

SOIL CONTAMINATION MONITORING

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Keywords: organic contaminants, inorganic contaminants; vadose zone; analytical techniques, soil monitoring, contamination, environment

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Summary

Soil contamination by naturally occurring and anthropogenic organic and inorganic chemicals is a serious human and environmental health problem in many industrialized and nonindustrialized nations. There is a wide range of types of soil contamination, and an equally wide range of methods and approaches to soil monitoring. Practical considerations such as how the data will be used, the data's required accuracy and precision, and the amount of money, staff, and instrumentation available for the analysis also play a part in the selection of appropriate soil contamination monitoring methods.

Several approaches to soil contamination monitoring include chemical, geophysical, and biological techniques. Chemical techniques are used to measure specific organic, inorganic, or radioactive contaminants in the soil using instruments such as a gas chromatograph, atomic absorption spectrometer, or mass spectrometer. Geophysical techniques examine changes in physical properties of the soil and the contaminants to address large areas of soil contamination.

They may not require any disturbance to the soil, but may not be useful for identifying each contaminant. Biological techniques use organisms as indicators of soil contamination, or byproducts of contaminant biodegradation processes to monitor or predict changes in soil contaminant concentrations over time.

Current developments in soil contamination monitoring include increased efficiency of soil contaminant extraction processes that improve contaminant recovery, development of laboratory instrumentation with enhanced detection limits or ease of use, and development of alternative techniques for soil contamination monitoring such as isotopic signatures or immunoassays.

In addition, on-site analyses allow monitoring of soil without removing it from the site using portable and hand-held meters, and field kits. Some are research-based techniques that may become standard for soil contamination monitoring. At this time, additional development of innovative techniques is warranted that produces cost-effective, robust, easily used and sensitive monitoring techniques for organic, inorganic, and radioactive contaminants in soil.

1. Introduction

Soil contamination by organic and inorganic contaminants has been recognized as an important problem in many areas of the industrialized nations. In addition, naturally occurring contaminants from radiological Earth sources and human and animal wastes (nutrients and pathogenic bacteria) all impact soil and sediments.

In many countries including the United States, land application of hazardous and radioactive wastes is used because it is economical relative to other types of waste disposal.

Industrial, military, and municipal waste disposal is often on the land surface or subsurface, that is, buried in both shallow and deep soils (Figure 1). Land applied contaminants filter through the soils and may impact ground water.

Waste disposal over several decades by application to land in shallow pits or ponds has become a problem in many countries that are now struggling with the task of remediating or cleaning up these areas.

Of special concern are areas that pose a direct threat to human and environmental health.

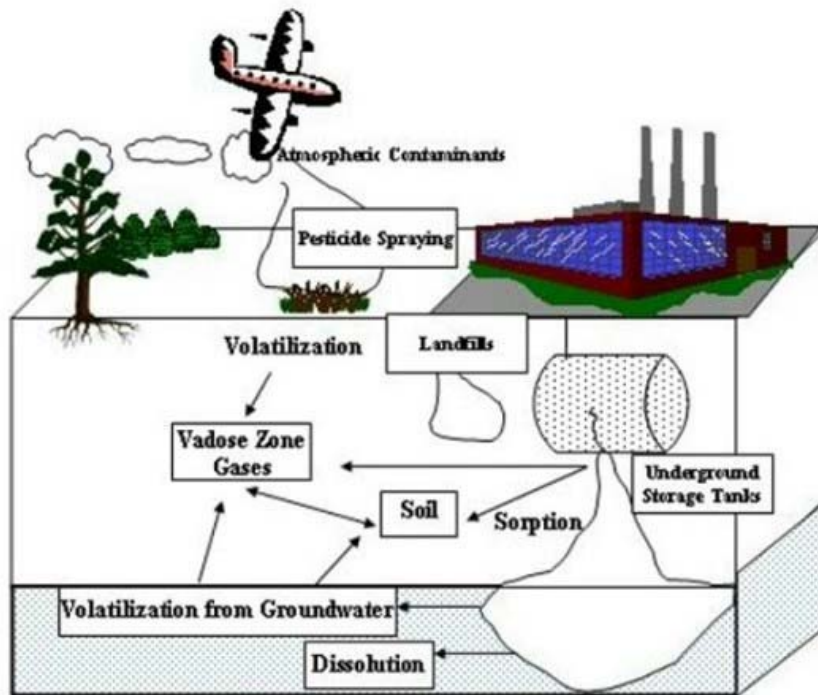


Figure 1. Soil contamination comes from multiple sources and is impacted by processes such as sorption to soil particles and volatilization into the vadose zone

Soils can become contaminated with a wide range of pollutants from various sources other than land disposal of wastes. Contaminants may be applied directly to the soil, as is the case with pesticides. Alternatively, chemicals in soils can occur as a result of air pollutants that fall out as wet or dry deposition and settle on aquatic or land surfaces. An example is the contamination of aquatic sediments from the deposition of hydrophobic chemicals emitted from hazardous waste incinerators. These pollutants fall out of the air onto lakes and are eventually trapped on the aquatic sediments where they can reside for many years.

Chemical pollutants in soils range in their properties from hydrophobic organic contaminants that are strongly associated with the soil, to more water soluble organic contaminants that are transported long distances and are partitioned primarily in the aqueous phase, to radioactive metals that have chemical characteristics like metals in addition to their radioactive properties. Because soil contamination ranges from metals, to complex organo-metallic compounds, to large and small molecular weight organic contaminants, soil monitoring presents many challenges and requires that varied techniques be used. Typical examples of soil contaminants occurring ubiquitously in the environment include hydrophobic polycyclic aromatic hydrocarbons (PAHs) which sorb readily to soils; chromium, a typical metallic contaminant in sediments associated with commercial harbors; tri-butyl tin, a complex organometallic compound used to prevent biofouling on ship hulls; and methyl tertiary butyl ether, a highly soluble gasoline additive which has been found to contaminate groundwater and sediments in several areas of the USA, particularly California.

Soil monitoring techniques are not only varied because of the range in chemical properties of the contaminants themselves, but also because the reason for which the monitoring is being done is varied. Some soil monitoring is used primarily as a screening test to estimate relative concentrations of contaminants or groups of contaminants. Some monitoring is required by local, state, or federal regulations and certified analytical laboratories are required to carry out the analyses. Other monitoring falls in between these two, and may be useful for monitoring the progress of natural attenuation, the natural cleaning up of contaminated soils due to chemical, biological, and physical processes in the environment. Each of these types of concerns requires a different level of analytical sophistication in terms of detection level, separation, and identification of specific chemical contaminants in soils. In addition, issues of cost, reliability of the measurement, and ease of the analysis are important in determining which analyses and for what purpose the analyses are used.

The main difficulty in soil monitoring arises from the nature of the soil matrix. Pollutants in water or in air generally are more easily measured than those associated with soil. This is due in large measure to the interaction of the contaminants with the soil particles themselves. Strong chemical and physical forces may act to bind the contaminants to the soil particles. Thus, if the monitoring technique requires that the chemicals be extracted or removed from the soil prior to analysis, the efficiency of the extraction process becomes crucial to the overall success of the analysis. A second problem is access to the contaminated soils. Land-applied contaminants migrate downward with time and become less accessible. Similarly, contaminants may be applied directly to deeper areas, and as depth of contaminated soils increases, monitoring techniques also may change.

The best techniques, generally speaking, are those that are nonobtrusive, inexpensive, and relatively easy to carry out using field sampling instruments. However, usually the reliability of the information and the difficulty of the analysis may be correlated, that is, the more reliable and sophisticated the analysis, the more difficult, time consuming and expensive it is. A big challenge in the field of soil monitoring is to provide relatively reliable soil monitoring methods that are easily carried out with minimal personnel training required and which use field-hardy, inexpensive instrumentation.

Certain techniques for soil monitoring have been used for several decades. These often are extensions of analytical chemistry techniques which have been adapted for soil analyses, or designed specifically for soil monitoring *in situ*, meaning in the field at the site of contamination. For example, traditional soil contamination monitoring would include the collection of the soil sample which is returned to the laboratory to measure inorganic and organic contaminants. Extraction of the contaminant from the soil is necessary. The extraction is followed by analysis by analytical methods such as gas chromatography, mass spectrometry, atomic adsorption spectrophotometry, fluorescence spectroscopy, and infrared nuclear magnetic resonance (NMR) spectroscopy (see *Laboratory-Based Analytical Technologies*).

Monitoring soil in the field without the benefit of laboratory analysis may be less expensive but adds uncertainty concerning the identification of specific chemicals. Field soil monitoring is carried out using specially designed instruments for nonobtrusive

sampling in which soils do not always have to be removed prior to analysis. Alternatively, laboratory instruments are modified to be carried into the field for use after soils have been collected. Field test kits and field instruments are usually smaller, more portable and more resistant to field conditions of wear and tear, travel, and other forms of physical abuse than laboratory instruments. Examples of *in situ* soil monitoring techniques include chemical analyses using modified laboratory instruments including a portable gas chromatograph or field kit that includes all reagents and a portable spectrometer for colorimetric analyses; physical analyses of the contaminated areas using electrical conductivity; and biological analyses that include an assessment of highly sensitive species as indicators of pollution, or biomarkers.

2. Properties of Soil Contaminants

Characteristic	Common abbreviation	Units	Environmental relevance
Molecular mass	MW	atomic mass units	Mass of a contaminant
Solubility	S	mg L ⁻¹ or g m ⁻³	Tendency of contaminant to dissolve in a liquid
Density	D	g cm ⁻³	Mass of a unit volume of contaminant
Vapor pressure	v.p.	Pa	Tendency of contaminant to exist in the air phase
Sorption coefficient	K _d	dimensionless	Partitioning of contaminant between sediment and water
Organic carbon partition coefficient	K _{oc}	dimensionless	Partitioning of contaminant between sediment and water, corrected for organic carbon content of soil
Octanol-water partition coefficient	K _{ow}	dimensionless	Partitioning of contaminant between lipids and water; Estimate of hydrophobicity
Henry's law constant	K _H	Pa·m ³ mole ⁻¹	Partitioning of contaminant between air and water
Radioactivity	None	Bq	Decay of a radionuclide; disintegrations per second

Table 1. Physical-chemical characteristics of contaminants that impact soil contamination monitoring

The most important physicochemical properties and commonly used coefficients are defined in Table 1. Knowing the physicochemical properties of a contaminant aids in determining which soil monitoring technique is appropriate. Solubility is one of the most readily available characteristics of contaminants and is defined as the concentration of a contaminant in equilibrium in a saturated solution at a given

temperature. Solubility(mg L^{-1}) is usually a function of the contaminant's molecular weight and density. Solubility information will provide an indication of the contaminant's ability to remain in the aqueous phase and not sorb onto soil particles.

Sorption is a process by which a contaminant is chemically or physically bound to the soil particle. In many cases, the greater the strength of the chemical bonds, the greater the extraction process required to break the bonds and release the contaminant for analysis. Sorption in natural soils may be a function of the amount of organic carbon or other sorptive materials naturally present in the soil. For this reason coefficients have been derived to express not only the amount of a contaminant sorbed to soil relative to that remaining in the liquid phase, often termed K_d , but also the amount of a contaminant sorbed to soil corrected for the amount of organic carbon present in the soil relative to the amount of contaminant remaining in the liquid phase, K_{oc} . Figure 2 shows a typical soil coring with lighter colored soil particles and decreasing organic carbon content with depth below land surface. The top layers of the soil will have a greater capacity to sorb hydrophobic contaminants than the deeper, sandier, less organic, carbon-rich soil. This sorption impacts the ease of extraction of the contaminant and therefore the ease of soil monitoring. Another coefficient, the octanol water partition coefficient (K_{ow}) is a second indirect indicator of the probability of a contaminant to sorb to soil and is a measure of hydrophobicity. It was derived to mimic partitioning between water and lipid materials such as those in organisms as an indicator of bioaccumulation of contaminants.

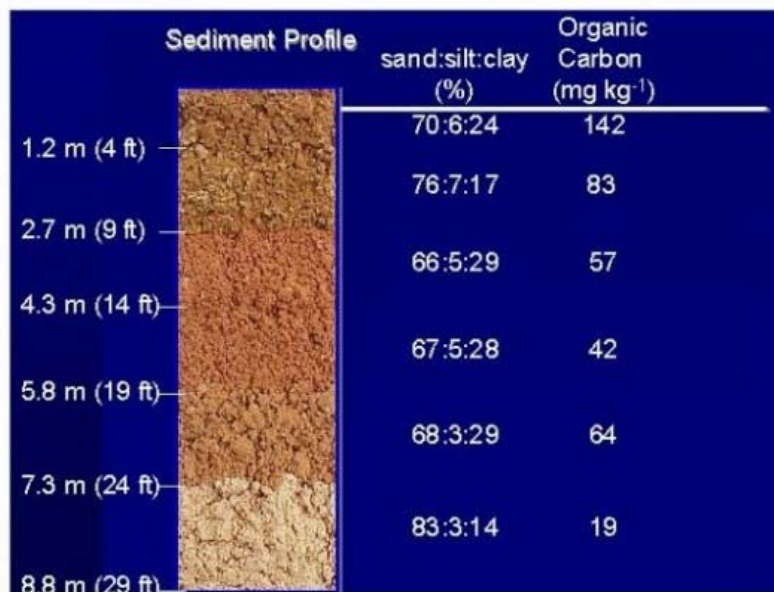


Figure 2. Soil profile showing typical reduction in organic carbon content with depth. Organic carbon increases sorption of contaminants to soil

Vapor pressure gives an indication of whether the contaminant is likely to volatilize or transfer to the vapor phase from soil or water. This is important from a quality assurance-quality control stand point to recognize the potential loss of sample during sample preparation and analysis. The same property can be used to advantage for monitoring contaminants with high vapor pressures by analyzing the contaminant in the

vapor phase without treatment of the soil to remove the contaminants. As with the coefficients for sorption, coefficients have been empirically determined to describe the relative distribution of contaminants between water and air. The Henry's Law coefficient ($\text{kPa m}^3 \text{mol}^{-1}$) is a useful tool for comparing the relative volatilities of contaminants from soil in the vadose zone into air spaces of the vadose zone. Henry's Law coefficients also are useful for determining what type of pretreatment, if any, is necessary prior to analysis and if analytical tools to measure gases can be useful for the analysis.

In addition to individual contaminants, often soil contaminants exist in complex mixtures composed of individual chemicals ranging from volatile low molecular compounds to hydrophobic high molecular weight compounds. Petroleum hydrocarbons and wood preserving solutions are examples and are present in many soils from spills, and leaks from underground and above-ground storage tanks and piping. Some individual contaminants and complex mixtures are termed nonaqueous phase liquids (NAPLs). These contaminants such as crude oils are combinations of several chemicals that are nonsoluble or minimally slightly in water. They remain as organic liquids immiscible in water rather than attaching to soil or dissolving in water. They are generally classified as DNAPLs (dense nonaqueous phase liquids) or LNAPLs (light nonaqueous phase liquids). DNAPLs include chlorinated solvents used in the dry-cleaning industry such as tetrachloroethylene (PCE) and trichloroethylene (TCE). These contaminants are more dense than water and therefore migrate readily through the soil and often reach the ground water. Once they reach the ground water they continue to sink and contaminate large areas of subsurface sediment and ground water. The vertical migration is stopped when a clay confining layer is reached. The DNAPLs pool at the bottom of the confining layer and then can migrate horizontally along the confining layer in an aquifer. Some slow molecular diffusion through the confining layer can occur.

LNAPLs are less dense than water, such as the lighter components of petroleum products including benzene, ethylbenzene, toluene, and meta- and para-xylene (collectively termed BTEX). If they are released on land they also can migrate through soil and reach the ground water. Instead of continuing to sink through the ground water when reaching the water table, these chemicals float on top of the water table and migrate horizontally with the ground water flow. Many of these chemicals are slightly soluble in water. Dissolution of the water soluble components can spread the contamination vertically through soil and sediment. However, this transport is small relative to horizontal transport.

Many NAPLs are regulated in drinking water at $\mu\text{g L}^{-1}$ concentrations, so even small concentrations in subsurface sediment and ground water are a concern. The NAPL pool acts as a reservoir of contamination through slow dissolution, and continues to contaminate surrounding ground water and sediment for many years. The physical properties of NAPLs make soil monitoring difficult because the sampling locations are critical for determining contaminant plume locations and NAPL concentrations in both sediment and ground water. Also, interactions between individual components of the complex mixtures impact the solubility of the individual compounds and their

partitioning between the immiscible liquid and the surrounding ground water and sediment.

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Biographical Sketch

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