

SITE REMEDIATION OF UNDERGROUND STORAGE TANK CONTAMINATION

Scot Journell, P.E., (Water Resources Associates, Inc.,
2702 North 44th Street, Suite #101B
Phoenix, Arizona 85008)

Abstract

Remedial techniques for sub-surface soil and water contamination are dependent on the lateral and vertical extent of petroleum hydrocarbon contamination and the type of petroleum hydrocarbons which have been released into the sub-surface. Specific remedial technologies are required for diesel fuel and heavy oils compared to the more volatile gasoline compounds.

Available remedial technologies for vadose zone contamination include excavation and treatment; soil vapor extraction and possible vapor burning; bioremediation; and chemical treatment. Remedial technologies for ground-water contamination include water recovery, contaminant volatilization, carbon adsorption, bioremediation and water reinjection. Specialized apparatuses are utilized when petroleum hydrocarbon product floating on the water table surface must be separated from the ground water.

A number of hydrologic considerations must be evaluated prior to any remediation scenario. These considerations include geologic characterization of the sub-surface soil matrix, and aquifer.

Introduction

Remedial techniques for subsurface soil and water contamination are dependent on the lateral and vertical extent of petroleum hydrocarbon contamination. Vadose zone contamination at depths of less than 20 feet is within reach of excavation and treatment methods which include landfill disposal, incineration enhanced vaporization, soil washing or surface bioremediation. When vadose zone contamination extends below depths of 20 feet then insitu methods are typically employed. These methods include soil vapor extraction, bioremediation and chemical treatment. When contamination extends vertically to include ground water then water recovery and treatment, bioremediation or chemical treatment are utilized. Variation in the total lateral extent of contamination primarily affects the unit cost of remediation. For large zones of contamination the higher front end cost of bioremediation or chemical treatment may be absorbed by a higher treated volume to result in reasonable unit cost. In addition to the physical constraints of the vertical and lateral extent of contamination, the selection of remedial techniques is dependent on the chemistry of the released hydrocarbon product.

Petroleum Hydrocarbon Contaminants

The major sources of petroleum hydrocarbon releases are underground storage tanks (USTs) and related piping. Table 1 lists the wide variety of petroleum hydrocarbon products which are stored in USTs.

TABLE 1. PETROLEUM PRODUCTS STORED IN UNDERGROUND STORAGE TANKS

Product

Power fuels - civil use

Aviation gasoline and additives

Grade 80

Grade 100

Grade 100LL (Low Lead)

Jet fuel and additives

Jet A (kerosene type)

Jet A-1 (kerosene type)

Jet B (wide cut or naphtha)

Automotive (motor gasoline) and additives

Leaded

Unleaded

Diesel fuel oil and additives, Nos. 1-D, 2-D, and 4-D

Gas turbine fuel oils, Nos. 0-GT, 1-GT, 2-GT, 3-GT, and 4-GT

Heating and illuminating oils

Fuel oils Nos. 1, 2, 4, 5, and 6

Kerosene

Solvents

Petroleum spirits, types 2, 3, and 4, and commercial hexane

Mineral spirits or Stoddard solvent (Type 1, petroleum spirit)

High-flash aromatic naphthas, types I and II

VM&P naphthas - moderately volatile hydrocarbon solvents, types I, II, and III

Petroleum extender oils, types 101, 102, 103, and 104

(Camp, Dresser, and McKee 1986)

Product Composition

There is a wide variation of chemical properties within the range of hydrocarbon products stored in UST's, however the most commonly stored products are fuels. These fuels are blends of hydrocarbon compounds. The compounds may be described by the number of carbon atoms in the molecule. In gasoline the compounds primarily range from four carbon atoms (C4) to twelve carbon atoms (C12). Kerosene ranges from C8 to C15 and diesel fuel ranges from C8 to C21 while fuel oil ranges from C9 to C20. The products with a greater percentage of high carbon compounds are sometimes referred to as being heavier than the products with a lower carbon range.

The fractional distillation process used to produce the hydrocarbon products does not completely separate the desired range of compounds from the smaller or lighter compounds. This aspect of the process allows the presence of the C5 through C9 aromatic hydrocarbons in heavier products such as diesel and fuel oil. These aromatic hydrocarbons include benzene, toluene, ethylbenzene and xlenes (BTEX) which are major constituents of gasoline. Table 2 shows typical concentrations of the BTEX compounds in selected products.

TABLE 2

PARAMETER	PRODUCT				
	GASOLINE	JET-A	DIESEL OIL	FURNACE OIL	HEATER OIL
Benzene	0.8	0.3	0.1	0.3	0.3
Toluene	12.0	1.4	0.7	1.4	1.6
Ethylbenzene	1.7	0.3	0.2	0.2	0.3
Total Xylenes	7.3	0.9	0.5	0.8	1.0
Total BTEX	21.8	2.9	0.15	2.7	3.2

The reported health effects of the BTEX compounds are greater than those of the heavier C10 through C20 compounds. The regulatory community has therefore focused on these constituent compounds and the presence of these compounds must be addressed in most fuel releases.

Subsurface Affects and Interactions

The constituent compounds of the petroleum product have different behaviors in the subsurface environment due to different physical and biological properties of the compounds. Selected properties for a group of constituent compounds are listed in Table 3. In this group of compounds, naphthalene (C10) may be considered representative of the heavier compounds and benzene is representative of the lighter compounds. Although naphthalene is actually an aromatic hydrocarbon the difference in molecular weight compared to benzene allows this comparison.

**TABLE 3
SELECTED PROPERTIES FOR A SELECTED GROUP
OF CONSTITUENT COMPOUNDS**

COMPOUND	<u>Fate and Transport</u>			
	Water Solubility at 20°C Coefficient (mg/L)	Vapor Pressure (torr) ¹	Degree of Biograd-ability	Adsorption
Benzene	1.780	75.0	Some	50
Toluene	515	22.0	Some	339
Xylene-M	175	5.0	Some	-
Xylene-O	162	6.0	Some	255
Xylene-P	198	6.5	Some	-
Ethylbenzene	152	7.0	Some	565
Naphthalene	31.1	1.0	Readily	976

Adapted from Maynard and Sanders, 1969 and Lyman et al 1982.

¹ At 20°C.

As Table 3 shows benzene is approximately 57 times more soluble in water than naphthalene. This results in a preferential partitioning of benzene into subsurface water. For this reason, benzene enters and moves with ground water more readily than the other constituent compounds. This may cause benzene to spread farther and faster than the heavier constituents. The solubility of naphthalene in water is relatively low. This indicates that the C9 and heavier compounds will be less likely to move laterally in ground water.

The vapor pressure of benzene is 75 times greater than that of naphthalene. This will result in a much more rapid volatilization of benzene into subsurface air voids. This difference results in a more rapid reduction of benzene concentrations by diffusion of vapors in the subsurface.

Table 3 shows that benzene is less biodegradable than naphthalene. This reflects the ability of natural processes to more readily attack the longer more complex compounds. Another important interaction is adsorption. The adsorption coefficient is a measure of the affinity of the compound for subsurface materials. Naphthalene has a higher affinity for subsurface material than benzene. Absorbed contaminants are much more difficult to remove from subsurface materials.

The combined effect of the physical properties on the released product over time is that the aromatic fraction of the product will move more readily into the subsurface due to the release and it will move more readily out of the subsurface materials due to remediation. This causes the composition of the released product to move toward the heavier range under natural processes and under remediation. The available remediation methods vary in effectiveness against the physical constraints and chemical properties of individual remediation sites.

Remedial Technologies

Vadose Zone Contaminants

Vadose zone contamination may be treated in situ or at the surface. Excavation and treatment is usually selected in cases where contaminants are within reach of excavating equipment. Rubber tired backhoes with an Extenda-Hoe configuration are able to excavate to depths of 17 feet.

Several limitations affect excavation. The most significant limitation is often imposed by interference of the excavation with the site business operations and site structures. Another significant limitation may be the possible need for shoring due to poor quality soils.

Surface Treatment. Several treatment methods may be applied to the excavated soil. The most rapid return of the site to a useful state may be accomplished through disposing of the material by landfill. In selection of this method the cost of transportation a dumping must be considered along with the cost of potential future liability problems at the landfill. The potential liability problem may be avoided by incineration. However the cost of incineration is so high that it is typically not considered unless the presence of a non-fuel hazardous substance causes the material to be considered a hazardous waste. Surface treatment at the site or a site related facility is another option for the disposition of excavated material. Enhanced volatilization is a surface treatment that works effectively volatile with hydrocarbons. This method ranges in technology from simple mechanical rototilling of the soil pile to enclosed low temperature heating and forced air flow through the soil. Although it is relatively simple, mechanical rototilling is very effective during warm seasons.

Another surface treatment option is soil washing. In this method the soil is slurried with water and surfactant or with a solvent. In the slurried phase the contaminant is separated from the soil particles and moved into the liquid. The liquid is then treated to capture and breakdown the contaminant. This method is effective on heavier, less volatile products such as diesel, heating oil or lubricating oil. The front end cost of constructing the treatment plant may cause this method to be considered only for larger remediations.

Bioremediation is also an effective method of surface treatment. In a surface application the soil is placed in a lined pit and covered with a liner material. The necessary nutrients and microbes are circulated through the soil by a system of pipes installed in the material.

In Situ Treatment. In situ methods are used when vadose zone contamination extends more deeply or when site facilities and operations prevent excavation. The most frequently used method for volatile hydrocarbons is vapor extraction. This is an enhanced volatilization method based on airflow through the vadose zone. The air flow is caused by applying a vacuum to a vadose zone well. This causes air to move through the soil mass into the extraction well. The volatile compounds partition into the air stream as it passes through the soil pores. The influx of fresh air through the ground surface and into the subsurface may be enhanced by construction of air injection wells. The effective depth of the method, at the minimum, extends to the full depth of the screened well interval. The radius of influence for extraction wells frequently extends more than 40 feet depending on the length of the perforated interval and the type of soil.

In most jurisdictions the vapor extraction system must be permitted as an emission source and treatment of the vapor stream may be required. Available treatment technologies include thermal destruction, carbon adsorption or catalytic destruction. Thermal units combine proven incinerator technology, moderate initial cost and moderate operating cost with near 100 percent destruction of vapor stream hydrocarbons. Carbon adsorption has a low initial cost however the operating cost for disposal or regeneration of spent carbon is high. This cost increases significantly when the contaminant load in the vapor stream is higher. Catalytic units have a high initial cost and complex systems which may be difficult to permit with local building and safety codes.

Bioremediation may be utilized as an insitu method. This method may be particularly useful for contamination by non-volatile hydrocarbons such as diesel or heating oil. In this application a system of injection and collection wells is used to move nutrients and microbes into and through the soil. Most contractors will perform a bench test on soil collected from the site prior to the remediation. The bench test typically utilizes a soil core of up to 15 feet in length which is collected by drilling. The test which may run for 90 days will verify the selected nutrient mix and group of microbes. In many cases the native soil microbes are effective when the nutrient mixture is applied. After a successful bench test then the field system may be constructed.

Obstructions to the use of bioremediation may be encountered when applying for site permits. The method has not received widespread endorsement by regulators. Objections to the method typically focus on potential impacts to the aquifer due to injection of microbes and nutrient mixtures. Some states may require that an Aquifer Protection Permit is obtained prior to the start of remediation. Such permitting may require extensive, costly site characterization and monitoring.

Chemical treatment is another insitu method that has been used. In this technique a chemical is applied to release the hydrocarbon from the soil and to break the longer carbon chains into lower carbon molecules. This chemical cracking allows remediation of heavier products such as diesel or heating oil. The process is similar to bioremediation in that the chemical is moved through the subsurface by a system of wells. The chemicals used may include surfactants, sulfides or hydrogen peroxide. This process may also require expensive permitting.

Ground Water Contaminants

The most commonly applied method of ground water remediation is to utilize recovery wells to pump the water to the surface and treat it with volatilization or carbon adsorption. The withdrawal wells must be located and constructed to maximize the capture of contaminated water. In some cases monitor wells used to delineate the lateral extent of ground water contamination may be converted to withdrawal wells. In other cases the site assessment information gathered from the monitor wells may show that the recovery and treatment effort would be optimized through installation of a separate recovery well or system of wells. These wells may be located downgradient from the contaminated water for the purpose of intercepting the contaminants. In some low transmissivity aquifers it may be possible to locate the wells within the area of contaminated water to reverse the existing gradient by withdrawal from the wells.

The most economical method for treatment of the recovered water is air stripping. In this method the water is cascaded through a column of open packing material as air is forced upward through the water. The volatile contaminants partition from the aqueous phase into the vapor phase. The rate of partitioning is governed by the concentration of contaminants, the ratio of air and water in contact and the length of contact time.

Another treatment method is carbon adsorption. In this application the recovered water is circulated through a bed of carbon. The hydrocarbons are adsorbed onto the carbon material. The unit cost of this treatment may be relatively high compared to air stripping due to the operating cost of changing, transporting and regenerating or disposing of the exhausted carbon. The rate of carbon use is controlled by the contaminant load in the water. In some cases air stripper discharge is passed through a carbon adsorption bed to remove residual concentrations of less volatile contaminants prior to discharge. Although not commonly applied, another method of treatment for recovered water is bioremediation. In this application the water is circulated through a series of biological reactor beds or vessels.

Treated water generated by a recovery effort may be disposed of by injection or infiltration into the subsurface or transfer to the local wastewater treatment system. Studied placement of infiltration areas for treated water may enable further modification of the site ground water gradient to reduce the number of required recovery wells. The treatment standards for discharge to sanitary sewer may actually be more stringent than applicable standards for re-injection into the subsurface.

Free Product

If free product is present on the ground water surface the remedial effort must begin with recovery of the product. The most common approach is to use a submersible pump to form a cone of depression which captures and holds the product. Another pump is then used to move the product to the surface. The product pump inlet may be placed in a skimmer which floats on the water/product interface or the inlet may be screened with a hydrophobic material that does not allow the water to pass into the pump.

Hydrologic Conditions

A number of hydrologic conditions must be evaluated prior to beginning remediation. The quality of the initial site assessment will affect the economy and effectiveness of the remediation. The character of subsurface materials in the vadose zone may exclude the application of some methods. In permeable soils in situ vadose zone methods are very effective because increased air flow, delivery of nutrients and microbes or delivery of chemicals is accomplished with fewer wells. In soils rich in organic matter the stronger adsorption of hydrocarbons may indicate chemical treatment. The presence of thin strata or lenses may reduce the effectiveness of in situ vadose zone methods.

The character of the aquifer will affect the design of recovery and treatment plans. In permeable aquifers with high flow rates the recovery wells must be located to intercept contaminants and treatment systems must be adequate to treat higher volumes of water. Low permeability vadose zone soils and aquifer materials may be well suited to bioremediation due to the reduced potential for nutrients and microbes to impact off site areas.

In each case the site operator, consultant and regulators must utilize a thorough site assessment, knowledge of hydrocarbon characteristics and selection of applicable technology to effect site remediation of underground storage tank contamination.

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