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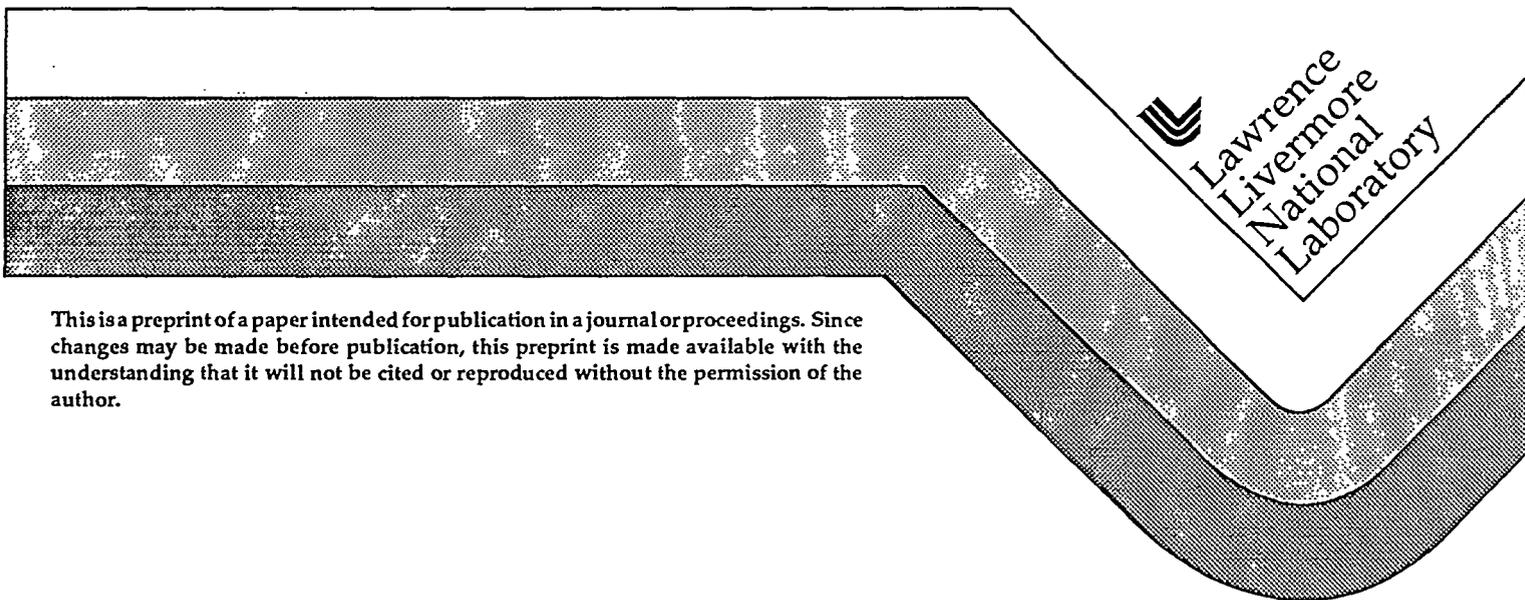
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## Innovative Technologies for In-Situ Remediation

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## INNOVATIVE TECHNOLOGIES FOR IN-SITU REMEDIATION

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### Abstract

LLNL is developing several innovative remediation technologies as long-term improvements to the current pump and treat approaches to cleaning up contaminated soils and groundwater. These technologies include dynamic underground stripping, *in-situ* microbial filters, and remediation using bremsstrahlung radiation.

Dynamic underground stripping is a system of thermal remediation and underground imaging techniques for use in rapid clean-up of localized underground spills of organic contaminants. It combines steam injection, direct electrical resistance heating, vacuum extraction, and tomographic imaging in a clean-up of an LLNL gasoline spill. *In-situ* microbial filters is a technique to remove organic contaminants, such as trichloroethylene, from groundwater as it naturally flows through a thin region of increased activity of the methanotrophic microbe, *Methylosinus*. The microbes can be inoculated in a fixed pattern as an emplaced subsurface filter, and the "filter" biodegrades trichloroethylene to below detectable limits. We have also conducted preliminary experiments using bremsstrahlung radiation to decompose volatile organic compounds, such as trichloroethylene, in groundwater and in vapor vacuum extracted from soil.

Concentrated underground organic contaminant plumes are one of the most prevalent groundwater contamination sources. The solvent or fuel can percolate deep into the earth, often into water-bearing regions. Collecting as a separate, liquid organic phase called dense non-aqueous-phase liquids (DNAPLs), or light NAPLs (LNAPLs), these contaminants provide a source term that continuously compromises surrounding groundwater. This type of spill is one of the most difficult environmental problems to remediate. Attempts to remove such material requires a huge amount of water which must be washed through the system to clean it, requiring decades. Traditional pump and treat approaches have not been successful. LLNL has developed several innovative technologies to clean up NAPL contamination. Detailed descriptions of these technologies described here can be found in [1].

### Dynamic Underground Stripping (Roger Aines)

The most advanced NAPL clean-up technology under development at LLNL is steam injection vacuum extraction and coupled with direct electrical resistance heating of the clay layers. This technique is being developed in collaboration with the University of California, Berkeley College of Engineering [2,3].

In a typical application, shown schematically in Fig. 1, the concentrated plume is surrounded by injection wells, with one or more extraction wells located in the center. The injection wells are screened in the more permeable areas; in less permeable areas, the well is completed for electrical heating (conductive packing material and a stainless steel electrode). Remediation begins with pumping of the extraction wells to depress the water table in the center of the pattern, followed by steam injection.

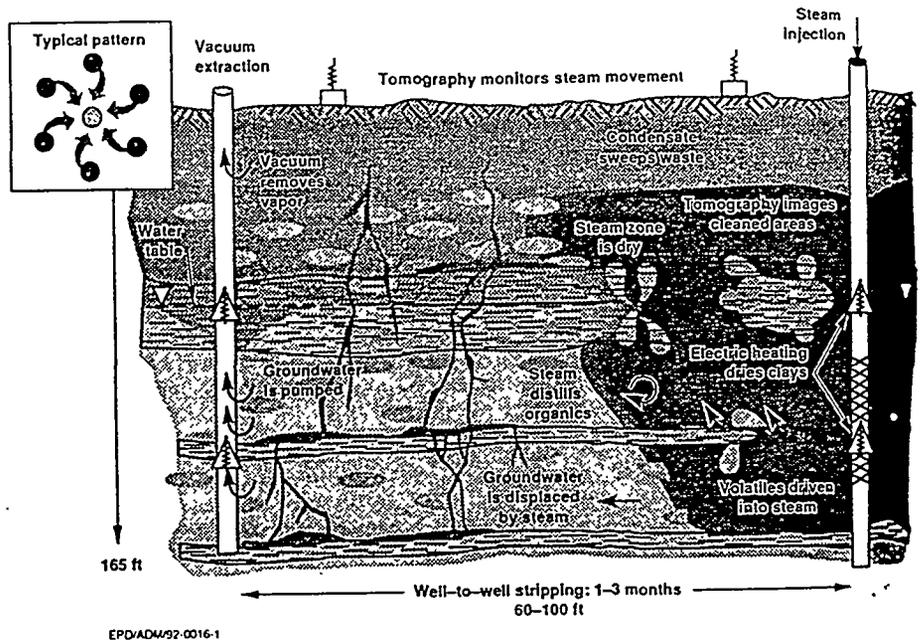


Fig. 1 Schematic of the Dynamic Underground Stripping process. The contaminant (ovals and streamers) is displaced toward the extraction well by steam injection and by electrical heating of the impermeable, clay-rich layers (shown by the horizontal-line pattern).

As steam is forced into the formation, the earth is heated to the boiling point of water. The advancing pressure front displaces groundwater toward the extraction well. Near the steam condensate front, organics are distilled into the vapor phase, transported to the front, and condensed there. The advancing steam zone displaces the condensed liquids toward the recovery well where they are pumped to the surface. The amount of heat required to bring the ground to 100 degrees C is the principal control on how much steam must be injected; pressure and steam delivery rate affect the rate at which the whole field can be heated and the shape of the advancing steam front.

When the steam reaches the extraction well, vacuum extraction becomes the most important removal mechanism. As steam input stops, a drop in steam zone pressure slightly reduces the boiling point of any residual water or contaminants (such as that held by capillary forces), forcing them to boil and convert to removable vapor. Our work has shown that it is possible to raise the initial ground temperature to  $>115^{\circ}\text{C}$ .

At this point in the process not all of the contaminated sediments may have been contacted by steam. Electrode assemblies placed in the impermeable layers are turned on, passing 480V current at several hundred amperes per electrode. This heats the clay and fine-grained sediments and causes water and contaminants trapped within to vaporize and be forced into the steam zones, where vacuum extraction can remove them. This heating may be followed by one or more additional steam injection phase for both contaminant removal and to keep permeable zones hot as groundwater returns.

The goal of the combined processes is to achieve a hot, dry, contaminant-free cylinder of earth. This creates a large contrast for geophysical imaging techniques to use in observing the areas that have and have not been heated. Among the methods demonstrated are electrical resistance tomography (ERT), seismic tomography, induction tomography, passive seismic monitoring, and temperature and conventional geophysical well logging in dedicated monitoring boreholes.

#### Gasoline Spill Clean-up

The LLNL Gasoline Spill site presents multiple challenges since the NAPL (gasoline) is both above the water table and dispersed in water-saturated soil (a three-phase system). The lithology is heterogeneous, with alluvial deposits consisting of interbedded sands, silts, and gravels. Approximately 17,000 gallons of gasoline were spilled, of which 5000 gallons is now trapped beneath the water table because of a 30-ft rise in the water table. The remainder is in the vadose zone. A significant amount of the vadose zone contamination has been removed by vacuum venting operations and ongoing natural bioremediation, which appears to be enhanced by the oxygen enrichment of the venting operation.

Current plans call for six injection wells around the periphery of the spill zone. Steam will be injected into the permeable zones at and below the water table, while the intervening layers will be electrically heated. Up to three extraction wells will be used to maintain the high groundwater removal rates required. The upper vadose zone will be avoided for the present in order to study and make use of the existing gasoline-degrading bacterial cultures in that region.

#### Clean Site Engineering Test

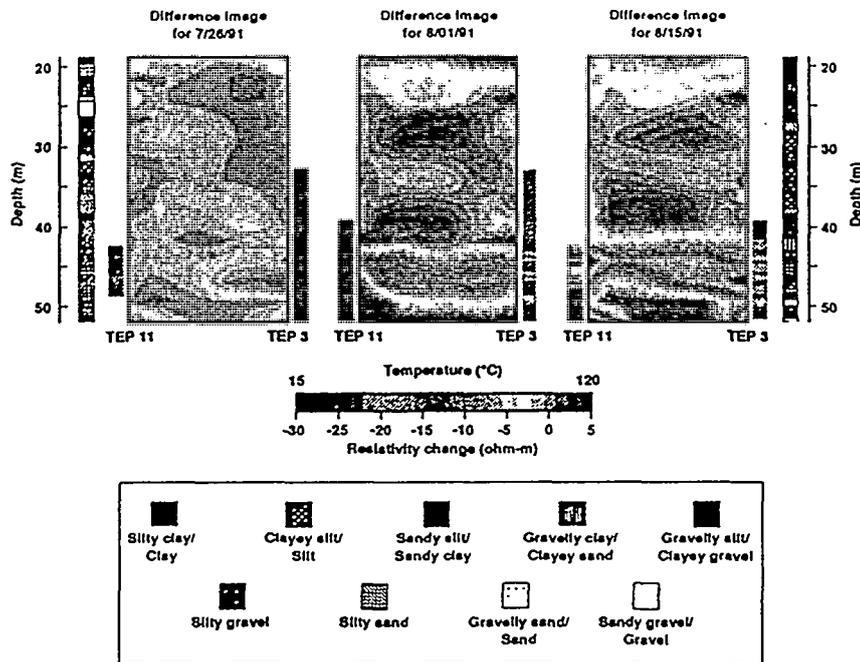
We have tested the technique at an uncontaminated site with geology similar to that at the Gasoline Spill Site approximately 400 yds southeast of the Spill Site. Because of the alluvial nature of the sediments in this area, only gross correlations of units can be made, but both sites contain permeable gravel layers interspersed with low-permeability silt and clay layers.

Twenty-three 165-ft-deep wells were installed at the Clean Site: 11 temperature and ERT imaging wells, three large-diameter monitoring wells for geophysical logging and cross-hole measurements, two extraction wells, three injection wells, and four combined electric heating/piezometer wells for water-level measurements. Ten additional 20-ft-deep wells were drilled at the southern edge of the site for a small-scale electrical heating test area.

An average of 8.5 gpm (as water) of 50-psi saturated steam was injected, and groundwater was extracted at about the same rate from an extraction well 65 ft away. Extraction was terminated 10 days later. A total of 295,000 gallons of water were injected as steam; 147,000 gallons were extracted. A total of 8,000 cubic meters were heated at a depth of 44 meters to over 100°C.

Current Status:

1. A steam zone can be established below the water table without excessive energy loss.
2. Six-electrode, three-phase heating of clay layers is appropriate for field application.
3. ERT proved the most successful technique for providing near-real-time imaging of the active processes between wells. Figure 2 shows a set of three images with accompanying temperature and information. ERT clearly shows the progress of the steam front as a zone of lowered resistivity.



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Fig. 2. Electrical resistance tomography views of the steam zone at the Clean Site engineering test. These are constructed by comparing initial baseline data with data taken during steaming. In the 7/26 image the injection plume has just entered the region between these wells, moving within the silty gravel layer, but no significant temperature rise is noted in the wells. By 8/01, the steam has reached both wells, and a significant temperature rise is seen in TEP 3. Development of two steam layers at the end of the test is seen in the 8/15 image.

## Conclusions

Installation of monitoring and treatment facilities is underway at the LLNL Gasoline-Spill Site. A full-scale electrical heating and steam injection demonstration is scheduled for the end of 1992.

### In-situ Microbial Filters (Richard Knapp)

The *in situ* microbial-filter strategy consists of increasing the microbial activity at the expanding boundaries of migrating contaminant plumes (Fig. 3). Microbial activity is enhanced and a subsurface filter established by pumping a pure strain of the naturally occurring methanotrophic microbe, *Methylosinus trichosporium* OB3b, into the aquifer through injection wells and by simultaneously withdrawing aquifer fluid from adjacent wells. A portion of the injected microbes attach to the soil or rock and form a thin, filter region. An appropriate choice of injection and withdrawal well locations and pumping rates permits this filter region to stretch continuously across the plume margins.

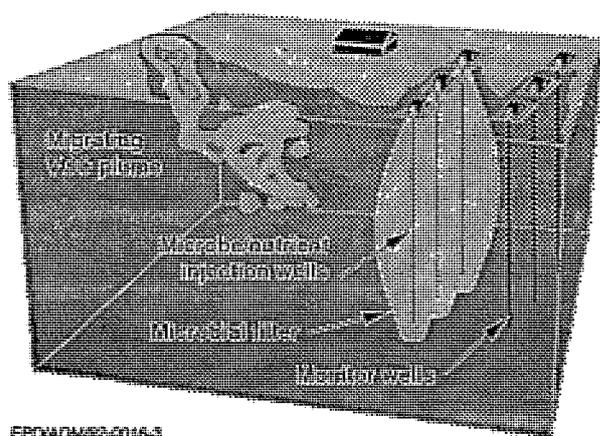


Fig. 3. The *in situ* microbial-filter approach. Microbial activity is enhanced at the expanding boundaries of a contaminant plume migrating downstream from a near-surface source region. A naturally occurring methanotroph is injected through two horizontal wells and forms a porous curtain. TCE-contaminated groundwater naturally flows through this region where it is bioremediated into  $\text{CO}_2$  and  $\text{Cl}^-$ . Groundwater enters the filter contaminated and leaves clean. Methanotrophs sporulate or lyse into harmless compounds after they have finished degrading TCE. Vertical monitoring wells are located downstream from the biofilter.

Contaminated groundwater naturally flows into the filter region, the attached microbial population degrades the contaminants at a rate greater than or equal to their transport rate through the region, and the groundwater exits clean. In this manner, further spread of the plume is prevented simultaneously with the remediation of the existing contamination. This approach also allows for concurrent volumetric treatment of the contaminant source by inoculation and for the emplacement of multiple filters across the expanding dimensions of the plume. Effective bioremediation over these small volumes in concert with multiple microbial filters results in a rapid cleanup of the entire plume.

*Methylosinus* is abundant in marine sediments or in soils. It has an absolute requirement for methane or methanol as a carbon and energy source. In the absence of this substrate, the microorganism will either disintegrate (lyse) or form spores that will remain dormant until there is an adequate substrate supply. This microbe is not pathogenic.

Methanotrophs contain enzyme systems called methane monoxygenases (MMOs) that allow them to grow on methane. Our target contaminant for remediation is TCE. *Methylosinus* catalyzes the first step in the oxidative breakdown of TCE; the initial intermediate is TCE epoxide, which rapidly and spontaneously reacts to ultimately form the innocuous compounds CO<sub>2</sub> and Cl<sup>-</sup>, a dissolved aqueous ion. No toxic intermediates are produced during this biodegradation. Chloroform can also be biodegraded by this organism.

Most current *in situ* bioremediation efforts focus on injecting nutrients into the subsurface to stimulate the indigenous population. Our approach, a radical departure from this, has two unique aspects: (1) the filter concept, whereby groundwater is decontaminated as it flows through a thin region of enhanced microbial activity instead of treating the entire volume of the plume simultaneously; and, (2) the inoculation approach [4-8]. Remediation could be accelerated by also inoculating the relatively small contaminant source region.

This inoculation approach has the potential to reduce problems encountered during *in situ* remediation when microbial populations are stimulated by means of nutrient injections. Although it has been used extensively in microbial-enhanced oil recovery, its feasibility for *in situ* biodegradation of volatile organic compounds (VOCs) (in particular low levels of chlorinated solvents such as TCE and chloroform in aqueous porous media) has not been proven.

#### Proof-of-Concept Experiment

We demonstrated the validity of the *in situ* microbial-filter concept by conducting a series of scaled laboratory experiments in a two-dimensional test bed that was 1.1 m long, 0.4 m high, and 0.1 m wide. It was packed with a nearly homogeneous sand with an overall permeability of about 8.5 D and a porosity of 34%. Fluid flow through this medium was at a constant rate of 1.5 cm/hr, a common rate for natural groundwater flow. The sand pack was sampled with fritted nickel probes extending horizontally through the entire width of the test bed and through ports at both the inlet and outlet of the test bed.

At the start of the experiments, *Methylosinus* bacteria were injected into this test bed to form an attached filter that was about 0.1 m thick in the flow direction. Microbial population balance measurements during inoculation indicated that about 8% of the injected microbes attached to the sand, the remaining inoculum was transported downstream by the ambient flow. Subsequent to this inoculation, a 24-hr pulse of TCE at a concentration of 108 ppb was injected into this simulated *in situ* microbial filter. Measurements of the aqueous TCE concentration made immediately in front of the emplaced filter showed the arrival of the pulse, whereas, no TCE was detected immediately downstream of the filter (Fig. 4). Our results from this proof-of-concept experiment suggest complete biodegradation of the TCE pulse.

After we completed the proof-of-concept experiment, we deconstructed the test bed and sampled the sand pack in the biofilter area. Measurements of the attached population counts and the metabolic activity of the attached population were made on these samples (Fig. 5). The attached population was 108 cells/mg of dry sand and was centered about where it was initially injected, but some downstream spread can be inferred. Measurements of attached microbial metabolic activity averaged 0.2-nmol of TCE oxidized per minute per gram of dry sand. The activity was skewed downstream from the attached population, perhaps suggesting a loss of activity in the upstream portions of the filter where the predominance of the biodegradation would have been accomplished.

### Conclusion

These results unequivocally demonstrate that microbes can be inoculated in a fixed pattern, that fluid can flow through this emplaced filter unimpeded, and that the filter effectively biodegrades aqueous contaminants to below detectable limits (<0.5-ppb TCE). When scaled to the field, our experimental success is even more dramatic because the results show that we can remediate a plume with a dimension of about 100 m in the direction of fluid flow.

### Remediation Using Bremsstrahlung Radiation (Stephen Matthews)

Ionizing radiation has been shown to radiolytically decompose halogenated hydrocarbons and other toxic chemical compounds. A dose of ionizing radiation, when applied, destroys these substances like an incinerator, rather than merely collect them like a carbon filter. Unlike an incinerator, however, radiolytic decomposition uses a non-nuclear electron beam accelerator that does not produce combustion products because the decomposition process occurs at ambient temperature.

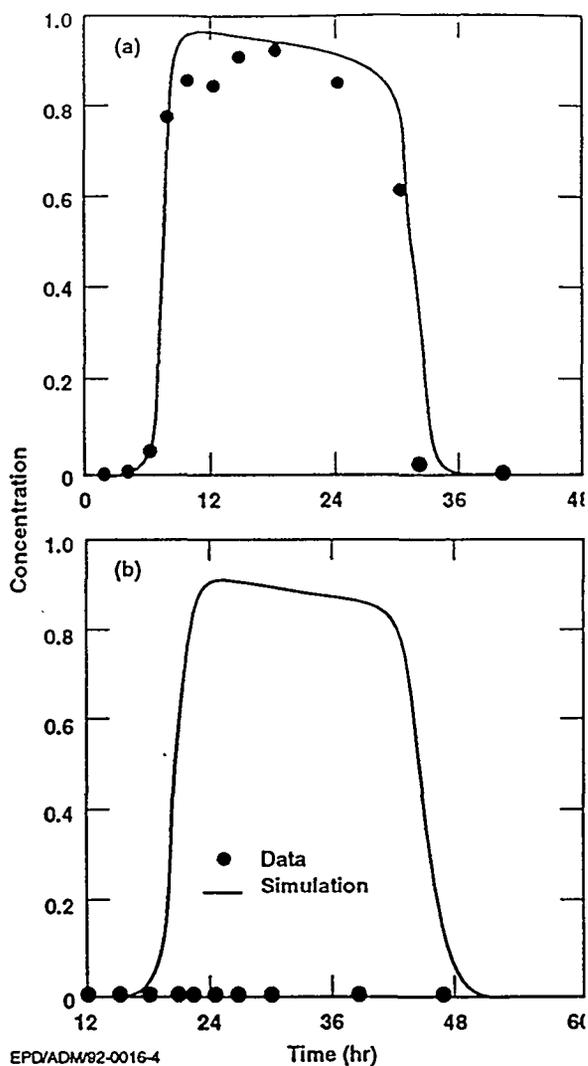
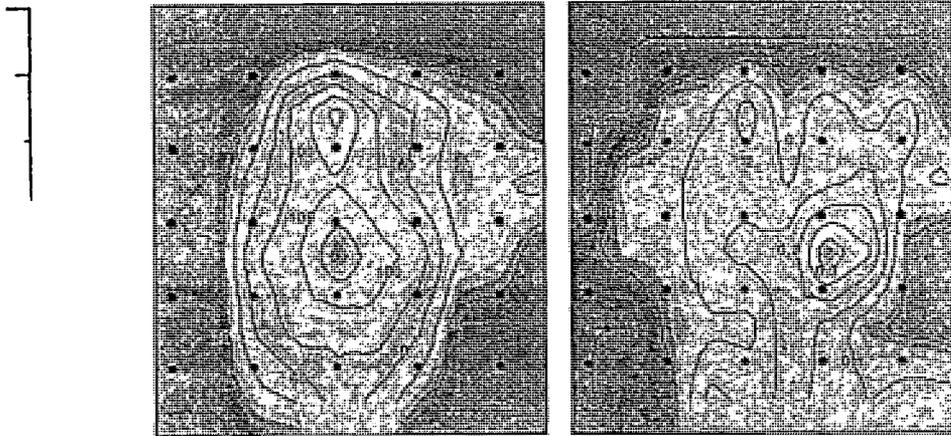


Fig. 4 (a) Experimental data and simulation of a TCE wave at a fritted-nickel sampling probe, located immediately before the biofilter in the first proof-of-concept experiment. The simulation assumes no biodegradation. Data suggest irreversible loss of TCE at this column, which is consistent with observed microbial activity outside the expected filter location. (b) Simulation of a TCE wave (with no biodegradation) and experimental data at a frit immediately after the biofilter. No measurable amount of TCE was transported through the filter region, suggesting complete biodegradation of the input pulse. Concentrations for both graphs are relative to the input 108-ppb pulse of TCE.



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Fig. 5 Measurements made 17 days after TCE inoculation through fritted-nickle sampling probes (black dots). (a) The attached microbial population (number of cells per microgram of dry sand). The TCE concentration is highest around the frit column at which they were injected, with some downstream (left-to-right) spreading. (b) The metabolic activity (nmo TCE oxidized per minute per gram of dry same) for the attached microbial population. Through the region of activity generally coincides with the attached population counts (see Fig. 4a), there is a downstream left-to-right skewing in the pattern.

We performed experiments in which radiation was used to decompose a variety of volatile organic compounds (VOCs). The VOCs were irradiated in groundwater, and in the vapor phase. The dose/destruction requirements were measured and the decomposition products were chemically examined. Four different electron accelerators were used to produce bremsstrahlung radiation to destroy toxic substances (bremsstrahlung is the technically correct name for the radiation produced by an x-ray machine). These accelerators provided electrons ranging in energy from 1.6 to 9 MeV and produced bremsstrahlung dose rates ranging from  $10^5$  to  $5 \times 10^{11}$  R/s. Toxic substances were also exposed to cobalt-60 gamma radiation at a rate of 400 R/s; cobalt-60 gamma radiation has an energy of 1.25 MeV. The experimental parameters of the five radiation sources are listed in Table 1.

Table 1.  
Accelerator and isotope radiation sources.

Source	Energy (MeV)	Max dose rate (R/s)
Pulserad	1.6	$5 \times 10^{11}$
Febetron	2.0	$5 \times 10^{10}$
ETA-11	2.0	$10^8$
Linatron	9.0	$10^5$
Cobalt-60	1.25	400

### VOCs in Groundwater

Groundwater from the LLNL site contains a mixture of four dissolved VOCs at concentrations up to 300 ppb: trichloroethylene (TCE), chloroform ( $\text{CHCl}_3$ ), carbon tetrachloride ( $\text{CCl}_4$ ), and polychloroethylene (PCE). Groundwater samples were placed in closed glass vials with no air space and then irradiated with various applied doses of ionizing radiation up to 1400 kR. The irradiated groundwater was then passed through a gas chromatograph (GC) and analyzed for VOC concentration.

The VOC concentration decreased in all the irradiated samples; the reduction depended primarily upon the applied radiation dose. The reduction in concentration as a function of applied dose for TCE is shown in Figure 6; a separate concentration curve is shown for each radiation source used.

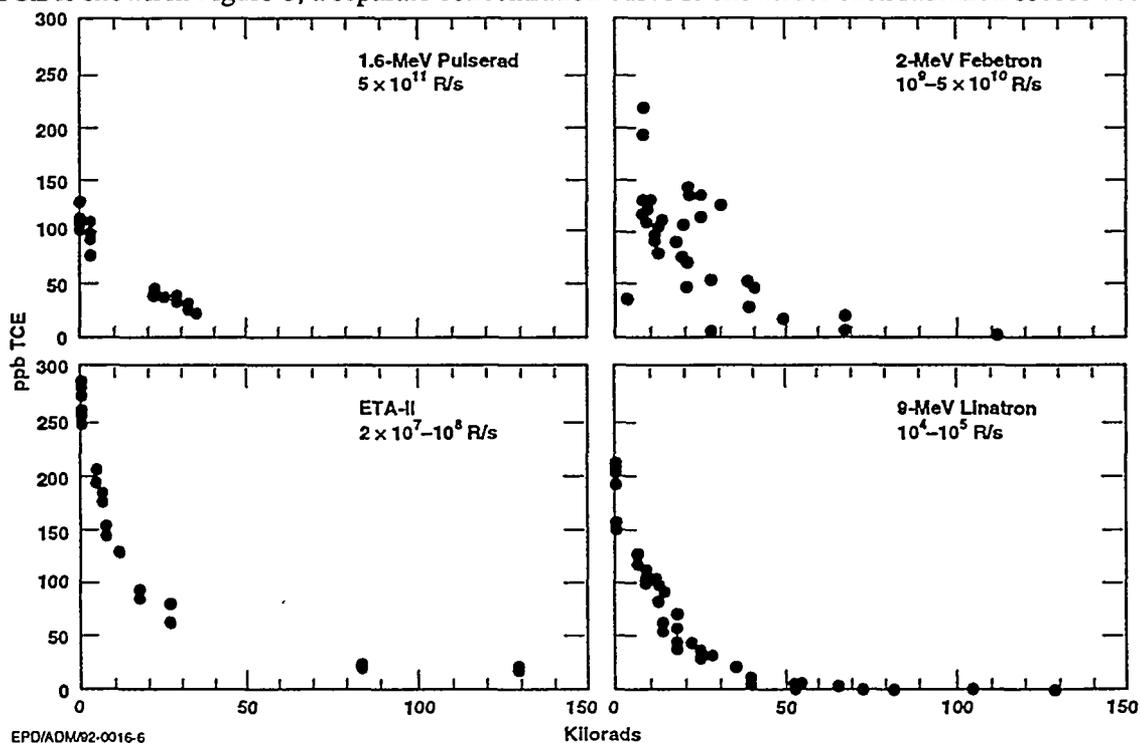


Fig 6. Radiolytically induced reduction of TCE concentration in Well MW-222 groundwater as a function of radiation dose provided by four accelerators.

These data indicate that the VOC concentration is reduced approximately exponentially with applied radiation dose.

The TCE and PCE required a smaller radiation dose for decomposition (by approximately one order of magnitude) than the  $\text{CHCl}_3$  or  $\text{CCl}_4$  required. Both the  $\text{CHCl}_3$  and  $\text{CCl}_4$  required a smaller  $1/e$  dose to reduce their concentration in groundwater when the irradiation was provided at high dose rate. No such dose rate dependence was observed in the decomposition of TCE or PCE.

We increased the VOC concentration in LLNL well water samples to 400 ppm, which simulates industrial waste. The spiked well water was then irradiated at the 9-MeV Linatron with applied doses up to 1400 kR. The irradiated water was examined with a GC and mass spectrograph (GC/MS) for VOC concentration and for identification and concentration of VOC decomposition products.

The reduction in concentration of all four VOCs in the spiked groundwater was approximately exponentially dependent on the radiation dose, in agreement with the earlier experiments.

Two of the irradiated spiked groundwater samples and an unirradiated control were examined for chloromethane, dichloromethane, hydrochloric acid, and chlorine gas. None of these products were found. The only observed difference between the irradiated and unirradiated samples was an increase in chloride ion concentration in the irradiated water. The chloride ion increase was dependent upon the radiation dose. A mass balance analysis showed that this increase could be approximately accounted for by the chlorine removed from the decomposed VOCs. Therefore the VOC decomposition products do not form significant amounts of new chlorinated hydrocarbons, and the chlorine from the decomposition is apparently completely mineralized. More sensitive mass-balance and chlorine speciation tests are in progress.

#### TCE Vapor

Since a common method for removing TCE from water and saturated soil is by vacuum extraction which produces an end product of TCE vapor mixed in air, we performed lab and field experiments to demonstrate that ionizing radiation breaks down TCE in the vapor phase. Laboratory samples of TCE vapor at concentrations of 480 ppmv were prepared in both humid and dry air and placed within stainless steel spherical shells at atmospheric pressure and ambient temperature. These shells were placed in front of the 9-MeV Linatron so that ionizing radiation could be applied to the gas inside. Identically filled unirradiated shells were used for controls.

Vapor samples were obtained from the spheres periodically during the process so that the reduction in TCE concentration could be measured as a function of applied dose. We found that the TCE concentration decreased approximately exponentially with applied dose; the decrease was the same in both humid and dry air. A dose of 100 kR is required to reduce TCE vapor at an initial concentration of 480 ppmv by a factor of  $1/e$ ; 300 kR reduces the TCE concentration to well below 1 ppmv.

Vacuum extraction wells are used at LLNL to remove TCE from areas where it has spilled into the soil. TCE vapor at a concentration of 200 ppmv was extracted and irradiated as described above. The irradiated TCE extraction sample was reduced in concentration by the radiation in a manner similar to the reduction observed in the laboratory-prepared TCE vapor samples. An approximate dose of 200 kR is required to reduce the TCE concentration in the extraction well sample by a factor of  $1/e$  and 450 kR is sufficient to reduce the concentration to below 1 ppmv.

The irradiated spheres containing the humid and dry laboratory-prepared TCE vapor and the irradiated TCE vapor from two LLNL wells were analyzed for TCE, phosgene, and other reaction products. No phosgene was found with a detection limit of less than 50 ppm. No TCE or other organics were found with a detection limit of 1 ppm. The condensed water from the humid irradiated TCE vapor sample was analyzed using a GC/MS and no organics were found to a limit of 1 ppm. All the irradiated vapors were found to consist of nothing but air to the limit of detection. Similar results were found in subsequent field tests at LLNL Site 300.

## Conclusion

These experiments demonstrate that TCE vapor in air can be decomposed by exposure to electron beam irradiation. An absorbed dose of 450 kR is sufficient to decompose TCE vapor from an initial concentration of 10,000 ppmv to a final concentration of 500 ppmv. This same applied dose can decompose TCE vapor from a starting concentration of 500 ppmv to a final concentration of less than 1 ppmv. No harmful decomposition products have been found.

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