

there has to be very careful planning and precise guidance (ideally using geographical positioning system (GPS)), accompanied by suitable supervision and monitoring, even although this may necessitate leaving significant areas untreated. Care must also be taken to ensure that that no leakage occurs from any storage stack in the woods and that all fertilizer bags are properly disposed of.

*See also:* **Health and Protection:** Biochemical and Physiological Aspects. **Soil Biology and Tree Growth:** Soil and its Relationship to Forest Productivity and Health. **Soil Development and Properties:** Nutrient Cycling. **Tree Physiology:** A Whole Tree Perspective; Mycorrhizae; Nutritional Physiology of Trees.

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## Soil Contamination and Amelioration

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### Introduction

Human activities have shaped and altered essentially all ecosystems on earth. Forest ecosystems are no exception to this and the effects of these activities can be observed throughout the forests of the world. While many of the activities leading to soil contamination have been necessary and positive (e.g., development of a sustainable agricultural system capable of feeding a growing world population), negative side effects are also widespread. Impacts range from clearly visible effects like unsustainable and large-scale logging and surface mining with all their associated problems of erosion, loss in soil fertility and productivity, and acid mine drainage, to less obvious effects including diffuse deposition of atmospheric pollutants or acid rain due to burning of fossil fuels. Many of these negative effects are reversible, and in particular, forested areas have the ability to buffer environmental impacts. Many physiological processes in forest systems such as evapotranspiration, photosynthesis, solute uptake, and effects of plant root exudates on contaminant degradation can be used to mitigate negative impacts and/or remediate existing contamination. This article focuses on forest soil contamination with regard to inorganic and organic contaminants and potential remedial strategies.

### Soil Contamination

Contamination is generally grouped by origin as resulting from point (direct) or nonpoint (diffuse) sources. Point sources of soil contamination include spills and leaks, local emissions, and land applications, while atmospheric deposition and agricultural runoff are the main nonpoint sources of contamination. Point sources such as industrial outfall pipes or chemical spills are discrete, localized, and can be readily assessed and delineated, while nonpoint sources are more difficult to assess due to the large areas that can be affected and multiple sources that may contribute to the problem. Inorganic contaminants like trace metals and in some cases radionuclides (e.g., Chernobyl accident in 1986) can originate as both point sources and nonpoint sources. Organic contamination generally results from point sources, although elevated levels of some recalcitrant

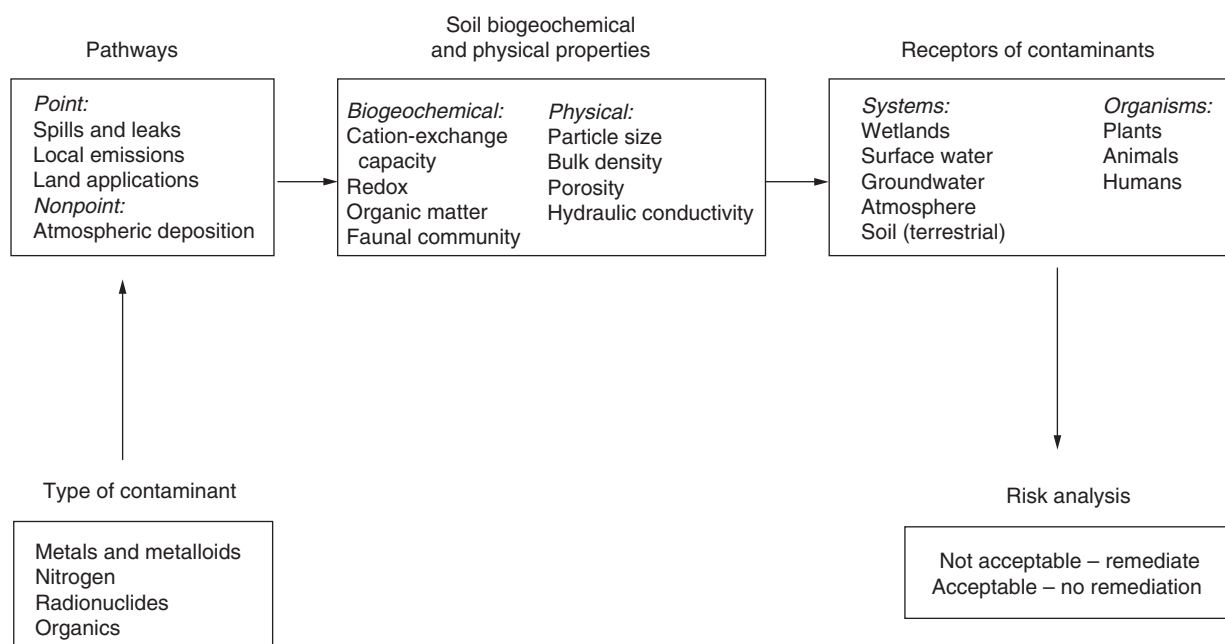
semivolatile organic compounds (SVOCs) including polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) are becoming more ubiquitous and are the result of atmospheric pollution and subsequent deposition.

Once contaminants enter the soil environment, they undergo a multitude of processes that affect their fate and subsurface mobility, which in turn alters their bioavailability and risk to potential human and ecological receptors. These processes include sorption and desorption (organic and inorganic contaminants), precipitation (inorganic contaminants) and dissolution (organic and inorganic contaminants), complexation (organic and inorganic contaminants), leaching (organic and inorganic contaminants), volatilization (mainly organic, but some inorganic contaminants), and degradation (organic contaminants). Biogeochemical and physical soil properties affecting the fate and transport of contaminants include pH, oxidation–reduction potential (redox conditions), organic matter (OM) content, and the amount of clay and sesquioxides present in soils. The amounts of OM and clays affect the cation-exchange capacity (CEC) of a soil, a variable that indicates the soil's ability to retain positively charged ions, some of which are contaminants such as many trace metals. Trace metals also form strong complexes with organic matter, which may lead to both immobilization due to complexation with insoluble organic matter in surface soils, as well as mobilization due to complexation with dissolved organic carbon (DOC).

Furthermore, nonionic organic contaminants have a strong affinity for soil organic matter, which in general renders them fairly immobile. Redox conditions affect the speciation, and therefore the mobility, of inorganic contaminants, as well as the geochemical environment for the potential degradation of organic contaminants. For example, many chlorinated organic compounds are completely degraded under reducing conditions, while most volatile organic compounds and explosives degrade more readily under aerobic conditions. For trace metals, pH is the master variable. With the exceptions of arsenic (As), molybdenum (Mo), selenium (Se), vanadium (V), and chromium (Cr), metals are more mobile under acidic soil conditions.

While this article focuses on soil contamination, it should be noted that soil contamination frequently leads to groundwater contamination. About 75% of all contaminated sites regulated under Federal programs in the USA involve groundwater contamination. Once in groundwater, contaminants that may have originated from a small localized area, such as a spill, may spread over a much larger area due to plume migration along a groundwater flow path or as separate-phase migration of a dense nonaqueous phase liquid (DNAPL) such as trichloroethylene (TCE). **Figure 1** conceptualizes soil contamination and remediation.

**Table 1** summarizes the main classes of contaminants commonly found in soils and some of their important characteristics.



**Figure 1** Conceptual model of soil contamination and remediation. Reproduced with permission from Adriano DC, Bollag JM, Frankenberger WT Jr., and Sims RC (1999) *Bioremediation of Contaminated Soils*. Madison, WI: American Society of Agronomy.

**Table 1** Contaminant classes and compounds commonly found in soils

<i>Contaminant class</i>	<i>Compound class</i>	<i>Example compounds</i>	<i>Environmental characteristics</i>	<i>Potential sources</i>	<i>Remedial options</i>
Inorganic contaminants	Salts	NaCl, MgCl <sub>2</sub>	High solubility/mobility; some plant toxicity; minimal human health risks	Ocean spray, roadside salts	Leaching; application of CaSO <sub>4</sub> · 2H <sub>2</sub> O
	Trace metal(loid)s	Hg, As, Pb, Cr, Cd	Mobility depending on pH and redox conditions; plant toxicity; significant human health risks	Metallurgy, paints, parent rock	Excavation; soil washing; liming; stabilization; phytoremediation
	Radionuclides	<sup>137</sup> Cs, <sup>238</sup> U, <sup>90</sup> Sr	Geochemical behavior similar to certain plant nutrients (K, Ca); human exposure to radioactivity	Nuclear reactors and weapons	Similar to trace metals; mainly stabilization and excavation
Organic contaminants	Polycyclic aromatic hydrocarbons (PAH)	Naphthalene, phenanthrene, benzo(a)pyrene	Varying solubilities and mobility; significant human health risks	Coal tars, asphalt, fossil fuels	Solidification; composting; chemical extraction
	Nitroaromatics	TNT, RDX, HMX; pesticides	Human health risks; risk of initiation	Military explosives; pesticides	Biodegradation; soil washing; composting; phytoremediation
	Phenols	Pentachlorophenol, phenol, nitrophenol	Bioavailability depending on soil pH and OM content; human health risk	Wood preservatives, solvents; refineries	Biodegradation; solidification; soil flushing; land farming
	Halogenated aromatics	PCBs, pesticides, dioxins	Low solubility; limited mobility; toxic to humans	Pesticides, waste incineration	Solidification; excavation; dehalogenation
	Halogenated aliphatics	TCE, PCE, CCl <sub>4</sub>	Present as NAPL and dissolved phase; high toxicity	Solvents, plastics	Bioremediation; chemical oxidation
	Petroleum hydrocarbons	Petroleum products (crude and refined oil)	Complex mixture of compounds; significant solubility/toxicity	Cars, refineries, industry	Land farming; thermal desorption, biodegradation

HMX, cyclotetramethylenetetranitramine; NAPL, nonaqueous phase liquid; PCBs, polychlorinated biphenyls; PCE, tetrachloroethylene; RDX, cyclotetramethylenetetranitramine; TCE, trichloroethylene; TNT, trinitrotoluene.

## Salt-Affected Soils

In general, two types of salt-affected soils are distinguished: saline soils that have high electrical conductivity ( $>4 \text{ dS m}^{-1}$ ) but low sodium content, and sodic soils that have high electrical conductivity ( $>4 \text{ dS m}^{-1}$ ) and high sodium content. Salinity affects soils in three ways:

1. Excess sodium (Na) can lead to the destruction of soil structure through its ability to disperse clays. This leads to decreased aeration and consequently, restricts root growth.
2. Excess salts in soil solution affect the osmotic potential of soil water. The increase in soil water potential (i.e., more negative) makes water harder

to extract and less available to plant roots, which can lead to water stress in plants.

3. The uptake of excess chloride can lead to direct damage to plant leaves. Roots of non salt tolerant plants have no mechanism to exclude the very mobile and soluble chloride ion. Once absorbed, chloride is quickly transported with the transpirational stream through the stem to the leaves, where it accumulates at the outer fringes of the leaves. This excess chloride leads to chlorosis of the leaves decreasing their capacity to conduct photosynthesis.

Four main sources of salinity exist. Three of these are anthropogenic sources with the fourth one being a natural source. A natural source of salts that may

affect the species composition of forests originates from ocean sprays. Due to strong winds in the vicinity of large bodies of water, small droplets of salt water can be carried inland from oceans and seas and deposited onto forests along coastlines. While this may not be considered 'contamination,' it can clearly affect soils and tree species composition within these forests.

The three main anthropogenic sources of salinity to forests originate from the use of roadside deicing salts in cold climates, the land application of wastewater and biosolids and accidental spills of brines from the production of oil. Deicing salts can be carried into forests along roadsides through splashes and runoff of melted snow. In general, these transport processes are limited to within a few meters of a road, although salt effects have been measured as far away as 200 m into a forest stand. While small areas of forested lands can be affected by deicing salts, the soil chemical and plant physiological effects are more visible in urban areas where other factors contribute to tree stress and mortality such as air pollution, confined rooting space, and physical tree damage from parked cars.

During the last two decades the practice of land application of wastewater and biosolids has become more common as a means to manage the large quantities of treated wastewater and sludges generated in the industrialized world. While this practice has great potential for the beneficial reuse of 'waste' by providing a cost-effective source of nutrients, organic matter, and irrigation water, it may also lead to increased soil salinity.

The production of oil produces large quantities of brine (mainly connate brines) that pose a serious problem for treatment and disposal. Occasionally, brine spills and slow seepage through unlined impoundments can contaminate forests. Unlike damage from deicing salts, concentrated brines can kill entire forest stands.

Amelioration of saline and sodic soils is generally accomplished by leaching soils with low-electrolyte water and by applying gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) or  $\text{CaCl}_2$  to the soil. In humid climates where infiltration exceeds evapotranspiration, it may be sufficient to stop the salt addition and allow for natural leaching of excess salts.

### Trace Metals and Metalloids

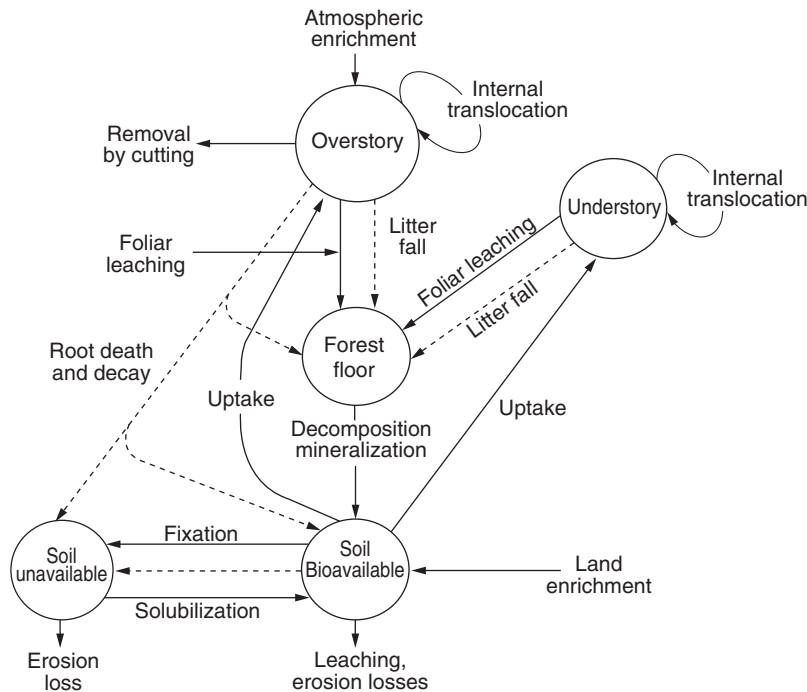
Contamination of agricultural and forest soils with trace metals and metalloids has been a major concern for many decades. While metals in contaminated agricultural soils can enter the food chain and increase human exposure and risk (both carcinogenic and noncarcinogenic risks), metals in forests are

mainly a potential problem for groundwater resources, ecological risk, and forest health.

There are both natural and anthropogenic sources contributing to elevated soil concentrations of trace metals. Natural sources are generally limited to weathering of parent rocks that contain appreciable concentrations of metals, and volcanic inputs. Anthropogenic sources are widespread and include fertilizers, pesticides, wastewater and biosolids, coal combustion residues, and atmospheric deposition. The main source of trace metals in natural forest ecosystems is atmospheric deposition. In intensively managed forest plantations, application of biosolids and the use of pesticides and fertilizers can also contribute trace metals to the system. Wood treatment facilities that used chromated copper arsenate (CCA) as a wood treatment product resulted in sites contaminated with arsenic and chromium as well as a variety of other (organic) constituents. Between 50% and 70% of contaminated sites regulated under Federal cleanup programs in the USA contain metals as major contaminants. Many of these sites, especially sites managed by the US Department of Defense and the US Department of Energy, contain large tracts of forested lands.

In general, forest soils are more acidic than agricultural soils, which are regularly limed and therefore, forest soils tend to have greater availability of trace metals. Among forest types, coniferous forests exhibit a lower soil pH than deciduous hardwood forests due to slower forest floor decomposition, greater concentrations of organic acids from decomposing litter, and lower contents of base cations. Furthermore, forest soils contain numerous old root channels that provide pathways for preferential water flow. Preferential flow bypasses the soil matrix, which may lead to increased mobility of contaminants to deeper depths. In addition, decomposing organic matter may yield appreciable concentrations of DOC to the soil solution, which can increase metal mobility due to metal-DOC complexes that move readily with percolation water. Therefore, potential subsurface metal mobility is higher in forested settings in comparison to agricultural systems. However, phytostabilization of metals in the root zone through root sorption (absorption and adsorption) may provide a mechanism for immobilization of otherwise mobile metal contaminants. **Figure 2** illustrates a generalized biogeochemical cycle for trace elements in forest ecosystems.

The most commonly found trace metals at contaminated sites include lead (Pb), cadmium (Cd), zinc (Zn), nickel (Ni), mercury (Hg), chromium (Cr), and arsenic (As). Forests (especially at higher elevations) sometimes act as 'filters' for airborne



**Figure 2** Generalized biogeochemical cycle for trace elements in forest ecosystems. Reproduced with permission from Adriano DC (2001) *Trace Elements in Terrestrial Environments*, 2nd edn. New York: Springer-Verlag.

metal contamination, rendering even remote forest stands into metal sinks. Lead is a widespread metal contaminant in forests due to airborne deposition and the use of forested areas as shooting ranges. In some alpine areas, for example, Pb concentrations of up to  $700 \text{ mg kg}^{-1}$  have been measured in forest soils far away from potential industrial point sources. Excess metal deposition in conjunction with acidic atmospheric deposition (i.e., 'acid rain') may lead to a decrease in forest health due to phytotoxic effects of metals, as well as create a potential groundwater problem. In Europe, the concept of calculating critical loads for deposition of metals to forest systems is commonly applied. Metal depositions below a critical load are considered harmless to the environment.

Unlike organic contaminants, metals do not degrade and have to be either immobilized or extracted. Potential technologies for remediating metals-contaminated soils are fairly limited and include *ex situ* technologies (e.g., excavation and disposal, incineration, soil washing, and thermal desorption) and *in situ* technologies (e.g., liming, solidification/stabilization, capping in place, electrokinetics, natural attenuation, and phytoremediation). Due to limited access in established forest stands, relatively low concentrations of metal contaminants, and the desire to apply less invasive approaches over larger areas, *in situ* approaches such as liming and

phytoremediation are the preferred options for metal-contaminated forest soils.

### Acid Deposition

Acid deposition, commonly referred to as 'acid rain,' has long been suspected as a contributing factor to the decline in forest vigor and the observed dieback of forests in central Europe, Scandinavia, and North America (USA and Canada). While agricultural soils and most soils under deciduous forests have sufficient capacity to buffer acidic atmospheric inputs, some coniferous forests, especially on shallow, nutrient-poor soils derived from 'acidic' parent rocks like granite, are susceptible to acid rain. Acid rain is a consequence of the combustion of fossil fuels, which leads to the emission of sulfur and nitrogen compounds (i.e.,  $\text{SO}_x$  and  $\text{NO}_x$ ) that form strong acids in contact with water (i.e.,  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$ ). While the emission of sulfur compounds has decreased dramatically over the past 30 years, the emission of nitrogen compounds has continued at a very high level. These acids accelerate the natural process of soil acidification under forest stands and may contribute as much as 40% to soil acidification. This process leads to excessive leaching of base cations (especially Ca and Mg), decreases a soil's acid neutralizing capacity, increases the mobility of potentially toxic trace metals, and releases excess

aluminum into soil solution. Elevated concentrations of aluminum are toxic to tree roots and cause an antagonistic effect on ion uptake (especially with Mg). In combination with an increasing ratio of aboveground to belowground biomass, such as observed in nitrogen-saturated forest systems of central Europe, this increases drought stress and the susceptibility to windfall and disease. The combined effects of these and other stresses such as shallow, naturally poor or acidic soils, drought conditions, management practices like removal of forest litter that lead to decreased fertility, other air pollutants, and animal damage are believed to be responsible for forest diebacks and the decline in tree vigor.

Strategies for mitigating these effects include continued efforts to limit the emissions of N- and S-containing compounds, improvements in forest management practices, and liming and fertilization of susceptible sites.

## Organic Contaminants

With the exception of some pesticides originating from agricultural runoff and carbonaceous particles originating from industrial coal processing, most organic contaminants are generated from point sources. However, recently there has been mounting evidence that many PAHs and PCBs can be found in areas far away from local point sources, indicating long-range transport as a significant source of forest soil contamination by organic compounds. Due to much higher concentrations of organic carbon in forest soils as compared to agricultural soils, organic contaminants originating from diffuse sources are usually found at much higher concentrations in forest soils. As previously mentioned, organic contaminants have a strong affinity for soil organic carbon.

Typical sources of organic contaminants include the combustion of organic materials such as coal, oil, or wood (PAHs), smelting processes (PCBs), pesticide production and application for agricultural, industrial, and residential pest control (dioxins, dichlorodiphenyltrichloroethane (DDT), chlorinated pesticides), accidental releases from oil producing facilities and during transportation of oil in tankers and (leaky) pipelines (petroleum hydrocarbons), wood treatment facilities (creosotes, pentachlorophenol (PCP)), production and use of explosives (cyclotetramethylenetrinitramine (RDX), trinitrotoluene (TNT), cyclotetramethylenetetranitramine (HMX)), and production and use of industrial solvents for dry-cleaning, degreasing, and plastics manufacturing (trichloroethylene (TCE), tetrachloroethylene (PCE), vinyl chloride).

Volatile organic compounds (VOCs), primarily in the form of BTEX (benzene, toluene, ethylbenzene,

and xylene) compounds, are generally found in localized areas. Over two-thirds of sites regulated under Federal programs in the USA contain VOCs, which are also primary contaminants in many underground storage tank sites. Unless spills occur in or near forested sites, forest stands are rarely affected by VOCs. Nonhalogenated VOCs readily degrade under a variety of conditions, and are therefore prime candidates for bioremediation and/or natural attenuation. Halogenated VOCs (such as TCE, PCE, CCl<sub>4</sub>) are also completely biodegradable, but require anaerobic conditions for the reductive dechlorination process to proceed.

Semivolatile organic carbons (SVOCs) include a large number of organic contaminants ranging from PAHs (such as naphthalene and pyrene), to PCBs (such as aroclors) to chlorobenzenes and chlorophenols, to pesticides and dioxins. There is a wide array of technologies available for the remediation of SVOCs, and with regard to contaminated forest soils, *in situ* biological approaches like bioremediation and phytoremediation appear to be the most applicable technologies.

Since the military uses large areas of land (quite often heavily forested as well) as military bases and for training purposes, these sites are greatly impacted by a wide variety of contaminants ranging from metals to solvents and explosives (including unexploded ordinance). More recently, perchlorate (ClO<sub>4</sub><sup>-</sup>) has been identified as a major contaminant on virtually every military site where it has been included as a target analyte. Consequently, inorganic and organic contaminants in soils (and groundwater) are frequently commingled at these sites. This poses a significant challenge for remediation efforts since many cleanup technologies are specific to contaminants or groups of contaminants. For soil (and groundwater) remediation, the application of bioremediation (especially by creating reducing conditions) may be a feasible and cost-effective approach to simultaneously treat a variety of contaminants. However, highly contaminated (and toxic) areas containing nitroaromatics (i.e., explosives) and/or other organic contaminants may continue to require excavation and incineration.

## Phytoremediation

A variety of *in situ* and *ex situ* remedial technologies are available to treat soils affected by the many contaminants described above. Environmental managers quite often prefer less invasive and more cost-effective approaches than excavation and disposal or incineration. Over the last two decades, phytoremediation has emerged as a feasible alternative to more

active and costly technologies, especially for large areas with relatively low levels of contamination.

Phytoremediation – more recently, the term ‘phytotechnologies’ has been introduced since this remedial approach covers a number of technologies and applications – is the use of plants to remediate or contain contaminants in soil, groundwater, surface water, and sediments. The technology is rapidly gaining acceptance within regulatory agencies as well as the public. In general, six main mechanisms are involved in the application of phytotechnologies:

1. Phytostabilization (inorganic and organic contaminants) is the use of plants to immobilize contaminants in soil, sediments, and groundwater through the absorption and accumulation into the roots, the adsorption onto the roots, or the precipitation or immobilization within the root zone.
2. Rhizodegradation (organic contaminants) refers to the breakdown of contaminants in soil through the bioactivity that exists in the rhizosphere (an area about 1 mm away from a root surface).
3. Phytoaccumulation (inorganic contaminants) is the process of metal- or salt-accumulating plants to translocate and concentrate inorganic contaminants into the roots and aboveground biomass.
4. Phytodegradation (organic contaminants) refers to the uptake of organic contaminants from soil, sediments, and water with subsequent transformation by the plants.
5. Phytovolatilization (inorganic and organic contaminants) is the mechanism of uptake and translocation of the contaminant into the leaves with subsequent release to the atmosphere through transpiration.
6. Evapotranspiration of plants can be used to significantly affect the local hydrology through interception of rain on leaf surfaces and transpirational uptake by the plant root system.

The first five mechanisms have been successfully used to remediate or contain contaminated soils, while the use of evapotranspiration applies more to groundwater contamination. Contaminated forested areas are good candidates for the application of these technologies since they are generally impacted over large areas, but at relatively low concentrations. Phytoremediation is limited by the effective rooting depth of plants, as well as the phytotoxicity and/or plant-availability of contaminants. Quite often, only a fraction of the total concentration of a specific contaminant is in a potentially bioavailable form that is accessible for plant uptake. However, given that many regulated environmental sites are actually

managed using a risk-based approach, it may be sufficient to remediate the bioavailable contaminant fraction rather than achieving a low total concentration of a specific contaminant.

**See also:** **Environment:** Impacts of Air Pollution on Forest Ecosystems; Impacts of Elevated CO<sub>2</sub> and Climate Change. **Health and Protection:** Biochemical and Physiological Aspects. **Silviculture:** Forest Rehabilitation. **Site-Specific Silviculture:** Reclamation of Mining Lands; Silviculture in Polluted Areas. **Soil Development and Properties:** Waste Treatment and Recycling.

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