Here Comes the Science:
Understanding the Technologies Used to Remediate Organic Pollutants

by Edward Sullivan

The contamination of soils and ground water by persistent organic chemicals not only presents a risk to human health and the environment, it also poses a great source of financial risk to the parties responsible for the cleaning up these pollutants. The financial risk can include a number of different elements including cost uncertainty for conducting the cleanup, third- party liabilities and natural resource damage (NRD) claims.

As nonscientists, risk managers can benefit from learning about the terms associated with these technologies, as well as the basic science behind some of the most commonly used remediation techniques, including ground water stripping, soil vapor extraction (SVE), air sparging, biosparging, bioventing, chemical oxidation and bioremediation.

Organic Chemicals

Simply put, an organic chemical is any chemical whose molecules include at least one carbon atom. There are many naturally occurring organic chemicals, such as methane, propane and the various hydrocarbon chemicals found in crude oil. With the onset of the industrial revolution, the chemical industry introduced thousands of new man-made or "synthetic" organic chemicals. Beginning in the 1940s, the synthetic organic chemical manufacturing industry began to ramp up significantly. Years of poor handling and disposal practices before the advent of environmentalism in the early 1970s resulted in any thousands of contaminated sites in the United States alone. It is now the responsibility of various responsible parties to clean up the contamination left behind by this legacy.

The environmental remediation industry is now in its third decade. Many lessons have been learned through the years and there are now a wide range of effective technologies available for cleaning up organic chemical contamination. Choosing the correct technology is paramount to completing a remediation that will not only be effective but also will minimize the financial risk associated with the cleanup.

In Situ vs. *Ex Situ*

Most environmental cleanup technologies can be applied either *in situ* or *ex situ*. *In situ* means the technology is delivered directly to the subsurface soils or ground water to treat the contaminants where they are located. *Ex situ* means the contaminants are removed from the ground, either by digging up contaminated soil or pumping contaminated ground water and treating the contamination in treatment facilities built at the site. The remediated soils or ground water are then either placed back into the ground or disposed off-site. The advantage to applying a technology *in-situ* is there is no need to construct treatment facilities. The benefit to treating *ex situ* is that more control can be exerted over the treatment process.

Stripping Technologies

Several remediation technologies take advantage of the volatile nature of certain organic chemicals. Volatility is the tendency of a chemical to change quickly from liquid to gaseous state. Anyone who has ever spilled paint thinner or nail polish remover and watched how quickly the spill evaporated can understand the concept of volatility. The most widely used cleanup methods that take advantage of chemical volatility are air stripping, SVE and air sparging.

Air stripping is as simple as it sounds. Contaminated ground water is pumped from the ground (thus it is an *ex situ* technology) and air is forced through water to strip the volatile contaminants from the ground water. The stripped chemicals, now in a gaseous state, are then captured and further treated to destroy or remove them from the air stream.

SVE works under the same principle but is used to remove contaminants from soil *in situ*. Soil, often erroneously thought to be solid, actually includes anywhere from 20% to 40% empty "void space" between soil grains. This void space is where contaminant molecules collect. Air is drawn through the soil voids by a series of vacuums and blowers. The air moving through the soil strips the contaminants from the soil voids and brings them in the gaseous state to the surface for collection and treatment.

Air sparging is similar to SVE, only it is applied *in situ* to clean up ground water rather than soil. Air is bubbled through the contaminated ground water, again to strip the contaminants. The contaminants, now in a gaseous state, are then drawn to the surface. SVE and air sparging are frequently used in tandem to clean up contaminants in soils above the water table and in ground water below the water table using the same blowers and vacuums.

Chemical Oxidation

Most people are familiar with the TV pitch-man who yells about the "power of OxiClean." The active ingredient in OxiClean is sodium percarbonate, a chemical oxidant that breaks down organic molecules. Just as chemical oxidants can remove organic stains like grass or oil from your laundry, so can they break down petroleum oil and other organic chemical pollutants in the subsurface. Usually applied *in situ*, chemical oxidants (such as peroxide, ozone, sodium, potassium permanganate, sodium persulfate and sodium percarbonate) can be injected into the ground where they interact with and break down organic pollutant molecules into harmless substances like carbon dioxide and water.

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An interesting emerging technology is the use of "chemical reduction" reactions to break down organic molecules. Chemical reduction reactions are the basically the opposite of chemical oxidation reactions in that they are characterized by the opposite flow of electrons between the two reactants. In chemical reduction reactions, electrons are transferred from the chemical reductant to the organic contaminant molecule being chemically reduced. Although beyond the scope of this article, this transfer of electrons is what chemically alters and breaks down the contaminant molecule. Nano-scale zero valent iron (nZVI) has shown significant promise as a chemical reductant. "Nano-scale" means that the iron particles are extremely small (less than the size of a typical bacteria cell). "Zero valent" means that the iron particles have an excess supply of electrons that can be released when the iron particles come into contact with the organic contaminants.

Bioremediation

Once thought to be basically sterile, subsurface soils and ground water environments are now known to contain untold numbers and varieties of naturally occurring micro-organisms. Just like humans, these micro-organisms must eat and breathe to survive.

In the mid 1980s, it was discovered at a number of gasoline spill sites that certain organic chemical pollutants in soil and ground water were mysteriously cleaning up by themselves. Upon further investigation it was determined that certain microbes in the ground were actually capable of "eating" the organic contaminant molecules to derive their electrons and carbon atoms and "breathing" oxygen. Just like with human consumption, the end product of this process is CO_2. However, as these oxygen-breathing or "aerobic" micro-organisms grow and multiply, they ultimately use up all the available oxygen in the subsurface environment thus shutting down their population growth and stopping the consumption of the organic pollutants.

In order to sustain the aerobic micro-organisms so they can consume all of the organic pollutant molecules, air, oxygen or oxygen-releasing compounds (ORC) can be injected into the ground to supply a continuing source of oxygen. The injection of air into the subsurface is called either bioventing (for soils) or biosparging (for ground water). Bioventing and biosparging are identical to SVE and air sparging except the air is injected at a much lower rate with the goal of promoting microbial growth rather than physically stripping contaminants from the soil or ground water. Organic chemicals amenable to aerobic bioremediation include many gasoline and petroleum compounds including benzene, toluene and xylene.

As bioremediation technologies evolved, people began injecting other materials along with oxygen into contaminated zones in the subsurface. For example, nutrients like nitrogen, phosphate or even vitamins can be used to bolster microbial populations. In addition, cultures of certain key microbes known to be especially capable of consuming target pollutant molecules can be grown and injected into the ground in a process called bioaugmentation.

Some microbes, known as "anaerobic" organisms, are capable of "breathing" other substances including nitrates, iron or sulfates in the absence of oxygen. The familiar rotten egg smell associated with swamps comes from anaerobic microbes that are "breathing" sulfate molecules and "exhaling" sulfide molecules. One innovative bioremediation technology promotes the growth of microbes that can consume contaminant molecules and breathe nitrate molecules. This is accomplished by injecting nitrate producing materials into the ground.

Perhaps the most fascinating bioremediation discovery was that certain microbes were capable of eating certain types of organic pollutant molecules and/or other simple naturally occurring organic molecules and actually "breathing" other types of contaminant molecules.

These micro-organisms, known as halorespirers, obtain electrons and carbon atoms from certain organic molecules and then transfer the electrons to other organic pollutant molecules to derive their energy. Since the microbes are not breathing oxygen, this is an anaerobic process. Injecting certain simple organic molecules (like simple sugars, molasses or soybean oil) into the ground as a food (i.e., carbon) source can promote the growth of these microbes and result in complete destruction of the chemicals they are "breathing." The chemicals amenable to this type of bioremediation include the commonly used solvents perchloroethene and trichloroethene. Today a number of anaerobic bioremediation amendments are commercially available including a product called HRC and various emulsified soy oil products. (For more information, see "Managing Environmental Risk with Bioremediation," in the April 2005 *RM*.) RM

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