Chapter 13
Subsurface Fate and Transport of Chemicals

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Glossary

Abiotic	Not relating to life, as in abiotic chemical reactions that occur independent of living organisms.
Absorption	Retention of a chemical within a solid material.
Adsorption	Adhesion of a chemical to the surface of a solid.
Advection	Transport of a solute within a fluid in the direction of the bulk fluid's flow.
Aerobic	Requiring oxygen.
Air sparging	Injecting air or oxygen into an aquifer.
Aliphatic	Organic compounds not containing an aromatic ring.
Anaerobic	Without oxygen.
Best management practice (BMP)	Techniques generally accepted as effective for achieving a particular goal, for example minimizing the environmental impact of remediation.
Biodegradation	Use of living organisms to clean up contaminated environmental media.
Biotic	Relating to life, as in a biotic reaction mediated by living organisms.
Bioventing	The addition of air (or oxygen) under, at times, an induced lowering of water table to promote aerobic biodegradation of subsurface contaminants in the unsaturated zone.

This chapter was originally published as part of the Encyclopedia of Sustainability Science and Technology edited by Robert A. Meyers. DOI:10.1007/978-1-4419-0851-3

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J.S. Gulliver (ed.), *Transport and Fate of Chemicals in the Environment: Selected Entries from the Encyclopedia of Sustainability Science and Technology*,
DOI 10.1007/978-1-4614-5731-2_13,

Catalytic oxidizer	Remediation technology equipment that uses a catalyst to accelerate the chemical oxidation of hydrocarbons with oxygen in a vapor effluent stream.
Chemisorption	Adhesion of a chemical to the surface of a solid, specifically through a chemical reaction occurring at the surface.
Confined aquifer	A water-bearing geologic strata that is situated between impermeable layers (clays and silt layers), leading to higher pressure of the groundwater in this unit.
Extraction well	A well used to remove liquid or gas from the subsurface.
Fate and transport	Encompasses how contaminants move through environmental media and how long the contaminants persist or how fast they are degraded.
Feasibility study	A document that describes and analyzes potential cleanup alternatives for a site and recommends selection of an effective and efficient alternative.
Green and sustainable remediation	Environmental cleanup that is designed and performed with consideration of the environmental impacts of the technologies used.
Half-life	Time required for half of the molecules of a chemical to decay or be degraded.
Henry’s law	Law that is used to describe the volatility of a chemical, by describing the equilibrium between the vapor phase and dissolved forms of the chemical.
Hydrocarbons	Chemical compounds that consist of carbon and hydrogen.
Hydrodynamic dispersion	Transport within a fluid in directions other than the primary direction of fluid flow. This process decreases contaminant concentrations while increasing the total volume of fluid contaminated.
Hydrodynamics	The process of the motion of groundwater.
Hydrogeology	Discipline dealing with the properties and characteristics of groundwater.
Hydrolysis	Reaction that splits a chemical into two parts by adding a water molecule, through addition of a hydrogen ion to one fragment of the chemical and addition of a hydroxyl group to the other fragment.
Hydrophobic	Having an aversion to water. Typically describes a contaminant that associates with nonpolar substances (such as oils and organic matter) rather than polar substances like water.
Injection well	A well used for injection of fluids, gases, and/or chemicals for remediation.

Inorganic	Describes chemicals that are not organic, including metals and common anions (sulfate, nitrate, etc.).
Interfacial tension	Tension at the interface between a liquid of one chemical and a solid, liquid, or gas of another chemical. One of the primary determinants of NAPL mobility in the subsurface.
Interim remedial action	A remedial action taken to address immediate risks to human health or the environment before long-term remedial goals are achieved.
Leaching	Dissolution of relatively soluble chemicals and removal by water transport.
Life cycle analysis (LCA)	Evaluation of the environmental impacts of all stages of a product or process.
Light nonaqueous phase liquid (LNAPL)	A nonaqueous phase liquid that is less dense than water and therefore floats on the water table, including petroleum hydrocarbon fuels and lubricating oils.
Liquid density	Mass per unit volume of a liquid.
Liquid viscosity	Resistance of a liquid to being deformed. Higher viscosity is associated with more resistance to flow, or less fluidity.
Lower explosive limit	The concentration of a compound in air below which it will not ignite.
Microaerophilic	Requiring only small amounts of oxygen.
Monoaromatic hydrocarbons (MAHs)	Organic chemicals containing one aromatic ring, which are common petroleum derivatives.
Nonaqueous phase liquid (NAPL)	A liquid, such as oil, that remains in a separate phase in the groundwater and can act as a source of organic contaminants to groundwater and soil.
Organic	Describes a category of chemicals that typically contain carbon with hydrogen, oxygen, and/or nitrogen. Most organic compounds can be degraded to carbon dioxide, water, and other simple components.
Oxidation	Chemical reaction in which a chemical of interest loses electrons. The chemical that takes the electrons is known as the *oxidant*. Includes "rusting" of metals and processes that degrade organic matter to carbon dioxide.
Partitioning	Distribution of a chemical between the solid, fluid, and/or gas phases, in proportions reflecting its affinity for each phase, as described by the *partition coefficient*.
Permeability	Tendency of a material to allow fluids to flow through it.

Persistent organic pollutants (POPs)	Chemicals that do not readily degrade under environmental conditions and, therefore, persist in environmental media.
Polychlorinated biphenyls (PCBs)	Organic chemicals with chlorine atoms attached to two benzene (aromatic) rings, which were widely used as dielectric and coolant fluids, for example in transformers.
Polycyclic aromatic hydrocarbons (PAHs)	Organic chemicals containing more than one aromatic ring, which are common by-products of coal combustion.
Porosity	Fraction of a material that is void space. Can be primary (original, from when the geological material was formed) or secondary (formed later, by selective dissolution or fracturing).
Precipitation	Formation of a solid from dissolved chemicals in a solution.
Preferential flow	Faster movement of groundwater through certain, more porous or permeable, portions of the subsurface, which can result in localized, rapid contaminant transport.
Redox	Term used to describe the related processes of reduction and oxidation.
Reduction	Chemical reaction in which electrons are gained by a chemical of interest. The chemical donating the electrons is known as the *reductant*. Includes the reduction of oxygen gas during aerobic respiration and the reduction of other chemicals (nitrate, iron, carbon dioxide) during anaerobic respiration.
Remedial action	Action taken to remove or contain a hazardous substance in the environment.
Remediation	Cleanup or other methods used to remove or contain hazardous materials.
Risk assessment	Qualitative and quantitative evaluation of the risk posed to human health and/or the environment by contaminants.
Saturated zone	The portion of the subsurface below the water table, where the pressure of water within the pores is at a pressure equal to or greater than atmospheric pressure.
Solubility	Ability of a chemical to dissolve into (i.e., mix with and become incorporated into) another substance. Unless otherwise specified, in an environmental context, solubility is typically used to refer to solubility of a chemical in water.

Sorption (verb: to sorb)	Attachment of a chemical to a solid, which removes the chemical from the dissolved phase. See also adsorption, absorption, and chemisorptions.
Speciation	The chemical form (phase, redox state, molecular structure) in which an element exists. Important determinant of metal mobility in the environment.
Subsurface	The zone beneath the surface of the earth, including geologic strata and groundwater.
Transport mechanisms	Processes by which contaminants move through the environment.
Unsaturated/vadose zone	The subsurface zone between land surface and the water table where the moisture content is less than atmospheric pressure (i.e., soil pores are not completely filled with water).
Vapor pressure	Pressure of the vapor of a chemical that exists in equilibrium with the chemical's solid or liquid phase.
Volatility	Tendency of a chemical to vaporize, or go into the gaseous phase.

Definition of the Subject and Its Importance

Since the onset of subsurface remediation in the 1970s, there has been a need for a more appropriate balance between the protectiveness of environmental cleanup technologies and the concept of environmental sustainability. This entry explores the implementation of innovative green and sustainable practices deemed appropriate for the remedial technologies that address the most common classes of persistent and toxic subsurface contaminants.

Introduction

Preceding and during the early timeframe of environmental remediation, there was a lack of concern and knowledge about the fate and persistence of chemicals released to the subsurface. There was a prevailing but unfounded assumption that the subsurface environment would sorb or attenuate almost unlimited amounts of contaminants. Much to our dismay, this has been shown to be false through major advancements in analytical chemistry techniques over the last 2 decades. Once subsurface transport mechanisms were understood, it became obvious that contaminants released at or near the surface may make their way deep into subsurface environments, including confined aquifers and bedrock settings. The fate and transport of environmental contaminants in subsurface environments are

Table 13.1 Summary of properties that affect fate and transport of organic and inorganic contaminants in the subsurface

Contaminant properties	
Organic contaminants	*Inorganic contaminants*
Solubility	Solubility
Fluid density	Redox (reduction-oxidation)
Viscosity	Speciation
Interfacial tension	Adsorption
Carbon partition coefficient	Reactivity
Henry's law constant	Vapor pressure
Biological degradation	
Vapor pressure	
Subsurface/hydrogeologic properties	
Rock type and characteristics	
Hydraulic conductivity	
Aquifer redox chemistry	
Specific surface area of minerals	

significantly affected by two categories of properties (Table 13.1): (1) the geologic characteristics of the subsurface environment, which defines the intrinsic properties of the soil (or rock) and imparts the characteristics of groundwater flow through that media, and (2) the properties of the contaminants, which define the physicochemical and biological processes that affect their fate and persistence.

The prevailing group of processes affecting subsurface fate and contaminant transport are hydrodynamic processes, partitioning, biotic reactions, and abiotic reactions. Hydrodynamic processes impact contaminant transport through groundwater advection, hydrodynamic dispersion, and potential preferential flow. Partitioning affects contaminant distribution and dispersal by allowing interchange of contaminant from one subsurface medium to another (e.g., soil, groundwater, soil gas) through means of adsorption, absorption, or chemisorption. Biotic reactions can affect contaminant transport by degradation (or immobilization) of the contaminant in oxidation or reduction reactions. More specifically, biotic processes, which occur under aerobic, microaerophilic, or anaerobic conditions, can lead to degradation or immobilization (by reaction or precipitation), depending on the type of contaminant. Abiotic reactions affect contaminant transport in the subsurface by promoting interactions between the contaminant and groundwater or stationary media (e.g., soil, bedrock), causing the contaminant to degrade or change in form (e.g., hydrolysis, redox reactions). These processes take place within the saturated zone and the unsaturated zone of the subsurface. Of these two subsurface zones, heightened concern is often paid to the saturated zone because contaminants are in direct contact with groundwater, which may be used as a potable or irrigational resource or for other purposes. The unsaturated zone, or vadose zone, overlies the saturated zone (i.e., above the water table) and is an important contributor to contaminant fate and transport through processes such as leaching and migration to the saturated groundwater zone.

Sources of chemicals released to the subsurface are varied, but generally include (1) underground and above ground storage tanks, (2) septic tanks, (3) agricultural activities, (4) municipal and industrial landfills and dumps, (5) regulated and abandoned hazardous waste sites, (6) injection wells, and (7) other industrial sites [1]. The types of chemicals that have been historically released to the subsurface and have the potential to cause adverse effects to human health or the environment are generally divided into organic compounds and inorganic compounds (or inorganic elements). Several of the more common classes of organic and inorganic contaminants found in soil and groundwater are as follows:

- Petroleum hydrocarbons and derivatives used as fuels such as gasoline, diesel fuel, jet fuel, and heating oil. These fuels consist of many organic chemical components, including monoaromatic hydrocarbons (MAHs) like benzene, toluene, ethylbenzene, and xylene (BTEX), and low-molecular-weight polycyclic aromatic hydrocarbons (PAHs), such as naphthalene, and are generally less dense in hydrocarbon fluid form than water, contain components that are highly volatile, and are sparingly to moderately soluble in water. When present as an immiscible phase (in water), they tend to persist over reasonably long time frames as light non-aqueous phase liquids (LNAPLs). However, LNAPL constituents will dissolve in water, sorb onto soils, and/or partition into the vapor phase.
- Chlorinated aliphatic hydrocarbons used as solvents, degreasers, and dry cleaning fluids, such as tetrachloroethylene (PCE), trichloroethylene (TCE), and carbon tetrachloride (CT). These compounds generally are distilled for use in industrial settings in a pure form or as relatively simple mixtures. When present as an immiscible phase, they generally are denser than water, highly volatile, and also sparingly soluble in water. Hence, they can exist as dense non-aqueous phase liquids (DNAPLs), dissolved in water, sorbed onto soils, and/or present in the vapor phase.
- Polychlorinated biphenyls (PCBs), pesticides, wood-preserving chemicals (such as creosote), and fossil fuel combustion/gas manufacturing gas by-products, such as coal tars and high-molecular-weight PAHs. These contaminants tend to be dense, highly viscous fluids (when present an immiscible phase) with constituents that sorb strongly onto soils, are nearly insoluble in water, exhibit low volatility, and are persistent in the subsurface environment because they chemically and biologically degrade very slowly. When present as an immiscible phase, they generally are found as DNAPL or are sorbed onto soils.
- Explosives and energetic compounds such as solid-rocket fuels and propellants, including trinitrotoluene (TNT), plastic explosives, perchlorate, and munitions components. These constituents are often found as solids on or near the land surface, although some (such as perchlorate) can be found dissolved in groundwater.
- Metals such as arsenic, lead, chromium (VI), mercury, cadmium, and others. These generally are found either dissolved in groundwater, present as elements in the solid phase, or present within the rock matrices as mineral components.

Each type of contaminant has a distinct set of physicochemical characteristics that define its behavior and migration within subsurface environments. Hydrogeology and rock/mineral geochemistry also have a significant influence on defining the fate and migration of contaminants. As a function of the contaminant's physicochemical properties and geologic characteristics, the above listed classes of organic chemicals exist in the subsurface as one or more of four phases: (1) mobile or residually entrapped nonaqueous phase liquid (NAPL), (2) dissolved phase in groundwater, (3) sorbed phase to solid aquifer media, and (4) vapor phase in soil gas. Both the properties of the chemical and that of the subsurface control the dynamic evolution of phase transfer, including the duration of time that these organic chemical remains within these phases following a spill or release. From the point of release, organic chemicals generally exist in the NAPL phase, with eventual partitioning to one or more of the other phases with time. Subsurface NAPLs can exist as a pure chemical or as a bulk mixture of chemicals.

Physical and chemical properties that have a major effect on the fate, transport, and persistence of the classes of typical organic contaminants are shown in Table 13.2. Properties such as solubility (in water) determine the degree to which a contaminant persists in the subsurface as an immiscible fluid or solid. If an immiscible fluid phase persists in the subsurface, fluid density governs whether the fluid acts as an LNAPL or DNAPL (e.g., petroleum hydrocarbons, with a fluid density less than 1 g/mL, form LNAPLs, whereas chlorinated hydrocarbons form DNAPLs). Properties like organic carbon partition coefficient (K_{oc}) and Henry's law constant effect the tendency of a chemical to partition under equilibrium conditions from a source release (e.g., contaminant liquid or solid) to subsurface media (e.g., soil, groundwater, and/or soil gas). The relatively high Henry's law constants and solubilities of hydrocarbons, for example, indicate that hydrocarbons are more likely to partition into air and groundwater than are PAHs, PCBs, and pesticides.

The half-lives for biological degradation of the contaminants, also shown in Table 13.2, provide an indication (using first order kinetics) of how quickly a chemical will biologically degrade in the subsurface. Petroleum hydrocarbons and chlorinated hydrocarbons have been observed to degrade under aerobic and anaerobic conditions, respectively, at reaction rates determined to be moderate to fast for both natural and engineered remedial systems. Conversely, PCBs and certain PAHs have been shown to undergo very slow to negligible rates of aerobic and/or anaerobic biodegradation in natural subsurface settings. Explosives and energetic compounds have been shown on a constituent by constituent basis to biologically or chemically degrade (in presence of reductants and oxidants, respectively) under subsurface conditions attainable with the aid of remedial technologies.

The most common inorganic compounds identified in the subsurface include metal contaminants. Although metals are natural constituents of soils, anthropogenic metals enter the soil through a variety of means including (1) leaching of municipal or industrial solid wastes, (2) storm water runoff and infiltration, (3) industrial by-products, (4) dredged materials, (5) mining and smelting operations, (6) atmospheric emissions from coal or oil combustion, (7) ash and

Table 13.2 Physicochemical properties of organic contaminants that affect contaminant fate, transport, and persistence (Refs. [2–5])

Class of contaminant	Henry's law constant (atm. m^3/mol)	Solubility (g/L)	Fluid density (g/cm^3)	log K_{oc}	Biodegradation half-life	
					Aerobic	Anaerobic
Chlorinated hydrocarbons	0.00674–0.015	0.15–6.3	1.2–1.6	0.4–2.4	4 weeks–1 year	11 weeks–4.5 years
Petroleum hydrocarbons	0.00046–0.015	0.03–200	0.86–0.88	1.5–3.6	2 days–6 months	8 days–2 years
Heavy PAHs	Minimal–0.0003	0.0000003–0.004	NA (solid)	1.3–7.5	12 days–5.2 years	50 days–21 years
PCBs	0.000003–750	0.00001–0.002	1.182–1.566	2.4–6.4	1.5–9 years	–
Pesticides	0.0000002–0.002	0.0000004–0.5	NA (solid)	2.1–6.3	2 days–16 years	1–294 days
Explosives/energetics	Minimal–0.00000002	0.13–250	NA (solid)	NA	4 weeks–6 months (TNT)	4 weeks–6 months (TNT)

NA not applicable

slag from coal or oil combustion, (8) and sludge residues from wastewater treatment. Typical metals identified as contaminants in subsurface environments include arsenic, chromium, cadmium, copper, lead, mercury, nickel, silver, and zinc. Radionuclides are a separate class of contaminants that are inorganic and due to their specificity are not discussed in this entry.

The physicochemical properties of inorganic chemicals that govern their fate, partitioning, and migration within subsurface environments include solubility, reduction–oxidation (redox) speciation, reactivity, and vapor pressure. Properties of subsurface media that play a defining role in the fate of inorganic contaminants within subsurface environments include rock type and characteristics (primary and secondary porosity, mineral composition, fracture density), hydraulic conductivity, redox chemistry, and specific surface area of minerals present. Metals are not degraded by biological or chemical reactions, though they can conveniently be rendered unavailable through precipitation reactions or transformed via oxidation/reduction reactions to less toxic species.

Properties of subsurface media that play a defining role in the fate, partitioning, and transport of organic contaminants within subsurface environments include rock type (i.e., porous or fracture flow), primary and secondary porosity, hydraulic conductivity, and total organic carbon.

Background

Beginning in the 1970s with the advent of subsurface remediation, the environmental industry invested heavily in remediation systems without an adequate understanding of the degree of contaminant cleanup (or the duration of the cleanup). Although these early efforts were well intended, the actions taken with the technologies utilized were not justified based on the costs of the cleanups, the overutilization of resources, the intensive amount of energy consumed, and the insufficient contaminant removal. Past presumptive remedies such as soil "excavation and off-site disposal" and groundwater "pump and treat" are prime examples of these generally wasteful remedies considered unsustainable onto the future.

Beyond this early misunderstanding about remedial technology selection to achieve efficient and sustained removal of subsurface contaminants, there has been a long-standing misperception that cleanup shall continue to pristine conditions, a goal that as turns out is largely unattainable in most circumstances. At the expense of nearly 2 decades of numerous examples of unsuccessful and costly cleanups, we have learned considerably from these early mistakes. Today, in many cases, there is a robust process and a wealth of regulatory guidance to determine more pragmatic yet adequate remedial action objectives and cleanup performance criteria. These cleanup goals and objectives are most often defined by human health risk assessment [6], ecological risk assessment [7], risk-based

Fig. 13.1 Key elements of green and sustainable remediation

corrective action [8, 9], or by what is reasonably achievable based on the best practicable remedial technology options (generally referred to as best available technology [BAT]).

In addition to these well-considered approaches that have provided a practicable risk-related basis for cleanup end goals, there is growing interest in the last 5 years to incorporate green and sustainable remediation (GSR) concepts throughout the remedial action process, while continuing to provide acceptable long-term protection of human health and the environment. As suggested by the Sustainable Remediation Forum (SURF), sustainable remediation is defined as a "remedy or combination of remedies whose net benefit on human health and the environment is maximized through the judicious use of limited resources" [10]. To this end, sustainable remediation employs solutions that minimize the environmental footprint while providing maximum net environmental benefit over the remedial lifecycle. To realize the benefits of sustainable remediation requires the use of green and/or renewable energy sources, conservation of water and energy, decreasing waste, and formulating integrated sustainability policies. With sustainable remediation, the goal should be to (1) develop and implement safe remedial solutions that are minimally disruptive to the environment, (2) realize energy savings through creative design and value engineering, (3) embrace waste minimization and recycling concepts, and (4) emit the least amount of pollutants and greenhouse gases to the atmosphere. To the extent practical, the following sustainability elements should be applied to remedial solutions incorporating GSR practices (Fig. 13.1): (1) short-and long-term energy and water consumption, (2) greenhouse gas emissions and air pollutants, (3) ecosystem impacts, (4) material consumption, and (5) waste minimization and/or recycling.

The recent recognition of the balance between adequacy of cleanup and sustainability concepts has not, in some cases, dispelled the notion of initiating cleanups with little thought to the protective character (human health and environmental), resource utilization, or safety of the action. As evidenced by the continued use of pump and treat systems, there are still regulatory mandates for cleanup with little decrease in contaminant mass (and therefore little decrease in overall risk). There are, in fact, examples of sites where natural attenuation is actively decreasing contaminant concentrations in the subsurface, yet the overseeing regulatory agencies require a more traditional, less sustainably oriented, significantly more costly approach because of outdated or arbitrary remediation goals set for the site. Clearly a new paradigm is warranted, whereby cleanup protectiveness of a remedy is balanced with sustainability elements. The analysis to establish this balance should be evaluated early in remedial planning, such as during a feasibility study of remedial alternatives. Incorporation of sustainability into the balancing criteria evaluated during a feasibility study would help to assure that this process happens. In the interim, many professionals in the environmental industry have been documenting sustainability metrics by qualitatively and/or quantitatively scoring the degree of sustainability core elements to be utilized on cleanup actions. Such evaluations have ranged from simple qualitative review of the available list of best management practices (BMPs), utilizing those that are applicable, to the performance of quantitative and complex life cycle analysis (LCAs) for optimization of the cleanup over the remedial lifetime. The following section provides valuable information on industry lessons learned from implemented LCAs and BMPs for sustainable remediation practices, as applied to the typical classes of subsurface contaminants described in this document.

Sustainable Remediation Practices for Classes of Typical Subsurface Contaminants

Remediation sites comprise a range of sizes, proximity to human and/or ecological receptors, proximity to man-made infrastructure, site accessibility, environmental complexity, type of contaminants and their chemical, physical, and toxicity characteristics, complexity of the circumstances surrounding the release(s), and so on. All of these factors affect the feasibility of corrective actions, and even the ability to implement any corrective action. Because of this, no generalized discussion of sustainable remediation practices can be complete, because the topic is simply too broad. However, the information described below, is comprised of remedial measures applied recently that can be characterized as sustainable practices.

With this in mind, this chapter will focus on sustainable practices honed over time for the general classes of subsurface contaminants discussed above. The discussions are premised on the following assumptions:

- Releases to the subsurface have stopped; i.e., that the pipelines have been repaired, the underground storage tanks have been removed, the uncontrolled landfill is no longer receiving toxic materials and has been capped, etc.

- Any discussion of “sources,” with regard to groundwater, refers to concentrated areas of contaminants such as NAPL or highly contaminated soils that are present but relatively stable.
- A risk assessment has been completed (if necessary), and remedial action objectives have been defined before remedial implementation.
- Emergency or interim measures (e.g., protection or replacement of domestic water supplies affected by the release) are in place as needed.
- Site characterization has progressed to a point where remediation methods can be considered within a feasibility study (FS) or a focused feasibility study (FFS).
- Remedial systems are designed to destroy (or remove) contaminants with the knowledge and benefit of exploiting the physical and/or chemical characteristics of the contaminants.
- Sustainable measures for the contaminants discussed have been optimized over time as a result of trial and error evaluation with full-scale remedial systems and technology innovation or breakthroughs.

These discussions readily address the lessons learned and resulting sustainable optimizations (or BMPs) of various technologies for typical contaminants.

Petroleum Hydrocarbons

Petroleum hydrocarbons, including MAHs and low-molecular-weight PAHs, often occur in persistent LNAPLs in the subsurface. Therefore, the primary method of remediation historically has relied on product recovery within a cone of depression produced by water table drawdown from groundwater pumping.

As a result of energy inefficiencies and high cost of groundwater extraction (and treatment), a more sustainable approach evolved involving product recovery with skimmer pumps. Skimmer pumps are designed to remove LNAPL from the water table surface. The skimmer floats on the water table and has an interval with a hydrophobic (water-rejecting) screen that is open to the LNAPL layer within a monitoring well. LNAPL is drawn into the skimmer and flows through a flexible tube to a reservoir where it is pumped to the surface. The following practices are often employed with product recovery systems to reduce energy consumption, minimize site impacts, and improve the overall sustainability of the treatment [11]:

- Power product recovery components or auxiliary equipment with low energy demand, such as renewable energy off-grid wind turbines or photovoltaic (PV) systems.
- Such systems relying on off-grid energy should be equipped with deep-cycle batteries to provide steady power.
- Eliminate the long-distance transport of incoming materials and equipment or outgoing remedial-derived wastes (i.e., recovered product). To that end, consolidate deliveries/pickups to avoid deploying partially filled vehicles.

- Recycle separated product (LNAPL) through local fuel or waste recyclers.
- Optimize product recovery through proper equipment sizing and frequent reassessment based on treatment performance.
- Establish operating or cleanup performance criteria that could trigger use of less intensive polishing technologies as cleanup progresses and LNAPL recovery rates decline.

Skimmer pumps are capable of removing LNAPL down to a sheen, but do not reduce dissolved contaminant concentrations or the mass of contaminants sorbed onto soil. In addition, skimmer pumps, unless supplemented with vacuum enhancements, generally are not capable of providing complete capture of a mobile accumulation of free-phase LNAPL that is migrating under natural subsurface conditions. In such cases, groundwater extraction is sparingly used to capture and contain the mobile, free-phase LNAPL for recovery. The following sustainable practices are often employed to minimize groundwater extraction while optimizing LNAPL capture:

- Perform groundwater capture zone analyses using empirical calculations or numerical groundwater modeling as basis of design for groundwater capture and, therefore, LNAPL containment.
- Calibrate and refine groundwater extraction network and flow rates with calculations or modeling after system startup with observed drawdown conditions from corrected groundwater elevations.
- Monitor and periodically optimize the groundwater extraction network and flow rates to maximize LNAPL recovery rates as a result of higher producing wells.
- Monitor extraction well change in head at a given rate over time, or specific capacity, to ensure continued efficient well operation. Rehabilitate wells periodically, if decreased specific capacity is observed, to maximize extraction well longevity.
- Design system to minimize the total amount of piping including length, surface area, bends, and elbows to maximize transport efficiency.
- Engineer extraction wells to maximize efficiency through decreased head loss and optimized flow rates by designing the well gravel pack to match the formation and using the largest feasible slot size to maximize open cross-sectional area. This decreases velocity and prevents migration of fines by allowing a less-turbulent flow into the well.

Sustainable features of skimmer pumps are that they require little energy to operate, and the energy can be obtained from sustainable sources such as solar panels (Fig. 13.2). Recovered LNAPL can be recycled to minimize waste. The method is relatively slow and inefficient for LNAPL removal, but it can be effective at small sites. Skimmer systems can be enhanced by applying a vacuum, which can speed up LNAPL recovery for a relatively minor additional energy input that could also be obtained from sustainable power sources. The use of skimmer pumps

Fig. 13.2 Example of solar powered system with photovoltaic panels for powering product skimming

generally does not exacerbate existing subsurface conditions or make additional remediation efforts more difficult or less effective.

Soil vapor extraction (SVE) can be effective at removal of volatile organic compounds (VOCs) of petroleum hydrocarbons within the unsaturated zone of the subsurface present as LNAPL, sorbed to contaminated soil, or in the vapor phase. One or more SVE wells (screened in the unsaturated zone above the water table) are constructed, and a vacuum system is installed and manifolded to the wells. The vacuum draws the soil air (which is contaminated with VOCs) out of the subsurface through a treatment system (described below). The contaminated vapors are replaced by fresh air from vent wells or from other parts of the subsurface. This allows the volatile fraction of the VOC to evaporate at a rate that is proportional to the Henry's law coefficient. These volatiles are then carried by the air into the SVE system, allowing for further evaporation into the fresher soil air, and so on.

SVE systems are efficient for VOC removal in the unsaturated zone primarily because volatiles preferentially partition into the vapor phase, and air is relatively easy to move in the subsurface compared to liquids. SVE systems tend to lose efficiency with age as the volatile fractions of the contaminants are removed and the less volatile fractions remain. Because not all of the components of refined petroleum hydrocarbons are volatile, SVE by itself cannot achieve complete subsurface remediation. In addition, SVE does not affect contaminants below the water table, because they are not in contact with the soil air. However, certain adaptations can be made to an SVE system to facilitate contaminant removal from the subsurface.

Examples of these adaptations include artificially lowering the water table to expose more soil contaminants to the air or forcing air into the aquifer below the water table to strip out the dissolved or sorbed volatile compounds in the saturated zone through a process known as air sparging.

Nearly all SVE systems require treatment of the vapors removed from the subsurface soil. The most efficient treatment depends on the contaminant concentrations within the vapor stream. Essentially, low concentrations are most cost effectively removed using a sorption medium such as granular activated carbon (GAC), which is a specific type of charcoal. GAC requires no energy input to remove organic compounds from soil vapors while deployed on an SVE system. Because GAC is an absorbent material, however, it does not destroy contaminants, but transfers them to another medium. Once most of the sorption sites are filled and "breakthrough" (i.e., contaminants are no longer captured by the absorbent material) occurs, GAC must be regenerated off-site (requiring energy) or replaced with virgin material (also requiring energy). The virgin material commonly used to manufacture GAC is coconut shells, which are a sustainable resource.

If vapor concentrations are too high, breakthrough will occur quickly and GAC change-out costs can become prohibitive. Above certain concentration threshold, however, a treatment method that uses a catalytic oxidizer may become the most appropriate choice. Catalytic oxidizers are energy intensive because their optimal performance occurs at a relatively high temperature (300–600°C). However, the oxidation of fuel components at sufficient concentrations releases heat that is used to maintain the optimal temperature, greatly increasing efficiency and decreasing or eliminating the need for external energy inputs. As a result, the sustainability of the remediation system is enhanced.

For very high concentrations of VOCs that approach or exceed the lower explosive limit of the vapors, high temperature oxidation of the fuel components can be used to actually run the SVE system in whole or in part. The technology uses an internal combustion engine powered by the extracted vapors and an auxiliary fuel source such as propane if needed. Under the right conditions, such a system requires no external power supply, and if a generator module is added, the system can supply power that can be used to operate lights or other electrical equipment onsite. Off-gas emissions from these units are equivalent to those from operating an automobile engine.

If properly used, SVE does not generally exacerbate existing subsurface conditions or make additional remediation efforts more difficult or less effective. If improperly vented, however, the negative pressure generated by the SVE can cause mounding of the water table that creates a hydraulic gradient capable of spreading LNAPL away from the vapor extraction well(s), possibly increasing the lateral extent of the contaminated area.

Most SVE systems have esthetic impacts that reduce their green characteristics. One undesirable aspect is that they tend to be noisy. This can be mitigated by methods such as surrounding the SVE unit with fences lined with commercially available sound-insulating blankets. Another undesirable aspect is that the systems have a visual impact. They typically are not large, with a footprint on the order of

10 m^2 or less and a height less than 3 m, but they have an "industrial" look about them. This could be mitigated with appropriate landscaping that could include components like fencing with small trees, shrubs, or even large potted plants. Typically, SVE systems are operated almost constantly for a period of approximately 2–3 years, so the esthetic impacts can be a substantial nuisance to nearby workers, passers-by, or residents. The following BMPs are examples of ways to promote a more sustainable SVE approach:

- Optimize extraction configuration and rates by manifolding several vapor points and periodically manipulating valves to minimize "dead zones" and reduce remediation timeframe, energy consumption, and noise.
- Utilize appropriate vapor treatment with GAC by vapor concentration (low concentrations – energy efficient; low concentrations result in infrequent change out; cat-ox for intermediate to high concentrations – appropriate concentrations improve oxidation efficiency; thermal oxidation for very high concentrations – can utilize contaminant vapors as a fuel source).

Multiphase extraction combines a pump system to remove LNAPL and contaminated groundwater along with SVE to remove soil vapors. The pump system has the effect of lowering the water table, creating a gradient for the LNAPL to migrate toward the extraction well while it removes contaminated water and LNAPL. This effect also exposes more of the subsurface to the soil air, enabling SVE to act on a larger volume of subsurface material.

If the water table is relatively shallow (less than about 8 m below land surface), removal of all three contaminant phases can be accomplished from the surface by applying SVE within the unsaturated zone along with suction to a downhole drop tube with its end located at or slightly below the oil–water interface. At the surface, the oil and water are separated. The oil can then be recycled (or used to power the internal combustion engine if appropriate), and the water gets treated and released back into the environment (Fig. 13.3).

Multiphase extraction can be energy intensive, but as with SVE, green and sustainable options exist. For example, the power to operate the system can sometimes be obtained from the petroleum hydrocarbon vapors and/or the LNAPL, considerably reducing or possibly eliminating the need for external power sources. Multiphase extraction generally is fast and effective, reducing overall energy use along with reducing long-term esthetic impacts from noise and infrastructure. It can be deployed quickly as all or part of an interim remedial action to mitigate urgent cleanup requirements and reduce the need for additional remedial actions that may be less sustainable. Even if it is not effective at a site, multiphase extraction generally does not exacerbate existing conditions or make additional remediation efforts more difficult or less effective. As with SVE, visual and noise impacts from the extraction system can represent an esthetic nuisance, but can be mitigated in a similar fashion with appropriate landscaping and noise dampening components. Although groundwater pumping (and treatment) is included in multiphase extraction for the purpose of exposing subsurface soil to unsaturated conditions, many of the pitfalls (e.g., energy-intensive systems, low dissolved

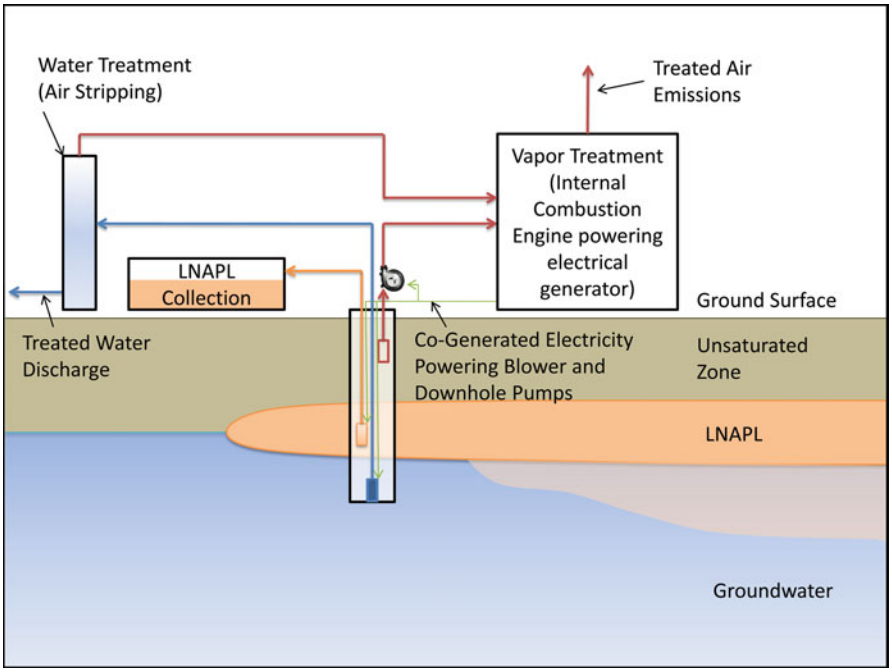

Fig. 13.3 Concept-level remedial strategy for green and sustainable multiphase NAPL recovery

phase contaminant removal, and high treatment cost) described earlier in this entry for pump and treat systems would also apply here. Therefore, caution is warranted when employing groundwater extraction and treatment for multiphase recovery or for product recovery. The following BMPs are offered to provide a sustainable approach to groundwater extraction and treatment with multiphase extraction systems:

- System design should consider modular treatment components that can be removed or added as needed.
- Variable frequency drive pumps can be used to optimize performance and reduce energy usage.
- Use of gravity flow where feasible to reduce the need for transfer pumps.
- System operation should have optimized extraction network to minimize pumping of clean water.
- Use of energy efficient equipment and green energy from alternative energy providers.
- Regenerate GAC onsite; recycle process residuals.

Monitored natural attenuation (MNA) is a highly sustainable remediation method that can be used for releases of petroleum hydrocarbon fuels, distillates, or contamination from other organic compounds. The method utilizes naturally occurring processes such as biodegradation to reduce contaminant mass and concentrations that are dissolved in groundwater, present as LNAPL, or sorbed to the soil. Biodegradation generally destroys most of the components of refined petroleum hydrocarbons, producing innocuous by-products such as carbon dioxide and water. As a result, MNA requires little to no external energy input and generates minimal waste.

Biodegradation of petroleum hydrocarbons readily occurs in many environments. Microbes have undergone natural selection for millennia, resulting in microbial communities that have evolved remarkable capabilities to utilize every bit of energy that can be extracted from oil constituents [12]. Biodegradation occurs even in extreme conditions. Fouling of fuel system components in aircraft due to microbial growth in kerosene-based jet fuel was recognized as early as 1956 [13]. For practical purposes, this means that in many (if not most) cases, degradation of refined petroleum hydrocarbons will proceed under natural conditions without external energy inputs.

MNA as the sole remediation method has certain limitations that must be addressed prior to and during implementation. First, it must be demonstrated that adverse impacts to human and ecological receptors are not occurring and are unlikely to occur in the future. Second, sufficient evidence for effective natural attenuation must be shown to exist at a given site. Such evidence can include among other things a demonstrably shrinking or stable dissolved plume, a reduction of dissolved concentrations in groundwater over time, and the use of stable isotopes to determine degradation rates. Third, long-term monitoring is required to ensure that conditions do not develop to change the efficacy of natural attenuation as a remedial action. MNA, in a practical sense, does not diverge from the activities associated with site investigation and monitoring. For this reason, the following BMPs utilized for site investigation are introduced with MNA activities [14]:

- Perform fewer field mobilizations through the use of flexible work plans and real-time field measurements as well as onsite mobile laboratory analyses to determine the next course of action during a single sampling event.
- Utilize small-scale direct push technology drilling equipment for invasive work or monitoring well installation to reduce fuel consumption, reduce drilling time, lower air emissions, lower water consumption, produce less noise, and minimize site clearing and physical impact.
- Use groundwater low-flow sampling equipment to minimize sampling purge volumes, reduce energy consumption, and reduced derived waste.
- Onsite treatment and recycling of MNA-derived wastes, including site clearing by onsite composting or landscaping and treatment/reuse of extracted groundwater for equipment decontamination.
- Collect the meteorological information (e.g., sun duration, wind direction and velocity) necessary to support the design and installation of off-grid alternative energy for auxiliary power for MNA monitoring.
- Use of solar or wind-powered telemetry systems to remotely transmit logging data directly to project offices.

In a variety of circumstances, MNA is used in conjunction with other methods that may not be sufficient to provide complete remediation of a site by themselves. There is a saying within the remediation industry that "90% of the remedial effort goes into cleaning up the last 10% of contamination." While this is not always true, monitored natural attenuation can provide a means in which the "last 10%" of the contamination does not have to be actively remediated because the final cleanup can be accomplished naturally and sustainably.

Enhanced bioremediation is designed to stimulate contaminant biodegradation by indigenous microbial populations [15]. Petroleum hydrocarbons degrade most rapidly under aerobic (i.e., oxygenated) conditions, although other electron acceptors may be utilized as reactants in biodegradation. Enhanced bioremediation of these compounds involves the injection of amendments to the contaminated subsurface to increase oxygen/electron acceptor concentration in the unsaturated and/or saturated zones. Enhanced bioremediation can supplement monitored natural attenuation in many cases to improve performance and reduce the time needed for complete remediation.

Several sustainable methods for promoting bioremediation by adding oxygen to the subsurface exist. One method used for soil remediation is known as bioventing. Bioventing works by injecting atmospheric air at low rates into the unsaturated subsurface zone to displace oxygen-depleted air, thereby stimulating the growth of aerobic microorganisms and improving biodegradation rates. Generally, the air is injected into the ground through well points screened in the contaminated unsaturated zone using a blower similar to that found on many SVE systems operated at low injection rates. Low air injection rates are important, particularly in populated areas, due to the potential for soil vapor migration into basements or other inhabited spaces. The low injection rates are advantageous for sustainable remediation, as external energy inputs are relatively low and could be supplied by renewable sources. A novel approach for air injection using mechanical windmill power (US Patent No. 6,109,358) represents a potential application of green bioventing technology.

Oxygen addition below the water table for bioremediation purposes can be accomplished through chemical or mechanical means. Proprietary slow-release oxygenating compounds for enhancing aerobic bioremediation are available in several forms, including powder (designed to be mixed with water), solids, and filter bags. Compounds in powder form generally are mixed with water and injected into the subsurface using direct push technology. Compounds in solid form or filter bags are typically suspended within the screened or open interval of monitoring-type wells.

Mechanical means of adding oxygen (for bioremediation or physical air stripping) below the water table usually takes the form of air sparging. Air sparging works by injecting air under pressure through one or more wells completely screened in the saturated zone for the purpose of providing oxygen to the groundwater. The air travels upward through the porous medium, along preferred flow paths that form a dendritic pattern (similar to the branches on a tree), until it reaches the unsaturated zone and becomes exposed to the soil.

Introduction of air in this manner will have two desirable outcomes if it is working well. First, the air will strip out volatile organic compounds from the water and saturated soil, transferring these compounds into the vapor phase where they can be removed through SVE (as needed). Second, the groundwater will pick up oxygen and become more aerobic, stimulating biodegradation. Air flow rate and injection pressure generally define whether physical air stripping (of VOCs) or in-place bioremediation will be the dominant process. If aerobic bioremediation is promoted through air introduction, the process is referred to as biosparging. The following sustainable BMPs can be applied to various types of bioremediation systems for treatment of petroleum hydrocarbons [15]:

- Maximize use of existing or new wells (to avoid resource overutilization) for addition of reagents that will act as electron acceptors in the biodegradation of petroleum hydrocarbons.
- Design and use of bioremediation recirculation cells allowing multiple passes of oxygenated groundwater through fewer wells.
- If oxygen additive is in liquid form, add to the subsurface via trickling gravity-feed system if high-pressure injections are unnecessary to assure proper distribution.
- If pressurized injection of air is required, evaluate the feasibility of pulsing rather than continuous injection to increase the efficiency of delivery.
- Employ modular, portable units that can be modified or incrementally reduced as needed.
- Employ photovoltaic panels or wind turbines to generate auxiliary power for trailer or for equipment, such as air blowers.

Physical air sparging (for the purposes of stripping and removing VOCs from the saturated zone) does not work at every site. It will not succeed if the dendritic patterns of the upwardly traveling sparge zone form with only a few branches, as contact between the air and the contaminants is essential. The efficacy of air sparging can be determined through relatively simple pilot tests, however.

Air sparging will require energy inputs to run the air pumps for a considerable period of time, depending on the size of the impacted area. The systems generally are run in conjunction with SVE, which is needed for vapor control, so 2–3 years of operation is not uncommon. If run with an SVE system, visual and noise esthetic impacts of air sparging are not substantially increased from an SVE system alone.

Phytoremediation is a remedial technology that uses plants to extract, destroy, and/or contain contaminants in environmental media. Petroleum hydrocarbons can be degraded within the plants or by plant by-products that are excreted into the soil, or volatilized into the atmosphere through transpiration.

To date, one of the most commonly implemented types of phytoremediation of petroleum hydrocarbons in shallow soils is rhizodegradation, or the destruction of contaminants by microbes whose activity is promoted by plant roots. Plants used for rhizodegradation include mulberry, hybrid poplars, grasses, cattails, and rice [16]. Phytodegradation, or destruction of the contaminants within the plant, and phytovolatilization of the contaminants can also be performed by a variety of trees, scrubs, and herbaceous plants.

Trees including poplars, cottonwoods, and willows can also be used to achieve hydraulic control to contain groundwater plumes. Often the same plants are used for both contaminant remediation and containment through hydraulic control. BMPs for phytoremediation include techniques for minimizing the impact of generic site operations, including energy conservation, waste minimization, and use of onsite resources.

The sustainability benefits of phytoremediation technologies include minimal site disturbance, leading to operational and esthetic benefits, and minimal energy inputs. Current technologies are limited in their applications by such factors as plants' limited contaminant tolerance, limited depth of influence of plant roots, and often lengthy remediation timeframes. Ongoing research and pilot studies are focused on developing new and improved methodologies for phytoremediation.

In situ chemical oxidation (also known as ISCO or Chem-Ox) is a method designed to oxidize contaminants using reactions that break apart chemical bonds, completely destroying the petroleum hydrocarbon compounds. The primary delivery method for the chemical oxidants is injecting them in liquid form into the aquifer using direct push methods or permanent injection wells. The method can work quite well at many sites, but like any remediation method, it is not universally applicable. Typical problems include daylighting (chemical oxidants flowing out onto the land surface or other inappropriate places), preferential oxidation of ambient organic carbon not related to contamination, desorbing of petroleum hydrocarbons from the soil into LNAPL form, and poor contact between the oxidant and the contaminants.

The sustainability advantages of ISCO is that it is fast acting, that it destroys contaminants rather than transferring them to another medium, and that it is injected using small equipment with a resultant small carbon footprint and minimal site disturbance. Direct push methods usually leave a boring with a diameter of 5 cm or less, which is filled in accordance with regulations and finished at the surface with a sod plug, asphalt patch, or other material such that little to no visual evidence of the hole exists. Remedial actions using ISCO are most applicable to small sites and generally are completed after two to six injection events, leaving no long-term esthetic impacts. Some or all of the following BMPs are examples of ways to promote a more sustainable ISCO approach:

- Minimize operational impact by constructing little to no long-term or permanent infrastructure.
- Use of extracted groundwater for onsite mixing of ISCO reagents.
- Use of direct push injections over injection wells if minimal injections are required.
- Reuse existing injection wells if multiple ISCO injection events are necessary.

Excavation and treatment or disposal is a remediation method not commonly associated with a green and sustainable approach. However, in many cases, it can be a direct and verifiable way of removing grossly contaminated material, which can then allow for more sustainable remedial methods to be implemented. Excavation can have many undesirable aspects during and after implementation, including things such as noise, dust, heavy equipment, large trucks, scarred landscapes, and so on. While these things may be necessary, they can be mitigated with proper planning and implementation of the remedial action. Some or all of the following BMPs are examples of ways that can help improve the green characteristics of excavation actions [17]:

- Devote time and resources to conducting low-impact site characterization (using direct push methods, field screening, etc.) both before and during the remedial action. Excavation footprints can sometimes be reduced if efforts are made to minimize the removal of clean material.
- Use appropriately sized equipment for excavation and hauling to minimize noise, dust, erosion, and fuel efficiency. Utilize energy efficient operating procedures such as minimizing idling and performing routine maintenance to improve fuel efficiency.
- Consider onsite treatment or using the closest treatment and disposal facility to minimize hauling. Purchase supplies that are produced locally and use local contractors when possible. Scout for local or onsite backfill material in the planning stages and during implementation.
- Salvage uncontaminated vegetation and organic debris for use as mulch or compost.
- Salvage uncontaminated objects and materials (such as steel, storage containers, etc.) for recycling, reuse, resale, or donation if possible.
- Revegetate and restore excavated areas as quickly as possible. Use native rather than imported plants. Judicious use of diverse plants and prior planning of final landforms can be utilized to create valuable habitat.

Chlorinated Hydrocarbons

Chlorinated aliphatic hydrocarbons, which include chlorinated VOCs, are important industrial chemicals frequently used as solvents for dry cleaning, degreasing, metal cleaning, paint stripping, and electronics. They tend to be highly volatile, toxic to humans, and denser than water. Common chlorinated solvents include chlorinated ethenes such as tetrachloroethylene (also known as perchloroethylene or PCE), trichloroethene (TCE), 1,2-dichloroethene (1,2-DCE), and vinyl chloride (VC); chlorinated ethanes such as 1,1,1-trichloroethane and 1,2-dichloroethane; and chlorinated methanes such as carbon tetrachloride, chloroform, and methylene chloride.

Like refined petroleum hydrocarbons, chlorinated VOCs can be found in the vapor phase, dissolved in groundwater, sorbed to soil, or as a NAPL. However, because chlorinated solvents are denser than water, NAPL will be present as DNAPL. Because of its higher density and other properties such as high viscosity, a DNAPL tends to be considerably harder to remove, destroy, or otherwise remediate than LNAPL.

Remediation methods for chlorinated VOCs include some that are the same as or similar to those discussed in the section on petroleum hydrocarbon remediation. These and other remediation methods are discussed below in the context of chlorinated hydrocarbons cleanup. However, the BMPs offered as sustainable practices discussed previously by technology for petroleum hydrocarbons have not been repeated in this section.

Soil vapor extraction (SVE) can be effective at removal of chlorinated VOCs present in the unsaturated zone of the subsurface that is sorbed to contaminated soil or present in the vapor phase. As described earlier, one or more SVE wells (screened in the unsaturated zone above the water table) are constructed and a vacuum system is installed with a manifold to the wells. The vacuum draws the air from the soil (which is contaminated with VOCs) out of the subsurface through a treatment system. The contaminated vapors are replaced by fresh air from vent wells or from other parts of the subsurface, allowing the VOCs to evaporate and drawn to the SVE for removal. Representative BMPs for SVE systems discussed in the previous section on petroleum hydrocarbons would be applicable for chlorinated VOCs with the exception of those related to vapor control technology.

Treatment of extracted soil vapor for chlorinated VOCs is more complicated than it is for fuel hydrocarbons. Chlorinated VOCs are not combustible, and when oxidized, one of the by-products is hydrochloric acid, which is highly corrosive, and can severely damage or ruin catalytic or thermal oxidizers. The vapors can be treated with GAC, but this is not green or sustainable and could result in considerable change-out expense if concentrations are high.

For higher concentrations, it is sometimes possible to recover the chlorinated solvents from the vapor stream for recycling. One method uses refrigerated condensation to recover VOCs from the vapor phase as liquid [18]. This type of technology is energy intensive, but can be considered a green remediation method based on the high efficiency of product recovery from the vapor stream.

Multiphase extraction is sometimes used to recover DNAPL, contaminated water, and soil vapor from the subsurface. DNAPL, however, is usually more viscous than LNAPL and is more prone to adhering to the soil matrix, making it difficult to draw the liquid into a well for product recovery. In most cases, the recoverable volume is small and the recovered solvent has been degraded to less than commercial quality, so recycling or reuse of the DNAPL generally would not be cost effective. As a result, most of the material would be disposed of off-site. As with the use of multiphase extraction for the recovery of petroleum hydrocarbons, caution is warranted when employing groundwater recovery and treatment. The BMPs offered for groundwater recovery with multiphase extraction of petroleum hydrocarbons would also apply to the recovery of chlorinated VOCs.

Monitored natural attenuation is a highly sustainable remediation method that can be very effective for the destruction of certain chlorinated hydrocarbons, particularly the chlorinated ethenes. The method exploits naturally occurring processes such as abiotic and biotic degradation to reduce contaminant mass and concentrations that are dissolved in groundwater, present as DNAPL, or sorbed to the soil. The process known as reductive dechlorination sequentially strips chlorine atoms off of each compound, starting with highly chlorinated compounds such as PCE and TCE through 1,2-DCE and VC, ultimately producing innocuous by-products such as carbon dioxide, chloride ions, and water. As with petroleum hydrocarbons, monitored natural attenuation of chlorinated ethenes requires little to no external energy input and generates minimal waste.

Biodegradation of chlorinated hydrocarbons through reductive dechlorination does not occur in all subsurface environments. Reductive dechlorination proceeds best under anaerobic (i.e., oxygen-depleted) conditions as opposed to the aerobic conditions that are most favorable for degradation of petroleum hydrocarbons. Additionally, reductive dechlorination requires both electron acceptors (i.e., the chlorinated ethenes) and electron donors (generally organic carbon that can come from anthropogenic sources such as landfill leachate or natural sources such as decaying vegetation) [19]. Third, microbial populations capable of facilitating reductive dechlorination are not always present, even if anaerobic conditions exist and adequate organic carbon is available. Therefore, even though MNA can be a green and sustainable remediation method, it is not always applicable or effective. In such cases, other methods need to be implemented.

Enhanced bioremediation, which is a method designed to stimulate contaminant biodegradation by indigenous microbial populations [15], can be a green and sustainable alternative similar to MNA. Enhanced bioremediation of chlorinated compounds involves the injection of amendments to the contaminated subsurface to promote bacterial processes that consume oxygen in the unsaturated and/or saturated zones, thereby initiating or enhancing reductive dechlorination. In cases where natural attenuation is actively occurring, enhanced bioremediation can supplement monitored natural attenuation to improve performance and reduce the time needed for complete remediation. If biodegradation is not occurring under natural conditions, enhanced bioremediation can initiate the process by creating conditions that are amenable to reductive dechlorination.

Enhanced biostimulation of chlorinated compounds typically uses fast-acting and/or slow-acting, food-grade carbon sources such as lactate, emulsified oils, molasses, or proprietary compounds developed specifically for this purpose. In many cases, injection of these carbon sources can be done with low energy input (such as controlled gravity feed), and they can be left in the subsurface because they are nontoxic and will eventually be completely consumed by the microbial populations. Enhanced bioremediation also destroys contaminants rather than transferring them to another medium, decreasing undesirable environmental impacts that can occur with some other remedial actions.

Like MNA, enhanced bioremediation can be used as a green and sustainable component of a larger scale remedial action involving media other than groundwater. Specific mixtures of carbon substrate can be used as needed to quickly induce anaerobic conditions or to react slowly and last longer. Other parameters, such as viscosity, density, emulsification, and so on, can be modified based on site conditions and remediation goals or requirements.

In some cases, the natural microbial populations are insufficient to degrade chlorinated hydrocarbons such as PCE and TCE to nontoxic endpoints, which can cause an undesirable buildup of 1,2-DCE and/or VC. Because VC is more toxic than TCE, this result is not acceptable from a regulatory or human health perspective. In such cases, bioaugmentation can be used, in which microbial consortia capable of complete degradation of chlorinated ethenes are grown in a laboratory, acclimated to site conditions, and injected into the subsurface with an appropriate carbon substrate. At present (2011), the only commercially available microbial consortia for this purpose are of the *Dehalococcoides* genus.

In situ chemical oxidation (also known as ISCO or Chem-Ox) is used to directly oxidize chlorinated hydrocarbons, typically by injection of oxidants in liquid form into the aquifer using direct push methods or permanent injection wells. The limitations to using ISCO for chlorinated hydrocarbons are similar to those discussed above for petroleum hydrocarbons and include daylighting, preferential oxidation of ambient organic carbon not related to contamination, and poor contact between the oxidant and the contaminants.

In situ chemical reduction can be used in place of or in conjunction with enhanced bioremediation. Its purpose is to chemically induce strongly reducing conditions capable of abiotically destroying chlorinated hydrocarbons. A typical reducing agent is zero valent iron (ZVI), which is a highly reactive metal that can be deployed as a powder in a permeable reactive barrier or injected into the subsurface in the form of a liquid suspension. The method is considered to be green and sustainable because it is long lasting, not harmful to the environment, and chemically destroys contaminants. The method also can have a residual effect of creating sustained reducing conditions in the subsurface that serve to enhance bioremediation, increasing its utility as a remedial tool.

Phytoremediation can be an effective technology for remediating chlorinated hydrocarbons in soil or groundwater. Plants used for phytodegradation of PCE, TCE, and DCE include poplars and cottonwoods. As discussed above, these trees can also be used to achieve hydraulic control to contain groundwater plumes. Rhizodegradation and phytovolatilization of chlorinated hydrocarbons have also been observed [16].

PCBs, Pesticides, and High-Molecular-Weight PAHs

PCBs, pesticides, and high-molecular weight PAHs are three of the most common classes of persistent organic pollutants (POPs), toxic chemicals that resist chemical and/or biological degradation and therefore persist in the environment. Although many of these compounds are now banned or highly regulated in the United States, their environmental persistence necessitates ongoing remediation efforts of historically contaminated sites.

Many POPs are polychlorinated or polycyclic aromatic compounds. The incorporation of multiple halogen atoms (chlorine, bromine, etc.) or multiple aromatic rings into organic compounds tends to make the compounds more difficult to degrade both chemically and biologically. Because POPs are difficult to degrade under environmental conditions, containment or ex situ treatments are typically required.

POPs are typically characterized by low solubility and, therefore, are most often found contaminating solid materials including soils and sediments. Incineration is often the presumed remedy for solid wastes contaminated with POPs, which are destroyed at high temperatures. Benefits of incineration include near-complete destruction of a wide variety of POPs and the ability to treat large volumes of contaminated material on relatively short timeframes. However, incineration can create toxic by-products (e.g., dioxins and furans) or volatilize heavy metals and, therefore, must be carefully engineered to prevent adverse health effects. Incineration also requires large quantities of energy to excavate the contaminated soil and to reach temperatures that often exceed 1,200°C.

Specialized technologies developed as alternatives to incineration include a variety of techniques for ex situ chemical degradation of POPs [20]. However, these technologies typically require high temperatures and caustic solutions or solvents, due to the innate stability of the chemicals. Onsite reuse of treated soil for backfilling can make these technologies somewhat greener. Vitrification can also be used to destroy POPs at high temperature, while containing any residual contaminants in the resulting glass, though this technology is not considered sustainable, due to excessive energy consumption. The large environmental impacts of most technologies for POP treatment highlight both the difficulty of treating these classes of contaminants and the need for additional innovation in this area of remediation.

In response to the need for innovation, various specialized technologies have been developed for bioremediation of PCBs and specific pesticides, typically via dechlorination. These technologies use specialized organic amendments, nutrients, or proteins to stimulate microbial activity that drives dechlorination of the POPs. Bioremediation is useful only for wastes with low POP concentrations, due to the much slower rate of degradation relative to more energy-intensive processes. Because of the specific nature of microbial processes and the difficulty of either dechlorinating or breaking the polyaromatic structure of POPs, technologies are often specific to the compounds for which they were developed and require testing for applicability to other POPs. These technologies are significantly more sustainable than incineration and chemical degradation processes, due to significantly lower energy requirements and waste production, and because some of the technologies can be utilized in situ at sites where conditions allow.

Another emerging technology uses mechanical agitation of POP-contaminated waste with a chemical reactant in a ball mill or similar machine to drive dechlorination, such as for PCBs. Although this technology requires excavation of the contaminated material, it has relatively low energy requirements, because mechanical energy is substituted for thermal energy in promoting degradation of the POPs. The sustainability of variations on this method is further affected by the nature of the chemical reactant used and waste products created.

Ongoing research into application of phytoremediation to POPs has revealed plants capable of phytoextraction and rhizodegradation of PCBs, pesticides, and PAHs. Phytoremediation is only possible where POP concentrations are low enough so that they are not toxic to the plants, and it is particularly promising for treatment of low-level pesticide contamination of surface soils. Where feasible, this technology offers a highly green and sustainable alternative to the high energy intensity and site disturbance required by most POP remediation technologies.

Explosives and Energetics

Explosive and energetic compounds that are in widespread use in military and industrial applications are common contaminants of concern, on account of their relative solubility and persistence in the environment. Common examples of these contaminants include perchlorate, 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX).

As with POPs, costly and energy-intensive remedial technologies such as incineration are often used to treat energetic compounds in soil. However, these compounds are less recalcitrant than POPs and can be degraded biologically under appropriate conditions.

Although microbial degradation of these compounds is typically slow, enhanced bioremediation of perchlorate, TNT, RMX, and HMX can be achieved by addition of a variety of carbon and/or nutrient amendments to groundwater, either in situ or ex situ. Investigations have shown that bacteria capable of degrading these energetic compounds, under both oxic and anoxic conditions, are widespread in the environment, but specific bacteria can also be added to promote degradation [21, 22]. Ex situ technologies that have been proven effective include a variety of bioreactors and composting operations. Organic energetic compounds (TNT, RMX, HMX) can be degraded to other organic by-products, or mineralized all the way to carbon dioxide. Perchlorate is reduced to chloride and oxygen gas.

Phytoremediation technologies for energetic compounds include rhizodegradation and phytodegradation of TNT by a variety of plants including hybrid poplars. Studies have also provided evidence for phytoremediation of perchlorate, RDX, and HMX. Constructed wetlands have also been found to be effective for remediating a variety of energetic compounds, through a combination of bioremediation and phytoremediation.

The BMPs and sustainability benefits of microbial degradation and phytoremediation of explosive and energetic compounds are similar to those discussed above for other classes of organic contaminants.

Metals

The diversity of metals and sources of metal contamination in the environment necessitates diverse contaminant- and site-specific remedial approaches. Common metal contaminants identified for remediation include arsenic, chromium, lead, and mercury. Modern and historical sources of metal contamination include mining and smelting operations (including acid mine drainage), steel production, landfills, firing ranges, battery recycling and disposal operations, metal plating facilities, wood treatment facilities, coal combustion by-products (e.g., coal ash), dyes and paints, lead arsenical pesticides, and leaded fuels.

Unlike organic contaminants, metals cannot be biologically or chemically degraded to innocuous by-products. Therefore, remediation of metals typically relies either on removal or on sequestration in solids, which limits mobility and potential exposure. Various methods exist for increasing the sustainability of technologies for both removal and sequestration.

In situ stabilization and geochemical fixation of metals uses chemical or biological processes to transform metals in soils or aquifers from soluble and/or toxic to insoluble and/or nontoxic forms. The chemistry of stabilization is dependent on the specific metal(s) of concern. Different metals have distinct properties that affect their mobility and bioavailability under different environmental conditions, and remedial technologies must be designed to address the specific site conditions relative to the properties of the metals of concern.

Redox state can be an important determinant of solubility and toxicity for redox-active metals, such as chromium, arsenic, iron, and manganese. For example, hexavalent (oxidized) chromium is much more soluble and toxic than trivalent (reduced) chromium, whereas iron and manganese are typically less soluble and toxic under oxidized conditions. Reducing conditions can also lead to sulfide production, and sequester metals through the formation of metal sulfide minerals. Therefore, addition of chemicals that stimulate reduction or oxygenation of the contaminated soils or aquifers can be designed to cause the metal(s) of concern to precipitate and become less bioavailable.

Various properties of soil and water geochemistry also affect metal behavior. Many metals are more soluble and bioavailable under acidic (low pH) conditions, and carbonate, in the form of lime or limestone, can be added to increase pH. The presence of other geochemical species (e.g., phosphates or organic matter) can cause metals such as lead, zinc, copper, cadmium, nickel, and uranium to be retained in the solid phase. Phosphate causes metals to precipitate, whereas addition of organic matter tends to increase metal sorption to soils. Addition of solids that tend to adsorb metals, such as iron oxyhydroxides, can also effectively sequester metals.

Implementation of in situ stabilization typically requires that an aqueous or solid chemical reactant be injected into the contaminated aquifer or mixed with impacted soils. Application of this technology in aquifers therefore requires the installation of injection wells, while remediation of soil requires equipment sufficient to mix to the depth of desired treatment. The BMPs for in situ stabilization include some discussed above for enhanced biodegradation and ISCO, technologies which require similar injection of reactants, and for excavation, which requires site disturbance similar to soil mixing.

As an in situ technology, stabilization offers relatively low energy requirements, as compared to extractive technologies. The environmental impacts of the stabilization as applied to groundwater are dependent on the frequency of injection events and level of automation of the system, which can minimize the number trips to the site for operations and maintenance of the injection system. Metals stabilization in soils has minimal energy requirements after the initial mixing. Use of recycled materials, such as composts, wood or coal fly ash, or red mud from the alumina industry, as treatment additives can further increase the overall sustainability of the remedial effort.

Limitations of this technology include the difficulty of achieving thorough mixing with the contaminated medium, possible limitations to future site use, and the necessity of treatability studies to demonstrate that metal solubilities will meet criteria after treatment. However, in sites where the contaminant and physical characteristics are well suited for in situ stabilization, it can be a highly effective and environmentally sustainable remedial option.

Phytoremediation of metals uses plants to extract and/or contain contaminants in environmental media. Whereas remediation of organic compounds by plants often focuses on contaminant degradation, phytoremediation of metals focuses on accumulating the metals within plant tissues, volatilizing them through the plants, stabilizing them in soils, or otherwise limiting metal mobility and bioavailability.

A wide variety of metals can be removed from solid materials or water through phytoextraction, which results in accumulation of metals in plant tissues. Plants used for phytoextraction are often chosen for their ability to tolerate and/or "hyperaccumulate" a specific metal of concern. For example, Chinese brake ferns are used to remove arsenic from shallow soils (Fig. 13.4). Because the metals are not degraded, plants typically must be harvested and disposed of as waste following metal uptake. Plants are also used for phytovolatilization of certain metals (e.g., selenium, mercury, and arsenic) through transpiration.

Plant-based containment technologies for metals include phytostabilization within the soil, achieved through chemical or biological processes that decrease metal solubility, and hydraulic control, which uses water uptake by trees to limit the mobility of dissolved metals.

Monitored natural attenuation, discussed in detail above in reference to organic contaminants, is also applicable to dissolved metals in aquifers, in cases where the natural groundwater chemistry results in immobilization of the contaminants. For example, hexavalent chromium may be naturally oxidized in aquifers with sufficient dissolved oxygen. Precipitation of metals at naturally high pH or adsorption of metals to solid materials present in the aquifer (e.g., minerals and organic matter) can also result in the attainment of remedial goals for dissolved metals.

As with remediation of organic contaminants, monitored natural attenuation of metals requires collection of evidence to indicate that natural attenuation is occurring and that no adverse impacts to humans or the environment are present. Where

Fig. 13.4 Use of Chinese brake ferns for remediation of arsenic in shallow soils

these conditions are met, this remedial strategy is a highly sustainable method for achieving remedial goals with minimal energy inputs.

Excavation is not typically considered a green or sustainable technology, due to its high energy demands and the need to contain excavated waste within a disposal facility. However, as discussed for petroleum hydrocarbons above, certain methods can be incorporated into excavation projects to improve their sustainability. For metals, one additional option is excavation followed by metal recycling, which can be an environmentally responsible remedial option for waste with high metals concentrations, such as slag from metal smelting operations and munitions from firing ranges. The economic feasibility of recycling is often dependent on the concentration of metals, the quantity of contaminated material, and proximity of recycling facilities.

Future Directions

This entry has provided practical concepts, value engineering principles, and BMPs for the current state of remedial technologies for the typical classes of environmental contaminants observed in the subsurface. These concepts and practices represent the qualitative principles currently utilized to improve or increase the sustainability of subsurface remediation.

Although these BMPs are helpful, is it not possible based on BMP application to evaluate their ultimate benefit to improving sustainability. In the near future, the environmental industry will move away from the general practice of subjectively reviewing and applying BMPs from a master list to the practice of applying project-specific, robust, quantitative analyses of sustainability benefit for a project. Green and sustainable remediation organizations like SURF have already created a compilation of comprehensive metrics (Metrics Toolbox) that can be used to evaluate, track, and forecast a remedy's ability to achieve certain outcomes in relation to sustainability goals [23]. In the future, metrics like those in SURF's Metrics Toolbox will be supplemented with a wider suite of metrics to perform analyses of sustainability key elements in remedial program decision making.

Although it is envisioned that greener remedies have a distinct place within regulatory programs, such as the US Environmental Protection Agency (EPA) Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) or Resource Conservation and Recovery Act (RCRA), program-specific regulatory criteria do not currently address the social and economic considerations of sustainability. The US EPA is presently attempting to clarify the role of green remediation within the CERCLA and RCRA programs; however, its ability to include the social and economic benefits in the remedy selection process may exceed the authority of these programs. The task of defining what is meant by the term "sustainable" in terms of remedial measures remains an ongoing effort [24] and will continue to evolve in coming decades through collaboration between researchers, regulators, and environmental remediation professionals.

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