Milligram
Mg	Megagram
MHz	Megahertz
min	Minute
Mn	Manganese
MPE	Multi-phase extraction
MTBE	Methyl tertiary-butyl ether
N	Nitrogen
n	Nano
NAD	Nicotinamide adenine dinucleotide
NAPL	Non-aqueous phase liquid
NH_3	Ammonia
Ni	Nickel
NO_3	Nitrate
P	Phosphorous
PAHs	Polycyclic aromatic hydrocarbons
Pb	Lead
PCBs	Polychlorinated biphenyls
PCDD	Polychlorinated dibenzo-*p*-dioxins
PCDF	Polychlorinated dibenzofurans

PCE	Perchloroethylene
PCP	Pentachlorophenol
PCPP	Pharmaceutical and personal care products
PFAS	Polyfluoroalkyl substances
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctanesulfonic acid
PFOSF	Perfluorooctanesulfonyl fluoride
PO_4	Phosphate
POPs	Persistent organic pollutants
PRB	Permeable reactive barrier
RDX	Royal demolition explosive
s	Second
Sb	Antimony
Sb_2O_3	Antimony trioxide
Se	Selenium
SO_4	Sulphate
Sr	Strontium
SVE	Soil vapor extraction
TCA	Trichloroethane
TCE	Trichloroethylene
TI	Thallium
TMB	Trimethylbenzene
TNT	Trinitrotoluene
TPH	Total petroleum hydrocarbons
U	Uranium
US EPA	United States Environmental Protection Agency
UV	Ultra-violet
V	Volt
VC	Vinyl chloride
VOC	Volatile organic compounds
W	Watts
WHO	World Health Organization
Zn	Zinc
ZVI	Zero-valent iron
µg	Microgram

1 Introduction

One of the major threats to the global environment addressed by the United States Environmental Protection Agency (US EPA) and World Health Organization (WHO) is ‘pollutants’. Pollutants are organic and inorganic man-made chemicals that contaminate the natural ecosystem. Due to industrialization and urbanization, the global chemical output grew from US$ of 171 billion in 1970 to 4.12 trillion by



In the figure, numerical from 1-10 signifies the scale/ranking of top ten key pollution problems with their respective source industry as detailed below:

1. Artisanal gold mining (Mercury pollution)
2. Industrial estates (Lead pollution)
3. Agricultural production (Pesticide pollution)
4. Lead smelting (Lead pollution)
5. Tannery operations (Chromium pollution)
6. Mining and ore processing (Mercury pollution)
7. Mining and ore processing (Lead pollution)
8. Lead-acid battery recycling (Lead pollution)
9. Naturally-occurring arsenic in groundwater (Arsenic pollution)
10. Pesticide manufacturing and storage (Pesticide pollution)

Fig. 1 Top ten toxic pollution problems and the estimated global population at risk. *Source*: Blacksmith Institute (2011)

2010 (Blacksmith Institute 2011). Mining activities, pesticides in agriculture, industrial manufacturing activities and accidents, vehicle emissions, and disposal of industrial effluents in natural waterbodies have been responsible for the outbreak of ten major toxic pollution problems in terms of number of people affected. These problems have subjected several million people at direct risk (see Fig. 1). The major source of toxic hot spots worldwide, viz., oil production along with its ancillary industries, does not appear in Fig. 1. It is because of the fact that sites that are contaminated by petrochemical industry tend to be neither abandoned nor defunct and are largely immune from regulatory control, and therefore this source has not been included in the list of world's top ten most toxic pollution problems by Blacksmith Institute (2011).

Over one thousand million pounds of toxic chemicals escape into groundwater and air annually. Currently, around two billion people worldwide drink contaminated water and breathe in high levels of toxic gases every day (GLIMUN 2009). These environmental pollutants can be broadly grouped into two kinds: firstly, priority (hazardous materials with a sufficient toxicological profile and regulated mitigation guidelines); and secondly, emerging (newly detected compounds that lack sufficient detection methods and regulated mitigation strategies) pollutants that include both organics and inorganics. The 21 POPs listed by Stockholm Convention (2010) include aldrin, chlordane, chlordecone, dieldrin, dichlorodiphenyltrichloroethane (DDT), endrin, heptachlor, hexachlorobenzene, α-hexachlorocyclohexane, β-hexachlorocyclohexane, hexabromobiphenyl, hexabromodiphenyl ether and heptabromodiphenyl ether, hexachlorobenzene (HCB), mirex, lindane (γ-hexachlorocyclohexane), toxaphene, pentachlorobenzene, tetrabromodiphenyl ether, pentabromodiphenyl ether, polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins (dioxins/PCDD), polychlorinated dibenzofurans (PCDF), perfluorooctanesulfonic acid (PFOS) and its salts, and perfluorooctanesulfonyl fluoride (PFOSF).

The priority inorganics listed by US EPA are metal(oid) and non-metals like cadmium (Cd), lead (Pb), antimony (Sb), arsenic (As), mercury (Hg), selenium (Se), silver (Ag), zinc (Zn), nickel (Ni), beryllium (Be), thallium (Ti), copper (Cu), nitrate (NO_3), ammonia (NH_3), sulphate (SO_4), phosphate (PO_4) and cyanide (CN). Chemicals that were not detected previously are being discovered in water and food. The most frequently conferred emerging pollutants include outsized classes of algal toxins, illegal drugs, nanoparticles, detergents, anti-fouling/foaming/corrosive chemicals, new pesticides, antimicrobials, disinfectants, antioxidants, flame retardants, chelating agents, artificial food preservatives, disruptive compounds, cosmetics, fuel additives, chemico-industrial by-products, man-made flourinated compounds, pharmaceutical and personal care products (PPCP), plasticizers and preservatives used to treat wood. Currently, the US EPA is investigating the contaminants of emerging concern (CECs) owing to the hazard they pose to health and ecology.

Toxic pesticides share the POPs listed in the elimination annexes under the Stockholm Convention. Though highly persistent, DDT is banned in many countries, but recent studies in South Africa continue to show up to 1930 ng DDT/g milk fat (Okonkwo et al. 2008). Limited use of banned chemicals like DDT in malaria vector control continues and remains controversial. In the US alone, about 34,000 Mg of PBDEs are exploited anually as flame retardants in automobiles, fabrics, furniture foams, construction materials, electronics and other appliances (McDonald 2005). PFAS like PFOS and PFOA persist in the environment (Buck et al. 2011) and bioaccumulate in human blood to a range of 30–44 μg/L causing bladder cancer and neurobehavioral alterations (Stockholm Convention 2005). According to the US EPA and European government agencies, from the 1990s onward much research costing billions of dollars was spent investigating the impact of carcinogenic POPs like PAHs and PCDD/Fs on people’s health (Jones and De Voogt 1999).

About 100 different highly toxic PAHs originate from the incomplete burning of coal/petroleum/natural gas/waste, wood treatments, industrial liquefaction and gasification processes. Higher levels of contamination of about 300 g PAHs/g soil were been recorded as having cancerous effects (Megharaj et al. 2011). MTBE spilled from car accidents is an additional model of a compound that is now noticed in waterbodies at higher concentrations, thus posing a threat to human health (Klinger et al. 2002). The US EPA (2004) estimates that over 50 million m^3 soils (77 %) of the current superfund sites are contaminated with metals. Pb, Cd, Zn and As are highly hazardous heavy metals that persist at contaminated spots and can damage health and the environment. WHO (2003) set a guideline of 10 μg/L of As in drinking water. Phytotoxic effect and acute toxicity of Pb, Cd and Zn at high concentrations cause tumour cells in later stages of accumulation in aquatic receptors. Continuous exposure to non-metals like CN and SO_4 that are widely applied in medicine, mining, agriculture and food industries cause lung disease, heart problems and stomach ulcers in humans (Baselt and Cravey 2008).

Contaminants like phthalates and bisphenol A have been used in plasticizers as well as cosmetics for more than 50 years, and their production reached a recent peak of 3 million Mg (Deblonde et al. 2011). Many PPCPs like illicit drugs have been detected in the surface and groundwater systems associated with wastewater disposal

Table 1 Use of chemicals in the global industrial sector and its projections by 2016

Significant sector	Specific chemicals used	Global market projection: Market value by 2011 (billion)	Global market projection: Anticipated increase (%) by 2016	Leading nations in market	Reference
Electronics	Heavy metals, rare earth metals, solvents, polymers and flame retardants	30.7	15–20	China, USA, Japan and Germany	BCC Research (2011)
Textile	Oils, waxes, surfactants, flame retardants and water repellents	19	30	China, Asian countries, Middle east countries, Africa, Central and Eastern Europe	PR Newswire (2012)
Flame retardants	Brominated and chlorinated organics and inorganics	5.1	8–10	USA, Europe, Asia-Pacific China, North America and Asian countries	Industry Experts (2011)
Cement	Petroleum coke, coal, Hg, acid gases, VOCs, PAHs and dioxins/furans	200	14	China, India and USA	USGS (2011)

that can potentially lead to immunity deficit, endocrine disruption, nerve disorders and DNA repair (Johnson et al. 2008). For instance, the high rate of vulture mortality in India was by the direct oral exposure to veterinary diclofenac through feeding diclofenac-treated livestock (Oaks et al. 2004). The widespread use and sorption behavior of disinfectants, hormones and sterols in personal care products such as shampoos, soaps, cosmetics, deodorants, skin-care lotions, mouth rinses and tooth pastes contaminate the biosphere. Exposure of the human body to genotoxic nanoparticles (chemically-synthesized metal nanoparticles) is increasing daily due to advances in technology.

Daughton (2004) noted that out of 22,000 unregulated organic and inorganic chemical pollutants, nearly 6000 are commercially available and only fewer than 200 of them are addressed by the current regulations of US EPA and WHO. Moreover, the projected aim to increase the market values (up to 14–30 %) of specific industrial sectors that commercially use ample quantities of chemicals like heavy metals, flame retardants, dioxins/furans and PAHs in the leading nations by 2016 (Table 1), would elevate the level of environmental pollutants. They will pose a serious threat to living organisms by 2050 (BCC Research 2011; Industry Experts 2011; USGS 2011; PR Newswire 2012). Trillions of dollars are expected to be spent for the clean up of polluted sites in the USA alone (Kuiper et al. 2004). It is therefore important to restrain these priorities and emerging pollutants by developing newer and more appropriate cost-effective remedial tools that are rapid, realistic and adaptable in many physical settings.

For more than a decade, the primary focus of environmental experts is to adopt risk-based management approaches to clean up polluted sites. The need for the effective risk-based remediation led to the development of several physical, chemical, thermal and biological ex-situ and in-situ technologies that are currently widely used at contaminated sites (Sharma and Reddy 2004). *In*-situ is 'in place' remediation, where the soil is not unearthed but treated in the original place of contamination. In-situ remediation is a good option, since excavation involving higher transport costs is not an option when the treatment site is large and/or of greater depth in the soil. However, due to the soil heterogeneity, it is quite challenging to achieve uniform remediation throughout the treatment area (Carberry and Wik 2001).

In contrast, ex-situ approaches comprise the excavation of impacted media from the subsurface for on-site treatment or off-site disposal and subsequent re-deposition of the cleaned up soil. Ex-situ treatment time is generally shorter than in-situ and provides more treatment uniformity due to the possibility to screen, homogenize and monitor the contaminants. However, the cost of ex-situ treatment is high as excavation is involved and in most cases in-situ remediation is employed to treat contaminated sites, and research is more focused on developing in-situ remedial techniques than ex-situ (Jain et al. 2011). In-situ remedial approaches available for the clean up of polluted sites are many as described below, and can be broadly classified as technologies suitable for: (1) soil/sludge/sediment treatments like chemical extraction, flushing, fracturing, thermal desorption, vitrification, bioaugmentation, biostimulation, phytoremediation and electrokinetic separation; (2) groundwater/fresh water/leachate treatments such as subsurface steaming, dual-phase extraction, air sparging, bioslurping, natural attenuation and air stripping; (3) containments like physical barriers and reactive treatment walls; and (4) hazardous gas emission treatments, for example chemical oxidation, membrane bioreactors and biofiltration. Integrating physico-chemical and biological technologies is widely practiced for better clean up of polluted sites. Recently, for promising detoxification and destruction of contaminants, novel systems like mixed cell culture system, microbial fuel cells, metagenomic approaches and nanoremediation have been developed for treating various types of site-specific pollutants.

Though several in-situ treatment methods exist to remediate polluted sites, selecting an appropriate site-specific remediation technology is challenging, but is critical for successful clean up of polluted sites. Hence, a comprehensive overview of all the available remediation technologies to date is necessary to choose the right technology for an anticipated pollutant. In this review, we critically evaluate and discuss the following: (1) technological profile of existing in-situ remediation technologies for priority and emerging pollutants; (2) recent innovative technologies for on-site pollutant remediation; and (3) current challenges as well as future prospects for developing innovative approaches to enhance the efficacy of remediation at contaminated sites.

2 Selection and Suitability of Remedial Measures

The process of removing harmful chemicals from the contaminated air, soil and water (removal), or treating the contaminated site in order to change the harmful chemicals into less harmful ones (treatment), or leaving the contaminants in the ground and taking steps to prevent them from entering into soil, water and air, and to avert their spread to the people (containment) is stated as ‘remediation’. The technological solutions that help to meet the site remediation goals within a reasonable period of time are collectively termed ‘remediation technology’. In the last decade, the number of remedial techniques has increased considerably. Comprehensive information of specific remedial options suited for individual pollutants are summarized in many studies (Khan et al. 2004; Juwarkar et al. 2010; Megharaj et al. 2011). Due to the availability of various remediation technologies, selecting the right strategy has become a vital component in the risk-based management of contaminated sites.

Many factors need to be well considered in choosing a suitable remedial solution to a polluted land issue (Vik et al. 2001). These include: (a) the goals of the remediation work, for example, the aim to protect the environment and human health enabling the restoration of a formerly used land, and to limit the potential liabilities of a land, (b) risk management, (c) sustainable development, (d) stakeholders’ views, (e) cost-benefit ratio, and (f) technological suitability and feasibility. Selection and suitability govern the promising outcomes of the process-based pollutant treatment. The factors that affect the suitability of remedial approaches are: (a) risk management applications (source reduction, pathway interruption and protection of receptors), (b) contaminants to be treated (type, concentration range, source, age and material handling characteristics), (c) remedial approach (removal, containment, rehabilitation, physical treatment, chemical treatment, biological treatment, solidification/stabilisation and thermal treatment), (d) process location (in-situ, ex-situ, on-site, off-site and in-vessel), (e) strategy (integrated approach, active or passive measures, long-term/low input, carrier-based measures and institutional measures), (f) implementation (process planning, site management, verification, monitoring, neighborhood impacts, aftercare and flexibility), and (g) outcome (recycling, destruction, removal, stabilisation and immobilization). Thus, considering the above factors, a right remediation technology can be selected for successful clean up of a problematic site. Available physical, chemical and biological technologies to remove pollutants in-place or in-situ are discussed below.

3 *In-Situ* Remediation Technologies for Soil and Groundwater

In-situ remediation technologies can be broadly classified as existing and emerging remedial options. Existing/established techniques include heating, soil flushing, fracturing, electrokinetic separation, physical barriers, soil vapor extraction, multi-phase extraction, air-sparging, natural attenuation, bioventing, bioaugmentation, biostimulation, and phytoremediation. Emerging techniques include microbial fuel cells, nanoremediation, genetic engineering, and photo-hetero microbial system. The following sections present a brief overview of the existing in-situ remedial options.

3.1 Heating

The focus of in-situ heating technique is to increase temperature, decrease viscosity and adsorption, and increase solubility, facilitating the recovery of volatile and semi-volatile compounds (Khaitan et al. 2006). Heating is a promising approach to remediate NAPLs (non-aqueous phase liquids) and DNAPLs (dense non-aqueous phase liquids) (Table 2). Electrical resistance heating, injection of hot air and steam, thermal conductive heating, electromagnetic heating (radiofrequency/microwave technology) and vitrification-enhanced thermal decontamination are the five fully-developed, short- to medium-term thermal treatment techniques (Triplett Kingston et al. 2010). Heating does not remove contaminants but modifies their biological, chemical and physical properties, and that of soils and groundwater. This makes them more amenable to remediation efforts like soil vapor extraction, air sparging, bioremediation, etc. Overall, heating improves the performance of other technologies which ultimately reduce the remedial time frames and costs involved.

3.1.1 Injection: Steam/Hot Air

Injection of steam/hot air was developed to enhance the recovery of oil from petroleum reservoirs. Here, hot air/steam is injected downstream to the polluted land surface through injection wells. Injected steam/hot air heat the contaminated soil, vaporizes the contaminants and the vapors are stored in a condensation tank from where they are recovered either by physical displacement, co-distillation, vacuum extraction or enhanced desorption (US EPA 2006). Steam is injected in a cyclical manner whenever the soil reaches the steam temperature. Udell and McCarter (1998) found that cyclic steam injection enhances mass transfer and accelerates the clean up process. Schmidt et al. (2002) confirmed that injection of steam with air accelerated the rate of pollutant removal. Combination of steam injection with auger mixing system (steam is injected through augers of specific design) proved to be effective (Davis 1998). Laboratory studies and field demonstrations also confirmed this technology's ability to effectively recover up to 99 % volatile and semi-volatile organics (VOCs and SVOCs) such as diesel or jet fuels and some chlorinated solvents from the subsurface (Heron et al. 2005). Efficiency and effectiveness of this process depend on site characteristics which determine the contaminant distribution and preferred flow path of the injected steam.

Table 2 Field demonstrations of in-situ heating technologies at US EPA superfund sites

Remediated site	Contaminants of concern	Volume treated	Initial contaminant level	Target temperature (°C)	Target power (kW)	Duration (months)	% Remediated	Outcome	Reference	Lessons learnt
Electrical resistance heating (ERH)										
1. Installation restoration site 5, Alameda Point, Alameda, California	TCA, EDC, DCE	1104 m^3 soil	9600 mg/kg	22–92	421,000	6	86.5	+	Cacciatore et al. (2003)	Extracted contaminated vapors can be condensed and treated using granular activated carbon for better recovery
2. US DOE, Young-Rainey STAR center, Largo, Florida	TCE, DCE, Methylene chloride, Toluene, Petroleum hydrocarbons	9930 m^3 aquifer	2500 kg	84	>400	4.5	99.8	++	Heron et al. (2005)	Combination of steam-enhanced extraction and ERH is effective in heating the treatment zones
3. Charleston naval complex, South Carolina	DCE, VC, TCE Halogenated VOCs	3287 m^3 soil	9890 mg/kg	89	278	9	86.0	+	FRTR (2005b)	ERH performance can be rectified by using enhanced reductive dechlorination
4. ICN Pharmaceuticals site, Portland, Oregon	TCE, DCE, VC, Benzene, Toluene	39,000 Mg soil	544,000 mg/kg	NA	950	8	99.0	++	Sutter (2012)	Creation of ‘hot floor’ and heat up ‘walls’ prevent vertical as well as lateral migrations of steam and DNAPLs

(continued)

Table 2 (continued)

Remediated site	Contaminants of concern	Volume treated	Initial contaminant level	Target temperature (°C)	Target power (kW)	Duration (months)	% Remediated	Outcome	Reference	Lessons learnt
5. Air force plant 4, Fort Worth, Texas	TCE, Halogenated VOCs	3000 m^3 soil	2770 mg/kg	60	1300–2000	2.5	95.0	++	US EPA (2012)	Six phase ERH is highly suitable to remediate DNAPLs at field conditions
Steam injections										
1. Lawrence Livermore national lab gasoline spill site, Livermore, US	BTEX	76,455 m^3 soil	287,690 kg	80–90	NA	7	99.9	++	US EPA (2012)	Dynamic underground stripping is suited for BTEX removal at large-scale
2. Savannah river site 321-M solvent storage tank area, Aiken, South Carolina	PCP, TCA	39,757 m^3 aquifer	12,156 kg	87	NA	7	99.0	++	FRTR (2012)	Dynamic underground steam stripping coupled with hydrous oxidation is suggestive to remediate high concentrations of contaminants
3. Former hazardous waste disposal site, Muehlacker, Germany	TCE, BTEX, Halogenated VOCs, Nonhalogenated VOCs	3000 m^3 soil	2500 kg	NA	100	10.0	95.0	++	US EPA (2012)	Monitoring of gas and liquid flow rates as well as temperature is a vital factor that decides the success of a heating system

4. A.G. Communications systems site, Warrnambool, Australia	TCE, DCE, Xylene, Benzene	NA	15,875 kg	84–140	294	6–8	99.9	++	US EPA (2003)	Steam-enhanced extraction coupled with SVE is a viable technology to cleanup hydrocarbons
5. Cape Canaveral air force station, Cape Canaveral, Florida	TCE	1070 m^3 soil	1000 mg/kg	100	NA	12–14	99.9	+	Robert et al. (2004)	Zero-valent iron injection is an alternative to steam injections. Also, integration of thermal treatments with reductive dechlorination is an innovative technology that increases the mass removal of DNAPLs
Conductive heating/ In-situ *thermal desorption* (*ISTD*)										
1. Confidential chemical manufacturing facility, Portland	DCE, TCE, Halogenated VOCs	9940 m^3 soil	NA	250	NA	6	99	++	TerraTherm (2000)	Thermal desorption combined with vacuum extraction is a suitable technology to remove organic compounds from soils
2. Terminal site 1, Richmond, California	PCP, TCE, DCE, VC	5120 m^3 sediment	2867 mg/kg	100	NA	9.0	99.9	++	TerraTherm (2010)	ISTD with dual-phase extraction is a promising technology at field-scale

(continued)

Table 2 (continued)

Remediated site	Contaminants of concern	Volume treated	Initial contaminant level	Target temperature (°C)	Target power (kW)	Duration (months)	% Remediated	Outcome	Reference	Lessons learnt
3. Naval air warfare site, West Trenton, New Jersey	TCE, DCE, VC	565 m^3 aquifer	277 mg/kg	100	4,93,000	3.5	99.0	+	Carmen (2010)	Controlled or lower groundwater flow is essential to enhance the rate of subsurface heating in shorter lifespan with accelerated VOC removal
4. Former electrical equipment service facility, Jacksonville, Florida	TCE, DCE, VC	NA	NA	100	NA	8	97	++	Amy et al. (2010)	Thermal conductive heating coupled with multi-phase extraction system is a potential technique for removal of chlorinated solvents
In-situ *radiofrequency heating* (*ISRH*)										
1. Bedrock site, Fort Lewis, Washington	TCA	850 m^3 fractured bedrock	2,50,000 mg/kg	50–60	NA	3	99.9	+	US EPA (2012)	Radio-frequency heating is suited to remediate contaminated bedrocks

2. Former petrol station, UK	BTEX, Petroleum hydrocarbons	480 m^3 Soil	1100 kg	50	30	2.0	99.0	++	Huon et al. (2012)	A mean soil temperature of more than 50 °C in the remediation volume reduces total remediation time by more than 80 % when compared to conventional ISRFH with SVE
Microwave heating										
Studies are available only at laboratory-scale										
Vitrification										
1. Oak Ridge national lab, Tennessee	Sr, Cs	NA for sludge	500 g	1500	29	5 days	99.9	++	Spalding et al. (1992)	Use of fillings like dolomitic limestone and native soil could help in reaching the processing temperature

++, Successful (Achieved remedial goals with >90 % contaminant removal); +, Partially successful (Remedial goals were not achieved in stipulated time, but >85 % contaminant was remediated); NA, Not available

Advantages of steam/hot air injection include the fact that relatively more rapid remediation is possible; excavation operations are not needed and target compounds are not pumped into the subsurface. Steam stripping/hot air injection treatments are not suitable for shallow treatment areas, but are effective in fractured rock settings (Davis et al. 2005). Major risks associated with steam/hot air injection is the displacement of contaminants by the injected fluids to areas other than recovery points and the high initial capital cost for steam injection. The problem of vertical confinement of injected steam into the vadose zone was overcome by injecting cold air above the steam injector (Hodges and Falta 2008). This costs around 51 US$ to remediate per m^3 contaminated site via steam/hot air injection (US EPA 2004).

Implementation of steam injections for cleaning up chlorinated solvents and petroleum hydrocarbons is very successful (nearly 99 % remediation) at field-scale (FRTR 2012). Dynamic underground steam stripping with hydrous oxidation (DUS/HPO) is a patented technology that helps remediate chlorinated contaminated soils at field-scale (US EPA 2001). For example, in the Savannah River superfund site in South Carolina, 39,520 m^3 of aquifer, consisting of interbedded sands and clays overlying a clayey aquitard with a groundwater depth of 44 m, contaminated with 31,100 kg chlorinated solvents (PCP and TCA), the DUS/HPO system of remediation was implemented. Nine injection wells in three clusters, three vapor extraction wells on perimeters and a combination groundwater/vapor extraction well in the center, were laid down in the treatment zone. About 20,593,440 L of steam with a heat content of 4747×10^{10} J was injected for 134 days and the source zone was heated up to 87 °C. Air was also injected by air stripping at 8 m^3/h to support HPO. When the vapors were subjected to dual phase and soil vapor extractions, the cumulative contaminant mass removal was 1000 kg TCE and 30,000 kg PCE (99.9 % remediated) after 7-month system operation (FRTR 2012). This coupled DUS/HPO technology successfully remediated 95 % BTEX, halogenated and non-halogenated VOCs in 2983 m^3 soil over 10 months. It involved proper monitoring of the physico-chemical characteristics like temperature, gas and liquid flow rate which are the critical factors that decide the success of a heating technology at field-level (US EPA 2001).

Nilsson et al. (2011) proved that steam stripping coupled with steam distillation can remove volatile and non-volatile hydrocarbons (jet fuel) even from an unsaturated zone of low permeability soils at bench-scale. The principle behind the technology is that injecting steam in the unsaturated zone of low permeability soils leads to a steady rise in the water saturation level, drastically changes the soil pore structure, and creates small fractures of micron size that act as better routes for the steam flow. The injected steam brings in contaminant vaporization. Second, heating the treatment zone to a temperature less than 100 °C in the presence of steam distillation enhances vaporization of the semivolatile and non-volatile NAPL compounds which ensures increased remedial activity. An experiment was conducted in soil spiked with decane, dodecane, methylcyclohexane, TMB and NAPL in a rectangular tank. The dry soil was humidified to bring in saturation of about 14.2 %. Dry steam of approximately 140–150 °C was injected for 10 h after which approximately 73–91 % of the NAPLs were removed. While studying the effect of steam-enhanced extraction technique coupled with soil vapor extraction at an Illinois superfund site contaminated with TCE, DCE, xylene and benzene, about 99.9 % remediation was achieved by heating the soil to a temperature of 84–140 °C for 6–8 months (US EPA 2003).

The remedial clean up of contaminated sites is not always achieved through steam stripping. Only a few field-level remediation studies have been partially successful (Table 2), where the remedial goals were not achieved within the targeted period of remediation despite the considerable reduction in the contaminant's total mass. One such example is the employment of steam injections to remediate 1070 m^3 of TCA-contaminated field at the air force station, Cape Canaveral, Florida. The remedial objective was to achieve 99.9 % remediation within 9 months of treatment. Though the soil was heated up to 100 °C, only 80 % of the VOCs were remediated in the targeted time and mostly the contaminants were bioavailable, and it took nearly 14 months to achieve 99.9 % remediation. Prolonged degradation was assumed to be due to lateral movement of contaminant to the previously treated zones which could be rectified by setting up a proper monitoring system (Robert et al. 2004). Overall, uncertainties in implementing steam injection heating at full-scale can be overcome by developing new systems of steam injections with defined operational control systems, e.g. flameless thermal oxidizer and a liquid vapor knockout system. It is recommended that off-gas stream can be monitored by using flame ionization detectors combined with dry electrolytic conductivity detectors. Thus, the most promising steam injection heating of NAPLs and DNAPLs can be improved by better system rectifications as suggested above.

3.1.2 Electrical Resistance Heating

Electrical resistance heating (ERH), developed in the early 1990s, became a commercial stand-alone method in 1997. In ERH, an electrode placed directly in zones of low permeability creates resistance to the flow of electric current. Electrical resistance heats the soil and evaporates the semi-volatile and volatile toxins as steam. The steam is then condensed and extracted vapors of the volatile organics are then treated conventionally by means of granular activated carbon (GAC) or oxidation. This technology mainly involves volatilization and steam stripping that enhances the contaminant removal speed and efficiency (Beyke 2000). However, some fraction of VOCs will be degraded in-situ naturally by hydrolysis, biodegradation and reductive dehalogenation by nanoparticles (for instance, Fe^0). ERH is applied either as three- or six-phase heating systems. Since the 1990s many full-scale six- as well as three-phase ERHs were demonstrated (McGee 2003). Today, six-phase hexagonal array and three-phase triangular array are applied to treat irregularly-shaped polluted sites where soils are heated by a low-frequency electric charge delivered through three/six electrodes in globular array.

Most applications of ERH focus on remediating chlorinated solvents and petroleum hydrocarbons (Triplett Kingston et al. 2010). About 99 % of the contaminants of low boiling point such as PCE and TCE were remediated successfully by ERHs either alone (US DOE 2005), or in combination with steam injection extraction

(Heron et al. 2005) as detailed in Table 2. In ERH, uniform heating is achieved throughout the treatment area by maintaining the temperature control monitoring points. It also provides the feasible physical conditions required for the release of contaminants from tight soil tensions to an unsaturated region, from where they are extracted either by multiphase or vapor recovery system. Yet, high concentrations of heavy hydrocarbons and organic carbon content interfere and prevent the recovery of some organic contaminants. Fractured bedrocks can only be heated by ERHs and not nonporous rocks. However, integration of ERH outlimits the treatability of soil vapor extraction and multiphase solvent extraction techniques regardless of the permeability of soil or water saturation level, almost to any physical setting (Heron et al. 2005). Treatment time by ERH is typically less than a year.

Recently, ERH has been used to treat contaminated sedimentary bedrocks, and field trials were held in Maryland, New Jersey and Indiana (Kluger and Beykle 2010). In 2006, at Annaolis, Maryland, tetrachloroethylene (TCE) contamination was observed extensively in surface soils. The site (765 m^2) was heavily cemented with dense, fine silt and sand layers that extended to 12 m beneath the ground level. The remedial objective was to reduce the TCE concentration by 95 % in the contaminated site. Bedrocks were heated up to 90 °C for 7 weeks. After the operation time, when the samples were assayed the initial TCE concentration declined by 99.9 % which was more than the anticipated goal and the study proved the reliability of ERH even for bedrock treatments. Truex et al. (2011) evaluated the co-effect of zero-valent iron (ZVI) and ERH for in-situ TCE remediation in an aquifer at field-level, and observed 85 % reduction of TCE in 60 days of heating, confirming that the success of remediation was due to enhanced in-situ dechlorination and minimization of TCE volatilization when using combined techniques. The problem of lateral migration of injected steam and DNAPLs away from the contaminated to uncontaminated zone was prevented by the creation of hot floor and heat-up walls, wherein 99 % remediation was observed in an age-old chlorinated solvent (TCE, DCE, VC, benzene and toluene)-containing site within 8 months of ERH treatment (Sutter 2012).

Electrical resistance heating has been implemented to date at field-level in various superfund sites (US DOE, Young-Rainey STAR center, Florida; ICN Pharmaceuticals site, Oregon; Air force plant, Texas; Charleston Naval complex, South Carolina and Installation restoration site, California). Six-phase ERH (US EPA 2012) was highly successful in remediating chlorinated solvents, halogenated VOCs- and BTEX-contaminated soils, groundwater and DNAPLs from >95–99 % in 3–8 months when the treatment temperature ranged from 60 to 80 °C with a target power of >400–2000 kW in most cases at full-scale. In 2003, the US DOE completed a full-scale NAPL remediation at the Young-Rainey STAR center, Florida. Contaminated zone extended to nearly 10 m below the subsurface and was about 900 m^2 in area representing a total treatment volume of 9120 m^3. The site was contaminated with approximately 2500 kg NAPL constituents such as TCE, DCE, methylene chloride, toluene and petroleum hydrocarbons. A combination of electrical resistance heating and steam-enhanced extraction was used to remediate the contaminated site. Within 6 weeks, nearly 1000-fold mass of the contaminant was removed when the site was heated to a target temperature of 84 °C. In less than 5 months, all the contaminant concentrations reached well below the remedial goals (99.8 % removal).

ERH is most successful when integrated with other in-situ techniques (Heron et al. 2005). Only in some cases ERH failed to achieve the remedial goal of >95 % of immobilized contaminant level in the limited time frame at field-scale. According to the reports of FRTR (2005a), the highly saturated condition of the soil reduced its electrical resistance and consequently the total remedial efficiency was only 86 % over 9 months even when the soil was heated to 89 °C. In such a scenario, the integration of reductive dechlorination with ERH could enhance the remediation process. Integration of ERH with several remedial systems and adoption of novel recovery systems other than GAC-like material are to be explored in the near future to overcome the partial failure when implemented at full-scale. According to US EPA (2012), it costs an estimated 42 and 96 US\$/m^3 at two full-scale ERH sites.

3.1.3 Electromagnetic Heating: Radio Frequency/Microwave

Radio frequency and microwave heating are in-situ processes that heat soil and enhance vapor extraction using electromagnetic energy. This technology had been used since the 1970s where bitumen was recovered from tar sand deposits. Radio frequency or microwave heating can be applied as identical to steam injection. The only difference is that antenna-like applicators are inserted into the exterior boreholes instead of steam. This technique can heat the soils over 300 °C. Generally, a set of frequencies (6.5, 13.5, 27.1 and 40.5 MHz for radio frequency, and 300 MHz to 300 GHz for microwave heating) assigned by the Federal Communications Commission (FCC) is used to remediate the volatile (PAHs and PCBs) as well as non-volatile (heavy metals) contaminants by electromagnetic heating (Appleton et al. 2005). Compared to conventional heating, radio frequency/microwave heating possesses the advantage of selective heating, shorter heating time, better process control and no direct contact with the heated material. It is also proved that microbial activity is not inhibited by electromagnetic fields (Jones et al. 2002). However, the technology is self-limiting because at one particular stage, the soil heats up and dries which stops the flow of current and limits the removal of the pollutant. Over the last decade, microwave technology has been integrated with UV illumination, pyrolysis and advanced oxidation processes for the conditioning and sanitation of sludge, regeneration of activated carbon and stabilization of heavy metals (Horikoshi et al. 2002; Klan and Vavrik 2006; Bo et al. 2006; Wu 2008).

Field-level application of electromagnetic heating is very limited. Especially, microwave heating is applied only at laboratory-level to clean up contaminated sites (Jones et al. 2002). Laboratory-scale trials using microwave energy to remediate contaminated soils focused mainly on the elimination of contaminants like PCBs, PAHs, HCB, chromium and heavy metals (Tai and Jou 1999; Abramovitch and Capracotta 2003; Liu and Yu 2006). Liu and Yu (2006) explored the role of GAC in microwave remediation of PCB-contaminated soil. More than 90 % PCB was remediated with 700 W microwave power after 15 min of irradiation when 200–500 °C temperature was maintained. Appleton et al. (2005) removed 99.8 % mercury, cyanides and PCBs in a very limited time span of 15 min to 3 h microwave treatment. To date, several studies proposed different microwave-incorporated remedial techniques only at lab-scale for various toxins in aqueous solutions, for example microwave irradiation in association with GAC (Bo et al. 2006), hydrogen peroxide (Klan and Vavrik 2006), UV/hydrogen peroxide (Han et al. 2004), titanium oxide nanotubes (Zhanqi et al. 2007), and UV/titanium mounted activated carbon (Liu et al. 2007). These were successful in removing 85–98 % toxins within 10–20 min microwave treatment. Thus, there is more potential to explore the performance of microwave heating in pilot- or field-scale in the near future.

On the other hand, radio frequency heating is applied at full/pilot-scale to remediate VOCs even in fractured bedrocks. Not many field-scale remediation studies are available for radio frequency heating compared to steam injection/electrical resistance heating. Huon et al. (2012) studied the effect of radiowave supported degradation of BTEX and petroleum hydrocarbons in a former petrol station site in the UK. The 99 % remediation achieved with a target temperature of 50 °C in 2 months indicated that when the target temperature is increased up to 50 °C, it attains the maximum degradation of VOCs at field-scale in a shorter period than usual. Recently, dielectric heating using radiofrequency energy is emerging as a novel choice for energy transfer applicable in quite a few remediation technologies, such as adsorptive-catalytic off-gas treatment, biodegradation, decontamination and/or drying of brickworks and thermal regeneration of drying agents in natural gas/biogas treatment (Huon et al. 2012). Overall, many possibilities exist to utilize the principle behind electromagnetic heating and employ its prime advantage of successful remediation in a short time at large-scale by designing new remedial systems. It costs about 150–250 US$ per Mg for small-scale electromagnetic heating clean up.

3.1.4 Thermal Conductive Heating/Thermal Desorption

After 12 years of improvement and full-scale demonstrations, thermal conduction heating, also known as thermal desorption, is currently a technically mature, cost-effective soil and groundwater remediation method with vacuum extraction (Heron 2008). In thermal conduction, vacuum and heat are simultaneously applied to subsurface land (to about 1 m), either with vacuum wells or surface heater blankets or with a group of vertical heaters operated at very high temperature (>500–900 °C). In this method, transport of radiant heat dominates near the heaters and most of the heating at greater soil depths is accounted by thermal conduction. As the source area gets heated up, pollutants in the soil are vaporized or destroyed either by boiling, evaporation, oxidation, pyrolysis or steam distillation (Baker and Heron 2004). Though thermal conduction heating is not designed to degrade organic pollutants, thermal desorbers can still be used to partially or completely remove the organic compounds depending upon the type of organics present and the temperature of the desorbers. Generally, the extracted hydrocarbons are discharged into the atmosphere after treating in an afterburner, carbon adsorption unit, condenser or catalytic oxidation chamber. Oxidizers and afterburners decompose the organic compounds. Carbon adsorption units and condensers trap the organics for disposal or for subsequent treatment.

A thermal remedial approach based on zone combustion method for the remediation of dioxin-contaminated zone was proposed by Kasai et al. (2000) and Harjanto et al. (2002). Stable thermal remediation of coke particles in the packed soil bed was employed in this method. In a laboratory-scale experiment, 90 % dioxin was removed from the soil, and the removal rate was improved with the pre-treatment (addition of limestone, pre-granulation and drying) of the contaminated soil. Thermal blankets and thermal wells proved to be greatly efficient in removing a diverse range of contaminants such as hydrocarbons, pesticides, PCBs, inorganics (Hg, As and Cd), DNAPLs, gasoline, combination of radionuclides, chlorinated solvents, carcinogens, etc. (Conley et al. 2000; TerraTherm 2010).

Generally, there are two types of thermal desorption systems based on the temperature employed: high temperature (HTTD: 315–537 °C) and low temperature (LTTD: 93–315 °C) thermal desorption systems. LTTD/hot gas decontamination is applicable for VOCs and fuels, wherein HTTD is useful to remove SVOCs, PAHs, PCBs and pesticides. Hot gas decontamination/LTTD removed 99.9 % explosives at the US Army Environmental Center, and is widely used to decontaminate the equipment and structures polluted with explosive residues using a temperature of 250 °C created by hot air (US EPA 2012). Time taken to clean up 20,000 Mg contaminated material was only 4 months with the LTTD system (FRTR 2005b). Another advantage is that the system's effectiveness is not affected by the subsurface heterogeneities compared to other methods. With reference to conductive heating, the distance between the wells is taken into account because the closer the wells are, the faster the desired temperature obtained with increased remedial efficiency (Bierschenk et al. 2004). Conductive heating operates best in unsaturated soil. In case of soils with low hydraulic conductivity, dewatering and combination of piping activities promote the pollutant degradability (US EPA 2004).

Compared to steam injection, vertical and horizontal sweep is very uniform in conductive heating/thermal desorption system. Also, ISTD is adaptable to many types of *ex*-situ processes. Since flow paths are created even in tight silt and clay layers, escape and capture of the vaporized waste product is relatively higher in this operation. Furthermore, improved transport of vaporized contaminants prevents the soil's drying and shrinking. In this system of heating, however, recovery of toxin depends on the toxin type. Also contaminant recovery is essential where metals are not subject to decomposition reactions like mercury. Other concerns include the need to control water recharge for the polluted regions located below the water table, site accessibility for better installation, and the high cost of material handling requirements. However, the combined effectiveness of both vapor and heat flow leaves no area untreated, yielding a sweep efficiency of nearly 100 %.

Conductive heating/in-situ thermal desorption is a successful, heating technique that could be exploited for field-scale remediation of NAPL-contaminated zone, much like steam/hot air injections and ERHs. Field studies conducted so far confirm the potential of conductive heating to remediate >95 % VOCs and SVOCs (TerraTherm 2000; Carmen 2010; TerraTherm 2010; Amy et al. 2010). *In*-situ thermal desorption with dual phase extraction is a promising technology at field-scale as it remediated 99.9 % PCP, TCE, DCE and VC from a sediment of 3915 m^3 volume in 9 months by employing heat of 100 °C (TerraTherm 2010). Amy et al. (2010) explained the positive effect (97 %) of combined application of multi-phase extraction and thermal conductive heating at field-scale over an 8-month period in a site contaminated with chlorinated solvents. TerraTherm (2000) recommended thermal desorption combined with vacuum extraction for removing volatile organics from soil at field-scale. Success of conductive heating depends on the controlled groundwater flow as it is essential to enhance the rate of subsurface heating in a shorter lifespan with accelerated VOC removal. Such controlled groundwater flow was successful in remediating 99 % TCE, DCE and VC in 566 m^3 contaminated aquifer within 3.5 months (Carmen 2010). Therefore, in the case of conductive heating to enhance its efficiency, special control systems must be designed in the near future. FRTR (2005b) estimated that the cost ranges from 35 to 250 US$ to treat per m^3 contaminated site by thermal conduction/desorption heating systems.

3.1.5 Vitrification

In-situ vitrification (ISV) has been employed since the late 1990s. It uses an extensive electrical heat of very high temperature (1600–2000 °C) so that most contaminants are volatilized (organics), while the remainder (heavy metals and radionuclides) are converted into chemically-inert, obsidian glass-like products (Dermatas and Meng 2003). Vitrification can be grouped into three processes on the basis of energy source: (a) electrical processes (electrical energy through graphite electrodes), (b) thermal processes (external heat and typical reactor), and (c) plasma processes (high energy received via electrical discharges) (Acar and Alshawabkeh 1993; Wait and Thomas 2003). Specifically, vitrification converts leachable sludge into an immobile solid so that wastes are prevented from contaminating the soil, groundwater and surface water.

In-situ vitrification is particularly suited to treat high-level radiowastes (US EPA 1997a) as it is a non-contact technology (workers are not exposed to any waste) with effective contaminant destruction and immobilization capacity (FRTR 2006). In this system, redisposal is not required after treatment and it is a best option when a site is difficult to clean or standards of clean up are high. The other advantages of vitrification are: a vitrified product may be usable; as it is an inert, impermeable solid, it reduces leaching for a greater time period; an extensive array of organic and inorganic pollutants can be treated; and both in-situ and *ex*-situ options are available. However, ISV has some limitations. Energy requirement and cost to treat contaminants at deeper depths are very high, and it requires special application methods (Thompson 2002). To ensure that the contaminants are completely immobilized, long-term monitoring is often required. *In*-situ vitrification is not applicable when contaminated soil is <2–7 m below ground level. To overcome the limitation of melt ejection event, Planar ISV was developed with some modification of conventional vitrification (replacement of the horizontal array of started path material by vertical planes), and successfully demonstrated at the Los Alamos national laboratory park in the late 1990s (Coel-Roback et al. 2003). ISV is applicable to sites with high clay content. To treat the materials in permeable aquifers, dewatering is required. At the same time dynamic compaction is required to treat sites with large voids (US EPA 1997b). The overall cost for in-situ vitrification ranges from 80 to 300 US\$/m^3 (Khan et al. 2004).

Dellisanti et al. (2009) presented an in-field joule heating vitrification method that completely melted tons of zinc- and lead-rich ceramic waste by progressive heating up to 1850 °C. Field studies related to in-situ vitrification application were carried out only in the late 1990s, and field-scale remediation studies of this specific technology are not available in recent years. Spalding et al. (1992) achieved 99.9 % remediation of strontium- and cesium-contaminated site in Tennessee within 5 days when the treatment zone was raised to a temperature of 1500 °C. Using filling materials helped to achieve the targeted treatment temperature in short time. In order to reduce the treatment cost involved in excavation in *ex*-situ vitrification mechanisms, in-situ vitrification could be an option (US EPA 1997a). The reason for the scarce applicability of this technology in recent years might be due its high treatment cost. If a suitable alternative to reduce the treatment cost is found, this means that vitrification can completely clean up even a very high contaminated site in a year. The scope of vitrification technology has increased to immobilizing high level nuclear waste so that it is easy to recycle nuclear fuel and reuse it. Thus, vitrification is a promising technology for managing nuclear waste and more system models are expected to be developed in the long-run (Vienna 2010).

Overall, among the in-situ thermal treatment technologies, electrical resistance heating, steam stripping and thermal conductive heating are the most widely exploited and successful ones at field-scale. In contrast, electromagnetic heating and vitrification technologies must be improved to overcome the existing limitations for a wider application.

3.2 Soil Flushing

Soil flushing is a developing technology that has been used successfully in the full-scale removal of organics. The US EPA completed the construction of a mobile soil flushing system during the early 1990s for use at spills and uncontrolled hazardous waste sites (FRTR 1999). In in-situ soil flushing, an aqueous solution or water is flooded into or sprayed over the contaminated surface, the pollutant bearing fluid is then collected by strategically placed wells or trenches and brought to the surface for removal or on-site treatment, recirculation and reinjection (Logsdon et al. 2002; Di Palma et al. 2003). Extracted fluids are always subjected to required treatments to meet the appropriate discharge standards before being released in the locality (Otterpohl 2002; Son et al. 2003). Flushing solutions may be water, acidic aqueous solutions, basic solutions, chelating or complexing agents, co-solvents or surfactants (US EPA 1990). Water will extract water-soluble constituents, while acidic solutions aid in removing metals such as Zn, Pb and some phenols. Chelating, reducing and complexing agents are useful to recover metals. Surfactants assist in the removal of hydrophobic organics (Logsdon et al. 2002; Alter et al. 2003). Generally, surfactants and co-solvent flooding technology are widely practiced for removing fuels and chlorinated solvents. Using a two-phase co-solvent flushing fungal biosorption process, in-situ remediation of DDT-contaminated soil was achieved by Juhasz et al. (2003).

Soil flushing is considered to be a mature technology due to its oil field applications. In relatively uniform and permeable soils, flushing is most efficient. However, high per cent soil, silt/clay content, surfactant adherence to soil, and reactions of flushing fluids with soil limit the efficiency of the flushing process (Reddy and Saichek 2003). The achievable treatment level varies depending on the soil hydraulic conductivity and contact as well as appropriateness of the flushing solution with the contaminant. Soil flushing is successful in treating pollutants that do not tend to sorb onto the soil and the ones that are fairly soluble in the extracting fluid. Acidity and alkalinity of the soil, and precipitation resulting from interaction between flushing fluid and soil interferes with the system's efficiency (Khan et al. 2004). It generally takes longer time to achieve clean up standards by soil flushing. However, the main key advantages of this remediation technique are that the recovered fluids are reusable and the process does not involve excavation as well as redisposal problems. This negates the cost and risks associated with the pollutant removal. Also, it is relatively very simple to design and operate (Reddy and Saichek 2003).

Of the uses of water, cyclodextrins, chelants and surfactants as flushing liquids, surfactant-enhanced remediation was widely employed to remediate sites contaminated with heavy metals and hydrocarbons at field-scale (Lee et al. 2005), pilot-scale (Svab et al. 2009), and laboratory-scale (Wang and Mulligan 2009). Soil flushing was able to achieve more than 90 % remediation at pilot-scale and more than 88 % remediation at field-scale when combined with a suitable cationic surfactant. When anionic surfactants were used for PCBs, it could achieve only 56 % remediation in 12 months. Thus, the type of surfactant used determines the success of soil flushing. Svab et al. (2009) studied the flushing process of a real PCB-contaminated site in which an aqueous solution of anionic surfactant (Spolapon AOS 146 solution of 40 g/L) was passed through 1.7 m^3 of polluted sandy soil. In 2.5 months, a decontamination efficiency of 56 % was achieved, but it could have been 90 % or above if duration of flushing was extended for another 6 months. Soil flushing with surfactant solution was reported to be a serious competitor to expensive thermal methods that are used to treat soils of low contamination levels as it is cost-effective and suited for both in-situ and *ex*-situ types.

Lee et al. (2005) found that 88 % TPH could be removed by flushing 2 % surfactant solution over the diesel-contaminated soil with a hydraulic conductivity of 2×10^{-4} cm/s for 44 days. Jawitz et al. (1998) confirmed that even complex NAPLs having more than 200 constituents could be remediated by flushing 5.5 % solution composed of surfactant (polyoxyethylene oleyl ether) and alcohol (pentanol) mixture.

Schnarr et al. (1998) proved the efficiency of in-situ chemical flushing using potassium permanganate at field-scale. Within 120 days, around 62 % of the initial source concentration of chlorinated solvents was reduced by flushing 10 g/L of potassium permanganate at total flow rates up to 100 L/day. Jawitz et al. (2000) reported the enhanced solubilization and extraction of DNAPLs at a former dry cleaning site in Jacksonville, Florida by in-situ alcohol flushing (95 % ethanol and 5 % water mixture over a period of 5 days). At a former manufactured gas plant site, Reddy et al. (2010) evaluated the enhanced remediation of soil contaminated with PAHs and heavy metals using different flushing agents, which included deionized water, chelant (0.2 M EDTA), cyclodextrin (10 % hydroxypropyl-β-cyclodextrin/HPCD) and surfactant (5 % Igepal CA-720). The effect of each flushing solution was tested in distinct column at a constant hydraulic gradient (1.2×10^{-4} cm/s).

The effects of rate limited solubilization or desorption of PAHs were also investigated by additional column tests using HPCD and Igepal at a lower hydraulic gradient (0.2×10^{-4} cm/s). EDTA (about 0.2 M) removed a maximum of 25–75 % of the toxic heavy metals from the soil under different hydraulic gradient conditions compared to other flushing agents. Also, the removal of PAHs depended on the micelle formation in surfactant-enhanced systems, whereas in the HPCD-enhanced system, it relied on the stereo-selective diffusion of hydrocarbons to the non-polar cavity of HPCD. Overall, the study showed that selectivity towards the target contaminant, flushing solution affinity and the existing hydraulic gradient condition determine the efficacy of contaminant removal in soil flushing systems. Lestan et al. (2008) also proved the efficiency of chelating agents like EDTA in remediating 60 % metals. Udovic et al. (2007) reported that EDTA could immobilize Pb by 83 % and that immobilization of Pb was enhanced (>6.5 times) by the use of earthworm, *Eisenia foetida*.

Cyclodextrin-enhanced vertical flushing (Blanford et al. 2001) and citric acid-enhanced flushing (Kantar and Honeyman 2012) methods successfully remediated uranium (98 %) and TCE (99 %) at field-scale. Kim et al. (2008) found that Co and Cs removal efficiency by electrokinetic flushing for 5 days was 6.8–7.7 times better than electrokinetic remediation alone. The field studies that were successful in remediating contaminants by flushing techniques, surface flushing in particular, are many as detailed in Table 3. Integration of electrokinetic remediation has gained momentum in recent years. Tsai et al. (2009) adopted a three-stage treatment train system that started with a preliminary biodegradable surfactant application followed by Fenton-like oxidation flushing and ended with enhanced bioremediation approach. They reported a TPH removal of 80 % from oil-contaminated soil. To attain 99 % remedial efficiency, which is currently around 60–80 %, much more integrated methods can be designed to enhance the efficacy of bioremediation by soil flushing. Also, exploring more avenues to reuse the recovered flushing solution with groundwater and separation of reusable surfactants from the flushing fluids, these strategies may improve the operational efficiency of the soil flushing system. Also, better monitoring systems for air emissions of volatile toxins from recovered flushing fluids should be established. The flushing cost depends on concentration and type of extraction fluid used. Roughly, 20–200 US$ was spent to treat a Mg of contaminated soil (US EPA 2012).

Table 3 Performance of notable in-situ soil flushing studies

Site	Key contaminant	Remediation (%)	Associated technology	Specific feature	Outcome	Type
1. Military vehicle repair shop site, Pusan, Korea	Petroleum hydrocarbons, Kerosene, Lubricating oils	88	Surfactant-enhanced remediation and steam injections	• Circulation of 2 % sorbitan monooleate surfactant solution in contaminated site • Chemically-enhanced treatment system with dissolved air floatation • Significant than flushing with water alone	√√	F
2. Oxidized mine tailing sandy soil sample, Bathurst, Canada	As, Pb, Cu, Zn	93	Surfactant-enhanced subsurface remediation	• Use of 70 pore column flushing • 0.1 % Biosurfactant (Rhamnolipids from *Pseudomonas aeruginosa* JBR425) in alkaline solution was flushed	√√	BS
3. OU1 site, Hill AFB, Layton, USA	TCA, Naphthalene, TCE, TMB, Decane	90	Cyclodextrin-enhanced vertical flushing	• 10 % Cyclodextrin was flushed for 10 days at the rate of 4.54 L/min	√√	F
4. Quartz soil, Mersin, Turkey	U	98	Citric acid-enhanced remediation	• Increasing concentration of citric acid increased the contaminant removal efficiency • Maintenance of slightly acidic to alkaline condition was required for better performance	√√	BS
5. Real PCB-contaminated soil, Czech Republic	PCB	56	Surfactant-enhanced remediation	• Use of anionic surfactant (Spolapon AOS 146) • Contaminant treatment time was 1 year which could be prolonged for attaining success	X	P
6. TCE-contaminated aquifer, Tucson, Arizona	TCE	99	Cyclodextrin-enhanced vertical flushing	• Use of self-controlled air strippers that reduced monitoring related factors • One pass cyclodextrin flush was cost-effective	√√	PS

7. Former manufactured gas plant site, New York, USA	PAHs, Heavy metals	50–75	Surfactant-enhanced remediation	• Performance of water, chelant (EDTA), surfactant (5 % Igepal), and cyclodextrin (10 % HPCD) was compared at a time • Surfactant-enhanced degradation was significantly efficient	√	P
8. US coast guard, Elizabeth, North Carolina	Jet fuel	98	Biodegradation	• Rate of biodegradation could be accelerated by injecting oxygen through injection pumps	√√	P
9. CFB Borden research site, Canada	PCE, TCE	62	*In*-situ oxidation	• Potassium permanganate was flushed at a rate of 100 L/day for 290 days • Effectiveness depends on the distribution and dissolution of DNAPLs on the subsurface	√	F
10. Winton's food and fuel, Palmer, USA	MTBE	>95	Multiphase extraction	• Remediation system installed was SVE and passive aquifer oxygenation system • Almost all MTBE was removed in 2 months	√√	F
11. Hill AFB, OU1 site, Florida	Jet fuel	99	Solvent-enhanced remediation and SVE	• A mixture of 70 % ethanol and 12 % pentanol in water was flushed	√√	F
12. Hill AFB OU2 site, Texas	TCE	99	Surfactant-enhanced remediation	• 8 % Surfactant, 4 % isopropanol, and 4 % NaCl were used for flushing	√√	F
13. Dover air force base test cell, USA	PCE	64	Solvent-enhanced remediation and SVE	• Co-solvent flushing was implemented • 70 % Ethanol was flushed	√	F
14. Hill air force base OU1 site, USA	Jet fuel, Chlorinated solvents	85	Solvent-enhanced remediation and SVE	• Co-solvent flushing was employed • 70 % Ethanol and 12 % pentanol was flushed	√√	F
15. Former dry cleaner site, Jacksonville, Florida	PCE	63	Solvent-enhanced remediation	• 95 % Ethanol was flushed in 3 days	√	F
16. Hill air force base, Utah	n-Decane, TMB, Naphthalene, DCB, Xylene	90–95	Surfactant- and solvent-enhanced remediation	• Microemulsion flushing was employed • 10 % Surfactant (polyoxyethylene), and 5.5 % pentanol was flushed in 18 days	√√	F

√√, Successful; √, Partially successful; X, Not successful; P, Pilot-scale; F, Field-scale; BS, Bench-scale

3.3 Fracturing: Pneumatic/Blast-Enhanced/Lasagna™/Hydro

Low-permeable and fine-grained soils that are a major challenge for in-situ pollutant removal by conventional techniques like soil vapor extraction and bioremediation can be treated by fracturing (Gafar et al. 2008). Fracturing techniques are categorised into pneumatic fracturing, blast-enhanced fracturing, Lasagna™ process for treating contaminated soils, and hydrofracturing for remediating contaminated waterbodies (FRTR 2012). Of all the available methods, hydrofracturing and pneumatic fracturing are the most widely used ones at full- or pilot-scale. These methods enhance the mass transfer of the pollutant in dense soils by creating new fractures and by making the existing fractures larger. Creating fractures helps to enhance the permeability and alter the path of liquid flow, thereby assisting in increasing the efficiency and cost-effectiveness of conventional in-situ treatment technologies. Fracturing also helps to reduce the number of extraction wells, labor and material costs required for treating the contaminated site. In the case of blast-enhanced fracturing, new fractures are created when the drilled boreholes are filled with explosives and detonated. It is applicable in sites with fractured bedrock formations (Miller 1996). Hydrofracturing is a pilot-scale technology where relatively high pressure fluid, especially water, is injected at modest rates into the source area that is to be fissured which initially creates a circular notch beneath the borehole. Later when biodegradable gel and slurry of sand is forced at high pressure, individual fractures are created.

Eventually, fractures become highly permeable as the gel degrades (Cipolla et al. 2008). To enhance the contaminant recovery, soil vapor extraction technology can be used in conjunction with the hydraulic fracturing process (Nilsson et al. 2011). Lasagna™ is an integrated technology that combines the principle of electroosmosis with fracturing, wherein fractures are created by hydraulic fracturing (Roulier et al. 2000). In pneumatic fracturing, existing fissures are enlarged and new fractures or channels are created by injecting highly pressurized air or other gases, and contaminant removal is accelerated by in-situ electrokinetics, enhanced in-situ biodegradation, soil vapor extraction and bioventing (Bhandari et al. 2007). This type of fracturing by gases is employed only when fractures are left to remain open without support for a longer period of time.

With no particular target group, fracturing is applicable to treat a diverse array of contaminants. It is used chiefly to fracture limestone, clay, silt, bedrocks and shale. However, fracturing does not work well in areas of high seismic activity and clay content. Usually, fractures are installed at 2–18 m below the subsurface. Even shallow fractures roughly between 2 and 8 m could be established. By itself, fracturing is not a remediation technology. To facilitate the reduction of concentration and mass of the contaminant, it has to be combined with other techniques. One of the noted advantages of fracturing is that it could extend the applicability of several other in-situ remedial approaches. For example, fracturing enhances fluid flow rate in the fissured zones in in-situ electrokinetics, enhances the delivery of nutrients and oxygen into inaccessible locations in case of in-situ biodegradation, creates fractured pathways to collect the injected air laden with contaminants in in-situ air sparging, and creates heating zones by injecting graphite into the fractures in in-situ vitrification. However, fracturing has some limitations: (1) final location of newly created fractures is uncontrollable; (2) fracturing near existing wells could damage the well casings and seals; (3) it creates new routes for unnecessary spread of contaminants; (4) prior investigations of the possible structures of trapped free product and underground utilities are always required; and (5) this technique is not appropriate for fill materials or disturbed soils (Nilsson et al. 2011).

Regarding hydraulic fracturing, relatively large volumes of solid materials are delivered to the subsurface as fillings for fractures that could slowly release nutrients and oxygen to improve in-situ aerobic degradation of toxins by microbes (Davies et al. 2012). Even an electrically conductive material like graphite is filled in the fractures to enhance electroosmosis and perhaps electrical heating for in-situ vitrification. Also, metal fractures like elemental iron are filled in the created fractures to degrade an extensive range of chlorinated compounds favoring reductive dechlorination (Comba et al. 2011). More successful field studies employing nanoparticles in fractures created either by pneumatic or hydraulic means are documented by Forman et al. (2010). At field fracturing, the medium allows the creation of pathways for distribution of nano-ZVI particles into clay as well as sandy soils (Saleh et al. 2008).

Several pilot-scale studies (Table 4) confirm that, when fracturing techniques are integrated with other in-situ treatment technologies, they could help to achieve the remedial goal (Nilsson et al. 2011). The first documented field study targeting chloroform and ZVI usage in remediating a VOC-contaminated site by pneumatic fracturing was at Hunters Point Shipyard, San Francisco, California by Forman et al. (2010). They reported that groundwater contaminated by TCE over 100 μg/L and PCE above 15 μg/L could be effectively treated by integrating ZVI with pneumatic fracturing. Another full-scale pilot demonstration of integrating pneumatic fracturing with bioremediation in a gasoline-contaminated site in-situ was done by Venkatraman et al. (1998). In an in-situ bioremediation zone set up, soil amendment delivery directly to the indigenous microbial populations, transport rates and subsurface air flow were enhanced by pneumatic fracturing system. The system operated for 50 weeks and it comprised periodic pumping of nitrate, ammonium and phosphate salts. Formation of a series of aerobic methanogenic and denitrifying bacterial degradation zones were indicated by off-gas data and 79 % of soil-phase benzene, toluene and xylenes were removed using the integrated approach. Accounting for all physical losses, mass balance calculations showed that biodegradation removed nearly 85 % of the total mass of BTEX. Nilsson et al. (2011) conducted a steam injection pilot-scale test in the unsaturated zone of a strongly heterogeneous fractured soil polluted by jet fuel. Formerly, sub-horizontal and sand-filled hydraulic fractures were created at three depths to stimulate the soil. Through one hydraulic fracture, steam was injected and from the remaining fractures, NAPL vapors were extracted by applying vacuum-enhanced extraction. Hydraulic fractures prevented the escape of injected steam and extracted gas/liquid. Concentration of total hydrocarbons was reduced by 70 % over the entire zone (1.5–5.5 m depth) and by 40 % in the upper target zone (1.5–3.9 m depth). A similar study using hydraulic fracturing with steam injection was reported by Tzovolou et al. (2010) in a field-scale.

Table 4 Performance of selected in-situ remediation studies at field- and pilot-scale

Site	Contaminants	Highlights/comments	Result	Scale	Reference
Soil fracturing					
1. Robert Gray army airfield, Ford Hood, Texas	Jet fuel	• Hydraulic fracturing combined with steam injection and electroheating of unsaturated zone of tight clay soils was employed • Pollutant removal efficiency was 77–86 %	√	P	US EPA (2012)
2. Petroleum-contaminated site, Saskatchewan, Canada	LNAPL, Petroleum hydrocarbons, Benzene, Toluene	• Dual-phase vacuum extraction with pneumatic fracturing enhancement system was suggested to be supportive for groundwater remediation • Bioslurping with enhancement of pneumatic fracturing achieved complete remediation at sites contaminated with very high concentration of hydrocarbons	√√	F	Zhang et al. (2009)
3. Gasoline-contaminated site, New Jersey	Benzene, Toluene, Xylene	• Integration of pneumatic fracturing with in-situ bioremediation was established • In in-situ bioremediation, for a period of 50 weeks, phosphate, nitrate, and ammonium salts were injected periodically which helped to remove 85 % BTX	√√	F	Venkatraman et al. (1998)
4. Hunters point shipyard, San Francisco, California	TCE, Chloroform	• Pneumatic injected micro-scale zero-valent iron was used to treat the chlorinated compounds • This technology was employed in target hotspot area where concentration of PCE and TCE exceeded 15 and 110 mg/kg, respectively	√√	F	Forman et al. (2010)
5. Military airport, Poland	Jet fuel	• Combination of steam injection with hydraulic fracturing was implemented • Average concentration of total hydrocarbon was reduced by 72 %	√	P	Nilsson et al. (2011)
Air sparging					
1. Contaminated site, Kansas	TCE, DCE	• *In*-situ ozone sparging was used • TCE concentration was reduced from 94 to 100 %	√√	F	Nelson et al. (1994)
2. Five points superette, Johnsonville, USA	MTBE	• About 98 % remediation of MTBE was achieved in 2 years of air sparging	√√	F	Wilson (2001)

3. Contaminated aquifer, Kalkaska, Michigan	BTEX	• Pulsed air injection was the technology used (combination of volatilization and biodegradation mechanism to enhance contaminant removal efficiency) • Increased average removal rate of hydrocarbons by a factor 3 compared to conventional air stripping system	√√	F	Yang et al. (2005)
4. Coastal plain sediments, New Jersey	TCA, TCE	• Air sparging combined with SVE was the best alternative to conventional pump-and-treat technology at field level	√√	F	Gordon (1998)
5. Petroleum hydrocarbon spilled site, Kaohsiung, Taiwan	BTEX	• More than 70 % BTEX was removed through biosparging in 10 month remedial period	√	F	Kao et al. (2008)
Physical barriers					
1. Nortel network site, Northern Ireland	TCE	• Zero-valent iron permeable reactive barrier was installed in groundwater • Additive remediation effect was achieved by reductive dechlorination due to zero-valent iron • Ten years performance evaluation of the established barrier system in different sites. Finally, 98 % remediation was achieved per site in 2 years	√√	F	Phillips et al. (2010)
Multi-phase extraction					
1. Sparks solvents/fuel site, Sparks, Nevada, USA	MTBE, PCE, TCE, Petroleum hydrocarbons	• Remediation system consisted of granular activated carbon/ fluidized bed reactor • 99 % Remediation was achieved after 2 years	√√	F	US EPA (2012)
2. BP at south of the border, South Carolina, USA	MTBE	• Air sparging with multi-phase extraction was implemented • Totally, 1350 m^2 area was treated • 88 % MTBE was removed, and the total remediation cost was US$ 2,14,000	√√	F	US EPA (2012)
3. Site at Texaco, Healdsburg, USA	Benzene, Ethylbenzene, MTBE, Butyl alcohol, Toluene	• Multi-phase extraction was combined with pump-and-treat technology • 97 % Remediation was achieved	√√	F	FRTR (2012)

(continued)

Table 4 (continued)

Site	Contaminants	Highlights/comments	Result	Scale	Reference
4. Greek petroleum refinery, Greece	LNAPLs	• Bioslurping technology was operated for 4 years • Significant groundwater contamination was not minimized by free-phase recovery (bioslurping), hence integration of air sparging was suggested	√	F	Gidarakos and Aivalioti (2007)
5. Confidential So., California, USA	Chlorinated volatile organics, DCA	• SVE system combined with thermal conductive heating along with high vacuum single pump extraction system employed • Around 3538 kg of DCA and CVOCs (99 %) were removed in 400 days • Costed about 58 US$/m^3	√√	P	US EPA (2012)
6. Sand pit, CFB, Borden, Canada	Hexane, Pentane	• Multi-phase extraction system was used • LNAPLs were recovered using a patented technology—‘Supersaturated Water Injection’ where nucleating CO_2 bubbles could volatilize LNAPLs • 50–70 % LNAPLs were removed which was comparatively higher than air sparging even when smaller volume of gas was injected	√√	P	FRTR (2012)
Electrokinetic remediation					
1. Chromated copper arsenate-treated waste wood, Denmark	As, Cr, Cu	• Electrodialytic remediation (combination of electrokinetics with low level direct current as cleaning agents) was established using electrodes of 60 V set up at increased distance (between 60 and 150 cm) than usual • 0.5 M Phosphoric acid and 5 % oxalic acid were used as additives to facilitate desorption of CCA compounds • Within 21 days, 82 % Cr, 88 % Cu, and 96 % As were removed	√√	P	Pedersen et al. (2005)
2. Red soil, Yingtan, Jiangxi Province	Cu	• 700 kg Cu-contaminated red soil was remediated using 80 V energy • 76 % Cu was removed in 140 days with the consumption of 224 kW h/m^3 energy	√√	P	Zhou et al. (2006)

3. 20-Year old chemical plant, China	Hexachlorobenzene, Zn	• 0.5 m^3 Sediment was treated under a constant voltage in a polyvinyl chloride reactor • 563 kW h/m^3 Energy was consumed in 6 months • Consumption of energy was subsequently increased periodically • Remedial per cent was <50 • Long-term ageing of sediment and co-occurrence of HCB and Zn was the reason behind low contaminant removal efficiency	X	P	Li et al. (2009a)
4. Military small arms training facility site, Boston	Pb	• Amendment of organic acid at the cathode-reduced voltage and energy requirement by 70 % and enhanced Pb extraction • Concentration of Pb was reduced by 85 % after 112 days of processing • Cost of treatment was between 14 and 18 US$/$m^3$/month	√√	P	US EPA (2012)
Bioventing					
1. Diesel oil contaminated site, Copenhagen, Denmark	Diesel	• About 96 % of 2000 mg/kg diesel oil was removed in 112 days of treatment using the coupled effect of bioventing, nutrient addition and oil-degrading bacteria	√√	F	Moller et al. (1996)
2. Transformer oil contaminated soils, Budapest, Ullatosu	EPH	• *In*-situ cyclodextrin-enhanced bioventing coupled with *ex*-situ nutrient addition was the technology employed • 99 % Remediation was achieved in 46 weeks	√√	P	Molnar et al. (2005)
3. Former petroleum refinery, West central region, USA	BTEX, Diesel, Gasoline	• Wind-assisted air injection technique removed 88–95 % pollutants • Long-term passive bioventing was highly successful as well as cost-effective, full-scale technology at remote locations with high, sustained wind speeds and permeability	√√	P	Zenker et al. (2005)
4. Flat Hill top site at a weather station, USA	TPH, BTEX	• Successful wind-driven bioventing stimulated remediation with no power requirement and minimal operation and maintenance • Monitoring indicated a 20 % oxygen delivery by wind-driven energy and greater than 90 % reduction in VOC concentrations in 2 months	√√	P	Dominguez et al. (2012)

(continued)

Table 4 (continued)

Site	Contaminants	Highlights/comments	Result	Scale	Reference
Natural attenuation					
1. Gasoline spill site, Garysburg, North Carolina	BTEX	• About 99 % BTEX was removed by natural attenuation along with iron-reducing biodegradation process in 2 years • Natural attenuation was the remedial option at the gasoline spill site to remediate the contaminated groundwater	√√	F	Kao and Wang (2001)
2. Canadian forces base, Borden	PAHs, Biphenyl, Carbazole	• After 14 years of treatment, only 3 of 11 contaminants were reduced significantly and the remaining were not remediated due to increasing mass flux and limited degradation potential • Greatest mass loss was associated with the compounds that have high solubility and low partitioning co-efficient	X	F	Fraser et al. (2008)
3. Low farmland, Andalusia, Spain	Diesel	• Stimulated natural attenuation was the best remedial measure for hydrocarbon degradation • Soil remediation by natural attenuation was enhanced by the practice of tilling or adding water which could enhance the contaminant evaporation	√	F	Serrano et al. (2008)
4. MGP site, New York	PAHs	• In a 14-year old groundwater natural attenuation process, 99 % contaminant was remediated • Monitored natural attenuation was a viable remedial strategy for groundwater sites impacted by PAHs	√√	F	Neuhauser et al. (2009)
5. Slag heaps, Temascaltepec, Mexico	Cd	• Role of plants and arbuscular mycorrhizal (AM) fungi with natural attenuation was substantiated • Glomalin protein of AM fungi was reported to sequester 0.028 mg/g Cd	√	F	Gonzalez-Chavez et al. (2009)
6. Campine region, Belgium, Netherland	Pb, Cd, Zn	• Phytoattenuation was used • Risk reduction and generation of an alternative income for agriculture as well as gradual reduction of the pollution levels were the main goals • Metal removal was low for Cd and Pb compared to Zn • Removal efficiency was enhanced by the introduction of winter crops for bioenergy purposes in crop rotation	√	F	Meers et al. (2010)

7. Military facility site, Korea	BTEX	• BTEX attenuation rate was 8.69×10^{-4}/day and the remediation time was 17.5 years • Rate of biodegradation and natural attenuation was very less and integration with other supportive remedial measures were suggested	X	F	Choi and Lee (2011)
Phytoremediation					
1. Metal-contaminated site, Dornach, Switzerland	Cu, Zn, Cd	• Only 10–30 % remediation was achieved by *Alyssum murale* and *Thlaspi caerulescens* • Limitations in phytoavailability of metals was due to the high soil pH	X	F	Kayser et al. (2000)
2. Houston site, USA	MTBE	• Phytohydraulic containment of MTBE was successfully achieved • About 36.5–67.0 % MTBE was removed after 1 year from the groundwater plume using poplar plants	√	F	Hong et al. (2001)
3. Dredged sediment disposal site, Belgium	Cd, Cu, Pb, Zn	• About 57 % of the heavy metals were significantly removed by implementing capping of willow trees for 1.5 years	√	F	Vervaeke et al. (2003)
4. Paint factory site, Czech Republic	PCB	• Austrian pine, black locust, ash and willow trees were tested • Austrian pine and black locust significantly increased the number of PCB degrading bacteria in the rhizosphere and helped to achieve >60 % remediation	√	F	Leigh et al. (2006)
5. Indian Harbor canal, USA	PAHs	• After 1 year of planting, nearly 70 % PAHs reduction was observed in the sediment samples raised with *Carex stricta*, *Tripsacum dactyloides* and *Panicum virgatum* compared to *Salix exigua*, *Populus* spp. and *Tripsacum dactyloides*	√	F	Euliss et al. (2008)
6. Agricultural soil, Witzwil, Switzerland	Cd, Cu, Zn	• Efficient remediation was achieved by the extraction of Cd using tobacco plants • Phytoextraction was aided by the application of 4.28 Mg sulphur/10,000 m^2/year	√	F	Fassler et al. (2012)

(continued)

Table 4 (continued)

Site	Contaminants	Highlights/comments	Result	Scale	Reference
7. Agricultural soil, Zhejiang, China	Phthalic acid esters	• Phytoremediation of phthalic acid esters by intercropping *Medicago sativa*, *Lolium perenne* and *Festuca arundinacea* • *M. sativa* in monoculture removed over 90 % of the contaminant • Intercrop of all the three plant species contained the highest shoot concentration of total phthalic acid esters of about 4.7 mg/kg dry wt.	√√	F	Ma et al. (2012)
Bioaugmentation					
1. Dover's air force base, DE	TCE	• Mixed enrichment culture capable of dechlorinating TCE to ethene was inoculated into the contaminated aquifer at 2×10^{11} cells/L • Groundwater was fed with lactate after bioaugmentation on day 1 • Within 90 days, VC and ethene disappeared in monitoring wells • After 509 days, TCE and DCE were fully dechlorinated to ethene	√√	F	Ellis et al. (2000)
2. USN hydrocarbon national environmental test site, Port Hueneme, California	MTBE	• A microbial consortium, MC-100, capable of degrading MTBE was inoculated • With 30 days of bioaugmentation and oxygen injection, MTBE was degraded to non-detectable level after 261 days	√√	F	Salanitro et al. (2000)
3. Bachman road residential wells site, San Diego, California	PCE	• *Desulfuromonas* sp. and *Dehalococcoides* sp. were bioaugmented in the contaminated groundwater • Complete dechlorination of PCE to ethene was observed in less than 50 days	√√	F	Lendvay et al. (2003)
4. Metal- and organic-contaminated soil, Tucson, Arizona	Cd, 2,4-D	• Dual bioaugmentation strategy with metal-detoxifying and organic-degrading microbial populations was adopted • Cd-resistant *Pseudomonas* sp. enhanced degradation of 2,4-D in reactors inoculated with *Ralstonia eutropha* • Dual bioaugmentation was effective at co-contaminant remediation	√√	P	Roane et al. (2001)

5. Kelly air force base, Texas, USA	PCE	• Bioaugmentation was carried out with a mixed culture containing *Dehalococcoides ethenogenes* to a density of 10^9 cells/L • Methanol and acetate were added as electron donors • Complete dechlorination was achieved after 142 days	√√	F	US EPA (2012)
6. Ho Chung mangrove swamp, Hong Kong, China	PAHs	• At the end of 2 weeks, natural attenuation based on the presence of indigenous microbes degraded more than 99 % PAHs, while biostimulation along with the addition of mineral salt medium degraded only 9 % PAHs	√	P	Yu et al. (2005)
7. Vegetable garden site soil, Pietermaritzburg	PAHs	• Combined application of biostimulation with ammonium phosphate and hydrogen peroxide enhanced PAH degradation by 100 % compared to biostimulation alone (90 %)	√	P	Atagana (2006)
8. MAG-1 area, Fort Dix, Burlington	Chlorinated ethenes	• *Dehalococcoides* sp. was bioaugmented into the contaminated aquifer • A density of 3.9×10^{13} cells/L showed significantly higher degradation with less remedial time compared to 3.9×10^{11} and 3.9×10^{12} cells/L	√√	F	Schaefer et al. (2010)
Biostimulation					
1. Site at Kururi, Japan	TCE	• Methane was used as the stimulator • Injection of methane, oxygen, nitrate and phosphate into the contaminated groundwater gradually stimulated the methane oxidizers in the aquifer, and about 10–20 % TCE was removed in a week	√√	F	Eguchi et al. (2001)
2. Old Rifle site, USA	U	• Acetate was used as the stimulator • Uranium was completely immobilized after 109 days by sulphur-reducing bacteria	√√	F	Yabusaki et al. (2007)
3. Polar desert site, Tanquary fiord, High Arctic	Petroleum hydrocarbons	• Diammonium phosphate along with surfactants was the best biostimulator for the degradation of petroleum hydrocarbons at extreme climatic conditions	√√	F	Sanscartier et al. (2009)
4. Oily sludge contaminated site, China	TPH, PAH	• Manure was used as a nutrient-rich biostimulator for hydrocarbon degradation	√√	F	Liu et al. (2010)

√√, Successful; √, Partially successful; X, Not successful; P, Pilot-scale; F, Field-scale

Table 5 Performance of electrokinetic remediation in combination with other technologies for the removal of organics

Contaminant	Combined technology					Remediation (%)	Reference
	F	B	S	U	L		
Hydrocarbons							
1. PAH	+	+	+	+	–	70–80	Park et al. (2005); Yang et al. (2005); Pham et al. (2009); Gomez et al. (2010)
2. Petroleum hydrocarbons	+	–	–	–	–	97	Tsai et al. (2009)
3. Diesel	–	+	–	–	–	64	Kim et al. (2010)
4. Phenol	–	+	–	–	+	80–95	Luo et al. (2006)
Chlorinated solvents							
1. TCE	+	–	–	–	+	75–90	Yang and Liu (2001); Harbottle et al. (2009)
2. VC	–	+	–	–	–	90	Tiehm et al. (2009)
Pesticides							
1. HCB	–	–	+	+	–	75–80	Oonnittan et al. (2009); Pham et al. (2009)
2. DDT	–	+	–	–	–	13	Karagunduz et al. (2007)

+, Technology implemented; –, Technology not implemented; F, Fenton's process; B, Bioremediation; S, Surfactant-enhanced remediation; U, Ultrasonic technology; L, Lasagna technology

However, more research is warranted to explore the fillings like nanoparticles or nutrient releasing solids for fractures that could aid the systems' efficiency. Ho et al. (1999) reported that Lasagna™ technology could successfully remediate phenol and TCE by 90 % when combined with electrokinetic remediation (Table 5). Performance studies of many more integrated remedial approaches like dual-phase extraction, bioslurping with fracturing as reported in US EPA (2012) can also be tested in field-scale to accelerate the current remedial percentages of 75–99.9 achieved in other conventional in-situ treatments. The approximate cost for pneumatic fracturing ranges from 8 to12 US$ per Mg. Based on creating 4–6 fractures per day, the cost of establishing hydrofractures is estimated to be 1000–1500 US$. In Lasagna™, cost is estimated to be 160–180 US$ per Mg for remediation in a year, 100–20 US$ per Mg if 3-year period is allowed for remediation (FRTR 2012).

3.4 Physical Barriers: Treatment Walls/Permeable Reactive Barriers

Barriers are the critical components such as designed covers/caps, slurry/permeable walls, landfills and grout curtains that are commonly used to restrict or control the movement of contaminant plumes in groundwater. Such physical barriers are generally well constructed with a multi-component system of highly impermeable material for long-term performance in order to eliminate the movement of the contaminant plume into aquifers and surface waterbodies (Inyang and de Brito Galvao 2004). This technology has been effective for a series of chemicals such as halogenated organics, chlorinated solvents, hydrocarbons, radionuclides and metals (US EPA 2012). Conditions that determine the efficiency of the physical barrier systems are properties of the barrier materials, component dimensions and system configurations. One of the widely implemented, viable, cost-effective subsurface barrier technologies is permeable reactive barriers (PRBs) (Scherer et al. 2000). In PRBs the flow of contaminated groundwater is not restricted, wherein they are allowed to pass over the barrier materials (reactive fluid) for the passive degradation or immobilization of contaminants. This treatment system can permanently restrict the contaminant migration to uncontaminated region and relatively decrease the volume of toxic contaminant residues by subsequent treatments (Testa and Winegardner 1990).

Generally, usage of physical barriers has the following advantages: minimized contaminant leaching; stabilization of contaminants by transforming the waste into a physical form that reduces the release potential of the contaminant; no need for excavation; passive remediation (no requirement for any energy input); potential for transfer of contaminants to other aquifers is minimal; and surface structures are not required except monitoring wells. Physical barrier systems also have their disadvantages: limited application to shallow plumes (<15 m); the risk that concentrated metals will be discharged into the groundwater if the reactive fluid is not removed in time; contaminated site should be well delineated and characterized before implementing the system; field data on the longevity of the reactive fluid and loss of permeability is scarce; site-specific constraints such as pH adjustment, subsurface utilities, inaccessibility, etc. may exist; and biological activity may limit the effectiveness of the reactive wall.

Many types of installation designs are currently available for PRBs like excavation and backfill (use of removable sheet piling and biodegradable polymer slurry), overlapping caissons (use of steel caissons), soil mixing (injecting and mixing reactive fluid with augers), high pressure jetting (injecting grouts to make impermeable walls), and vertical hydraulic fracturing (pumping gel containing reactive media into fractures created in permeable sands). All these techniques are utilized for establishing several barrier designs (Benner et al. 2001). Funnel-and-gate (vertical impermeable sheet pilings or slurry walls) and continuous trench (trench excavated and refilled with reactive material) design of PRBs are being implemented at field-scale by the US EPA (Strigel et al. 2001). Of the two, funnel-and-gate is more cost-effective for large or deeper contaminated plumes because voluminous reactive material is required for continuous trench design. In funnel-and-gate design, slurry walls, sheet pipes and other materials used to form the funnel are often easier and more economical to install than reactive walls. Plumes with mixed contaminants can be funnelled through a gate with multiple reactive walls in a series for achieving better remediation (Anderson and Mesa 2006).

A wide range of materials like ZVI, calcite/limestone, zeolite, metal oxides, microorganisms, polymers and organics (straw, hay, peat, wood, leaf mulch, mushroom compost and municipal solid waste), have been exploited as reactive materials to remediate contaminated groundwater. US EPA (2012) listed several sites where PRBs successfully remediated organics and inorganics (Table 6).

Table 6 Successful PRB reactive materials at field-scale in superfund sites

Site	Contaminants	Successful reactive materials	Construction	Reliability
1. Aircraft maintenance facility, Southern Oregon, USA	TCE	Zero-valent iron (ZVI) pellets	Funnel-and-gate	++
2. Watervliet arsenal superfund site, Watervliet, New York	Halogenated VOCs	Mixtures of ZVI, sand and concrete	Continuous trench	++
3. FE warren air force base, Cheyenne, Wyoming	TCE, DCE, VC	ZVI particle and sand	Trench box	++
4. Former industrial site, Belfast, Northern Ireland	TCE, DCE	ZVI particle	Slurry wall funnel as well as in-situ reactive vessel	++
5. Nickel rim mine site, Sudbury, Ontario, Canada	Pb, Co, Cd, Cu, Ni, Zn, NO_3, SO_4	Leaf compost, peat, sewage sludge, manure, sawdust, wood waste, composted leaf mulch, pine mulch, pine bark and microbes (*Geobacter metallireducens* and *Alteromonas putrefaciens*)	Cut and fill	++
6. Tonolli superfund site, Nesquehoing, Pennsylvania	Pb, Cu, Cd, As, Zn	Limestone	Continuous trench	–
7. Former mill site, Monticello, Utah	U, As, Mn, Se	ZVI particle	Funnel-and-gate	++
8. Former industrial site, Brunnam Gebirge, Austria	PAH, BTE, TCE, DCE	Activated carbon	Adsorptive reaction with hydraulic barrier	++
9. Solar pods plume, Golden, Colorado	NO_3, U	ZVI particle and wood chips	Reaction vessels	++
10. Chalk river lab, Ontario, Canada	Sr	Zeolite	Funnel-and-gate	+
11. Y-12 Oak ridge national lab, Tennessee	U, HNO_3	Iron oxides	Funnel-and-gate as well as Continuous trench	++

++, Successful technology; +, Partially successful technology; –, Unsuccessful technology

Gilbert et al. (2003) concluded that municipal compost is not an appropriate carbon source to support continuous activity of sulphate-reducing bacteria under high flow rates when a mixture of ZVI, limestone and compost was used as an additive in PRB laid to remove metal in acid-mine drainage. Funnel-and-gate design of PRB successfully remediated the sites contaminated with TCE, U, As, Mn and strontium so far in the US EPA superfund sites at Oregon, Utah, and in Canada using reactive materials like ZVI and zeolite. Also, 75–90 % removal of Pb, Cu, Cd, As, Zn, U and nitrate was observed in the superfund sites of New York, Pennsylvania and Tennessee using mixtures of sand and concrete, ZVI and iron oxides as reactive materials in continuous trench PRB system. A successful PRB installation in Ontario employed municipal compost, leaf compost and wood chips to remove nickel from an acid-mine drainage contaminated aquifer (US EPA 2012). There are many positive results for using anoxic limestone drains as a barrier material for decontaminating Pb and acid groundwater (Maynard 2005).

The majority of installed PRBs use ZVI as a reactive medium at field-level. Wilkin et al. (2006) noted that a ZVI permeable reactive barrier is effective in reducing the concentration of Cr from 1500 μg/L to <1 μg/L in 8 years at the US coast guard support centre near Elizabeth City, North Carolina. A recent field study at a network site in Northern Ireland indicated that 98 % remediation was achieved by using ZVI permeable reactive barrier in 2 years at a long-term high TCE-contaminated site (Phillips et al. 2010). Benner (2000) observed 90 % reduction in sulphate concentration in the organic carbon barrier at Nickel Rim, Ontario. Bayer et al. (2004) suggested that the problem of not achieving full aquifer restoration within a reasonable time frame using pump-and-treat technology can be rectified by integrating it with the barrier system. This is because vertical, physical hydraulic barriers such as sheet piles or slurry walls in the field could potentially minimize the pumping required to gain a thorough capture of a given polluted zone. Also, Waybrant et al. (2002) found that PRBs can potentially enhance bacterial sulphate reduction and metal sulphide precipitation which will help to prevent the associated release of dissolved metals and acid-mine drainage in a contaminated aquifer.

Of all these studies, the use of PRBs in association with microbes to promote biodegradation of contaminants is increasing rapidly. For the PRBs to be more effective in the future, cheap, widely available reactive fluid materials can be tested, and optimised barrier systems could be framed to overcome the constraints of heterogeneous sites, and the technology might be more economical and promising for wide range of pollutants. In other words, value-added or innovative materials can be evaluated as additives for barriers to enhance the containment system performance.

3.5 Soil Vapor Extraction

One of the most widely accepted, cost-effective soil remedial approaches for treating SVOCs and VOCs is soil vapor extraction (SVE). It is also known as vacuum extraction, soil venting as well as in-situ enhanced volatilization (Zhan and Park 2002).

In this method, through horizontal/vertical wells, vacuum is applied to create a concentration/pressure gradient that induces the removal of gas phase volatiles from soil. Vapors of volatile constituents are drawn towards the extraction wells and then treated with the carbon absorption technique before being emitted into the atmosphere or reinjected to the subsurface. This method is also used in air stripping and groundwater pumping for treating contaminated groundwater. In areas of higher groundwater levels, water table depression pumps are often used to offset the effect of upwelling induced by high pressure vacuum. SVE is more effective in treating more volatile and lighter petroleum compounds like gasoline (Zhan and Park 2002). It only promotes the in-situ degradation of low volatile organics and not their complete removal as the process involves continuous air flow through the soil. Generally, almost all petroleum products can be remediated by integrating SVE with bioventing, steam injections, radio frequency heating techniques, because volatility of the heavier contaminant will be accelerated by hot air injections (Qin et al. 2009). However, the energy requirement for volatility enhancement should be considered to reduce the capital cost. Using this method, naphthalene, perchloroethylene, benzene, toluene, xylene, biphenyl, TCE, TCA and gasoline have all been successfully removed from the zone of contamination.

SVE could treat large volumes of soil at reasonable cost in a short time (a few months to 2 years) with minimal soil disturbance (Barnes et al. 2002). It is also advantageous due to its proven performance at field- and pilot-scale, readily available equipment and easy installation, minimal site disturbance, compatibility with other technologies and applicability at sites with free products. However, the applicability of this method is limited to sites with a low water table (>1 m below ground level) and volatile compounds. Also, soil characteristics like structure, stratification, permeability and moisture content greatly affect the performance of the system as the ease and rate of vapor movement through the soil is impacted by these soil factors (RAAG 2000). Usually, low permeability, high moisture content and preferential flow behaviors by layering/fractures can extend remedial times by limiting the air flow through the soil pores. Other restrictions of this method include the need for air emission permits, requirement for expensive treatment of atmospheric release of extracted vapors, treatment of only unsaturated soil zone and need for integration with other technologies to reduce the contaminant concentration to more than 90 %. Recently, different types of subsurface covers have been established to avoid surface water infiltration that could limit the air flow rates, subsequently reducing the fugitive vapor emissions (Boudouch et al. 2009).

Almost in all the in-situ techniques at field-scale, SVE is the principal recovery system (Table 7). Cho et al. (1997) used SVE in combination with biodegradation to successfully remediate 98 % jet-fuel at the US coast guard facility, Elizabeth City, North Carolina. Hoier et al. (2007) successfully remediated 77 % TCE using the pneumatic SVE technique. The operational cost varied from 20 to 50 US$ per Mg of contaminated soil. A pilot SVE system installed at a small landfill at the Savannah River site was successful to address TCE contamination present in the layered vadose zone (Switzer and Kosson 2007). In the study by Noonkester et al. (2005), sets of 2–3 extraction wells laid in the vadose zone of high chlorinated

Table 7 Status of in-situ soil vapor extraction studies

Site	Key contaminant	Remediation (%)	Associated technology	Specific feature	Outcome	Nature	Reference
1. Canadian forces base, Borden, Ontario	PCE	60	None	• 60 % PCE was removed after 250 days • Heterogeneity of the system (changing well configuration, pulsed pumping, and use of short screen drive points to localize the flow) is the reason for the decreased mass removal	X	F	Fountain (1998)
2. Winton's food and fuel, Palmer, USA	MTBE	>95	Multi-phase extraction	• Remediation system installed was SVE and passive aquifer oxygenation • Almost all MTBE was removed in 2 months	√√	F	US EPA (2012)
3. US coast guard, North Carolina	Jet fuel	98	Biodegradation	• Rate of biodegradation could be accelerated by injecting oxygen through injection pumps	√√	P	Cho et al. (1997)
4. TCE-contaminated soil, Denmark	TCE	>77	Pneumatic SVE	• Enforcing large pressure drops on the system to enhance recovery from low-permeable areas was achieved by pneumatic SVE • Pneumatic venting increased removal rates of the contaminant by 77 %	√	BS	Hoier et al. (2007)

(continued)

Table 7 (continued)

Site	Key contaminant	Remediation (%)	Associated technology	Specific feature	Outcome	Nature	Reference
5. Former Kelly air force base, San Antonia, Texas	TCE	97	Electrical resistance Heating	• Over 544 kg chlorinated solvents were treated in an area over 14 × 10^5 m^2 • Soil was heated up to 90 °C • In 14 months, contaminant was successfully removed	√√	F	US EPA (2012)
6. Beach soil, Porto, Portugal	Benzene	85–94	Bioremediation	• Soil with higher organic matter content was more populated by indigenous microorganisms that enhanced the contaminant degradation • Organic matter content had opposite effects on the remediation of soils through the combination of SVE and bioremediation • Higher natural organic matter hindered SVE but enhanced bioremediation	√	F	Soares et al. (2010)

√√, Successful; √, Partially successful; X, Not successful; P, Pilot-scale; F, Field-scale; BS, Bench-scale solvent-contaminated site were treated using SVE at 1 month intervals. Up to 3 months, it allowed continuous operation of the SVE system to individual wells for rebound of the contaminants between treatments. The process of operation intended to maximize contaminant recovery from individual wells and reduced the overall capital investment and the SVE system's operating cost. Kirtland and Aelion (2000) reported that continuous air sparging/SVE is effective in removing 87 % petroleum hydrocarbons from low permeability soil in 44 days. SVE with electrical resistance heating was able to remediate 97 % of a TCE-contaminated superfund site in a month by heating the contaminated zone to about 90 °C (US EPA 2012). Soares et al. (2010) studied the effect of bioremediation with the SVE system in a benzene-contaminated site. They found that high organic matter in soil could hinder the SVE system's operation though it was able to elevate the indigenous microbial population. Although there have been several SVE success stories, the system's performance depends on soil heterogeneity which is a crucial factor for successful remediation.

3.6 Electrokinetic Remediation

Electrokinetic (EK) remediation has emerged as a highly explored remediation technology at pilot-scale in the twenty-first century. EK remediation is also known as electrochemical decontamination, electrokinetic soil processing or electromigration. It makes use of electric current to treat slurries and soils contaminated with heavy metals, radionuclides and mixed inorganic species or certain organic compounds. When an electric current is applied in the contaminated soil, an acid is produced in the anode compartment that is transported across the soil and desorbs the pollutants from the soil surface (Cameselle et al. 2013). It also initiates electromigration of contaminants existing in the pore fluids and those present at the electrodes and form an electric potential difference which may lead to electroosmosis generated flushing of different contaminant classes (Bonilla et al. 2000; Virkutyte et al. 2002). In general, EK remediation is a controlled co-application of electroosmosis and electrical migration with electrolysis at the electrodes.

Generally, EK separation works well for low permeable soils composed of clays or silt clay mixtures. For efficient performance the presence of a pore fluid in the soil pores both to transport the contaminants injected into or extracted from the soil mass and also to conduct the electrical field is required. It may be likely to saturate certain partially saturated soils by electromagnetic advection of the analyte; however, it is required under such circumstances to engineer the process (Reddy and Chinthamreddy 2003). Many reports depict the success of electrokinetics in combination with other technologies such as Fenton's process, Lasagna treatment, ultrasonic extraction techniques and bioremediation to remediate sites contaminated with heavy metals like Pb, Cr, Zn, Hg, Fe, Mg and Cd (Zhou et al. 2005; Li et al. 1998); radionuclides like thorium, radium and uranyl; polar organic compounds such as acetic acid and phenol; and nonpolar compounds like benzene, toluene, ethylene and xylene (Gomes et al. 2012) as depicted in Table 5. This technique is mainly utilized to inject nutrients, electron acceptors and other additives into the contaminated zones so that the in-situ biodegradation process could be achieved for better contaminant degradation of more than 85 % (Pedersen et al. 2005). Generally the construction of conventional subsurface barriers like slurry walls, sheet-pile cut-off walls and grout curtains used in EK remediation is expensive and may require heavy machinery. In such cases, portability and ease of installation of electrodes surrounding the contaminated zone makes EK barriers a better alternative to conventional methods. In addition, the EK method provides early responses which helps to minimize the spread of the contaminant in time. Generally, the formation of undesirable products by the oxidation/reduction process and interference by buried metallic constituents/high moisture content of the soil limit the system's efficiency.

EK remediation is proposed more in conjunction with other in-situ remedial techniques especially for injection of surfactants (Oonnittan et al. 2009; Wan et al. 2011) that enhance the solubility and transport of the contaminant; for contaminant extraction using penetrating probes for toxin precipitation in migrating plumes; for injection of grouts for waste containment and soil stabilization; for leak detection systems in containment barriers and repair of failing containment barriers; and for pore fluid and soil characterization. Also, investigations on injecting chemical conditioners at the cathode and anode that would modify the chemical reaction at the electrode thereby enhancing the system efficiency are currently increasing day-by-day (Li et al. 2009a). So far, chemical conditioners like acetic acid, thorium ions and chelating agents such as EDTA, ammonium ions, etc. have been explored to enhance the performance of EK remediation (Lestan et al. 2008). Zhou et al. (2006) remediated 76 % of Cu using 80 V power in 140 days. Alshawabkeh et al. (2005) found that when organic acid was amended at the cathode region of the EK remedial system, it reduced the energy requirement by 70 % and enhanced the degradation of Pb by 85 % in 112 days of treatment. Pedersen et al. (2005) evaluated the effect of phosphoric acid and oxalic acid as additives to facilitate the efficient removal of Cr, Cu and As in the waste wood field site in Denmark by EK remediation. By passing an electric current of 60 V for 21 days, removal of the heavy metals was 82–96 %.

Electrochemically-enhanced oxidation is an emerging and promising approach for treating contaminated groundwater systems. Presently, EK remediation is used to remediate widespread organics like that of heavy metals in conjunction with other techniques (Alshawabkeh et al. 2005). EK remediation with Fenton's process was successful in removing 99.7 % phenol, 80 % PAH and 75 % TCE (Yang and Liu 2001). With surfactant and cosolvent-enhanced remediation, EK remediation was successful in remediating 75–80 % PAHs and chlorinated solvents using SDS, Igepal, Butylamine, Tween 89, HPCD, etc. (Saichek and Reddy 2005). Bioremediation, ultrasonic technology and Lasagna technologies were also integrated with EK remediation to remove 75–95 % organic pollutants (Ho et al. 1995; Luo et al. 2006; Huang et al. 2012).

Overall, this technology is quite tempting for field implementation since it constitutes a solution to cost-prohibitive remedial sites. The only concern is to achieve the complete clean up by reducing the energy and power requirement by using various natural energy resources which can be explored by further research. Yuan et al. (2009)

conducted a preliminary study to consider the use of a solar cell to generate an electric field for EK remediation of Cd-contaminated soil instead of direct current (DC) power supply. The EK remediation mediated by solar cell was found to drive the electromigration of Cd in contaminated soil and achieved comparatively higher removal efficiency by the high output potential generated, and was influenced by weather conditions. Moreover, the greater life time (20 years) and low running cost by the use of solar cells relatively reduced energy expenditure when compared with the traditional DC power supply. Wan et al. (2010) and Yang and Chang (2011) reported that an integrated strategy of electrokinetics coupled with nanotechnology/permeable reactive barriers along with the use of surfactants could help to achieve the remedial goals in short periods. Full-scale cost estimate of this system is about 117 US$ per m^3 soil. On the whole the scope for field remediation using electrokinetics is more promising.

3.7 Multi 3-Phase/Dual-Phase/Vacuum-Enhanced Extraction/Bioslurping

One of the best available technologies for treating saturated levels of VOCs that reached the groundwater table is multi-phase extraction (MPE). MPE is also termed bioslurping or vacuum-enhanced extraction or dual-phase extraction (DPE). In MPE, pumps of very high vacuum are used to remove various combinations of contaminated groundwater, hydrocarbon vapor and separate phase petroleum products from the subsurface. Extracted fluids and vapors are then re-injected or disposed into the subsurface (US EPA 2012). MPE typically maximizes the pollutant extraction rates especially in layered and fine grained soils. Increasing air phase permeability and by lowering the water table helps to maximize the effectiveness of SVE in the vadose zone. MPE could clean up different phases of contaminants (dissolved, vapor, residual and non-aqueous) in both saturated and vadose zones compared to the conventional pumping systems that address only two phases (Abriola and Pinder 1985). Complete removal of the contaminant is established by dissolution, volatilization and advective transport. In general, MPE can act as an ideal alternative to potentially applicable techniques like SVE and pump-and-treat.

The applicability of MPE is governed mainly by soil characteristics and to a lesser extent contaminant properties like hydraulic conductivity of the soil, and volatility/vapor pressure of the contaminant. MPE is most applicable to VOCs like petroleum hydrocarbons (BTEX), degreasing agents (TCE) and chlorinated as well as non-chlorinated solvents. Studies also tend to state that MPE is rarely applicable to treat non-volatile contaminants, provided airflow is kept higher by subsequent introduction of oxygen that could stimulate biodegradation (Rahbeh and Mohtar 2007).

MPE is effective even on moderate to low permeable soils. Even in low permeability settings when other in-situ remedial techniques are applied, where excavation is the major need, MPE could remove the contaminant source without excavation, and reduce the duration and cost of remediation (Hassanizadeh and Gray 1979).

It also reduces the number of recovery wells and is effective for capillary zone removal. Besides, it increases the total fluid recovery, maximizes aquifer transmissivity at the wellhead and minimizes the free product dispersal. On the other hand, requirement of vacuum pump or blower and more potential treatments, initial startup, adjustment periods, depth limitations and higher capital costs compared to conventional pumping approaches are disadvantages of the MPE system. Generally, when the target contaminants include long-chained hydrocarbons, the MPE of contaminants such as liquids and vapors is combined with bioventing, air sparging, or bioremediation. Use of DPE with these technologies shortens the clean up time at a site contaminated with VOCs and fuels. To recover groundwater in higher yielding aquifers, this technique can be used with the pump-and-treat method (Kram 1993). However, site geology and contaminant distribution limit the effectiveness of the system.

MPE can be designed and implemented in three main forms: single pump, dual pump, and bioslurping. In the single pump system, contaminants are extracted in both liquid and vapor phase by employing one vacuum pump which may be a liquid-ring pump/a jet pump/a blower. Single pump MPE, also termed 'vacuum groundwater extraction', is limited to 9 m depth below groundwater though it is best suited to treating low permeable soils. Bioslurping is the same as the single pump MPE scheme; however, the drop tube in a bioslurping application is generally set below the liquid-air interface and is very effective for free-product recovery. Due to increased airflow, in-situ aerobic biodegradation is enhanced in bioslurping. Yen et al. (2003) assessed the recovery of petroleum hydrocarbons in contaminated unconfined aquifer by bioslurping. Gidarakos and Aivalioti (2007) studied the long-term and large-scale application of bioslurping of a Greek petroleum refinery site. They found that 4-year application of bioslurping over a 1,000,000 m^2 contaminated site can potentially remove LNAPLs, but appropriate groundwater remediation techniques like air stripping were recommended to directly treat the groundwater. Dual-phase system uses a surface blower to extract vapors and two pumps to extract liquids from the well. Dual-pump systems, just a combination of groundwater recovery systems and SVE, are generally easier with short treatment time (6 months to 2 years), and applicable over a wide range of site conditions compared to single-pump systems although the equipment costs are higher (US EPA 2012). Three-pump systems are also available.

Studies indicated that continuous temporary DPE treatment is more promising than pulsed/intermittent permanent DPE systems because pulsed DPE hinders enhanced biodegradation and the product recovery. Furthermore, in almost all of the in-situ groundwater remediation studies using other conventional techniques (SVP/thermal conduction heating), MPE systems are widely implemented which assures complete remediation of VOCs as suggested by Nelson et al. (2009). Bierschenk et al. (2004) also reported that 99 % DCA and CVOCs was recovered by high vacuum pump extraction system when the contaminated site was subjected to thermal conductive heating for 400 days. Nelson et al. (2009) made use of a patented technology named 'supersaturated water injection (SWI) system' where nucleating gas bubbles could volatilize LNAPLs. In this study, an LNAPL composed of 103 kg of volatile pentane, 30 kg of non-volatile soltrol and hexane was emplaced at residual saturation below the water table. The SWI technology removed 50 % less volatile hexane and 78 % pentane. The mass removed was comparatively higher to that expected by air sparging. Rahbeh and Mohtar (2007) studied the positive effect of multi-phase transport models to full-scale treatment by air sparging and SVE of BTEX-contaminated site. A similar field study envisaging the success of air sparging with MPE was done by Jang and Aral (2009).

Likewise, there are more prospects to integrate MPE system with other conventional remedial technologies to enhance their efficiency. However, the technology could be improved by implementing an automated operational system to reduce labor costs and improve safety, minimizing size of treatment to access more limited space, integrating with pneumatic or hydraulic fracturing in extremely low permeability formations, etc. The technology requires approximately 30–75 US$ per m^3 for its operation (FRTR 2012).

3.8 Air Sparging

Air sparging, also known as ‘in-situ volatilization’ and ‘in-situ air stripping’, involves the injection of gas (usually air/oxygen) under pressure into the subsurface saturated zone in order to volatilize the contaminants sorbed onto the soil surface as well as dissolved in the groundwater by increasing the subsurface oxygen concentrations (US EPA 2012). The injected air flows through the saturated and vadose zones, volatilizes the contaminants and migrate them upwards to the vadose zone, from where they are either subjected to bioremediation or removed by SVE system. Air sparging is one of the best stimulators for biodegradation of pollutants as it is always documented to be a supporter of microflora in the contaminated sites, especially for aerobic soils (Brennerova et al. 2009). Since 1980, in-situ air sparging had been used to remediate a broad range of VOCs and SVOCs (Khan et al. 2004) including diesel, jet fuel, oils, greases, gasoline, chlorinated solvents and fuels. This technique is less applicable for treating fuels like diesel and kerosene, and more applicable to remediate sites contaminated with BTEX as they are readily transferable from the dissolved phase to the gaseous phase. Air sparging performs better only when it is combined with other remediation techniques like SVE and pump-and-treat.

This technology has a few merits: minimal disturbance of treatment zone by implementation; easily installable and readily available equipment; very low treatment time usually shorter than 1–3 years when the conditions are optimized; less costly (20–50 US$/Mg) compared to other in-situ treatment systems; and no post-treatment requirements/recovered product disposal related issues. Air sparging is unsuccessful for non-biodegradable and non-strippable contaminants, silt/clay sediment sites, and when the vertical pathways of air becomes hampered (Kirtland and Aelion 2000; Benner et al. 2002). Neither is this technique suited for treating stratified soils and confined aquifers, and when air is sparged into the contaminated zone, this risks contaminants migrating into the uncontaminated zones. Besides, field-level implementation of air sparging requires a comprehensive pilot study beforehand to ensure the contaminant migration and vapor control limit which consumes additional time and cost (Tomlinson et al. 2003; Adams and Ready 2003).

An in-situ air sparging system with multiple injection wells performed better than a single injection well in-situ air sparging system and was effective in capturing and remediating the detoured contaminant plume (Jang and Aral 2009). At field-scale, Kao et al. (2008) showed >70 % BTEX removal within 20 months at an average groundwater temperature of 18 °C through the biosparging system. They explained that biosparging operation caused the shifting of anaerobic to aerobic conditions inside the BTEX plume which increased the population of heterotrophs that aided in BTEX biodegradation. Aivalioti and Gidarakos (2008) reported 99 % removal of BTEX at the aquifer (600 m^2) of a Greek petroleum refinery site in 5 months by biosparging. At bench-scale, a surfactant (sodiumdodecylbenzene sulfonate)-enhanced air sparging system that involved nitrogen gas at a steady flow rate of 0.12 L/min removed about 78 % PCE from a contaminated aquifer (Kim et al. 2009). The use of biosurfactants along with air sparging for removing volatile contaminants was recommended by Abdel-Moghny et al. (2012).

Available literature (Table 4) indicates that air sparging when combined with other conventional techniques like SVE or volatilization/biodegradation mechanisms is cost-effective and efficient in treating petroleum contaminants at large-scale (Kao et al. 2008). Jennifer (2008) proved that an air sparging system that ran for 3 days in a BTEX-contaminated groundwater could remove 21 % residue by volatilization, 22 % by biodegradation, and 0.1 % by leakage—the three usual processes that occur in every biosparging mechanism. Liang and Chen (2010) evaluated the complete destruction of BTEX in a contaminated site using iron-activated persulfate chemical oxidation coupled with a wet scrubbing system. Complete BTEX removal was achieved by the use of a citric acid chelated iron activator. Hence, there are more prospects to enhance the efficacy of air sparging-related remedial systems by developing continuous systems (e.g., pulsed air injection) integrated with eco-friendly remedial technologies that are more economical.

3.9 Bioventing

Bioventing stimulates the in-situ aerobic biodegradation of fuels, non-halogenated VOCs, SVOCs, herbicides and pesticides by the delivery of oxygen to the contaminated plume. Unlike biosparging where nutrients and or air pumped into the saturated zone, this system injects or extracts air through an unsaturated zone. In contrast to SVE, bioventing uses low air flow rates that are necessary to maintain microbial activity. Optimal flow rates maximize the biodegradation process and minimize contaminant volatilization as vapors pass gradually through biologically active soil (Lee et al. 2001). Since low air volume is required for the process, it could even degrade semi-volatile organic compounds in low permeability soils.

Conventional bioventing systems use an electric blower to deliver oxygen to the subsurface wells. Natural air-exchange is used in the passive bioventing systems to deliver oxygen via bioventing wells to the subsurface with a one-way valve that helps to maintain a controlled air flow relative to the drop in atmospheric pressure (Kao et al. 2001). This technology is most applicable for mid-weight petroleum products like diesel compared to heavier compounds which generally take longer to biodegrade; lighter compounds tend to volatilize quickly and can be treated better along with the SVE system. Halogenated organics are also treatable by this technique, but this is less effective. A cometabolite is required to biodegrade chlorinated compounds using this system (Sui et al. 2006). Where sites are contaminated with high concentrations of organic compounds or heavy metals, this technology is not applicable because the higher contaminant concentrations hinder microbial growth. It is ineffective in treating areas with very high water tables as well as soils with low moisture content which affects soil aeration, and in turn, the microbial survivality (Dupont 1993).

All that bioventing requires is the presence of indigenous microbes that are able to degrade the pollutant of concern along with oxygen and nutrients required for microbial growth. Bioavailability of the contaminant also matters a lot. Bioventing is a very simple, inexpensive and publicly accepted technology, where the used equipment requires only low maintenance and can be left unattended for longer periods of time. It needs only a short treatment period between 6 months to 2 years and generally does not require off-gas treatments. Yet, this technology cannot always reach low clean up limits. Mostly, saturated soils are difficult to aerate and saturated soil zones of low air permeability are created by the fluctuating water tables which constrain the system (Barnette et al. 2005).

At pilot-scale, bioventing was highly successful (Molnar et al. 2005; Dominguez et al. 2012). Cometabolic bioventing effectively degraded 95 % TCE in unsaturated soil zone when methane was used as the growth substrate (Sui et al. 2006). Moller et al. (1996) studied the effects of inoculation of oil-degrading bacterium, nutrient addition and bioventing on bioremediation of diesel in unsaturated soils. With 112 days of monitoring, about 96 % degradation was achieved. The influence of cyclodextrin-enhanced bioventing in soils, contaminated with transformer oil, was reported by Molnar et al. (2005). The average transformer oil concentration in 50 m^3 of contaminated soil was about 20,000 mg/kg and 1.0 mg/L in groundwater. *Ex*-situ physico-chemical treatment of groundwater was also combined along with in-situ bioventing of the unsaturated zone. Application of nutrients together with 50 % randomly methylated-beta-cyclodextrins (RAMEB) three times during a 46-week experimental period caused a significant reduction in the soil TPH concentration by 99 %.

Hvidberg (2007) conducted a novel treatment train consisting of an enclosure, in-situ alkaline hydrolysis, pump-and-treat and bioventing, and remediated 95 % of a large pesticide-contaminated site located on Denmark's north-western coast. Using small-scale respirometers containing soil contaminated with gasoline, the effects of forms and concentration of nitrogen as well as soil water content along with microbes on biodegradation rate of gasoline were determined (US EPA 2012).

Results indicated that soil water content of 18 % and C:N ratio of 10:1 are highly suited to bring about effective gasoline degradation. Also, bacteria were the dominant organisms involved in gasoline degradation. Magalhaes et al. (2009) combined an air-injection bioventing system and a biotrickling filter for the treatment of toluene-contaminated soil over a short period of time, and observed about 99 % removal of toluene in just 5 days.

Recently, sustainable wind-driven bioventing technology was proposed by Dominguez et al. (2012) at pilot-scale to decontaminate petroleum hydrocarbons. Because of the diurnal and seasonal wind drifts of the site, natural air pulsing occurred and bioventing was able to reduce 90 % VOCs in 2 months though the total treatment time without adding an energy source was 15 months; by doing so, energy equivalent to 20,000 kW/h/year was saved. Naturally, the drop in the amount of energy reduced the extent of greenhouse gases produced (an equivalent of approximately 12 Mg of CO_2/year). They also reported that the wind-driven method is highly cost-effective as it can maximize available resources by using existing groundwater wells and minimize water consumption as well as waste generation resulting from the installation of new wells. Zenker et al. (2005) suggested that long-term passive bioventing by using wind-driven energy is a cost-effective, full-scale, in-situ remediation technology to treat VOCs at remote locations with high, sustained wind speeds and permeable vadose zones. Thus, there are more prospects to explore the degradability of bioventing, especially the passive system, as that of the wind-driven systems for varied mixed contaminants in large-scale. Typically, bioventing costs about 20 US$ to treat per m^3 soil (Juwarkar et al. 2010).

3.10 Natural Attenuation

Natural attenuation/in-situ bioremediation/bioattenuation/passive remediation/intrinsic remediation was not an acceptable technology until 1994. Only by 1998, US EPA recognized bioattenuation as a viable technique to remediate groundwater and soil in its superfund sites, and it has now been accepted as a valid method for treating petroleum-contaminated sites by several state underground storage tank programs (US EPA 2012). So far, many projects have been successfully completed in the superfund sites as presented in Table 8. To date, several studies are being reported with this technology at full-scale. This technique employs the use of natural processes to reduce the concentration of contaminants at polluted sites and restrict the spread of pollutants from chemical spills. In case of natural attenuation, pollutants are simply left in place and the naturally-occurring processes like dispersion, volatilization, dilution, radioactive decay, biodegradation and sorption of the toxins onto the soil clay/organic matter help to clean up the site. Biological degradation reduces contaminant mass; simple dilution or dispersion reduces the contaminant concentrations; and adsorption helps to bind the contaminants to soil particles and prevent the contaminant migration. In this way, the environmental contaminants are left undisturbed (Khan et al. 2004).

Table 8 Recent application of natural attenuation at US superfund sites (US EPA 2012)

Site	Contaminant
^{G} Altus Air Force Base, Altus, Oklahoma	TCE
^{S} Wyckoff/Eagle Harbor, Puget Sound, Washington	Hg
^{G} Naval Surface Warfare Center, Indian Head, Maryland	Perchlorate
^{S} Louisiana Pipeline Terminals, Gulf Coast, Louisiana	PAHs
^{S} Ketchikan Pulp Company Site, Ketchikan, Alaska	NH_3, Sulfides, Methylphenol
^{S} Bremerton Naval Complex, Bremerton, Washington	PCBs, Hg

^{G} Groundwater; ^{S} Sediment

Natural attenuation processes can be categorised as destructive (where contaminants are destroyed) and non-destructive (where the concentration of the contaminant is reduced) (Gelman and Binstock 2008). This remediation technology is a proactive approach that is mostly mislabelled as the 'walk away' or 'do nothing' technique to site clean up that focuses on the authentication and monitoring of natural clean up methods other than relying completely on engineered systems (Khan and Husain 2002). Bioattenuation is mainly employed for removing herbicides, non-halogenated VOCs and SVOCs, fuels and pesticides from aquifer or soil particularly hydrophobic organics of high molecular weight like PAHs (Clement et al. 2000; Hejazi 2002; Nobre and Nobre 2004). This process could be applied for halogenated VOCs and SVOCs, but it may require longer treatment times. Surface geology, microbiology and hydrology decide the success of the bioattenuation processes. Before a site is processed by natural attenuation, it is necessary to assess the efficacy of natural processes that are occurring to reduce the contaminant levels over time. The treatment zone should be situated in a region remote from the potential receptors with less risk to ecology or public health. Bioattenuation is highly applicable for low to high permeable soils because high permeability speeds up the contaminant migration. Low permeability prevents the air, water and nutrients from dispersing throughout the soil and slows down the contaminant breakdown.

Several packages are offered for predictive modelling of bioattenuation. For instance, BIOSCREEN to stimulate bioattenuation from petroleum fuel discharges and BTEX, BIOCHLOR for chlorinated solvents, Bioredox-MT3DMS for chlorinated solvents and petroleum hydrocarbons, and BIOSLURP for NAPLs (Mulligan and Yong 2004). Natural attenuation is quite simple compared to other techniques where it is possible to be carried out with little/no site disturbance. This method could be used with other methods as pre- or post-treatment options at contaminated sites. However, this technique often needs a longer clean up period to achieve the remediation objectives compared to other conventional techniques and is generally very slow, where long-term monitoring is required. Performance of natural attenuation systems is often unpredictable. Generally, the by-products are ecologically more risky than the parent compounds. For instance, VC, the degradation product of TCE, is more toxic than TCE itself. Also, resolubilization and desorption of pollutants could occur and the modelling data need to be evaluated with caution as it is subjected to significant uncertainty. Cost of natural attenuation treatment is variable and no specific cost estimate is available (Khan et al. 2004).

Gonzalez-Chavez et al. (2009) carried out a field-scale natural attenuation study with the help of Arbuscular Mycorrhizal (AM) fungi and plants in a slag heap polluted with highly available Cd. The experimental results confirmed that glomalin protein produced by AM fungi could cause Cd stabilization, and use of plants and AM fungi aid the natural attenuation process. Bento et al. (2005) compared the biological degradation of TPH-polluted soil collected from the USA and China with natural attenuation, and concluded that natural attenuation increased (fourfold) the microbial activity and TPH degradation activity. Johnson et al. (2003) reviewed the potential of benzene degradation under a range of anaerobic groundwater conditions by natural attenuation. Many studies on the biodegradation of PAHs have been done but our knowledge of biodegradation behavior in the field compared to BTEX or chlorinated solvents is limited (Juhasz and Naidu 2000; Rogers et al. 2002).

Margesin and Schinner (2001) reported that natural attenuation is an eco-friendly technology that could significantly remove diesel oil even under unfavorable conditions, for instance, those present at about 3000 m above sea level in an alpine glacier. Using the mass flux method of detection, Kao and Wang (2001) reported 99 % BTEX degradation by natural attenuation at field-scale. Asta et al. (2010) observed that even very high concentrations (up to 4 mg/L) of As(III) and As(V) acidic discharge of the abandoned Tinto Santa Rosa mine in the Iberian pyritic belt, Spain, could be bioattenuated by sorption using iron oxyhydroxysulphate and iron oxyhydroxide as stream bed precipitates. Serrano et al. (2008) concluded that after a diesel spill in agricultural soil, most of the aliphatic hydrocarbons persist in the subsurface (up to 0.1 m) and volatilization was the main cause for the decline in aliphatic hydrocarbon concentration. Also, natural attenuation was the main source of aliphatic hydrocarbon degradation in soil when pH, moisture and temperature of the soil were optimized in the order of increasing microbial enzyme activity. A significant decrease (99 %) in dissolved mono and polycyclic hydrocarbon concentration was observed in a 14 year-old manufactured gas plant site subjected to monitored natural attenuation (Neuhauser et al. 2009).

Meers et al. (2010) introduced an analogy of phytoattenuation where the concept of natural attenuation and phytoremediation was integrated with a risk-based approach. They conducted a field experiment using energy crop (maize) that could result in the production of 33,000–46,000 kW h/10,000 m^2 of renewable electrical and thermal energy annually which by exchange of fossil energy would imply a decline of about 21×10^7 kg/m^2/year CO_2 if used to substitute a coal-fed power plant. They also detected a significant yearly decline of 0–5 mg/kg Zn in the subsurface though not Cd and Pb. A long-term natural attenuation study was conducted by Fraser et al. (2008) at a site that was contaminated by naphthalene, phenol, xylene, methyl naphthalene, acenaphthene, biphenyl, anthracene, dibenzofuran, fluorene, phenanthrene and carbazole. More than 90 % of naphthalene, biphenyl and carbazole entering the plume were completely removed after a 14-year attenuation process. Concentration of the remaining pollutants, however, was observed to be expanding due to limited degradation potential and increased mass flux.

Biotransformation emerged as the major process that controls the natural attenuation mechanism. Cozzarelli et al. (2011) conceptualized natural attenuation processes in landfill leachate plumes. He et al. (2010) found that enhanced reductive dechlorination could mobilize As at field-scale. Choi and Lee (2011) suggested the integration of some active remedial measures with biodegradation and natural attenuation to achieve the anticipated remedial goal in short time. Macias et al. (2012) conducted the natural pre-treatment and passive remediation of highly contaminated acid-mine drainage. Their results confirmed that coupled application of natural Fe-oxidising lagoon pretreatments and limestone-DAS (reactive substrate) passive treatments is a viable and potential approach to remediate acid-mine drainages contaminated with high concentrations of heavy metals. All these studies dictate that although natural attenuation is an eco-friendly technique, it takes a couple of years to achieve the anticipated remedial goal. Hence, integrating suitable remedial techniques that could support the attenuation processes are required to reduce the remedial time in the near future.

3.11 Phytoremediation

Phytoremediation involves the use of vegetation (grasses/plants/trees), its associated microorganisms and enzymes to remove, destroy, immobilize or contain pollutants from contaminated media. Some plants have the potential to accumulate large amounts of heavy metals that are not exploited in their function, and are generally known as‘hyperaccumulators’ (Susarla et al. 2002). Plants with the ability to take up and process or degrade even organics for their physiological needs are also referred to as hyperaccumulators (Vouillamoz and Mike 2001). Compared to other technologies although phytoremediation is time-consuming, it is the most cost-effective of the other remedial approaches as very large volumes of contaminated soil can be treated in-situ where excavation is not required (Mench et al. 2010). Most information related to phytoremediation is associated to its application in soil at field and laboratory level, and its utility in groundwater remediation is increasing interest (Juwarkar et al. 2010).

Phytoremediation is of five types: (1) phytotransformation (appropriate to treat both water and soil where pollutant remediation occurs by means of plant metabolism), (2) rhizofiltration (a water remediation method where pollutants are accumulated by the plant roots), (3) phytostimulation (microbial degradation is stimulated by plant activity in the root zone), (4) phytoextraction (contaminant uptake from the soil), and (5) phytostabilization (reducing the contaminant migration using plants) (Barcelo and Poschenrieder 2003; Gosh and Singh 2005). Phytoremediation is used to treat PAHs, PCBs, petroleum hydrocarbons, heavy metals, radionuclides, non-aromatic chlorinated solvents, organophosphate insecticides, explosives, BTEX, surplus mineral and nitrotoluene ammunition wastes (Nedunuri et al. 2000; Barac et al. 2004; Sheng and Gong 2006; Leigh et al. 2006; Al-Qurainy and Abdel-Megeed 2009; Ahmadpour et al. 2012). Phytoremediation is also applied in landfill covers, buffer regions for agricultural run-off, industrial wastewater, and drinking water treatments (Mench et al. 2010).

The use of phytoremediation is, generally its application has several limitations before it can be implemented at a site. First of all, it is vital that the polluted site to be remediated should be able to suitably support the plant growth followed by the availability of feasible growth conditions (weather, soil properties like nutrient availability, texture, pH and moisture). The second limitation is that phytoremediation is applicable only at shallow depths (upper 0.2–0.25 m of the soil horizon). Only in some cases can deeper depths be remediated when it is integrated with other technologies or some hybrid trees (for example, poplar trees that could grow to a depth of 5 m). Third, since it takes time for the establishment of plants in the remedial sites it is not suitable for rapid treatments. Phytoremediation is also restricted by the rate of root growth as denser root mass is ideal to contact more pollutants and slower growth rates increase the treatment time (Yang 2008; Gerhardt et al. 2009). Even winter could shut down the system completely as plants become dormant. Clean up generally takes more than one growing season.

Another problem is the risk of bioaccumulating the contaminant in the food chain as there is a potential for plant-eating animals to be exposed to the contaminants when they eat the phytoaccumulators. To avoid such circumstances, 'phytomining' is practised where plants are harvested and disposed or destroyed after the extraction of reusable metals (Chaney et al. 2007). Even overhead nettings and perimeter fencing are mounted to prevent animals grazing on contaminated plant materials. Phytoremediation is suited only to lower contaminant concentrations as very high contaminant levels could restrict the establishment of phytoremediators (Vishnoi and Srivastava 2008). Finally, it is recommended to confirm that transpiration and unwanted volatilization of the toxins to the atmosphere through plant uptake does not occur. On the whole, to assess the fate of the contaminants, sites undergoing phytoremediation must be continuously monitored.

Comparable advantages are evident in the phytoremediation system. Phytoremediation is an aesthetically-pleasing, passive and solar energy-driven technique that is able to treat outsized contaminants with minimal site disturbance along with minimal generation of secondary wastes where the end products are only CO_2 and H_2O, but not any hazardous toxins. This technique is low cost for treating large-scale contaminated sites with low contaminant concentrations (Mench et al. 2010). Usually, the unused top soil could be used for agriculture. About 5–18 US$ is expended to clean up an m^2 contaminated site by plants. So far, numerous plant species were tested for their ability to remediate organic and inorganic contaminants like pesticides, PAHs, chlorinated solvents, diesel, phenol, BTEX, Cr, Cd, Zn, Ni, Cu, As, Hg, Mn, Co, Pb, Se, U, N and P at field-scale as summarized in Table 9. Over the last 10 years, the potential use of trees as a suitable vegetation cover for polluted sites has also received increasing attention (US EPA 2012).

James (2001) and Pulford et al. (2002) proposed that deep rooting plants could reduce highly toxic Cr(VI) to Cr(III) since organic products of root metabolism could act as reducing agents. Research on the application of phytoremediating plant with inorganic, organic and bio-amendments revealed promising results (Green and Hoffnagle 2004). Banuelos et al. (2005) reported that Indian mustard can be genetically modified to produce more biomass in the polluted soil and hyperaccumulate

Table 9 Plants used in phytoremediation for the removal of selected organic and inorganic pollutants

Contaminant	Plant used
Pesticides	*Artemisia annua*, *Kochia sieversiana*, *Kochia scoparia*, *Xanthium strumarium*, *Oryza sativa* cv. Nipponbare, *Lemna minor*, *Elodea canadensis*, *Cabomba aquatic*, *Pisum sativum*, *Cucurbita pepo*, *Eichhornia crassipes*, *Corbicula fluminea*, *Pistia stratiotes*, *Lemna minor*
PAHs	*Lolium multiflorum*, *Lolium perenne*, *Betula pendula*, *Galega orientalis*, *Brassica campestris*, *Cordia subcordata*, *Festuca arundinacea*, *Melilotus officinalis*, *Panicum virgatum*, *Astragalus membranaceus*, *Aeschynomene indica*, *Avena sativa*, *Capsicum annum*, *Pinus strobus*, *Salix viminalis*
Chlorinated solvents	*Arabidopsis thaliana*, *Festuca arundinacea*, *Panicum virgatum*, *Cucurbita pepo*, *Populus* sp., *Salix* sp., *Brassica napus*, *Hydroponic Leucaena*, *Elodea canadensis*
Diesel	*Pinus sylvestris*, *Pinus sativum*, *Festuca rubra*, *Lolium perenne*, *Trifolium repens*, *Jatropha curcas*, *Cyprus rotundus*, *Salix alba*
Phenol	*Vetiveria zizanoides*, *Astragalus chrysopteru*, *Hordeum vulgare*, *Typha angustifolia*
BTEX	*Paspalum vaginatum*, *Zoysia tenuifolia*, *Galega orientalis*, *Populus deltoides*
Cr	*Trigonella foenum-graecum* L., *Spinacia oleracea* L., *Brassica campestris* L., *Helianthus annuus*, *Eichhornia crassipes*, *Callitriche cophocarpa*, *Polianthes tuberosa*, *Genipa Americana*
Cd	*Thlaspi caerulescens*, *Lolium perenne* cv. *Elka*, *Solanum nigrum*, *Trifolium repens*, *Brassica napus*, *Populus canadensis*, *Populus deltoides*, *Juncus subsecundus*, *Ricinus communis*, *Alyssum* sp., *Typha domingensis*
Zn	*Tithonia diversifolia*, *Helianthus annuus*, *Paulownia tomentosa*, *Arabidopsis halleri*, *Thlaspi caerulescens*, *Salix caprea*, *Anthyllis vulneraria*, *Lupinus albus*, *Azolla caroliniana*, *Picris divaricata*
Ni	*Alyssum corsicum*, *Alyssum murale*, *Alyssum lesbiacum*, *Thlaspi goesingense*, *Sebertia acuminata*, *Lycopersicon esculentum*, *Solanum nigrum*, *Amaranthus* sp., *Populus alba*, *Spirodela polyrhiza*
Cu	*Zea mays*, *Aeolanthus biformifolius*, *Commelina communis*, *Elsholtzia splendens*, *Brassica juncea*, *Baccharis sarothroides*, *Aldama dentata*, *Lemna gibba*, *Onobrychis viciifolia*, *Dyera costulata*, *Lemna minor*
As	*Arundo donax*, *Tagetes erecta*, *Tagetes patula*; *Pteris vittata*, *Pityrogramma calomelanos*, *Helianthus annuus*, *Agrostis tenuis*, *Chrysopogon zizanioides*, *Cynara cardunculus*
Hg	*Eichhornia crassipes*, *Pistia stratiotes*, *Scirpus tabernaemontani*, *Colocasia esculenta*, *Silene vulgaris*, *Elodea nuttallii*, *Brassica juncea*, *Azolla pinnata*
Mn	*Eichhornia crassipes*, *Phytolacca americana*, *Phytolacca acinosa*, *Vigna unguiculata*, *Alyssum* sp., *Typha angustifolia*, *Phragmites* sp.
Co	*Glycine max*, *Pistia stratiotes*, *Ambrosia artemisiifolia*, *Pleurotus pulmonarius*
Pb	*Vetiveria zizanioides*, *Thlaspi praecox*, *Mimosa pudica*, *Brassica juncea*, *Ambrosia artemisiifolia*, *Apocynum cannabinum*, *Bidens triplinervia*, *Zea mays*, *Typha latifolia*, *Salix* sp., *Lemna minor*
Se	*Brassica napus*, *Festuca arundinacea*, *Spartina patens*, *Arabidopsis thaliana*, *Pteris vittata*, *Stanleya pinnata*
U	*Helianthus annuus*, *Phragmites* sp., *Lagonychium farctum*, *Vetiveria zizanioides*
B	*Lemna gibba*, *Salvinia natans*, *Populus* sp., *Vetiveria zizanioides*
N and P	*Thalia geniculata*, *Onenathe javanica*, *Phyla lanceolata*, *Eichhornia crassipes*, *Ipomoea aquatica*, *Pistia stratiotes*, *Populus deltoides*, *Chlorella vulgaris*

Se in a short time. Ma et al. (2001) demonstrated that Chinese brake fern (*Pteris vittata*) could hyperaccumulate 22,000 mg/kg As in their shoots. Gumaelius et al. (2004) also indicated that *P. vittata* could accumulate 200-fold higher As than any other vegetation. Raskin and Ensley (2000) showed that sunflower had greater ability to remove Pb from leaf compared to corn, spinach, Indian mustard, tobacco and rye.

Plants like sunflower, corn, spinach, Indian mustard, tobacco and rye have been tested for their potential to accumulate Pb from effluent, wherein sunflower showed the highest potential to remove Pb (Raskin and Ensley 2000). A field experiment by Zhuang et al. (2007) revealed that *Rumex crispus* is an ideal candidate for phytoextraction of Zn and Cd from soil. Another field trial conducted by Shu et al. (2004) compared the growth and metal accumulation ability of four grasses (*Imparata cylindrica* var. *major*, *Paspalum notatum*, *Vetiveria zizanioides* and *Cynodon dactylon*) supplemented with and without complex fertilizer (NPK) and domestic refuse. The results showed that among the grass species selected for phytostabilization and phytoextraction of metal-contaminated soils, *V. zizanioides* was the best choice. About 70 % loss of total petroleum hydrocarbons was recorded after one year's growth of *Carox exigua*, *Panicum virgatum*, *Tripsacum dactyloides* and *Vicia faba* (Euliss et al. 2008). Diab (2008) observed 47 % degradation of total petroleum hydrocarbons in 60 days by *V. faba*.

Komarek et al. (2008) explored the influence of chelant-enhanced phytoextraction of heavy metals. They confirmed that adding EDTA significantly increased the translocation rate of Pb content in poplar plants. A similar field study by Zhuang et al. (2005) indicated the great potential of *Viola baoshaensis* for removing Pb, Cd and Zn in the presence of ammonium additives/EDTA. Otto et al. (2008) indicated that narrow plant filter strips could commendably decrease herbicide run-off from agricultural soils because of the plants' ability to promote infiltration, delay surface runoff and adsorb herbicides. Root zone effects in a constructed wetland system were noticed using plant growth-promoting rhizobactera like *Rhizobium leguminosarum* and *Pseudomonas aeruginosa* by Radwan et al. (2007). Mendelssohn et al. (1995) conducted a multidisciplinary experimental program to evaluate the use of bioremediation products such as microbial seeding, inorganic fertilizer and soil oxidant, as a means of oil biodegradation enhancers in coastal salt marshes with *Sagittaria alterniflora*. Their experimental results showed that fertilizer application enhanced the rate of phytoremediation at wetlands, and degradation of oil was greater in the drained condition than in the flooded condition.

An AM fungus colonized the phytoremediators that were raised in a metal(loid) remediating site and aided in the nutrient acquisition for their host plants (Meharg 2001). Manceau et al. (2008) reported that two common wetland plants, *Iris pseudacorus* and *Phragmites australis*, transformed Cu into metallic nano-sized particles near and in root zones colonized by AM fungi. The role of potential amendments like gravel sludge, biosolids, oxides of Fe, Mn, Al and Ti, coal fly ashes, ZVI grit and alkaline materials in phytostabilization was reviewed in the literature (Friesl et al. 2006; Kumpiene et al. 2008; Mench et al. 2009; Vangronsveld et al. 2009). Mench et al. (2007) reported that a long-lasting phytostabilization effect was obtained for ZVI grit product and biosolids. According to McGrath et al. (2006), in a 3-year cropping season, *Thlaspi caerulescens* crop extracted up to 0.4 % Zn and 3 % Cd, and the maximum annual removal was 0.4 g Zn, and 0.07 g Cd m^{-2}. Vervaeke et al. (2003) conducted a field trial implementing green capping using willow trees in sediment contaminated with Cd, Cu, Pb and Zn. It was found that after 1.5 years nearly 57 % mineral oil was significantly reduced in the sediment with a pronounced 79 % decrease in the root zone. Euliss et al. (2008) conducted a field study and discovered that about 70 % PAHs from the contaminated sediment could be remediated by planting *C. stricta*, *T. dactyloides* and *P. virgatum* over a 1 year period. Hong et al. (2001) achieved phytohydraulic containment and 36.5–67.0 % methyl tert-butyl ether (MTBE) removal from a groundwater plume using poplar plants. Hultgren et al. (2009) observed 100 % phenanthrene and 80 % pyrene degradation efficiency in the presence of *Salix viminalis*, but merely 63 and 68 % PAH degradation was achieved without plants. Fassler et al. (2012) indicated that application of elemental sulphur helps to enhance the phytoextraction of metals at real contaminated sites.

Phytoremediation of phthalic acid esters by intercropping *Medicago sativa*, *Lolium perenne* and *Festuca arundinacea* was demonstrated by Ma et al. (2012) in the largest e-waste recycling site in China. Over 80 % of the phthalic acid esters were removed by effective monocropping of *Medicago sativa* and intercropping of all the three crops. Galazka et al. (2012) studied the effect of *Festuca pratensis* with and without the inoculation by diazotrophic bacteria (*Azospirillum* spp. and *Pseudomonas stutzeri*) on the degradation of a mixture of PAHs and diesel fuel. It was observed that inoculation of diazotrophs with phytoremediators helped to achieve more than 70 % remediation. Under aerobic conditions, surfactant solution (Tween 80) was effective in the rhizodegradation of oil with added benefit on the indigenous soil microbes (Memarian and Ramamurthy 2012). These days, transgenic/genetically modified plants are emerging as a promising technology which is discussed in the later part of this review under emerging techniques. In most field studies, only 50–70 % remediation was achieved at least with 1 year of treatment time. Solutions to achieve >90 % remediation in most cases by reducing the treatment time should be worked out in future by integrating the plants with supportive physico-bio-chemical elements.

3.12 Bioaugmentation

Biostimulation and bioaugmentation possess the ultimate goal of decontamination through biotransformation (Brar et al. 2006). Bioaugmentation and biostimulation can be either an in-situ or *ex*-situ treatment process. A handful of successful field-scale studies have confirmed the performance of biostimulation and bioaugmentation as stand-alone and integrated systems (Table 10). Rather than nutrient load, specialization and selectivity of inoculated microbes determine the bioremediation potential (Hamdi et al. 2007). In bioaugmentation, metabolic activity of indigenous

Table 10 Bioaugmentation and biostimulation: successful case studies at field-/pilot-scale

Research group	Year	Contaminant	Technology		Stimulants		
			BS	BA	Fertilizer	Surfactant	Others
[f] Sanscartier et al.	2009	TPH and PAHs	♣	–	♣	♣	♣ (1)
[f] Tsutsumi et al.	2000	Crude oil	–	♣	–	♣	–
[f] Duke et al.	2000	Crude oil and fuel oil	♣	–	♣	–	♣ (2)
[f] Lendvay et al.	2003	PCE, DCE	♣	♣	♣	–	–
[f] Delille et al.	2002	Crude oil	♣	–	♣	–	♣ (3)
[f] US EPA	2012	PCE, DCE	♣	♣	–	–	♣ (4)
[p] Straube et al.	2003	PAHs	♣	♣	♣	–	–
[p] Yu et al.	2005	PAHs	–	♣	–	–	–
[p] Atagana	2006	PAHs	♣	♣	♣	–	♣ (4)
[f] Maes et al.	2006	DCA	♣	♣	–	–	♣ (4)
[f] Jimenez et al.	2006	PAHs	♣	–	♣	–	–
[p] Malina and Zawierucha	2007	TPH and PAHs	♣	♣	–	–	♣ (4)
[f] Garcia-Blanco et al.	2007	Crude oil	♣	–	♣	–	–
[p] Jacques et al.	2008	PAHs	♣	–	–	–	–
[f] Kauppi et al.	2011	TPH and PAHs	♣	♣	♣	–	–

[f] Field-scale study; [p] Pilot-scale study; BS, Biostimulation; BA, Bioaugmentation; '♣', Implemented/used specific technology/stimulant; '–', Technology/stimulant was not implemented/used; 'Others' include: (1) Moisture and temperature amendments, (2) Forced aeration, (3) Fish compost, and (4) Electron donors/acceptors like acetate, methanol, ethanol, hydrogen peroxide, etc.

soil microbes is further enhanced by inoculating consortia or single cells of microbes containing genes for biodegradation so that these genes are transferred to indigenous and rhizospheric microbes (Gentry et al. 2004). Genetically modified organisms or indigenous or allochthonous wild types are the specialized organisms that are included in bioaugmentation. According to Dejonghe et al. (2001), bioaugmentation corresponds to an increase in the genetic diversity or gene pool of the targeted site.

Rhizoremediation, suggested by Kuiper et al. (2004), is indeed one form of bioaugmentation. Mrozik and Piotrowska-Seget (2010), El Fantroussi and Agathos (2005), and Iwamoto and Nasu (2001) stated that bioaugmentation is applicable only when biostimulation and bioattenuation fails. The major factors affecting bioaugmentation are: (1) environmental (temperature, pH, moisture content, electrical conductivity, availability of electron acceptors, availability of nutrients and toxic molecules); (2) microbial (horizontal gene transfer of wild type strains and genetically modified organisms, microbial interactions and mutation, microbial diversity, toxic metabolites produced from degradation compounds, metabolic activity or enzyme induction and activity); (3) physico-chemical bioavailability of contaminants (solubility in water, complexation, stability, toxicity of pollutants, mass transfer limitations and irreversible sorption); (4) growth substrates (bioavailability and concentrations of contaminants and substrates, limiting factors like NPK and preference of other substrates other than the contaminants); and (5) aerobic or anaerobic process (electron acceptor/donor availability and reduction/oxidant potential).

Generally, microbes that express catabolically superior toxin-degrading enzymes and are highly resistant to environmental stresses should be selected for bioaugmentation (Singer et al. 2005). According to Belotte et al. (2003), the best bioaugmentation approach is to preselect the microorganisms from their own physical setting. Experiments conducted so far in bioaugmentation used fungi belonging to the genera, *Verticillium*, *Penicillium*, *Mucor*, *Aspergillus* and *Absidia*, and gram-negative bacteria like *Sphingomonas*, *Pseudomonas*, *Flavobacterium*, *Alcaligenes* and *Achromobacter* (Mrozik and Piotrowska-Seget 2010). Mostly, all types of pollutants are subjected to bioaugmentation, and there is no specific category of target pollutant to treat. For pollutants of less water solubility (PCBs and PAHs), it is essential to use the surfactant-producing strains so that the contaminants are made more bioavailable (Dua et al. 2002; Johnsen et al. 2005; Mrozik and Piotrowska-Seget 2010). It will be more favorable to make use of a strain that could produce a surfactant and degrade the targeted pollutant. In many cases a single strain was shown to be less effective than consortia (Kuiper et al. 2004), because the toxic intermediate of the degradative pathway of one strain in a consortium may be further degraded by other strains possessing suitable catabolic pathways.

Bioaugmentation has five general sustainability criteria which add to its merits. They are: its ability to harness or mimic a natural process, elimination of energy or natural resource consumption, reduction or no release of toxic gases into the atmosphere, permanent contaminant-destroying ability, and reusability or recycling ability of inactive lands or discarded materials. However, the main disadvantage is the requirement of voluminous microbes for large-scale treatment of sites contaminated with high concentrations of pollutants where cost might be high and the variability and uncertainty exist with regard to the acclimated microbes. The major disadvantage is that it takes a long time (up to several years) to achieve the remedial goal since the system is slow. So far, no accurate cost estimation is available for this technology as it is highly variable.

The ability of the native soil microbes to degrade PAHs in a long-term polluted soil was reported by Li et al. (2009b). They also found that after supplementing a microbial consortium comprising three bacteria belonging to the genera *Zoogloea*, *Flavobacterium* and *Bacillus*, and five different fungi, *Aspergillus niger*, *Penicillium chrysogenum*, *Alternaria alternata*, *Phanerochaete chrysosporium* and *Cuuninghamella* sp., the degradation rate of PAHs significantly increased to 41.3 %. Alisi et al. (2009) studied the degradation of phenanthrene and diesel oil using microbial consortium of selected native strains and observed a removal of 75 % total hydrocarbon and 60 % isoprenoid in 42 days. A group of bacteria isolated from a gasoline-polluted soil was encapsulated as enriched consortia in gellan gum microbeads by Moslemy et al. (2002). The encapsulated cells exhibited a higher gasoline degradation rate with a shorter lag phase compared to their free cell counterparts at the corresponding microbial concentrations. Monard et al. (2008) found a significant increase in atrazine mineralization by earthworm digestion in soils bioaugmented by *Chelatobacter heintzii* and *Pseudomonas* sp. Olaniran et al. (2006)

reported that EDC was remediated completely by a synthetic consortium made of *Klebsiella* sp., *Bacillus cereus*, *B. subtilis*, *Achromobacter xylosoxidans*, *Acinetobacter* sp., *Pseudomonas aeruginosa* and *Acinetobacter haemolyticus*, where the microbes' survival was enhanced by supplying NPK in the ratio of 3:1:6.

Until now, only on-sites like pristine places and hot springs were given attention for strain selection. Verstraete et al. (2007) suggested that deep sea/underground should also be explored. Gentry et al. (2004) observed chlorobenzoate degradation by activated soils. Van der Gast et al. (2004) reported 85 % degradation of processing waste metal fluids by a consortium of four indigenous bacterial strains assembled on the basis of their degradation abilities and tolerance to fluctuating chemistry of the treated fluid. Plangklang and Reungsang (2009) studied the importance of 'formulation' of an inoculum which is a crucial factor that affects the viability of pollutant-degrading microbes, and noticed that immobilized *Burkholderia cepacia* on corn corb involved in carbofuran degradation could survive for 30 days compared to the free cells. Recently, few commercial inocula have only been tested in bioaugmentation systems at laboratory level, but not in field-scale. KB-1™ and Bio-Dechlor INOCULUM™, composed of consortia of multiple *Dehalococcoides* sp. with other bacterial types (PCE-cis-DCE dechlorinators, fermenters and acetogens) were used for remediation of groundwater (Loffler and Edwards 2006).

Enzyveba—a patented, stable and complex consortium of eukaryotic and prokaryotic organisms, used by Marcopolo Engineering SpA, Italy—was tested and proved to be: firstly, a bioactivator of landfills/composting facilities/wastewater treatment plants; and secondly, a commercial degrader of diesel fuels (Di Toro et al. 2008). Van Dillewijin et al. (2007) showed that axenic plants inoculated with a plant growth-promoting bacterium (*Pseudomonas putida*) could remove 80–88 % trinitrotoluene. Lebeau et al. (2008) reported that bioaugmentation increased the accumulation of metals by plant shoots to a factor of 5.0 without any obvious difference between the degrading microbe types (either bacteria or fungi). Using 10^{12} CFU/kg inoculum, 80 % degradation of dichlorodibenzo-*p*-dioxin was achieved compared to 10^{10} CFU/kg inoculum where only 46 % degradation was achieved (Hong et al. 2007).

At field-scale, the effect of soil bioaugmentation was confirmed for trinitrotoluene (Van Dillewijin et al. 2007) and atrazine (Strong et al. 2000). Truu et al. (2003) and Juhanson et al. (2009) demonstrated the combined effect of phytoremediation and bioaugmentation in full-scale. Zhang et al. (2008) treated the largest soil surface of 7000 m^2 by bioaugmentation (*Cunninghamella echinulata* and *Enterobacter cloacae* as a consortium) for salt- and petroleum-contaminated soil in which wheat straw enhanced petroleum degradation with subsequent salt leaching. Diplock et al. (2009) reported that it generally takes three times longer for conducting field trials by bioaugmentation compared to laboratory studies. Length of treatment at field-scale has been reported to extend from a few weeks to nearly 3 years (Hesselsoe et al. 2008; Juhanson et al. 2009). Further research should formulate a commercial inoculum for diverse contaminant types and make the bioaugmentation approach more mechanized so that inoculated organisms' role is better understood when removing pollutants. Also, strategies to reduce the remedial time and integration with other biological tools to increase the remedial effects could be used along with further implementation of comparable field studies using other technologies.

As in most cases, bioaugmentation fails at field-scale which is assumed to be due to unfavorable soil physico-chemical factors and antibiotics produced by the native microbes that harm the artificially-inoculated microbes. A new approach of using an enzyme-based, cell-free product was proposed by Scott et al. (2008) to remediate atrazine-contaminated fluids. The cell-free approach is limited in that is applicable only to efficient and viable enzymes that do not rely on diffusible cofactors like NAD, etc. However, enzyme immobilization on carriers would make them highly stable and resistant to changes caused by substrate concentrations, pH, temperature, etc. Hence, it is important to select a cost-effective carrier material for the enzyme product as well as study different mechanisms for the efficient delivery of enzymes into the natural ecosystem.

3.13 Biostimulation

Biostimulation refers to the addition of specialized growth-limiting nutrients such as carbon, nitrogen and phosphorous in contaminated sites so that naturally-occurring microbes are present in sufficient numbers and types to degrade the waste effectively (Trindade et al. 2005). As such, biodegradation is enhanced by the amendment of water-based solutions such as electron acceptors, nutrients and other additives (Juwarkar et al. 2010). Acetate, sulphate, nitrate, ethanol and electrodes are the electron donors that are used in biostimulation of contaminated sites. Herbicides, pesticides, fuels, non-halogenated SVOCs, VOCs, heavy metals and radionuclides like U were successfully removed via biostimulation at field-scale (Eguchi et al. 2001; Brar et al. 2006). While it is applicable, it is less effective to degrade halogenated organics. This approach requires the presence of indigenous microbes that are potent to degrade a target pollutant. Likewise, it is problematic that the toxins are bioavailable and not tightly sorbed to the soil particles. Although the cost of biostimulation technologies tends to change depending on the site, it is considered one of the cheapest remedial alternatives applicable for both soil and groundwater. This technology is not suited for sites contaminated with high concentrations of pollutants as it would hinder the microbial growth. Tight, impermeable subsurface lithology makes it difficult to spread the water-based solution throughout the treatment zone. Fractures create preferential pathways in the subsurface, from where the nutrient solution could preferentially flow and aid the microbial activity.

The extensive use of biostimulation as a promising remedial approach has several limitations, most of these being concerned with soil heterogeneity. Every site has its own unique soil chemistry, hydrology and geology affecting the native microbial populations available for degradation. For instance, iron-rich soils support bigger populations of strains like *Geobacter* sp. that utilize iron as its electron acceptor that could concurrently reduce heavy metals like U (Bopp et al. 2010). However, iron-poor soils do not support the survival of such bacterial strains and are harder to remediate. Co-contamination additionally creates some problems as one contaminant could be toxic to the microbes stimulated to degrade the other contaminant (Atagana 2006). A co-contaminant may also increase the mobility of the contaminant.

For example, use of gasoline additives always increases the migration of BTEX in groundwater (Da Silva et al. 2005). Non-target microbial consumption or loss of stimulant due to diffusion away from the treatment zone can inhibit the ideal growth of decontaminating bacteria. For example, during U reduction, anaerobic environments with low nitrate levels prevent the electron donors from being consumed by bacteria that use nitrate or oxygen as terminal electron acceptors (Yabusaki et al. 2007). Further, long-term monitoring is required to validate the effectiveness of the biostimulation system particularly with regard to heavy metal contamination. Hence, the above limitations must be rectified if biostimulation is to become a more reliable technology.

Almost in all cases, biostimulation is applied in conjunction with bioaugmentation (Table 10). In a study to determine the efficiency of biostimulation in restoring oil-contaminated coastal marsh dominated by *Spartina alterniflora* through the addition of phosphorous and nitrogen under temperate condition, Garcia-Blanco et al. (2007) reported that >80–90 % oil disappeared after 20 weeks. Biostimulation of a petroleum spilled site was successful in Bellingham, Washington when the activity and population of sulphur-reducing bacteria such as *Desulfobacter* sp. that could degrade petroleum was stimulated by the addition of growth limiting nutrient (sulphate) (Bhowmik et al. 2009). By the injection of hydrogen peroxide into ground wells, aerobic conditions favorable for PAHs degradation were established by Menendez-Vega et al. (2007). Adding an electron donor such as lactate increased the degradation rate of PECs to VC (Hirschorn et al. 2007). After 2 years of ethanol (electron donor) amendment, U(VI) was reduced to 1.0 µM from 5 µM in a radionuclides-contaminated site at Oak Ridge, Tennessee as ethanol stimulated the activity of sulphur-reducing bacteria (Wu et al. 2006a).

Yabusaki et al. (2007) conducted a field experiment at the Old Rifle site in Western Colorado and observed complete immobilization of U(VI) in groundwater by iron-reducing *Geobacter* sp. whose activity was stimulated by acetate amendment. Eguchi et al. (2001) reported that removal of 10–20 % TCE in a week was achieved by methane oxidizers due to the stimulation of growth by the supply of growth-limiting nutrients such as methane, oxygen, nitrate and phosphate. Hamdi et al. (2007) observed degradation of pyrene (63 %) and benzo(a)pyrene (21 %) within a few weeks when the activity of the PAH degraders was stimulated by the addition of biostimulants like decaying rice straw and sludge compost. Similarly, Wu et al. (2008) demonstrated the ability of ground corn cob to stimulate PAH degradability of *Monilinia* sp. About 82–95 % TCE was dechlorinated to ethene when the dechlorinated culture (*Dehalococcoides* strain KB-1) was supplied with enough growth-limiting elements like methanol, ethanol, acetate and lactate as mixtures (Hood et al. 2008). Increase in PAH degradation by *Pseudomonas aeruginosa* strain 64 using biostimulators (ground rice hulls and dried bloods) was reported by Straube et al. (2003).

Enhanced bioremediation of petroleum hydrocarbons (up to 96 %) was achieved by Sarkar et al. (2005) by the amendment of inorganic fertilizers and biosolids. A similar study was conducted by Delille et al. (2009) using a commercial fertilizer to remediate diesel oil in Antarctica's coastal sea. While studying the effect of fertilizer as a stimulating agent to aid biological degradation of synthetic diesel oil at extreme temperature, Horel and Schiewer (2009) reported that fertilizer applications could stimulate the contaminant degradation up to three and eight times higher at 20 and 6 °C, respectively, compared to nutrient deficient conditions. The optimal CNP ratio (range of 100:9:2/199:10:1/250:10:3) required to commence any in-situ BTEX remedial measure was reported by Wolicka et al. (2009).

Use of biosurfactants to aid biodegradation of pollutants along with biostimulants was also demonstrated (Ron and Rosenberg 2002; Bordoloi and Konwar 2009; Hazra et al. 2012). In recent years, numerous organisms that could produce biosurfactants were identified and used in conjunction with bioaugmentation and biostimulation. Lipopeptides produced by *Rhodococcus* sp., *Bacillus subtilis* and *Nocardiopsis alba* (Abdel-Mawgoud et al. 2009; Haddad et al. 2009; Gandhimathi et al. 2009), glycolipid from *Pseudozyma hubeiensis* and *Nocardiopsis lucentensis* (Fukuoka et al. 2008; Kiran et al. 2010), glucolipid and trehalose lipid from *Rhodococcus erythropolis* (Peng et al. 2007), rhamnolipid produced by *Pseudomonas aeruginosa* and *Burkholderia plantari* (Chen et al. 2007; Abdel-Mawgoud et al. 2009; Hormann et al. 2010) are the biosurfactants used so far for the bioremediation of affected areas. Apparently, the combined application of biostimulation and bioaugmentation with biosurfactant is a promising approach to speed up the remedial mechanism (Baek et al. 2007; Tyagi et al. 2011). Though biostimulation has proved to be effective with organic and inorganic contaminants, additional field experiments should be conducted to develop good models for the widespread use of biostimulation systems. Also, by confirming that biostimulation decreases toxin levels within a shorter time frame and by improving the ease of implementation, biostimulation could be demonstrated as an ideal strategy for degrading environmental contaminants at large-scale.

3.14 Biosorption

Additionally, an effective biological technique that is just as good as bioaccumulation or biostimulation is biosorption where either natural resources or microorganisms are used. Biosorption is gaining importance owing to its inherent advantages (low cost by use of industrial, agricultural and waste biomass; process operation under ranging pH and temperature as the biosorbent is active; easy storage or use; ability of the binding sites to accommodate a variety of ions; higher degree of rapid toxicant uptake; high possibility of biosorbent regeneration and reuse with possible toxicant recovery) over bioaccumulation processes (Vijayaraghavan and Yun 2008). Biosorption is generally used for the removal of pollutants from water, especially those that are not easily biodegradable such as metals and dyes. A variety of biomaterials, including industrial and agricultural wastes, bacteria, fungi and algae are known for their biosorption potentials. Juwarkar et al. (2010), Vijayaraghavan and Yun (2008), Volesky (2006), and Loukidou et al. (2004) vividly discussed the biosorption process in their reviews. Melo and D’Souza (2004), Tunali et al. (2005), and Aravindhan et al. (2004) demonstrated Cr biosorption by seaweed and fungal biomass. Successful sorption was reported for Cd by red alga (Sari and Tuzen 2008), rice polish agricultural waste (Kumar and Bandyopadhyay 2006), wheat bran (Singh et al. 2006), and black gram husk (Saeed and Iqbal 2003). Sorption of Cu by lichen biomass immobilized in grape stalks (Ekmekyapar et al. 2006), spent grains (Lu and Gibb 2008), marine alga (Da Silva et al. 2002), green alga (Deng et al. 2007), activated carbon (Esmaeili et al. 2008), and polysulfone matrices (Beolchini et al. 2003); Ni sorption by cone biomass (Malkoc 2006); biosorption of Pb with the use of polymerized banana stem (Noeline et al. 2005); and sorption of Zn by orange peel cellulose with fungal cells immobilized in Ca-alginate beads (Lai et al. 2008), mature jamun (King et al. 2008) and neem tree barks/leaves (Arshad et al. 2008) have been reported. Bhattacharyya and Sharma (2004) suggested neem leaf powder as a suitable sorbent of dyes. New remedial approach such as the use of bioreactive organoclays which result in accelerated sorption and biodegradation/transformation of noxious pollutants of concern like Cr was reported by Sarkar et al. (2011). Using seaweed-based treatment technology as a biosorbent for remediating complex metals in wastewaters is a recently advanced option available for site clean up (Ahmady-Asbchin et al. 2009).

Thus, remedial in-situ technologies are quite promising for a wide range of pollutants and are becoming more sophisticated. Of all the available in-situ remedial techniques, bioaugmentation with biostimulation, biosorption, rhizoremediation, surfactant-enhanced remediation and EK remediation are considered to be promising for rapid degradation of contaminants because they are ecofriendly and cost-effective.

4 Emerging Technologies

Of the conventional technologies that are discussed above, physico-chemical methods such as heating, flushing, etc. are generally costly and the remedial approach is often incomplete due to the conversion of parent compounds into transformation products which are more recalcitrant and equally hazardous to non-target organisms. On the other hand, biological remediation processes like phytoremediation, bioaugmentation, etc. offer an environmentally friendly and economically feasible option to remove hazardous toxins from the environment. Since the natural ability of plants and microbes for decontamination is exploited and the organic pollutants in theory could be completely mineralized to water and CO_2 without any residual effects, along with the intended reduction in bioavailability of the target contaminant with cost-effectiveness, currently bioremediation is mainly focused on further developments such as integrating a few promising physico-chemical technologies (Megharaj et al. 2011; Rayu et al. 2012). In this context, the use of microbial fuel cells, nanoparticles, transgenic plants and microbes, and photo-hetero microbial consortia approaches has entered a new phase and leading to improvements in how well existing risk-based environmental remedial systems perform. These emerging technologies are mostly biological and expected to give rise to the birth of an ‘era of green biotechnology' in the near future. The massive exploitation of these recently advancing novel remediation approaches will bring about a rapid + reliable + low cost + risk-based contaminant clean up strategy.

4.1 Microbial Fuel Cells

A microbial fuel cell (MFC), also known as 'green power generation system' is a bioelectrochemical device that converts chemical energy into electrical energy by the catalytic reaction of microorganisms on organic compounds or metals (Aelterman et al. 2009). Generally, microbial metabolism is harnessed through fuel cells to convert organic materials or wastewaters into hydrogen, electricity and industrially useful chemicals while remediating the polluted environmental sites (Erable et al. 2012). In the last few years, MFC-related investigations have been intensified due to the promise of sustainable energy production from organic wastes. MFCs are highly adaptable and have greater potential to deliver energy in a sustainable fashion; however, their widespread application is feasible only after major improvements have been made. There are different types of MFCs as can be seen in Fig. 2 (Kim et al. 2002; Rabaey and Verstraete 2005; Logan et al. 2006; Liang et al. 2007). Mediator-less MFC includes plant-MFC (microbes aerobically breakdown and release electrons from small mass carbohydrates that are exuded from plant roots as a result of photosynthesis), metal-reducing MFC (use of microbes that possess the ability to reduce Fe(III) to Fe(II) during the oxidation of the carbonaceous

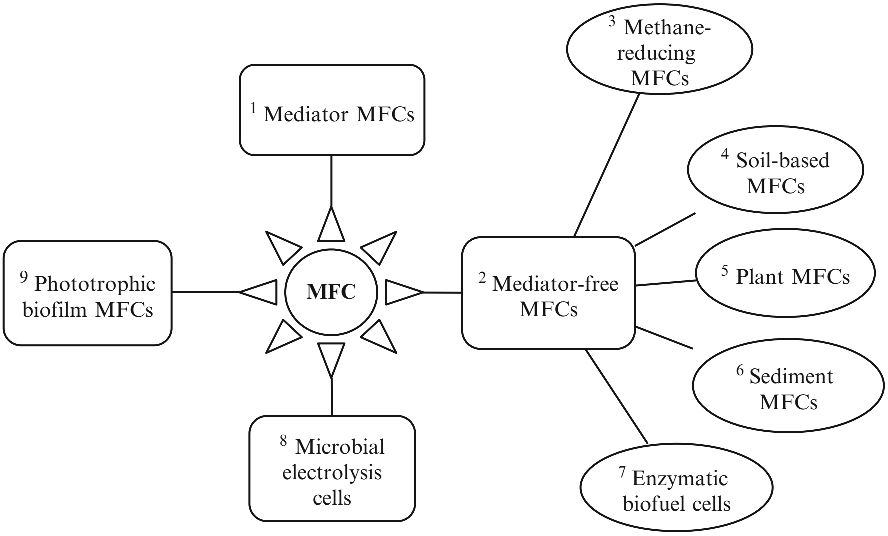


Fig. 2 Microbial fuel cell (MFC) types. Superscript indicates the reference for each technology: [1]Logan et al. (2006); [2]Nwokocha et al. (2012); [3]Lee et al. (2008); [4]Ringelberg et al. (2011); [5]Strik et al. (2008); [6]Donovan et al. (2011); [7]Huang et al. (2011); [8]Jeremiasse et al. (2010); [9]Strik et al. (2008)

substrate to CO_2), enzymatic biofuel cells (enzymatic biocathodes), and sediment MFC types (anode placed in nutrient-rich marine sediments and cathode placed in seawater above the sediment and the resulting voltage gradient generates power in marine environments) (Nwokocha et al. 2012). Generated electrons and protons (by means of a proton-exchange membrane) flow through a load to the cathode and subsequent reduction of oxygen ions by protons produces water. To produce a sufficient rate of oxygen reduction, catalysts like platinum and iron-tetra methoxy phenyl porphyrin were used (Logan 2010). Water thus produced is pure and thereby this process is highly suited for its application in remediation and water purification while generating electricity (Scott and Murano 2007). The power output by this system is generally low and variable; however, up to 90 % columbic efficiency could be achieved (Clauwert et al. 2008; Lee et al. 2008).

The function and efficiency of MFCs depend on the nature of the carbon source used, design and configuration of the fuel cell, nature and type of the electrons and proton-exchange membrane in usage, nature of inoculum and presence of electron acceptors as mediators. Different feedstocks including organic acids, alcohols, acetate, proteins, amino acids, inorganic sulphides, industrial effluents such as paper recycling sludge, brewery effluent, and food processing effluents were applied for the production of electricity using MFCs (Lee et al. 2008). MFC is a very efficient and clean method for energy production because when plant-MFCs are globally implemented, the production of dangerous greenhouse gases by the plants in natural ecosystem will be reduced while generating electricity. Also, MFC can be operated indoors or within communities and can be used as a private source of power for houses. It utilizes a very low temperature of 18–35 °C for energy production. Furthermore, MFCs are considered to be renewable and sustainable energy sources since energy is tapped from already existing feedstocks such as organic waste and wastewaters. Plant-MFCs can capture solar energy which is renewable as well as available for approximately 5.5 billion years (Rozendal et al. 2008). Moreover, production of energy from industrial wastewater and effluents represents energy savings which can be invested into cost-effective, ever-green energy production at large-scale as this system is neither expensive nor time-consuming.

Drastic reduction in the proton transfer, ohmic losses caused by electrical resistance to the electrode, electrode and proton-exchange chamber, activation losses or leaching to voltage loss, and electron quenching reactions (competing reactions such as fermentation, methanogenesis, respiration result in electron loss) limit electricity generation in MFCs (Clauwert et al. 2008). In spite of these limitations, MFC technology is a viable option in the race to obtain green energy from natural wastes. Overall, MFC can be used to clean up all contaminant types as well as radioactive elements from the ground. No clear cut details are available on the total cost involved in contaminated site clean up when using this technology.

Rhoads et al. (2005) and Clauwaert et al. (2007) observed the reduction and successive reoxidation of Mn(II) coupled with oxygenation reduction in enzymatic (biocathode) fuel cells. Pure culture of *Geobacter metallireducens* is able to oxidize toluene, benzoate and petroleum hydrocarbons using an electrode as the terminal electron acceptor (Bond et al. 2002; Lin et al. 2005; Zhang et al. 2010a). Also, an electron transfer system was reported with *Geobacter* sp. or consortia using nitrate, tetrachloroethene, U(VI), Cr (VI) as electron acceptors (Strycharz et al. 2008; Cao et al. 2009; Tandukar et al. 2009). Huang et al. (2010) reported an enhancement in Cr(VI) reduction (2.4 mg/g VSS/h) and energy generation (2.4 W/m^3) from biocathode MFCs using native bacteria isolated from Cr(VI)-contaminated zone. A higher power output along with biodegradation of toluene, benzene and naphthalene (36–94 %) of organic-rich sediment was obtained by Yuan et al. (2010a) in a novel tubular air-cathode MFC with a cloth cathode assembly loaded with an external resistance of 30 Ω in 6 months. Catal et al. (2009) observed simultaneous electricity generation and Se removal in single chamber MFC with glucose and acetate as carbon sources. In 72 h, 99 % of 200 mg/L Se was removed with an increased columbic efficiency of 38 %.

Zhang et al. (2009) investigated the feasibility of pyridine biodegradation in a two-chamber MFC with an electrical resistance of 100 Ω. With complete pyridine degradation in 12 h, maximal voltage of 623 mV and a maximal power density of 1.7 W/m^3 were obtained in 90 days when glucose was supplemented at a concentration of 500 mg/L. Huang et al. (2011) observed 27 % of Cr(VI) reduction and 61 % of power generation below 22 °C at a pH of 5.0 in a biocatalytic graphite fiber cathode MFC. Jang et al. (2006) observed over 85 % nitriloacetic acid was removed under anaerobic conditions using oligotrophic and copiotrophic MFCs when nitriloacetic acid was supplied as a sole source of carbon. Aulenta et al. (2009) recommended the use of conductive materials to manipulate and control a range of microbial bioprocesses, and also suggested the implications of novel biosensors for MFCs. Yuan et al. (2010b) reported a novel bioelectrochemical method to successfully degrade nitrophenol using power derived from a MFC when acetate was used as a potential substrate. A higher power density was obtained with a reduction rate constant of 0.41/h when the MFC had a higher output voltage of 0.5 V. Devasahayam and Masih (2012) recorded a maximum voltage of 779 mV when a resistance of 100 Ω was applied along with the use of 0.4 % sucrose as substrate using *E. coli*. Scott-Emuakpor et al. (2012) successfully demonstrated the use of a tungsten trioxide-based photoelectrocatalytic fuel cell system for water treatment of dichlorophenols which is a new technology for mineralization of organic contaminants.

Luo et al. (2011) studied the combined effect of MFCs with Fenton-like technique to degrade refractory pollutants and generate electricity in both cathode and anode chambers. At a pH of 3.0, maximum power density of 15.9 W/m^3 was achieved with 100 % furfural removal. Luo et al. (2009) achieved 95 % phenol degradation within 60 h with a maximum power density of 28.3 W/m^3 by using graphite packed MFC with a ferricyanide cathode. Thus, studies relating to MFC in remediation are numerous at bench-scale as listed in Table 11. This potential for energy production linked to contaminant clean up is expected to be improved further for full-scale implementation as MFCs have been used at field-scale only by a few research bodies like Queensland University in Australia. There are challenges in obtaining genetically modified strains of exoelectrogenous anaerobic microbes to improve energy production and survival in MFC, designing novel MFCs to overcome existing shortfalls, and use of novel catalysts to aid the system efficiency. These are being researched currently and are expected to lead to further innovations in remedial research.

Table 11 Recent MFC remedial studies carried out at bench-scale

Contaminant	Substrate	Contaminant reduction (%)	Duration (days)	Reference
1. Uranium	–	87	40	US EPA (2012)
2. Nitrate	Acetate	95	45	Lefebvre et al. (2008)
3. Phenol	–	95	2.5	Luo et al. (2009)
4. Pyridine	Glucose	100	90	Zhang et al. (2009)
5. Toluene, Benzene, Naphthalene	–	36–94	185	Yuan et al. (2010a)
6. Nitrophenol	Acetate	26.9	60	Yuan et al. (2010b)
7. Chromium	–	80	20	Huang et al. (2011)
8. PAHs	–	75.54	18	Mohan and Chandrasekhar (2011)
9. Furfural	–	100	0.5	Luo et al. (2011)
10. Phenol	–	100	10	Huang et al. (2011)

4.2 Nanoremediation

Of late, nanoremediation has become one of the main foci of research and development with great potential for contaminated site clean up and protecting the environment from pollution. Nanoremediation involves the application of reactive materials (1.0–100 nm size) which initiate both catalysis and chemical reduction of the contaminants of concern and result in detoxification and transformation of pollutants. The small size and novel surface coatings of the nanoparticles enable them to be more widely distributed in comparison to larger-sized particles, and this unique property makes them best suited for in-situ applications (Tratnyek and Johnson 2006). The maximum surface area-to-weight ratio of nanoparticles maximizes the adsorptive surfaces onto which the contaminants like As get bound and immobilized (Karn et al. 2009). Nano-sized particles provide a solution for faster and more cost-effective site remediation as their reaction is much more effective than other materials.

So far, nano-scale zeolites, metal oxides, carbon nanotubes, noble metals and titanium dioxide have been evaluated for use in nanoremediation (Karn et al. 2009). Of these, currently nano-scale zero-valent iron (nZVI) is widely used in groundwater remediation (Rajan 2011). Nanotechnology has also been attributed towards reducing the NAPLs from underground oil tanks by in-situ use of a material utilizing nano-sized oxides (Jiemvarangkul et al. 2011). Generally, this reactive nanoremediation strategy focuses mainly on the organic pollutants, and seems to work well for chlorinated solvents such as PCBs (tested by US Air Force). When injected as slurry, nanoparticles drift along with the flow of groundwater, effectively creating an 'anti-pollution plume'. Also, it enables remediation in deeper soils that are not accessed even by pump-and-treat methods. It is compatible even with other technologies like phytoremediation and aid as an expanding tool for contaminant clean up. But, particle-particle aggregation because of their small size limits its mobility in the natural environment (Phenrat et al. 2008). In such a case, polymer coating is suggested to improve their mobility. Even they could be unexpectedly carried away to longer distances in the environment depending upon the groundwater composition and hydrological conditions (Novikov et al. 2006). In addition, self-aggregation property of the nanomaterials with suspended solids or sediments increases their possibility to enter into food chain or drinking water source that lead to their entry into humans and other living organisms causing oxidative stress response, pulmonary toxicity, mutagenesis and cell death (Wiesner et al. 2006). Removing the nanoparticles form the environment may also represent a significant problem due to their small size.

Copper, iron and silver nanoparticles have been shown to cause ecotoxicological effects on micro- and macro-flora/fauna (Boxall et al. 2007). The environmental risks of nanoparticles remain unanswered beyond their positive effects in removing the contaminants. More understanding as well as quantification of toxicity, possible hazards, mobility, stability, bioavailability, and recalcitrance of manufactured nanoparticles are needed (Zhu et al. 2012) since US EPA has suspected the likelihood of biomagnification of nanoparticles. Thus, to expand the applicability of nanoremediation to full-scale, there is a need to improve engineering applications using nanotechnology for in-situ applications, increase research to assess the effects of nanoparticles on ecological and public health, and develop analytical tools to quantify and monitor the manufactured nanoparticles in the bionetwork.

In a pilot test, Henn and Waddill (2006) found that ZVI could decrease the concentration of TCE in about 6–9 months. Cao et al. (2005) also found the ability of ZVI to completely reduce perchlorate to chloride without producing any intermediates. About 99 % As removal was shown using 12 nm dia ferrous oxide nanoparticles at bench-scale (Rickerby and Morrison 2007). In other field test conducted in Europe and North America, nZVI was effective in reducing Cr(VI) and chlorinated solvents (Mace et al. 2006). Ability of nZVI to migrate even to a depth of 6 m was proved in a field study conducted at Naval Air Station, Jacksonville that helped to reduce 99 % TCE concentrations (Gavaskar et al. 2005). Also, ZVI was effective in the removal of different metals like Cr(VI), U(VI) and Co(II) (Uzum et al. 2008). Ability of gold nanoparticles supported on alumina to remove Hg from drinking water and reduction of Cr(VI) through sorption by cerium oxide nanoparticles was reported by Lisha and Pradeep (2009) and Recillas et al. (2010). Shipley et al. (2011) used nZVI impregnated with clays to adsorb and degrade heavy metals like Zn and Cu from wastewater. By adopting this practice of advanced adsorption, limitations of conventional adsorption technology (low efficiency and high operational cost) could be overcome as the use of nanoparticles is cost-effective in the remediation of various pollutants in aqueous solution including heavy metals, PCBs and nitrocompounds (Li et al. 2006).

Skubal et al. (2002) modified the surface of titanium dioxide nanoparticles with thiolactic acid (a bi-dental chelating agent) and used it for removing Cd from wastewaters. Zaera (2012) reported the use of nanotechnology for the manufacture of better-defined catalysts that aid the environmental remediation. Zhang et al. (2010b) proved the ability of iron nanoparticles (core size of 15 nm) coated with ferromagnetic carbon to effectively reduce >95 % of Cr(VI) in wastewater by means of carbon shell physical adsorption which was much higher than the remediation by commercially available iron nanoparticles. ZVI nanoparticles with a dia of <90 nm and specific surface area of 25 m^2/g removed up to 96 % of atrazine (100 mg/L) within 72 h under anoxic conditions (Bezbaruah et al. 2009a). At lab-scale, in a batch and column experiment reductive immobilization of chromate in soil and water using stabilized iron particles was shown by Xu and Zhao (2007). Tungittiplakorn et al. (2004) demonstrated the ability of engineered nanoparticles (amphiphilic polyurethane nanoparticle of 17–97 nm dia) for soil remediation of PAHs (80 %). Ghauch et al. (2009) reported the removal of antibiotics from water using iron nanoparticles.

Xiao et al. (2010) recommended the use of multivalent carbon nanotube-reinforced polyacrylic acid/polyvinyl alcohol nanofibrous mats for generating other functionalized nanofiber-based complex materials with enhanced mechanical properties for applications in environmental remediation, catalysis, sensing and biochemical sciences. Palladium nanoparticles bioprecipitated on *Shewanella oneidensis* and encapsulated in polyurethane removed 98 % TCE in 22 h (Hennebel et al. 2009). He et al. (2007) stabilized Fe-Pd nanoparticle with sodium carboxymethyl cellulose which resulted in successful dechlorination of TCE in groundwater and soil. Crane et al. (2011) studied the combined effect of ZVI particle and nano-Fe_3O_4 for U removal (>98 % within 2 h) from carbonate-rich water sample collected from Lisava valley, Banat, Romania. Decabrominated diphenyl ether (a class of the emerging pollutant) and polybrominated diphenyl ether were removed up to 90 % within 40 min by treating with ZVI nanoparticles (Shih and Tai 2010). Nano-ZVI particles of 10–90 nm encapsulated in biodegradable calcium alginate beads were capable of degrading 89–91 % TCE in 2 h (Bezbaruah et al. 2011). About 96–99 % As and Cr along with phosphate were removed by mixed magnetite-maghemite nanoparticles at a pH 2.0 (Chowdhury and Yanful 2010). Singhal et al. (2012) observed 98 % malathion remediation by using ZVI at a pH of 8.2 in 12 h.

Calcium peroxide nanoparticles have been used as an innovative agent for in-situ chemical oxidation by Olyaie et al. (2012). Noubactep and Care (2010) recommended the use of Fe-Pb nanoparticles for reductive dechlorination of lindane. Li et al. (2010) proposed foam delivery of nanoparticles for vadose-zone remediation. There are much more advanced laboratory studies in the emerging field of nanoremediation involving the application of bimetallic, stabilized, engineered, polymeric nanoparticles for the remediation of organics and inorganics as listed in Table 12. Thus, nanoparticles are highly promising to remediate more than 95 % contaminants in few hours at bench-scale. However, at pilot-scale when tested in the superfund sites by US EPA, nanoparticles removed 60 % contaminant in few weeks (Table 13). Field-scale implementations of chemical/synthetic nanoparticles, available in large number, are expected in the near future. But, full-scale use of nanoparticles obtained from green synthesis is yet in the bench-scale level, and requires more attention in future research.

Amaladhas et al. (2012) synthesized silver nanoparticles from leaf extract of *Cassia angustifolia* that have antibacterial effect against *E. coli* and *Salmonella* sp.

Table 12 Nanoremediation studies and their success

Nanoparticles	Contaminant	Remediation (%)	Reference
1. Amphiphilic polyurethane nanoparticle [b]	PAHs	80	Tungittiplakorn et al. (2004)
2. Starch-stabilized Fe-Pd [b]	PCB	80	He and Zhao (2005)
3. ZVI [f]	TCE	99	Henn and Waddill (2006)
4. ZVI [b]	Cr(VI)	90	Xu and Zhao (2007)
5. ZVI [b]	Atrazine	96	Bezbaruah et al. (2009b)
6. Carboxymethyl cellulose and polyacrylic acid stabilized ZVI [b]	RDX	98.3	Naja et al. (2008)
7. ZVI entrapped in biopolymer, calcium alginate beads [b]	NO_3	50–73	Bezbaruah et al. (2009a)
8. Electrochemically-stabilized maghemite nanoparticle [b]	As(V)	99	Park et al. (2009)
9. ZVI [f]	TCE	99	Gavaskar et al. (2005)
10. Biopalladium polyurethane nano cubes [b]	TCE	98	Hennebel et al. (2009)
11. Carboxymethyl cellulose-stabilized iron [b]	Hg	99	Xiong et al. (2009)
12. Multivalent carbon nanotube-reinforced polyacrylic acid/polyvinyl alcohol nanofibrous mat [b]	TCE	93	Xiao et al. (2010)
13. ZVI [b]	DBDE	90	(Shih and Yai 2010)
14. Ferromagnetic carbon coated iron nanoparticle [b]	Cr(VI)	95	Zhang et al. (2010b)
15. Magnetite and maghemite [b]	As, Cr, PO_4	96–99	Chowdhury and Yanful (2010)
16. Carboxymethyl cellulose-stabilized iron [b]	Cr(VI)	100	Wan et al. (2010)
17. Iron oxide [b]	As(V)	>90	Shipley et al. (2011)
18. Iron nanoparticle in alginate biopolymer [b]	TCE	89–91	Bezbaruah et al. (2011)
19. Magnetite and ZVI [b]	U	98	Crane et al. (2011)
20. Fe-Ni [b]	Cr(VI)	75	Kadu et al. (2011)
21. ZVI [b]	Malathion	98	Singhal et al. (2012)

[b] Bench-scale; [f] Field-scale

along with pollutant-degrading capabilities. Saha et al. (2009) reported green phytochemical synthesis of calcium alginate stabilized Au and Ag nanoparticles (solid-phase biopolymer-based catalyst) for nitrophenol reduction. Virkutyte and Varma (2011) recommended the green synthesis of metal nanoparticles which could be used as enzymes and biodegradable polymers in surface functionalization and stabilization applications. Smuleac et al. (2011) discussed about membranes containing reactive Fe/Pd and Fe nanoparticles embedded in polymer film which was

Table 13 Nanoremedial full-scale studies conducted at superfund sites by US EPA (2012)

Site	Technology	Duration of operation (months)	Contaminant reduction	Outcome	Objective met??
1. Alabama soil, Northern Alabama	Nano-scale ZVI	1	40–61 % TCE, PCE, PCBs	• Confirmed the effectiveness, mobility, and ability of nZVI to degrade contaminants	Yes
2. Dry cleaning facility site 45, Parris island, South Carolina	Emulsified ZVI and nano-scale iron	32	86 % DNAPL	• Achieved 75 % DNAPL mass removal	Yes
3. Hanford site 100, Washington	Nano ZVI	12	70 % Cr(VI)	• Reduction of Cr(VI) under the influence of iron injection • No adverse groundwater quality effects by nZVI injection that would impact human or environmental receptors • No significant loss of permeability in the aquifer	Yes
4. Space launch complex 34, Cape Canaveral, Florida	Emulsified ZVI	8	60 % TCE	• 50 % TCE removal • No change in aquifer quality due to EZVI treatment • No environmental impact due to EZVI injection	Yes
5. Parris island, Port Royal, South Carolina	Emulsified ZVI	30	65 % TCE, DCE, VC	• Evaluated long-term performance of nano-scale EZVI injected into the saturated zone to enhance in-situ dehalogenation of DNAPLs containing TCE	Yes
6. Penn-Michigan manufacturing site, West Lafayette, Ohio	Ohio-swellable organo-silica-nanoparticle	9	40 % TCE	• Achieved less than 5 μg/L TCE	No
7. Pharmaceutical facility, Research triangle park, North Carolina	Bi-metallic nanoparticles	3	90 % TCE, DCE, VC	• Achieved considerable source mass reduction	Yes
8. Picatinny arsenal, rockaway township, New Jersey	Nano-scale ZVI	12	54 μg/L TCE, 180 μg/L CCl_4	• Achieved a final concentration of 2 μg/L CCl_4, and 1 μg/L TCE	No

prepared by using a non-toxic, biodegradable green tea extract instead of the most commonly used sodium borohydride. Gold nanoparticles termed as 'green gold' were prepared using leaf extract of *Terminalia catappa* by Ankamwar (2010). A rapid and reliable process for green synthesis of nano-sized materials using microwave irradiation and supernatant of *Bacillus subtilis* culture was reported by Saifuddin et al. (2009). Baruwati and Varma (2009) synthesized metal nanoparticle form the grape pomace extract which is almost like achieving a high value product from waste. Table 14 presents the biological sources for the green synthesis of different nanoparticles that may have potential in their use in bioremediation. Overall, combination of green nanoparticle synthesis and biological remedial processes with nanotechnology are the emerging, remarkable and innovative remedial approaches.

4.3 Transgenic Plants and Microbes

Advances in protein and genetic engineering techniques opened up new avenues for the development of genetically modified microorganisms (GMOs) and plants to function as 'exclusive biocatalysts' in which certain desirable enzymes or degradation pathways from diverse organism are brought together in a single host with the aim to perform specific reactions (Van Aken 2009; Demain and Vaishnav 2009). In genetic engineering, catabolic genes associated with insertion sequences are rapidly disseminated or DNA is shuffled among the microbial groups to expand the novel degradative pathway (Maestri and Marmiroli 2011). Engineering of catabolic enzymes enhances the degradative rates or broadens the substrate specificity. When a single strain is constructed by genetic engineering to perform a number of related or unrelated metabolic activities, the predictability and efficiency of the process gets significantly enhanced and the recombinant organism is able to degrade a wide range of recalcitrant pollutant rapidly within a shorter time period. Even the use of genes that encode the biosynthetic pathway of biosurfactant could improve the rate of biological degradation by increasing the pollutant bioavailability in the natural ecosystem. Also, the genes conferring resistance to critical stress factors enhance both the survival and performance of the designed catalyst (Dua et al. 2002).

Metabolic engineering approaches also involve deletion strategies for removing competitive reactive pathways (Kind et al. 2011). Mixtures of inorganic and organic chemicals that are even at high concentrations could be possibly treated at a time by GMOs (Singh et al. 2011). New evidences on the metabolic pathways and bottlenecks of degradation are still accumulating, resulting in the need to accentuate the use of available molecular approaches (Megharaj et al. 2011). However, there is a problem with the introduction of GMOs into the environment because of the legal restrictions on their release into the natural ecosystem, additional energy needs imposed by the existence of engineered genetic materials in the bacterial cells, and the low survival of the foreign strains that have been introduced into the real problematic lands (Maiti and Maiti 2011). In such a case, the survival rate of the foreign microbial strains could be enhanced by the use of species reinforced by root

Table 14 Nanomaterials synthesized from biological sources

Nanoparticle	Biological source
Ag	1. *Capsicum annuum* L. extract 2. Coffee (*Coffea arabica*) and tea (*Camellia sinensis*) extracts 3. Leaf broth of *Magnolia kobus* 4. In-vitro cultures of *Brassica juncea* 5. Culture filtrate of *Phoma glomerata* 6. *Opuntia ficus-indica* mediated synthesis 7. *Cassia fistula* leaf broth 8. *Cacumen platycladi* extract 9. Electrochemically active biofilm (bacteria) 10. Culture filtrate of *Trichoderma harzianum* 11. Culture filtrate of *Aspergillus niger*
Au	1. Leaf extract of *Tamarindus indica* 2. Extracts of *Cymbopogon flexuosus* 3. *Rhodopseudomonas capsulata* 4. Cell mass of *Stenotrophomonas maltophilia* 5. Leaf extract of *Terminalia catappa* 6. Leaf extract of *Coleus amboinicus* 7. Leaves of zero-calorie *Stevia rebaudiana* 8. Dried flower extract of *Carthamus tinctorius*
Fe	1. *Camellia sinensis* extract
Metallic	1. Sweet desert willow (*Chilopsis linearis*) 2. *Vitis vinifera* extract
Oxide	1. *Fusarium oxysporum* with precursor salt (barium acetate and potassium hexafluorotitanate) 2. Extract of *Physalis alkekengi*
Ag protein	1. Leaf extract of *Piper betle*
Magnetic Fe_2O_3	1. Regenerated cellulose films
Sb_2S_3	1. Microbial synthesis by *Serratia marcescens*
PLA	1. Leaf extracts of medicinally important plants (*Syzygium cumini*, *Bauhinia variegata*, *Cedrus deodara*, *Lonicera japonica* and *Elaeocarpus sphaericus*)
Fe, Fe/Pd	1. *Camellia sinensis* extract
Au, Ag, Zn, Magnetic Fe_2O_3	1. Biomass of *Medicago sativa*
Au, Ag	1. Fruit extract of *Emblica officinalis* 2. *Cinnamomum camphora* extract 3. Leaf extract of *Camellia sinensis* 4. Biomass of *Cinnamomum camphora* leaf 5. *Sorghum bicolor* powder 6. *Hibiscus rosa sinensis* leaf extract 7. Leaf extract of *Zingiber officinale*
Au–Ag–Cu alloy	1. In-vivo *Brassica juncea* plant

colonizers (plants) that would have a selective advantage over other factors. Thus, judicial blocks can be overcome with the use of plants rather than microorganisms as ‘engineered environmental biosystems’. For remediation purpose, it is, therefore, a potential approach to use plants, and selectively support the metabolism of pollutant-degrading rhizosphere organisms. By improving symbiotic microorganisms, the potential of degrading bacteria (engineered endophytes) to colonize the roots can be manipulated (Weyens et al. 2009; Abhilash et al. 2012). Further, the engineered endophytic strains increase the phytoremediation of water-soluble VOCs (Barac et al. 2004). GM plants could be developed as they significantly help to reduce the need for agrochemicals required for crop growth thereby reducing the environmental pollution.

On the other hand, plants containing transgenes are either responsible for metabolism of organic compound or result in better uptake of inorganic mixtures so that the pollutant accumulated plants could be removed and destroyed which ultimately prevent the pollutant migration to zones where they pose a threat to the public health (Seth 2012). Either the use of GMOs as such or engineered endophytes or transgenic plants are being called for large-scale implementations to remove contaminants more effectively from the environment (Cherian and Oliveira 2005). However, the possibility of imbalanced food chain, unintended gene transfer through cross pollination leading to unknown effects on other plants/organisms and allergic properties by the unintended change in the genetic make-up of the livings in the biosphere by GMOs with great potential to harm human health limits the use of GM materials widely at full-scale in the natural ecosystem by the regulatory bodies. Whatever it is, this situation would change in the long-run. After 10–20 years from now, GMOs would find a promising remedial phase in the real contaminated site clean up approaches. Classes of contaminant to be treated, nature of recipient plants, target genes, source of transgenes, final result of transformation and patents for the transgenic plants or microbes are the critical components of a GM system. Success of a GM system mainly relies on choosing a promoter sequence among constitutive promoters with high levels of expression (Halpin 2005). Both organic and inorganic pollutants such as chlorinated solvents, halogenated/petroleum hydrocarbons and heavy metals could be treated by transgenic plants and microbes. There is no data on the cost details pertaining to GMO-related remedial practices.

A transgenic system for soil As removal was tested by Dhankher et al. (2002) in *Arabidopsis thaliana* by introducing two genes, glutamylcysteine synthetase (GCS) and arsenate reductase C (*arsC*) from *E. coli*. The transgenic plant accumulated 2–3 times more As/g. Similarly, transgenic *Arabidopsis thlaspi* showed plant tolerance towards Ni and Cd due to antioxidative defense mechanism (Boominathan and Doran 2003; Freeman et al. 2004). Transgenic *Arabidopsis* and tobacco plants that carried bacterial organo-mercury reductase (*merA*) and mercury lyase (*merB*) genes were able to absorb methyl mercury and elemental Hg(II) from soil, releasing volatile Hg(0) from foliage into air (Rugh et al. 2000). LeDuc et al. (2004) reported increased uptake and volatilization of Se by Indian mustard and *Arabidopsis* when a gene encoding the selenocysteine methyltransferase was cloned from *Astragalus bisulcatus* (Se-hyperaccumulator) to the two test plants. Transgenic plants with improved potential for TNT removal was reported by Gullner et al. (2001) and Hannink et al. (2001). Zhou et al. (2013) recently suggested the use of transgenic hairy roots developed by *Agrobacterium rhizogenes* in phytoremediation of organic and inorganic pollutants. Wu et al. (2006b) demonstrated the engineered plant-microbe symbiosis for rhizoremediation of inorganic mixtures. About 40 % Cd accumulation by sunflower roots with engineered rhizobacterium (*Pseudomonas putida* 06909) was achieved. While studying the ability of GM plants in phytoremediation of heavy metals and metalloid contaminated soil or sediments, Kotrba et al. (2009) observed successful promotion of Cd, Pb, Cu, As and Se phytoextraction by transgenic approaches. Brim et al. (2006) reported that the engineered *Deinococcus radiodurans* strain cloned with *tod* and *xyl* genes of *P. putida* was able to degrade organic contaminants.

Weyens et al. (2009) reported a successful field-scale phytoremediation of 90 % by poplar trees grown with TCE-degrading engineered endophyte (*Pseudomonas putida*) at a TCE-contaminated site. Weyens et al. (2013) achieved increased accumulation of Cd and toluene by inoculating the willow tree with Cd-resistant, and siderophore- and IAA-producing engineered *Burkholderia vietnamiensis* BU61 as a donor of the pTOM-TCE plasmid. Hu et al. (2012) reported 84 % PAH removal by the use of genetically engineered higher eukaryotic lines. Sood et al. (2010) developed novel yeast (*Candida digboiensis*) strain that could remove 72 % heneicosane in 8 days at pH 3.0, and 40 mg of eicosane in 50 ml minimal salts medium in 10 days. Paul et al. (2005) suggested the production of suicidal GMOs for safe and efficient remediation. Brim et al. (2006) developed a radiation-resistant *Deinococcus radiodurans* strain, by the cloned expression of *xyl* and *tod* genes of *Pseudomonas putida* for toluene degradation, and achieved complete oxidation of toluene under both complex and minimal nutrient conditions. Ripp et al. (2000) conducted a field study in USA using *Pseudomonas fluorescens*, carrying a naphthalene-degrading plasmid (pUTK21) mutagenized by transposition insertion of *lux* gene, to remediate PAH-contaminated site. Recently, Cao et al. (2012) recommended the use of a stable GMO producing rhamnolipid for pyrene removal from the contaminated soil. Wide array of studies employed GMOs and plants for the degradation of contaminants at lab-scale (Table 15). All that is required is to broaden the utility of GMOs and plants for large-scale pollutant clean ups.

4.4 Microbial Consortia in Photo-Hetero Microbial System

One of the most vital components of bioremediation is microbes. More commonly, bacteria, yeast, seaweeds, algae, fungi and actinomycetes that are isolated from the contaminated sites are evaluated for their efficiency in contaminant degradation at laboratories, and once they are confirmed to possess the catabolic genes that degrade the target contaminant, they are reinoculated into the real contaminated sites (Filali et al. 2000). In most studies, single species that could survive in the laboratory conditions where a feasible environment is provided will find it too complex to survive and get adapted to natural environments when the site constitutes complex pollutants at high concentrations. In such a case, microbial consortium can be developed so that multiple interactions among the microbial population can take place which can make the microbes more robust to the environmental fluctuations.

The first and foremost advantage of using microbial consortia is the ability of a microbe to detect and respond to the presence of another microbe either by exchanging dedicated molecular signals or by trading metabolites. This will lead to the second important merit of division of labor. As a result, microbial consortia perform several functions at a time with accelerated speed that are impossible for individual strains or species. Consortia of bacteria, bacteria and fungi or bacteria and algae are currently being developed and utilized for environmental implications (Sannasi et al. 2006; Subashchandrabose et al. 2011). One of the problems that rest with the consortia is the issue of compatibility between the two organisms that are brought together. It is expected that one must not hinder the growth of the other. Use of algal–bacterial consortia is much more beneficial than bacterial consortia, or bacterial–fungal consortia in the remediation of pollutants (Subashchandrabose et al. 2011). It is because, cyanobacteria or microalgae release a variety of light weight compounds and extrapolymeric compounds composed of nucleic acids, lipids, proteins, excretion products and fermentation products that serve as microbial growth substrates which, in turn, enhance the degradation potential of aliphatic and aromatic contaminants by the bacteria (Kirkwood et al. 2006). Fuels, non-halogenated VOCs, SVOCs, herbicides, heavy metals, pesticides and radionuclides could be treated by microbial consortia. To overcome the limitations pertaining to the use of microbial consortia at real contaminated site in the presence of mixed high contaminant levels, 'engineering microbial consortia' (Brenner et al. 2008) could be developed and used in the near future. Cost estimates are not available for this system.

Thavamani et al. (2012) demonstrated the potential of a bacterial consortium (*Alcaligenes* sp., *Pseudomonas* sp., *Pandorea* sp. and *Paenibacillus* sp.) for field-scale bioremediation of high molecular weight PAHs (pyrene and BaP) with heavy metal (Cd) tolerance in a long-term PAH-contaminated soil. More than 90 % anthracene, phenanthrene and fluoranthene, 77 % pyrene and 48 % BaP were degraded during the 60-day incubation. A consortium composed of bacteria—three gram-positive genera, *Micrococcus*, *Arthrobacter* and *Bacillus*; and six gram-negative genera, *Agrobacterium* sp., *Xanthomonas* sp., *Chryseomonas* sp., *Flavobacterium* sp., *Serratia* sp. and *Pseudomonas* sp.—all isolated from metal-contaminated site, reduced 38–52 % Cr, 17–28 % Cu and 3–17 % Pb at a pH range of 6.0–8.0 (Sannasi et al. 2006).

Recently, Gojgic-Cvijovic et al. (2012) achieved 82–88 % and 86–91 % TPH degradation in petroleum sludge and polluted soil, respectively, by the use of bacterial consortium (*Pseudomonas* sp., *Achromobacter* sp., *Bacillus* sp. and *Micromonospora* sp.). PAHs bioremediation was reported with a bacterial consortium enriched from the contaminated soil (initial PAH concentration was 9362.1 μg/kg) collected from the US EPA Superfund site by Mao et al. (2012). Addition of 10–20 % suspension from bacterial consortium (*Mesorhizobium* sp., *Alcaligenes* sp. and *Bacillus* sp.) was able to remove 20–35 % PAHs in 56 days. Pino and Penuela (2011) tested the simultaneous degradation of chlorpyrifos and methyl parathion by the consortium composed of *Pseudomonas putida*, *Proteus vulgaris*, *Bacillus* sp., *P. aeruginosa*, *Acinetobacter* sp., *Citrobacter freundii*, *Stenotrophomonas* sp.,

Table 15 Transgenic plants and microorganisms in bioremediation

Recipient plant/organism	Introduced gene	Contaminant	Reference
Arabidopsis thaliana	*ArsC*—Arsenate reductase gene	As	Dhankher et al. (2002)
Nicotiana tabacum	*CYP76B1*–Cytochrome P450 Monoxygenase gene	Herbicide	Didierjean et al. (2002)
Brassica juncea	Selenocysteine lyase	Se	Pilon et al. (2003)
B. juncea	γ-*ECS*, *GS*—Glutamycysteine synthetase and Glutathione synthetase gene	Atrazine, Dinitrobenzene, Phenanthrene, Metolachlor	Flocco et al. (2004)
A. thaliana	*hGSHS*—Homoglutathione synthetase	Herbicide	Sugiyama and Sekiya (2005)
A. thaliana	*NfsA*—Nitroreductase gene	Nitroreductase	Kurumata et al. (2005)
Poplus nigra	*YCFI*— Yeast protein	Cd, Cr, Cu	Bittsanszky et al. (2005)
N. tabacum	*GstI-6His*—Glutathione S-transferases gene	Alachlor	Karavangeli et al. (2005)
Lycopersicon esculentum	*tpxI*—Peroxidases gene	Phenol	Wevar Oller et al. (2005)
Deinococcus radiodurans	*merA* gene	Hg	Brim et al. (2000)
N. tabacum	*Gly* I, *Gly* II—Glyoxalase gene	Zn	Singla-Pareek et al. (2006)
A. thaliana	*XplA* and *XplB* from *Rhodococcus rhodochorus*	RDX	Rylott et al. (2006)
N. tabacum	*Bphc* from PCB-degrading bacteria	PCB	Novakova et al. (2009)
N. tabacum	*rh1A*, *rh1B*—Rhamnosyl transferase gene	Al	Brichkova et al. (2007)
N. tabacum	*DbfB*—Biphenyl dioxygenase	Chlorobiphenyls	Mohammadi et al. (2007)
A. thaliana	*BrMT1*—Metallothionein type 1 gene	Cd	Kim et al. (2007)
Populus trenula x, *Populus alba*	*CYP450 3EI* from rabbit	TCE, VC, CCl_4, Chloroform	Doty et al. (2007)
N. tabacum	*Dh1A*, *Dh1B*—Haloalkane dehalogenase gene	Dichloroethane	Mena-Benitez et al. (2008)
Oryza sativa	*CYP1A1* from human	Chlorotoluron, Norflurazon	Kawahigashi et al. (2008)
E. coli	*MerR*/*CadC*/*ZntR*/*Pmer*/*PcadA*/*PzntA* gene	Cd, Zn, Hg, Pb	Bondarenko et al. (2008)
E. coli	*As III* S-adenosylmethionine methyltransferase gene	As	Yuan et al. (2008)
A. thaliana	*743B4*, *73C1* genes	TNT	Gandia-Herrero et al. (2008)

N. tabacum	*TvGST* gene	Anthracene	Dixit et al. (2011)
Populus tremuloides	*pnrA* from *Pseudomonas putida*	TNT	Van Dillewijn et al. (2008)
N. tabacum	*Tpx 1* and *tpx 2* from *Lycopersicon esculentum*	Phenol	Sosa Alderete et al. (2009)
A. thaliana	*merP*	Hg	Ruiz and Daniell (2009)
A. thaliana	*MerP*—Metal tolerant and accumulation gene	Hg	Hsieh et al. (2009)
Caulobacter crescentus	*RsaA-6H*—Fusion protein	Cd	Patel et al. (2010)
Pelargonium sp.	*HPS/HPI*—Fusion protein	Formaldehyde	Song et al. (2010)
N. tabacum	*ppk/mer*, *T/merB*	Hg	Nagata et al. (2010)
C. crescentus, *Sphingomonas desiccabilis*, *Bacillus idriensis*	*arsM* gene	As	Liu et al. (2011)
Pseudomonas aeruginosa	*rhlABRI*—Cassette that produces rhamnolipid	PAHs	Cao et al. (2012)

Flavobacterium sp. and *Klebsiella* sp. isolated from highly polluted soils in Moravia, Columbia. In culture media augmented with each of the pesticide, the consortium was able to remove 72 % methyl parathion and 39 % chlorpyrifos. When glucose was supplemented, about 97–98 % of the pesticide was degraded in 120 h by the bacterial consortium. Kumar et al. (2012) identified *Pseudomonas*, *Bacillus*, *Pannonibacter* and *Ochrobacterum* species from the paper mill and agro-based pulp which were capable of reducing COD up to 86.5 % in black water and 66 % in black liquor and black water at a pH of 6.8 and 35 °C when enriched with phosphorous and nitrogen along with trace elements. Congeevaram et al. (2007) found that a consortium of *Micrococcus* sp. and *Aspergillus* sp. was able to remove 90 % Ni(II) and Cr(VI) around pH 5.0, and tolerant to a Cr level of 10,000 mg/L. Within 42 days, about 95.3 % BaP was degraded when *Mucor* sp. and *Bacillus* sp. were co-immobilized on vermiculite (Su et al. 2006).

A new bioremediation method for petroleum-contaminated soil using AM fungi and bacteria was investigated by Chen et al. (2009) at Petro China of Chandqing, Shaanxi, China. Both *Glomus caledonium* and *Bacillus subtilis* removed 92.6 % TPH in 60 days. Caceres et al. (2008) reported the transformation of an organophosphorous pesticide, fenamiphos, to non-toxic fenamiphos sulfone by a consortium of five different cyanobacteria and microalgal species. Munoz et al. (2005) showed the complete degradation of acetonitrile by the consortium of *Chlorella sorokiniana* and *Comamonas* sp. in a column photobioreactor. Zhong et al. (2011) demonstrated MTBE degradation by a mixed microalgal–bacterial system (*Methylibium petroleiphilum* and *Chlorella ellipsoidea*). There are many studies that confirmed the efficiency of algal–bacterial system in the degradation of phenols, hydrocarbons and heavy metals as listed in Table 16. The current requirement is to increase the use of these microbial consortia at full-scale and develop different formulations like immobilized mixed cultures in a nutritious substrate that would assure more remedial success as well as cost-effectiveness when commercialized as a product.

5 Challenges and Prospects

An in-depth revisiting of the available literature on techniques applicable for in-situ remediation indicated that the application of remedial tools is growing rapidly day-by-day, of which bioremediation has taken upper hand over physical and chemical treatment systems although physico-chemical techniques like EK remediation are successful. It is because, chemical and physical techniques are almost energy intensive and evolve greenhouse gases which increase the intensity of global warming, and are not considered to be ecologically and economically secure. However, existing bioremedial strategies also suffer from a number of limitations such as lesser degradation potential of microbial community during on-site remediation, less bioavailability of pollutants on temporal and spatial scales, and lack of benchmark standards for efficiency and pollutant toxicity testing of bioremediation for their increased field applicability (Table 17). As a result, currently focus is

Table 16 Degradation of environmental pollutants by microbial consortia

Consortia	Pollutant and Removal %	Reference
Bacterial consortium		
1. *Pseudomonas* sp., *Serratia* sp., *Flavobacterium* sp., *Chryseomonas* sp., *Xanthomonas* sp., *Agrobacterium* sp., *Bacillus* sp., *Arthrobacter* sp., *Micrococcus* sp.	Cr(VI) 38–52; Cu(II) 17–28; Pb(II) 3–17	Sannasi et al. (2006)
2. *Alcaligenes* sp., *Pseudomonas* sp., *Pandorea* sp., *Paenibacillus* sp.	HMW and PAHs 48–90	Thavamani et al. (2012)
3. *Acinetobacter* sp., *Pseudomonas putida*, *Bacillus* sp., *P. aeruginosa*, *Citrobacter freundii*, *Stenotrophomonas* sp., *Flavobacterium* sp., *Proteus vulgaris*, *Klebsiella* sp.	Chlorpyrifos, Methyl parathion 39–72	Pino and Penuela (2011)
4. *Mesorhizobium* sp., *Alcaligenes* sp., *Bacillus* sp.	PAHs 20–35	Mao et al. (2012)
5. *Pseudomonas* sp., *Achromobacter* sp., *Bacillus* sp., *Micromonospora* sp.	TPH 82–91	Gojgic-Cvijovic et al. (2012)
Bacterial–Fungal consortium		
1. *Mucor* sp., *Bacillus* sp.	BaP 95.3	Su et al. (2006)
2. *Micrococcus* sp., *Aspergillus* sp.	Cr(VI) 90; Ni(II) 90	Congeevaram et al. (2007)
3. *Glomus caledonium*, *Bacillus subtilis*	TPH 92.6	Chen et al. (2009)
4. *Sphingobacterium* sp., *Bacillus cereus*, *Achromobacter insolitus*	Phenanthrene 25–100	Janbandhu and Fulekar (2011)
Bacterial–Algal consortium		
1. *Chlorella sorokiniana*, *Sphingomonas yanoikuyae*, *Pseudomonas migulae*	Phenanthrene 15	Munoz et al. (2003)
2. *Chlorella* sp., *Scenedesmus obliquus*, *Stichococcus* sp., *Phormidium* sp., *Rhodococcus* sp., *Kibdelosporangium aridum*	Ni and Cu 62; Zn 90; Fe 64; Mn 70	Safonova et al. (2004)
3. *Pseudoanabaena* sp., *Pseudomonas* sp.	Phenol 95	Kirkwood et al. (2006)
4. *Selanastrum capricornutum*, *Mycobacterium* sp.	BaP 73	Warshawsky et al. (2007)
5. *Phormidium* sp., *Oscillatoria* sp., *Chroococcus* sp., *Burkholderia cepacia*	Diesel 99.5	Chavan and Mukherji (2008)
6. *Scenedesmus obliquus*, *Sphingomonas* sp., *Bacillus cepacia*, *Pseudomonas* sp., *Pandoraea pnomenusa*	Naphthalene, Phenanthrene and Fluorene 100	Tang et al. (2010)

rendered to develop advanced green remedial procedures which facilitate the emergence of new, promising bioremediation techniques like MFCs with high cost-benefit ratio where they perform a dual role of contaminated site clean up as well as electricity generation.

Most of the emerging technologies are only biological and the widely researched technologies for advancement and commercialization are also related to the family of bioremediation. Currently, there is a possibility to integrate successful physico-chemical methods with biological tools to accelerate the remedial efficiency at real contaminated sites. Also, emerging technologies like MFCs are not widely implemented at field-scale as they require system designing (define the components, modules, interfaces and data needed for setting up the MFC system). In such cases, appropriate models for implementation at full-scale are required to be engineered. Similarly, nanoremediation has prospects to synthesize eco-friendly green nanoparticles utilizing the natural resources which are so far not implemented at field-scale. Also, regulations are to be developed for the field application of transgenic plants and microbes so that they could be harnessed for large-scale risk-based remedial approaches. Photo-hetero microbial systems can be studied in-depth for their potential to produce economically viable products like biofuels, enzymes, etc. that could ensure an economical return when environmental clean up is done.

In relation to the vision to develop a less energy intensive and a non-greenhouse gas evolving remedial technique to support the ease of global living beings, it is highly necessary to develop and use a battery of bioassays to monitor and test the efficacy of remediation during the operation of each remedial technique in order to ensure the system efficiency and economy (Megharaj et al. 2000). Since remedial technologies available for emerging contaminant removal are scarce, research should be focused more on the development of large-scale advanced emerging technologies to ensure risk-based clean up of emerging priority pollutants. Hence, application of the principle of less energy intensive, function-directed, no greenhouse gas evolving remedial technology with high cost-benefit ratio is adequate to minimize the risks caused by the persistence and further spreading of priority and emerging pollutants in the ecosphere.

6 Summary

A global hot topics of concern are ‘pollution’ and ‘remediation’. World-wide annual release of billion pounds of chemical toxins into the bionetwork, and global population risk of around 2.0 billion people by complications caused by persistent priority pollutants like pesticides, petroleum hydrocarbons, heavy metals, halogenated materials, nitroaromatic compounds, solvents and phthalate esters, as well as by newly emerging, noxious contaminants such as flame retardants, pharmaceutical and personal care products, illicit drugs and industrial byproducts are the currently spoken issues of alarming distress for the livings in the biome.

Currently, decontaminating the pollutants in the environment is a major policy priority in most developed and developing countries as people are exposed to toxicants at dangerous levels that cause deleterious health effects (Ludlow and Roux 2012). Several physical, chemical, thermal and biological remedial options are available for removing the pollutants from the ecosystem. Of them, a number of strategies are available to remove the pollutants in-situ, and the available in-situ

Table 17 Advantages and disadvantages of the existing in-situ remediation techniques

Technology	Advantages	Disadvantages
Thermal		
1. Steam injection/Conductive/Radio frequency/Vitrification	• Potentially rapid remediation • High temperature treatments increase VOC removal efficiency from clay soils • Less site monitoring • Can enhance the efficiency of other in-situ remedial measures such as air sparging	• Unsuited for deeper depths (>65 m) • Initial capital cost is high • Potential to be expensive • Operating difficulties by soil debris • Unsuited for unsaturated soil • Interferences by soil properties • Need for extensive characterization of the site to determine the preferred path of treatment (for ex., steam injection)
2. Electrical resistance heating	• Adaptable to treat all soil types • Suited for sedimentary bedrocks • Depth independent • Effective in fractured zones	• Heat loss on small sites • Interference by co-contaminants
3. Thermal desorption	• Shorter treatment time • Appropriate to treat contaminant mixtures • Applicable to remediate heterogeneous sites	• High extensive material handling needs • Damage of processor unit • Material binding problems • Need for stabilization • Chance of contaminant migration to non-impacted areas • Difficulty in treating near occupied sites • Post-treatment effects on soil properties (for ex., soil shrinkage, sterility)

(continued)

Table 17 (continued)

Technology	Advantages	Disadvantages
Physical/Chemical		
1. Soil flushing	• Effective in soils with low silt or clay content • Reusability of recovered fluids • Simple design and operation	• Lengthy remediation time • Costly above ground treatments • Hydraulic control requirement • Extractant post treatment requirement • Surfactant adherence to soil • Contaminant mobility problems • Underground injection control regulations and land disposal restrictions limit selection and use of flushing solution • Requires greater understanding of the site geology • Not suited to treat mixture of hazardous substances
2. Fracturing	• Effective to treat low-permeable and fine-grained soils • Enhanced mass transfer of the contaminant in dense soils • Reduced treatment cost	• Unsuited for seismic bedrocks • Potential for contaminant spread • Fractures close in non-clayey soil • Lack of idea on trapped free product
3. Electrokinetic separation	• Most effective in clays • Compatible with most of the techniques • Early treatment response • Highly targetable (treat specific area) • Viable method to treat inorganic and organic compounds in porous media • Competitive in cost and remedial efficiency over other methods • Less energy intensive over *ex*-situ methods	• Decreasing efficiency with increasing soil moisture and unfavourable site conditions (cation exchange capacity, salinity, organic content, etc.) • Interference by buried soil metals • Formation of undesirable products in soil by redox reaction • Not suited for contaminant mixtures with varying concentrations • Not suited to treat non-polar contaminants • Post-treatment disposal requirements

4. Physical barriers	• Passive treatment system • Reduced exposure to contaminants • Relatively less maintenance and operational cost • Site is able to be in use while treatment is occurring • Barriers may last long	• Large rocks below ground may present a problem during construction • Installation requires excavation, produces substantial quantities of spoils that must be disposed of • Lengthy time for cleanup and monitoring • Reactivity of the barrier may get significantly reduced by environmental stress • Assessment of performance is difficult
5. Soil vapor extraction	• Cost-effective • Applicable to remediate large sites in short time • Minimal soil disturbance • Easy installation • Compatible with other techniques	• Reduced removal rates in soils with high organic & moisture content • Residual treatment before disposal • Unsuited for saturated zone, low permeability or heterogeneous soil • Limited applicability only to volatiles • Not suited to remediate mixture of chemicals
6. Multi-phase extraction	• Minimum disturbance to site operations • Proven performance in low-permeable soils • Short treatment times • Can be combined with other technologies • Can be used under buildings and other locations that cannot be excavated	• Expensive to implement at sites with medium to high permeable soils • Requires specialized equipment with sophisticated control capacity • Requires monitoring and control during operation
7. Air sparging	• Best stimulator of pollutant biodegradation • Supports microflora at contaminated sites • Easy implementation • Less costly • Remediate broad range of volatiles in short time • No post-treatment requirements	• Inappropriate for silt & clay sediments • Inefficient for non-strippable toxins • Inefficiency in high permeable zones • Flow of dangerous vapors • Influence of site specific conditions • Risks of contaminant migration

(continued)

Table 17 (continued)

Technology	Advantages	Disadvantages
Biological		
1. Natural attenuation	• Natural process • Reduced remediation cost • Reduced long-term risks • Minimal disturbance above ground • No disorder to existing soil biological communities • Post-disposal site is not required	• Reliability is not predictable • Slow process • Program duration affects cost • Need for regular and long-term monitoring • Natural events like storms or human activities may cause resuspension of contaminated sediments • Integration of several disciplines (microbiology, chemistry, hydrogeology, etc.) is needed
2. Bioventing	• Economic • Efficient in treating unsaturated soils • Creates biologically active soils • Short treatment time • Simple • Low maintenance	• Unsuitable for low permeable, clayey soils • Inefficiency in saturated zone and sites with shallow contamination • Not suited to treat sites with high contamination
3. Bioremediation (Bioaugmentation and biostimulation)	• Natural process • Cost-effective • Less energy requirement • Minimal site disruption • Less manual supervision • Toxic chemicals are destroyed • Low capital expenditure • Reduced exposure to public or site personnel	• Slow process • Chance of incomplete degradation resulting in toxic by-products • Process is sensitive to the level of toxicity and environmental conditions • Not suited to completely remove heavy metals • Not suited to biodegrade almost all chemicals • Unsuited for soils with low permeability • Gaps in the understanding of microbial ecology, gene expression and physiology • Performance evaluation is uncertain

4. Phytoremediation	• Less expensive • Green approach • Aesthetically pleasing • After plant establishment, there are chances to flourish wildlife • Easily monitored • Preserves environment in more natural state	• Limited to shallow sites with low levels of contamination • Restricted to sites with contamination as deep as the roots of the phytoremediating plants • Retarded remediation efficacy in sites with high contaminant concentration • Complete treatment shutdown if selected plants are dormant or root growth rate is very slow • Need for post treatment of used plants • Chances for air pollution by burning of plant leaves that were used to phytoremediate a field • Slow treatment • Food chain could be adversely affected by bioaccumulation of contaminants into the plants • Need for large surface area • Contaminant transfer from soil to air • Seasonal interferences • Mass transfer limitations

physico-chemical techniques like EK remediation, heating, etc. are the most promising for on-site contaminant clean up. Bioremediation that harnesses the potential of microbes is widely adopted for full-scale contaminant removal either by biostimulation or bioaugmentation or phytoremediation. However, the successful physico-chemical techniques are not advantageous as they are energy intensive and pave way for global warming by letting out greenhouse gases into the atmosphere. On the other hand, though bioremediation is cost-effective and eco-friendly, it suffers from limitations due to the low bioavailability of pollutants on spatial and temporal scale, poor performance of microbial groups in real contaminated sites, and lack of bench-mark values for evaluating the efficacy and toxicity reduction by bioremediation for their widespread field applications. Considering the above constraints of the existing technologies, advanced techniques using MFCs, nanomaterials, transgenic microbes and plants, and photo-hetero microbial systems have been recently developed which are mostly biological with more prospects of high remedial efficiency in short span along with the potential to harness electricity and by-products like biofuels that add to the economy. However, the in-situ emerging technologies are not widely employed at field-scale due to the lack of system designing for large-scale implementations and regulatory limitations. Therefore, the current prospect as well as a challenge in the field of environmental remediation is to develop a regulated, less energy intensive, no greenhouse gas evolving remediation technology with high cost-benefit ratio for field-scale remediation of soil/sludge/sediment/groundwater/surface water/leachate/air emissions along with the development of bioassay techniques for determining the toxicity and efficiency of each remedial technology at the time of operation.

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