Microbes and Molasses

A Successful Partnership

By Cindy Argentine

Washington Square Mall in Germantown, Wis., wasn't much of a destination in the late 1990s. Stores that had operated there for 20 years had been abandoned. Buildings were in disrepair. Weeds grew up between cracks in the parking lot. Even worse was a problem hiding underground. A toxic chemical called perchloroethylene (PCE) had leaked into the groundwater and was present at levels 400 times greater than allowed in drinking water.

Today, that same location is an attractive shopping center with a grocery store, specialty shops, and plenty of cars in the newly paved parking lot. The contamination has virtually disappeared, and PCE can no longer be detected in the groundwater.

What was the key to this transformation? About 250 gallons of molasses—a dark, thick syrup made from sugar cane—and millions of microbes already living underground. Engineers injected the molasses into the soil and groundwater, and that helped the bacteria break down the toxic chemicals.

This technology is a type of bioremediation—the process of using living organisms to fix environmental problems. The name "bioremediation" makes sense when you consider the word's roots: "bio" means life, and "remediate" comes from "remedy," a solution to a problem.

"Bioremediation is almost like farming," says John Wilson, a forerunner in the field of bioremediation and a chemist with the U.S. Environmental Protection Agency. "You prepare the ground, you fertilize it, you create that environment for the organisms to grow and flourish, and then you get the results you want."

The trick with bioremediation is to understand what type of bacteria you need and then to create the conditions they like best, Wilson adds. In the case of Washington Square Mall, "anaerobic" bacteria were needed. These bacteria live without oxygen. They use other chemical compounds—such as PCE—to produce the energy they need to live.

Engineers find out what chemical compounds are missing in the bacteria's natural environment, and then they try to supply them. This way, the bacteria can thrive and thereby break down the toxic compounds.

Source of the toxic pollution

Where did the toxic pollution at Washington Square Mall come from? Scientists believe it was from a dry cleaning shop that operated there from the 1970s through the 1990s. When clothes are "dry" cleaned, they are washed in a chemical solvent instead of in water and detergent.

Ever since the 1960s, PCE has been the most common solvent used for dry cleaning. People working in the dry cleaning industry call it "perc"—short for perchloroethylene. It's great for removing grease and stains, and since it is not flammable or explosive like the solvents used in earlier decades, it was considered safer to use. The problem is that PCE is not safe to breathe or ingest in significant quantities because it can affect the liver and brain and may cause cancer.

Washington Square Mall was not the only place with PCE contamination. According to the State Coalition for Remediation of Drycleaners, there are more than 17,000 contaminated dry cleaning sites out of 23,000 active dry cleaners in the United States. Finding ways to pay for and clean up all of these sites is an ongoing problem. Any technology that offers a solution serves an important need.

Washington Square Mall was abandoned after a toxic chemical known as PCE leaked into the groundwater.

After cleanup of the soil and groundwater, Washington Square Mall is now an attractive shopping center.

PHOTOS: ARCADIS US, INC., MILWAUKEE, WIS.

How dry cleaning got messy

At many sites, such as Washington Square Mall, the pollution probably did not happen overnight. It likely resulted from a series of small releases over time.

PCE is a dense liquid at room temperature, and it's often stored within dry cleaning machines as well as in drums or small tanks at a site. Whenever it is transferred from one container to another, there is a potential for a spill.

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PCE was released in other ways, too. Hoses leaked, fittings came loose, and equipment occasionally malfunctioned. Sometimes wastewater containing PCE was emptied down drains to the sewer, and any cracks in the sewer pipes carried it straight to the underlying soil and groundwater. Any or all of these things may have happened at dry cleaners throughout the United States.

In the 1970s and 1980s, when most of the original environmental laws in the United States were written, businesses began paying more attention to how the chemicals they used were classified and disposed. Many businesses tightened their processes and upgraded their equipment to reduce the amount of PCE being released into the environment. But much of the contamination had already occurred.

In 1989, as required by the Safe Drinking Water Act, the government set limits on the concentrations of several toxic chemicals (including PCE) allowed in drinking water. Federal and some state governments now limit the concentration of PCE in drinking water to 5 parts per billion (ppb). Below the Washington Square Mall, its concentration was 2,000 ppb in the groundwater and 80,000 ppb in the soil.

Transforming the mall

Luckily, this story doesn't end with just identifying the problem. A real estate developer knew that some sort of cleanup could be done, and in 1998 his company decided to purchase the contaminated site, clean it, and build a grocery store there.

According to U.S. law, site owners are responsible for cleaning up their sites, and they also risk lawsuits from anyone affected by the environmental contamination. Knowing this, the buyer contacted the Wisconsin Department of Natural Resources and enrolled in a program that would protect his company from being liable. This program prevents site owners from being liable for any future cleanup costs or associated lawsuits as long as the owners determine where the pollution is and then clean it to designated standards.

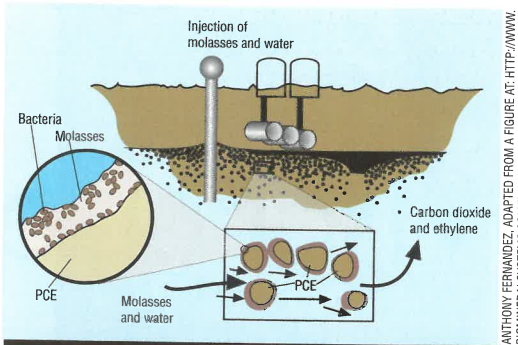
Theresa Evanson, a scientist with the Wisconsin Department of Natural Resources, says this program is a great motivator for cleanup. "Buyers are basically given a guarantee that when they finish their cleanup, they are done," she says.

The developers of Washington Square Mall embraced this approach. They hired an environmental engineering firm to identify the types of contaminants in the soil, measure their concentrations, and pinpoint how far they had traveled. Based on this information, the firm designed a program to remediate the site.

Cleanup began in August 1998. Using earth-moving equipment, the firm dug a 14-foot-deep hole and excavated about 3,000 tons of contaminated soil. Trucks carried this soil off-site for disposal in a hazardous waste landfill.

Bioremediation began later that same month to treat the remaining contamination, primarily in the groundwater. The cleanup team installed 182 temporary wells and 12 fixed wells in a grid-like pattern over the area of groundwater contamination. They injected a solution of molasses and water into the wells (Fig. 1). During the following year, they injected molasses four or five more times.

Bacteria already present at the site immediately went to work. Six months after the initial injection, the concentration of PCE was near zero at some of the monitoring wells. A year later, the concentrations of PCE had decreased so much that the chemical could no longer be detected. The cleanup was a success.



ANTHONY FERNANDEZ, ADAPTED FROM A FIGURE AT: HTTP://WWW.BIOMINERALSYSTEMS.COM/E1.PHP

Figure 1. At Washington Square Mall, molasses was pumped into soil and groundwater to stimulate naturally occurring bacteria to consume toxic PCE and turn it into harmless ethylene.

Destroying contaminants with sugar

So, how do the bacteria destroy PCE? Like other living creatures, bacteria require energy to survive. To produce this energy, some bacteria use molecules that are toxic to people—such as PCE—but are not harmful to the bacteria. At Washington Square Mall, these bacteria were able to change PCE into harmless compounds such as ethylene (C_2H_4).

Both PCE and ethylene have similar molecular structures (Fig. 2), but PCE has chlorine atoms while ethylene has hydrogen atoms.

By adding sugar-rich molasses to the water underground, scientists provide a food source for some bacteria and a source of hydrogen atoms and electrons that certain types of bacteria use as they interact with and break down PCE and other chlorinated compounds in the groundwater.

Scientists believe that the metabolism of the bacteria involves breaking the carbon-chlorine bond in PCE. Hydrogen atoms then

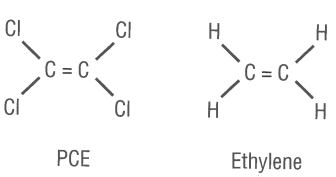
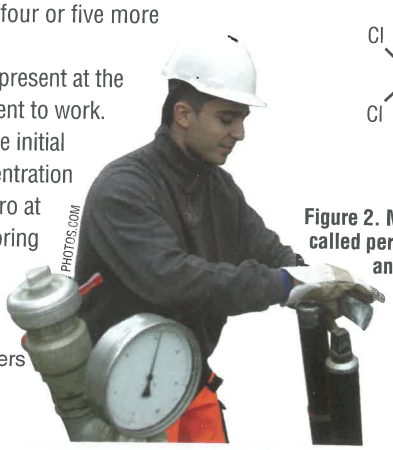


Figure 2. Molecular structures of PCE (C_2Cl_4), also called perchloroethylene or tetrachloroethylene, and of ethylene (C_2H_4), also called ethene.



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take the place of chlorine atoms, transforming PCE into a new molecule. In many cases, it appears that the chlorine atoms are stripped off one by one, with hydrogen atoms taking their place, which eventually leads to simple ethylene. The chemical reactions involved in this process are summarized in Fig. 3.

In each step, dechlorination occurs through a sequence of oxidation and reduction reactions, in which electrons are transferred between reactants (Table 1).

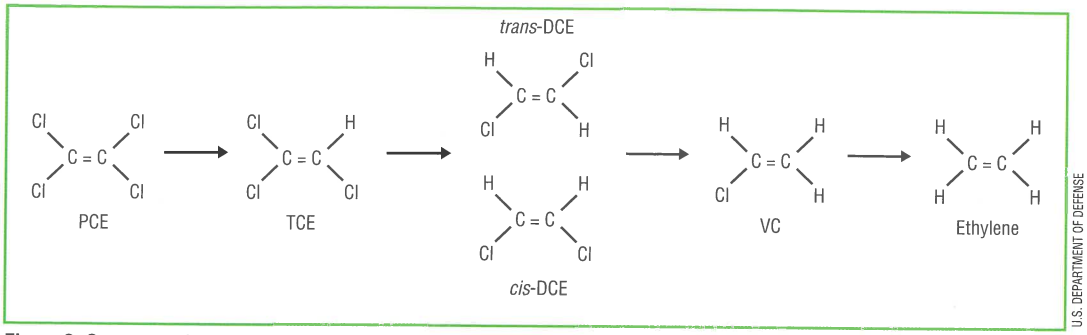

Figure 3. Summary of the steps leading to the transformation of PCE into ethylene by bacteria in soil. The chemical reactions are provided in Table 1. PCE, perchloroethylene; TCE, trichloroethylene; DCE, dichloroethylene; VC, vinyl chloride.

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A growing business

PCE is only one of many contaminants that can be treated with bioremediation. Oil spills in the soil or groundwater were the first applications and rely on the fact that some bacteria feed on the hydrocarbons present in oil. Unlike the bacteria that break down PCE, these bacteria need oxygen to survive. Once they have used up the oxygen in the soil or groundwater, they stop working. Scientists have engineered ways to enrich soil with oxygen so that bacteria can complete these cleanups.

Bill Newman, a chemist and the president of a bioremediation company, is one of those scientists. His company, Remediation and Natural Attenuation Services, designs unique cleanup methods based on the type of contamination and the chemistry of the local soil and groundwater. For microbes that reduce chlorinated compounds such as PCE, his firm patented an emulsified vegetable that works as an alternative to molasses when injected in the soil.

ARCADIS US, INC., MILWAUKEE, WIS.

To treat the groundwater contamination at Washington Square Mall, an environmental consulting firm installed temporary wells into which a solution of molasses and water was injected underground.

Oxidation reaction (loss of electrons):							
$C_6H_{12}O_6$	+	$6\ H_2O$ →	$6\ CO_2$	+	$24\ H^+$	+	$24\ e^-$
Glucose (from molasses)		**Water**	**Carbon dioxide**		**Hydrogen ions**		
Reduction reactions (gain of electrons):							
$3\ C_2Cl_4$	+	$3\ H^+$	+ $6\ e^-$ →	$3\ C_2HCl_3$	+	$3\ Cl^-$	
PCE		**Hydrogen ions**		**TCE**		**Chloride ions**	
$3\ C_2HCl_3$	+	$3\ H^+$	+ $6\ e^-$ →	$3\ C_2H_2Cl_2$	+	$3\ Cl^-$	
TCE		**Hydrogen ions**		**DCE**		**Chloride ions**	
$3\ C_2H_2Cl_2$	+	$3\ H^+$	+ $6\ e^-$ →	$3\ C_2H_3Cl$	+	$3\ Cl^-$	
DCE		**Hydrogen ions**		**VC**		**Chloride ions**	
$3\ C_2H_3Cl$	+	$3\ H^+$	+ $6\ e^-$ →	$3\ C_2H_4$	+	$3\ Cl^-$	
VC		**Hydrogen ions**		**Ethylene**		**Chloride ions**	
Overall reaction:							
$C_6H_{12}O_6$ +	$3\ C_2Cl_4$ +	$6\ H_2O$ →	$6\ CO_2$	+	$3\ C_2H_4$ +	$12\ Cl^-$	+ $12\ H^+$
Glucose	**PCE**	**Water**	**Carbon dioxide**		**Ethylene**	**Chloride ions**	**Hydrogen ions**

Table 1. Oxidation reduction reactions resulting in the transformatioon of PCE into ethylene by bacteria in soil. PCE, perchloroethylene; TCE, trichloroethylene; DCE, dichloroethylene; VC, vinyl chloride.

The Washington Square Mall revitalization project has been a significant stepping stone in the acceptance and understanding of bioremediation. Following the success at this site, the Wisconsin Department of Natural Resources allowed bioremediation at a larger site in Glendale, Wis., where concentrations of PCE were even higher. The source at that location was believed to be a machine shop that used chlorinated solvents as a degreaser. Similarly to Washington Square Mall, bioremediation reduced contamination to below-detection limits. Contaminated sites throughout the country, including several major military bases, are also being revitalized with this technology.

Bioremediation is ingenious: It uses naturally occurring microorganisms to clean up toxic waste. The concept sounds simple, but the actual process is complex. Environmental scientists are still studying the biology and chemistry of exactly how it works, and they are trying to apply it in different geologic conditions. Says Wilson, "The best thing about bioremediation is that it does more than simply monitor or contain an environmental problem. It eliminates it." *CM*

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