# HYDROGEN RELEASE COMPOUND (HRC®): A NOVEL TECHNOLOGY FOR THE BIOREMEDIATION OF CHLORINATED HYDROCARBONS

S.S. Koenigsberg

*Regenesis Bioremediation Products, 1011 Calle Sombra, San Clemente, CA 92673-6244; Phone: (949) 366-8000; Fax: (949) 443-3145; e-mail: steve@regenesis.com.*

## ABSTRACT

Hydrogen Release Compound (HRC®) is a simple, passive, low-cost, and long-term option for the anaerobic bioremediation of chlorinated hydrocarbons (CHs) via reductive dehalogenation. Applications to the remediation of other compounds, such as MTBE and perchlorate, that are anaerobically degradable by other reductive mechanisms, are in progress. HRC should be viewed as a tool for the enhancement of natural attenuation at sites that would otherwise require high levels of capital investment and operating expense. HRC is a proprietary, food quality, polylactate ester that, upon being deposited into the subsurface, slowly degrades to lactic acid. Lactic acid is then metabolized to hydrogen, which in turn drives the reductive dechlorination of CHs. This has been demonstrated effectively in the laboratory and in the field. HRC can be manufactured as a moderately flowable, injectable material, or as a thicker, implantable hard gel, to facilitate localized treatment and passive barrier designs. HRC is best utilized for the remediation of dissolved-phase plumes and the associated hydrophobically sorbed contaminant. The use of HRC is contraindicated for free-phase DNAPL unless the total mass to be remediated is within the scope of economic feasibility in comparison to alternative treatments. Evidence suggests there is competition between reductive dehalogenators and methanogens in which the methanogens compete for the use of hydrogen in the conversion of carbon dioxide to methane. Some researchers believe that a low concentration of hydrogen favors the reductive dehalogenators and starves out the methanogens. The objective, therefore, is to keep hydrogen concentrations low. The time-release feature of HRC, which is based on the hydrolysis rate of lactic acid from the ester and the subsequent lag time to hydrogen conversion, facilitates this objective. HRC, therefore, becomes a passive form of enhanced natural attenuation in contrast to the more capital- and management-intensive alternatives now available. Laboratory and field results will be presented, the latter expanding on the first uses of HRC by various members of the engineering and consulting firm community.

***Key words:*** *reductive dechlorination, bioremediation, hydrogen, hydrogen release compound*

## INTRODUCTION

Hydrogen Release Compound (HRC) offers a passive, low-cost treatment option for *in situ* anaerobic bioremediation of chlorinated hydrocarbons (CHs). HRC is a proprietary, environmentally safe, food quality, polylactate ester specially formulated for the slow release of lactic acid upon hydration. Bioremediation with HRC is a multi-step process. Indigenous anaerobic microbes metabolize the lactic acid generated by HRC, into several other organic acids and produce hydrogen along the way. The resulting hydrogen can be used by reductive dehalogenators which are capable of dechlorinating CHs. Major target compounds in this group include PCE, TCE, TCA, and their derivatives.

HRC can be manufactured as a moderately flowable, injectable material liquid that can be pressure injected using various direct-push technologies. This material can facilitate anaerobic remediation for about six months to one year or more depending on site conditions. When manufactured as a thicker, hard gel, it can be applied to wells in canisters or be used to implant borings. The latter option may offer many years of continuous release depending on site conditions. In either

venue, HRC provides a long-lasting, time-released hydrogen source to enhance the reduction of a variety of contaminants. The following summarizes the key advantages of HRC:

1) Low maintenance, low cost and non-invasive—Unlike actively engineered systems, continuous mechanical operation and maintenance is eliminated, dramatically reducing overall operations and maintenance costs. Injection applications are relatively non-invasive allowing undisturbed operation of commercial facilities during treatment installation and offering lack of visibility during the working phase.

2) Constant and persistent hydrogen source—As a function of the controllable viscosity, HRC will remain where emplaced and generate highly diffusible organic acids and hydrogen slowly over time. Since CH plumes are difficult to locate, a continuous, highly diffusible series of substrates increases the effectiveness of contact, containment, and remediation,

3) Enhance desorption of CHs—The continuous hydrogen source provided by HRC can reduce dissolved-phase CH concentrations. This creates a larger concentration gradient which in turn facilitates desorption of hydrophobically sorbed CHs from the soil matrix.

4) Favored reductive dechlorination over possible competing methanogenic activity—Results from several university studies suggest that there is competition for hydrogen between the reductive dechlorinators and methanogens. While methanogen survival is favored under elevated hydrogen conditions, reductive dechlorinators may be best supported in conditions of more moderate hydrogen concentration.

## METHODS AND RESULTS

### *HRC Microcosm Studies with TCE*

The use of HRC for remediation of TCE was studied in 200 ml test tube experiments in which the release of lactic acid from HRC was measured as a function of bacterial concentration and HRC concentration. In the experiments, 10 grams of sterilized sand were added to each test tube followed by a solution of TCE with a concentration up to 140 mg/L. Various quantities of bacteria, capable of metabolizing TCE, were then added. Finally, 0.5 or 1.5 grams of HRC were added to each test tube. Each day, 6 mL samples were taken and analyzed for TCE and lactic acid.

Results indicate that TCE was remediated under all conditions. Results from one representative experiment are presented in Figure 1, which shows that reduction in TCE follows an increase in lactic acid release. It is important to note that most of the initial drop in TCE (within the first hour) was due to adsorption of TCE on the sand. This TCE eventually desorbed from the soil as the dissolved-phase TCE was remediated during the progression of the experiment.

### *Aquifer Simulation Vessel (ASV) Studies*

The Aquifer Simulation Vessel (ASV) is used to establish the influence of important field-scale parameters on the efficacy of HRC. The ASV consists of a horizontal six-inch diameter/six-foot

length pipe. The ASVs are designed to allow measurement at six-inch intervals along the pipe. Each pipe is packed with actual contaminated soil from the field. HRC is placed in the system at the "CH-water" inlet side, such that the flowing water will pass through the HRC and then move through the pipe. The water can be added with various levels of CHs and remediation rates measured. The distribution of lactic acid and its breakdown products can also be measured.

In the initial studies, the ability of HRC to facilitate the reductive dechlorination of TCE was measured. In the experiments, an ASV was filled with soil. Then, the TCE was added to the soil at the CH-water inlet side at a concentration of approximately 6 mg/L. The ASV was allowed to acclimate over a period of six days during which baseline TCE-concentration profiles were developed. Finally, a "slug" of HRC was added to the inlet side and the system was run at a flow rate of 0.5 ft/day for a period of nine days. Results from one experiment, in which TCE levels were measured at days one, six, and nine at each six-inch interval along the ASV, are presented in Figure 2.

These studies evolved from fundamental bioreactor work undertaken by Dr. William Farone of Applied Power Concepts, Inc. with the guidance and enrichment cultures of Dr. Joseph Hughes of Rice University. The Farone studies ultimately led to the development of a "Chemical Dynamics Model" for CH remediation with polylactate esters, as described below.

***A Chemical Dynamics Model for CH Remediation with Polylactate Esters***

A chemical mechanistic model of all of the reactions involved in CH remediation with polylactate esters, including absorption and desorption of all the chemical species, is postulated based on coupled elementary rate equations. The equations are solved simultaneously to match laboratory remediation data in closed systems using solutions containing initial concentrations of TCE up to 100 mg/L. A key feature of the model formulation that was required to simulate the laboratory data is the importance of microbial populations in controlling the rate of biotransformation of the CHs as well as controlling the rate of hydrolysis of the esters and the rate of production of hydrogen from the lactic acid. The results support the hypothesis that the wide variation in rate constants for CH degradation is related to microbial populations and hydrogen availability.

The test system involves two 200 ml test tubes containing 10 grams of soil and 160 ml of liquid with 10 and 25 mg/L of TCE (concentrations as high as 100 mg/L have been used). An alternative system using the ASV device was also employed. Numerical analysis of the coupled differential equations was carried out by the Runga-Kutta-Gill algorithm. The model was programmed in Visual Basic for Applications as a series of macros in an Excel spreadsheet. The full model is available at www.regenesis.com, in a paper entitled "A Chemical Dynamics Model for CH Remediation with Polylactate Esters" (W.A. Farone, S.S. Koenigsberg and J. Hughes, 1999).

In conclusion, standard chemical kinetic formulations are useful in predicting concentrations of chemical species in active dechlorinating systems using a polylactate ester that releases lactic acid.

Modeling the effect of bacterial concentration as a catalyst with the order determined by the data appears to provide a reasonable understanding of the experimental data.

***Field Study—Single Well Application***

The effects of HRC-containing canisters in a single well were studied at a site in Florida. Eleven, 4' long and 4" wide canisters with small holes, each containing about 25 pounds of sorbitol polylactate ester (SPL) hard gel, were placed in a five-inch monitoring well containing moderate concentrations of TCE, cis-1,2-DCE, and VC. The contaminant plume, contained in a fine- to medium-grained sand aquifer, measured 120 feet in length by 60 feet in width. Due to a flat gradient, groundwater velocity is estimated to be less than 0.1 foot per day. Reductions in contaminant concentrations in the well are presented in Figure 5. Following three months of treatment, reductions in TCE, cis-1,2-DCE, and VC were 96%, 98%, and 99%, respectively. Absence of DO and highly negative redox levels confirmed that a highly reduced environment had been created.

***Field Study—Recirculating Well System***

As a supplementary trial to a USEPA SITE demonstration program, Maureen Dooley and other staff at Harding Lawson Associates tested the efficacy of HRC in remediating CHs in a recirculating well system. In the field cell, groundwater is extracted from the three downgradient wells and injected into the three wells 17 feet upgradient. Five, 2-inch PVC monitoring wells are positioned between the injection and extraction wells. Three, 4' long and 4" wide canisters with small holes, each containing about 25 pounds of sorbitol polylactate ester (SPL) hard gel, were placed into each of the three injection wells. The canisters were exposed to a vertical flow rate of .25 gal/min for 250 days, at which time the pump was shut down; about 20% of the HRC was still present and left in place.

Results through day 206 indicate significant reductions in the concentration of all cVOCs. TCE concentrations at the beginning of the study averaged 9,900 ug/L and were reduced to <10 ug/L in less than seven months. Initial PCE concentrations of approximately 740 ug/L were reduced to <1 ug/L. Average DCE levels of 2,500 ug/L decreased to <100 ug/L. Vinyl chloride levels rose from an average of 250 ug/L to 3,000 ug/L (a strong indication of enhanced biological reductive activity) and then decreased to <100 ug/L. Total mass reduction was calculated to be 97% based on the average concentration of cVOCs in the treatment cell. After 50 days upon HRC application, redox levels dropped from +100mv to less than -50mv across the entire cell. Redox levels were maintained within a range of -150 to -50mv over the remaining duration of the study. Data collected two months following shutdown of the recirculation pump at day 310 showed that there was only a limited rebound in the concentration of cVOCs within the treatment cell. Changes in cVOC concentrations at well EPA-2, which is in the center of the test cell between the injection and extraction wells, through day 310 of the study are graphically presented in Figure 6.

Based on these results, Harding Lawson Associates concluded the following: 1) complete biodegradation of PCE, TCE, and daughter products was demonstrated; 2) DCE and VC biodegradation rates were rapid under HRC-enhanced anaerobic conditions; 3) sulfate-reducing and iron-reducing conditions appeared to be the predominant microbiological conditions across the treatment cell; 4) enhanced biodegradation was observed 17 feet downgradient of the injection points indicating HRC affected conditions beyond the area immediately surrounding the injection well; and 5) there was little rebound observed within the treatment cell after the recirculating system was shut down, suggesting significant reduction of residual cVOCs.

***Field Study—Full-Scale Injection TCE Remediation in New York***

A site in New York was contaminated with TCE at concentrations reaching 26,000 ppb in a clay aquifer; depth to groundwater was about five feet bgs. Under the management of Susan Boyle and staff at Haley and Aldrich, approximately 500 pounds of glycerol polylactate ester (GPL) HRC were injected into borings spaced five feet on center in a 560-square-foot grid. Following 166 days of treatment with HRC, total TCE mass was reduced by 66%. Initial increases in cis-1,2-DCE and vinyl chloride mass, in addition to an overall 69% reduction in sulfate mass, a 292% increase in dissolved iron, and the appearance of ethene, support the occurrence of enhanced biological reductive dechlorination of TCE. TCE, cis-1,2-DCE, and VC overall mass changes are presented in Figure 7. The cost of the HRC and its injection was $10,500 for this relatively tight spacing.

***Field Study—Full-Scale Injection PCE Remediation in Orlando, Florida***

A commercial dry cleaning facility released PCE into groundwater underlying a shopping center complex. PCE and TCE concentrations ranged from 4 - 8,784 ug/L within the target aquifer. The target "surface" aquifer is composed of silty-clayey fine-grained sand and clay and is divided into an upper and lower zone by a clay unit. The upper aquifer section is approximately 12-30 feet below ground surface (bgs) and the lower aquifer section is 35-45 feet bgs. Groundwater flow direction is to the northeast at a velocity of 0.04 foot per day. Under the management of Duane Graves, Mike Lodato, and staff at IT Corporation, approximately 6,810 pounds of the GPL-HRC were injected into a 14,600-square-foot area via 145 direct-push points spaced 10 feet on center. Concentration contour plots depicting changes in PCE, TCE, and cis-1,2-DCE following 43 days of treatment with HRC are presented in Figure 8. Data indicates overall reductions in PCE, TCE, and cis-1,2-DCE mass of 98%, 77%, and 54%, respectively. The cost of the HRC and its injection was $60,400 for this more common spacing.

***Field Study—Full-Scale Injection PCE Remediation in Hurlburt Field, Florida***

At a major military base in the Southeast, PCE and TCE were released over a long period of time. These releases were the result of fueling and maintenance operations at the facility's POL fuel yard and contaminated the aquifer underlying the facility. Within the target "intermediate" aquifer,

the releases resulted in a co-mingled plume of PCE, TCE, DCE, and VC. Concentrations of these constituents range up to 500-600ug/L. The intermediate aquifer extends from 40-50 feet below ground surface and consists of layers of sand, silty sand, and clay lenses. Groundwater flow direction is to the south-southwest at an estimated velocity of approximately 0.35 foot per day. Under the management of Will Harms and staff at URS Greiner, approximately 6,000 pounds of the GPL-HRC were injected into the contaminated saturated zone via 25 direct-push points spaced 5 feet on center within a 500-square-foot area.

Changes in PCE, TCE, cis-1,2-DCE, and VC masses following 55 days of treatment with HRC are graphically presented in Figure 9. A slight increase in PCE is an important indicator of a continual PCE source on the site. In support of the effectiveness of HRC, overall TCE mass was reduced by 72% despite the continual PCE source. TCE biodegradation daughter products cis-1,2-DCE, VC, and ethene masses increased by 227%, 1,957%, and 343%, respectively, further supporting the effectiveness of HRC in enhancing biodegradation of PCE and TCE on the site. Treatment and monitoring are ongoing. The cost of the HRC and its injection was $42,000 for this relatively tight spacing.

***Field Study—Full-Scale Injection TCE Remediation in New Jersey***

An East Coast manufacturing facility released TCE into the groundwater underlying the facility. TCE and degradation daughter product concentrations ranged from 140 to 6,200 ug/L within the medium-coarse-grained sandy aquifer. HRC was applied within an interval extending from approximately 5 to 20 feet below ground surface. Groundwater flow direction is to the north-northeast at a velocity of approximately one foot per day. Approximately 500 pounds of HRC were applied via 15 direct-push points in a barrier array. Spacing between barrier points was 5 feet on center.

Overall PCE, TCE, and cis-1,2-DCE mass changes following 128 days of treatment with HRC are presented in Figure 10. PCE, TCE, and cis-1,2-DCE masses were reduced by 41%, 53%, and 67%, respectively.

***Field Study-–The Original Pilot-Scale Injection for PCE Remediation in Wisconsin***

At a dry cleaner site in Wisconsin, Jack Sheldon and staff at Montgomery Watson, performed the first HRC injection study. The site was contaminated with high levels of PCE and 240 pounds of GPL-HRC were injected at 12 delivery points in a 60-square-foot area as depicted in Figure 11. The groundwater velocity was on the order of .1 ft./per day.

Approximately eight months following the installation of HRC, PCE mass was reduced 126 grams, representing a reduction of 80%. PCE degradation rates in the HRC-injected zone were 11.5 times faster than background rates at day 70 and 4.9 times faster at day 120. These rates are conservative as they compare the change in activity at the well most proximal to the HRC injection (MW8) to the well most distal (MW1). The rates would be at least an order of magnitude higher if MW 8 were compared to various natural attenuation rates across the site – rather than MW1 that

may have been influenced by hydrogen.

Concurrent increases in PCE-degradation daughter products, TCE, DCE, and VC, were also documented as was further sequential degradation through some of the daughter products themselves at different times. These total changes in mass over time for all the CAHs are presented in Figure 12. Concentration contour plots showing changes PCE, TCE, and DCE at days 0, 120, and 253 are presented in Figure 13. The continued effects of a single cost-effective application of HRC are demonstrated to be present for at least 253 days. This study had a higher cost due to its research nature; however, the cost of HRC and injection was only $4,400 in this limited area with tight spacing.

Although not shown, there were mass balances between parent and daughter products of between 27% and 46%, an important indicator that the HRC injections facilitated contaminant removal by biodegradation. There were several other indicators that the proper conditions for facilitating reductive dechlorination were established, including: highly negative redox levels, significant reductions in sulfate and nitrate, increased dissolved hydrogen levels, and a substantial increase in total plate counts for anaerobic bacteria. Note that the dissolved hydrogen levels as presented at Day 149 (Figure 11) are in the 2-10 nM range that is considered by some to be optimal for reductive dechlorination at the expense of methanogenesis.

## CONCLUSIONS

Hydrogen Release Compound (HRC™) has been demonstrated to be a simple, passive, low-cost, and long-term option for the anaerobic bioremediation of chlorinated hydrocarbons (CHs) via reductive dehalogenation. HRC should be viewed as a tool for the enhancement of natural attenuation at sites that would otherwise require high levels of capital investment and operating expense.

HRC is best utilized for the remediation of dissolved-phase plumes and the associated hydrophobically sorbed contaminant. The use of HRC is contraindicated for free-phase DNAPL unless the total mass to be remediated is within the scope of economic feasibility in comparison to alternative treatments. Results of ongoing and future research as well as the results of commercial applications, where permission is granted, can be accessed on the Web at www.regenesis.com.

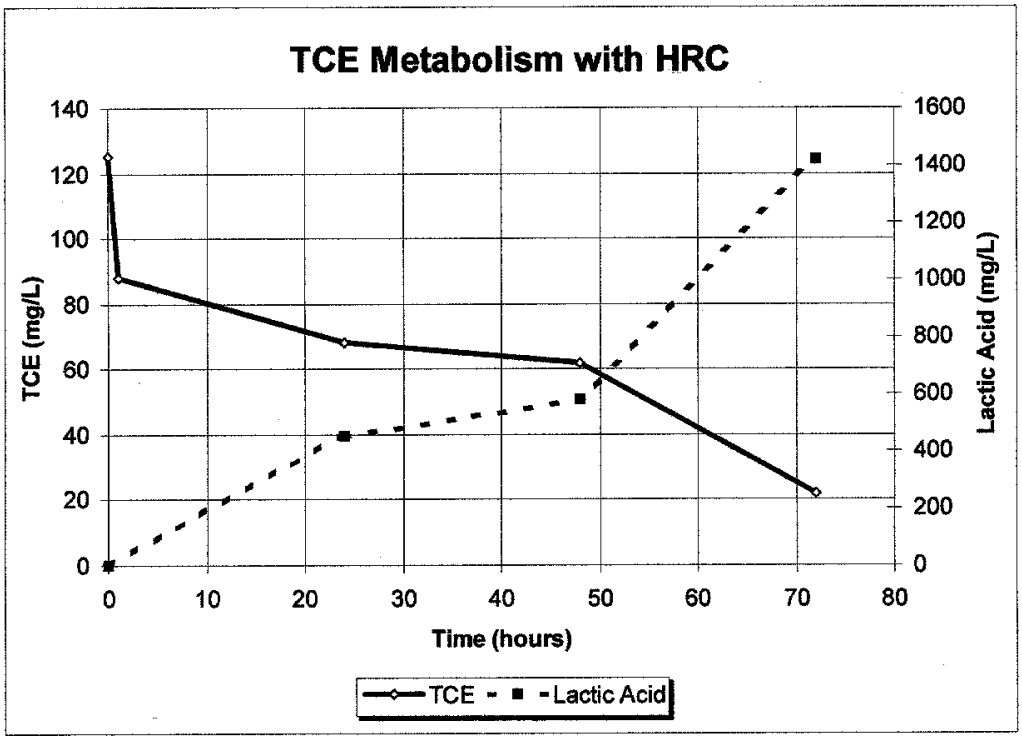


**FIGURE 1.** HRC microcosm study results comparing rate of release of lactic acid from HRC to rate of TCE degradation.

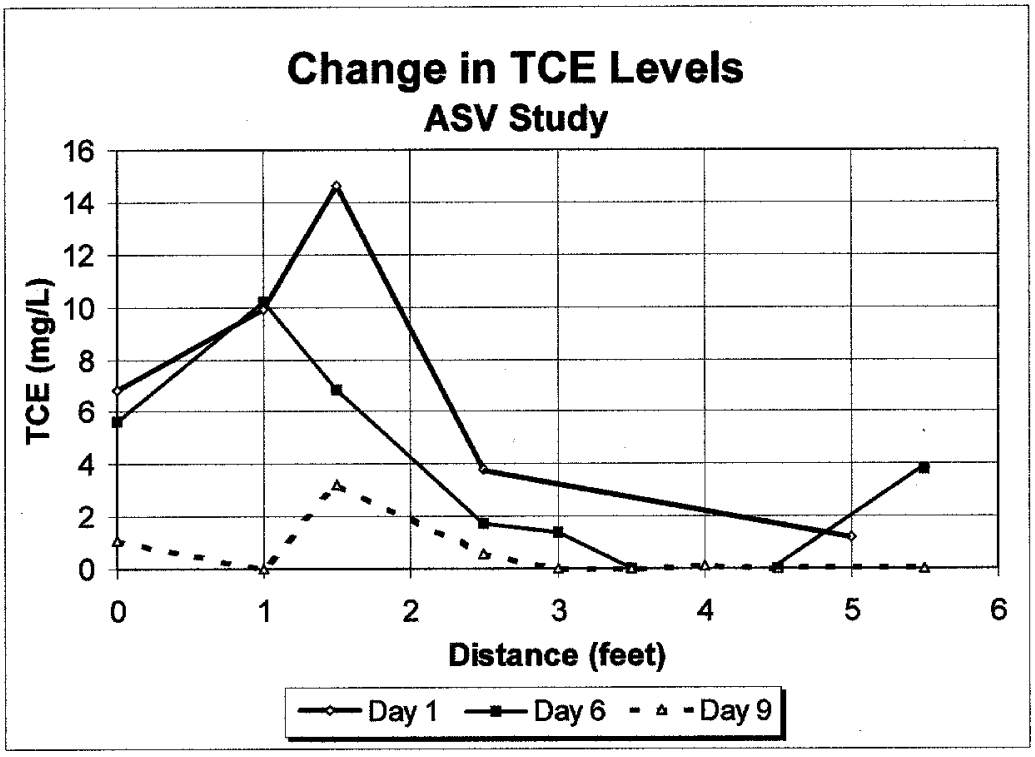


**FIGURE 2.** Aquifer Simulation Vessel (ASV) TCE degradation study.

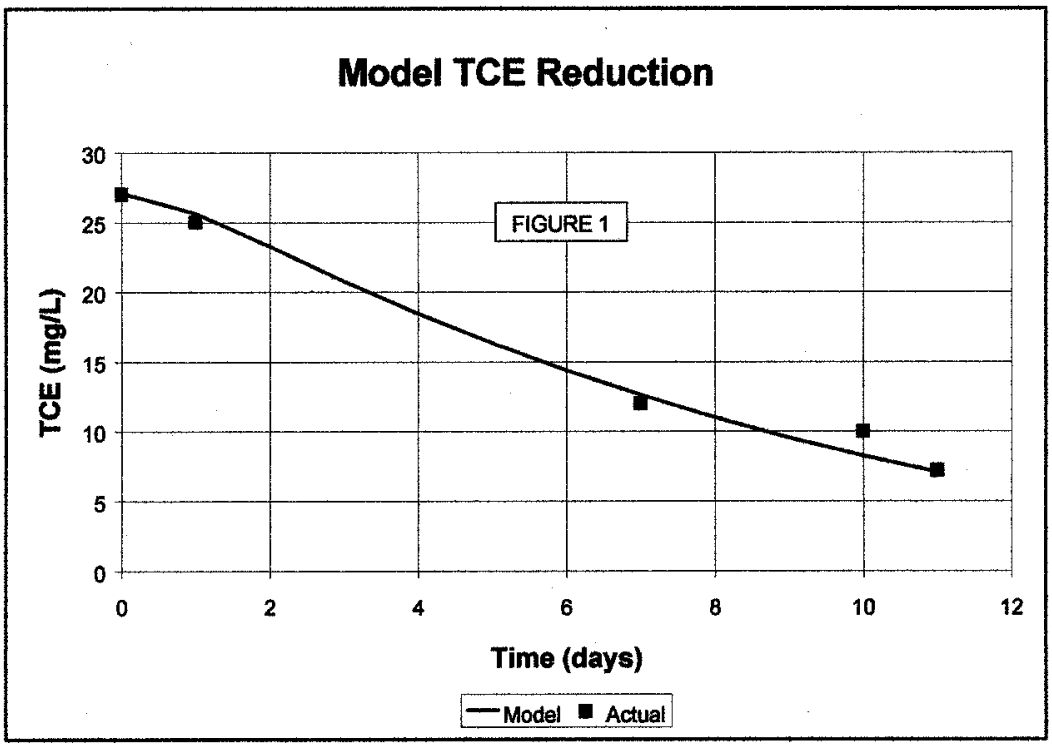


**FIGURE 3.** Results of TCE reduction model vs. experiment.

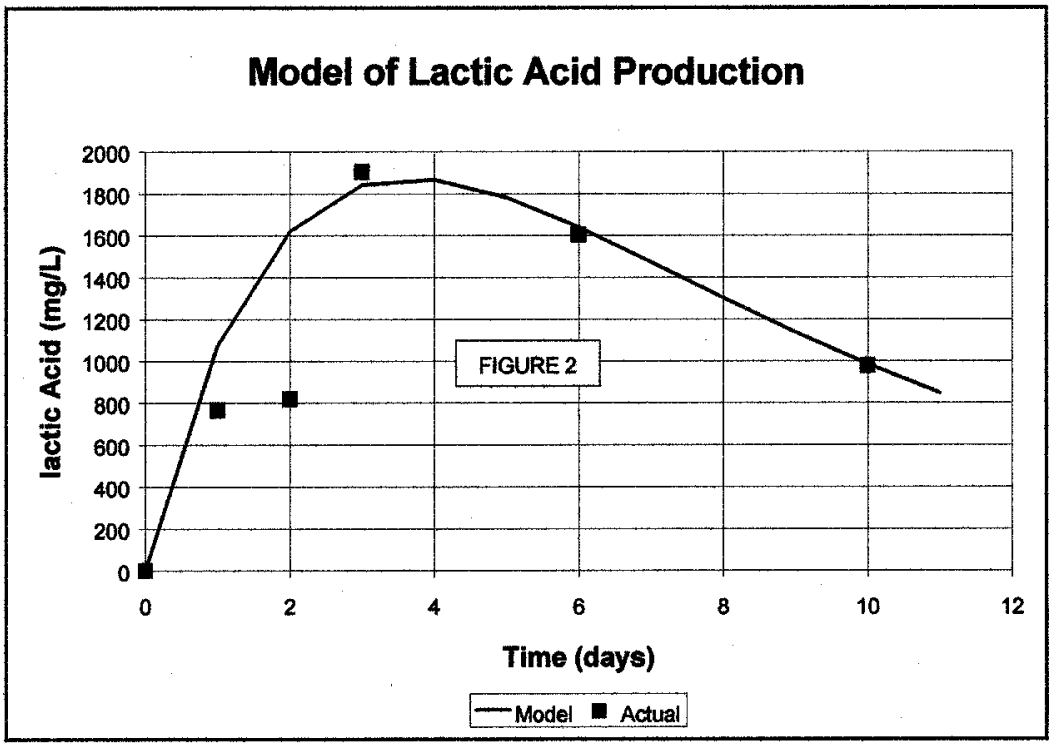


**FIGURE 4.** Results of lactic acid production model vs. experiment.

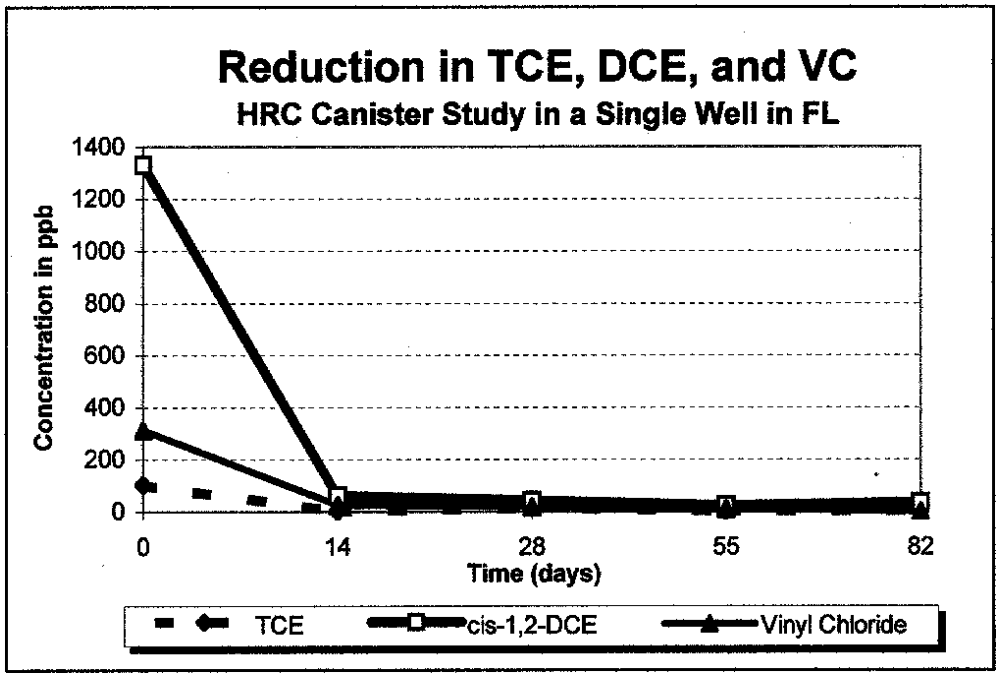


**FIGURE 5.** HRC single-well study in FL -Reduction of TCE, DCE and VC.

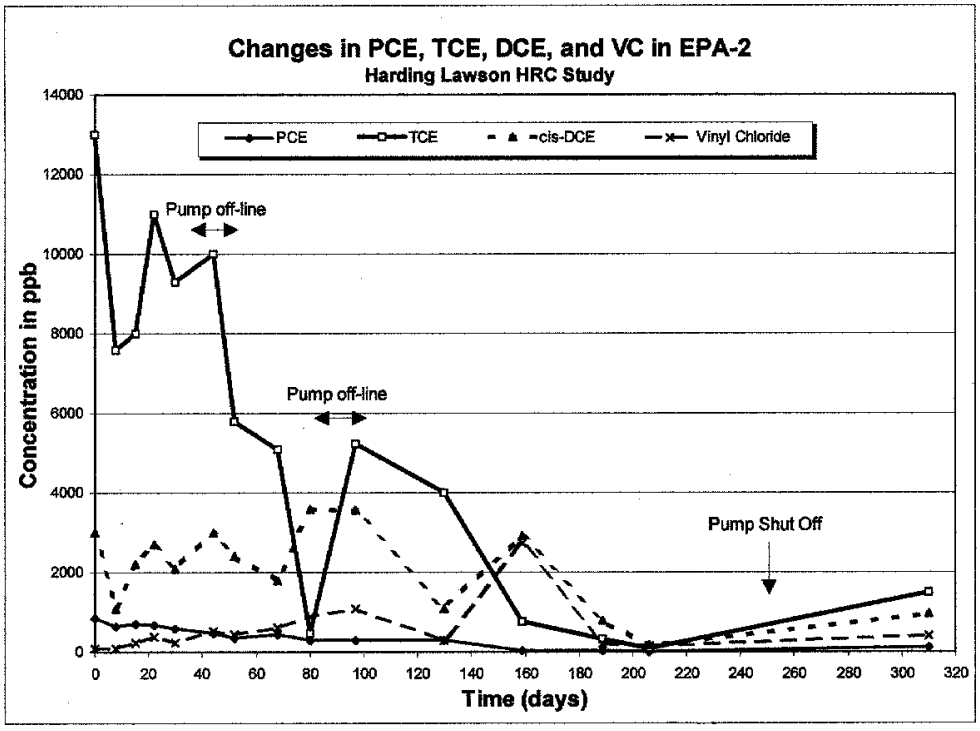


**FIGURE 6.** Recirculating well system study with HLA—changes in PCE, TCE, DCE and VC over 310 days of treatment with HRC.

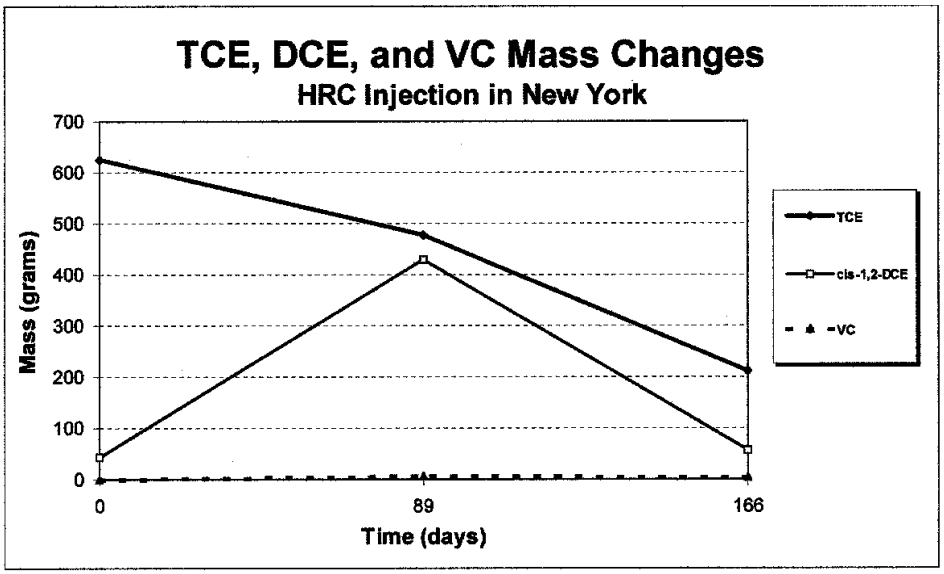


**FIGURE 7.** Full-scale injection TCE remediation in New York results.

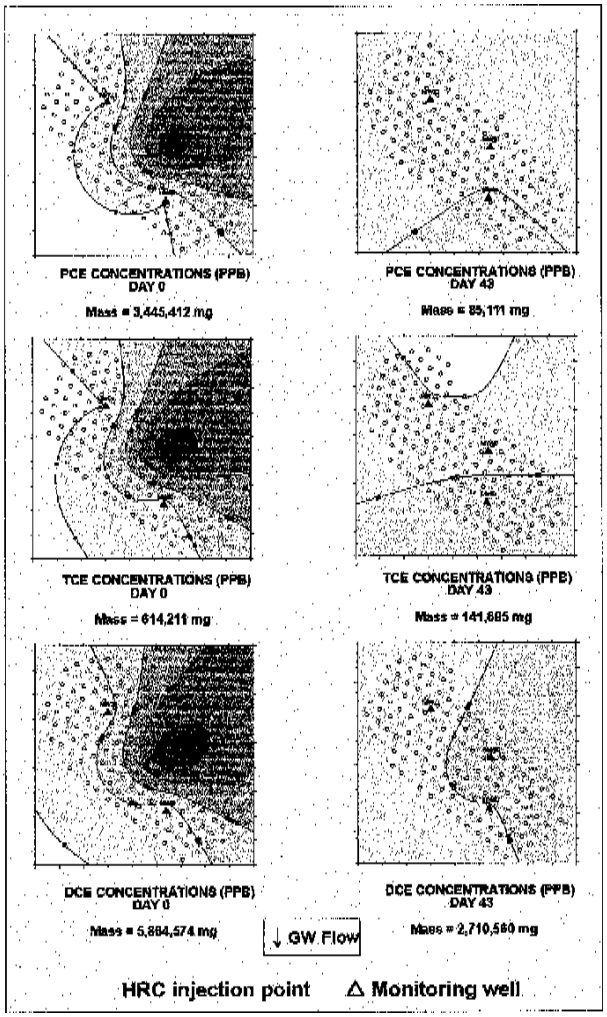


**Figure 8.** Full-scale injection in Florida, changes in PCE, TCE and cis-1,2-DCE.

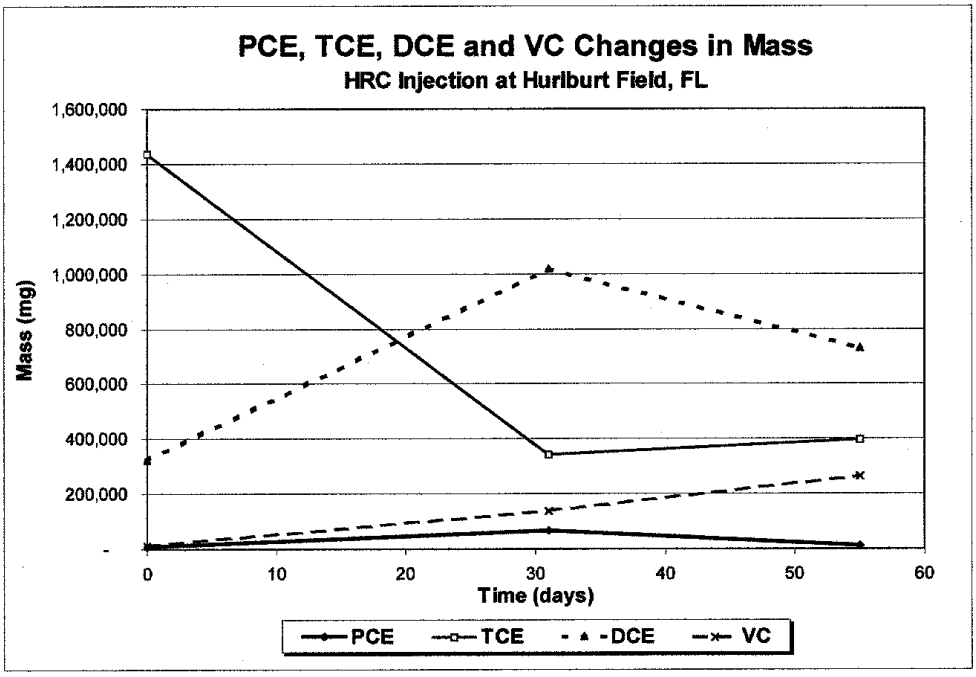


**Figure 9**. Change in PCE, TCE, cis-1,2-DCE, and VC at Hurlburt Field, Florida.

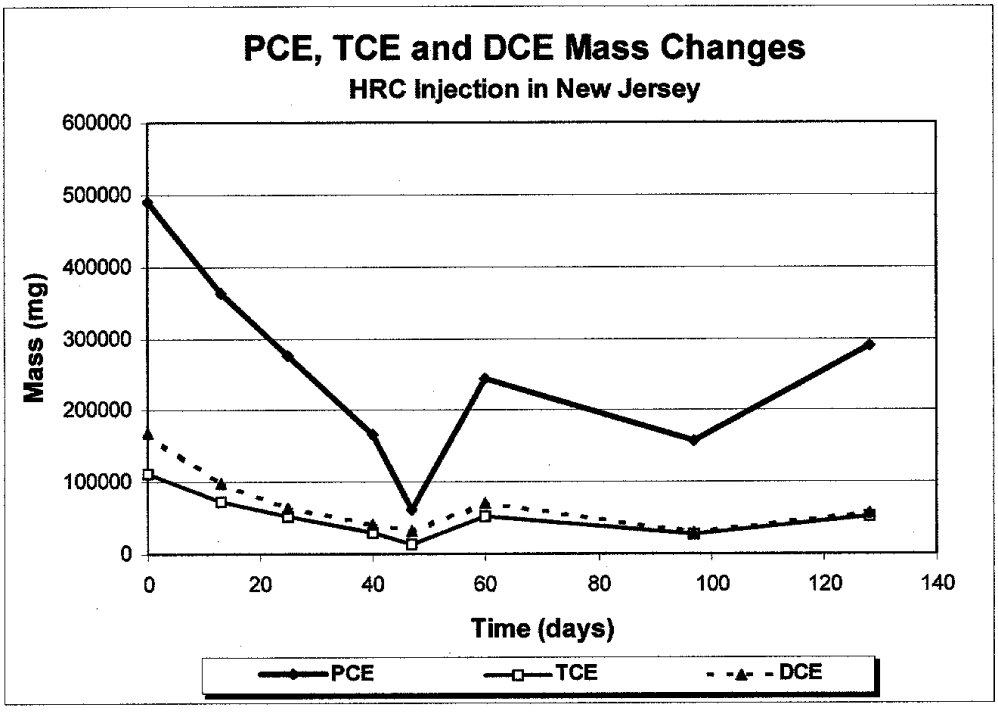


**Figure 10.** Change in PCE, TCE, and cis-1,2-DCE at New Jersey.

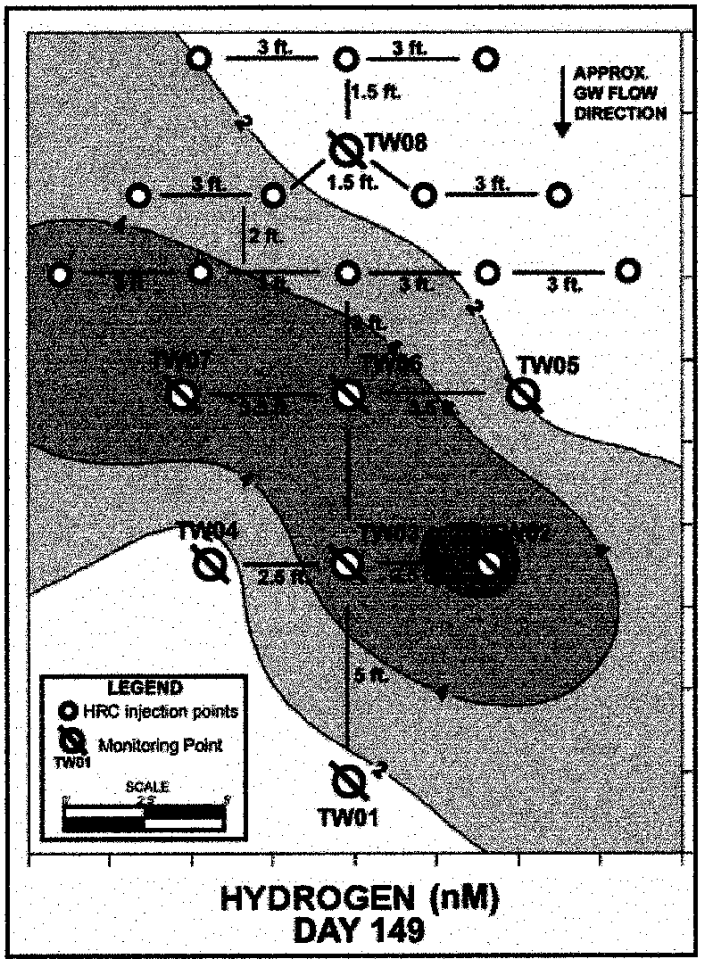


**FIGURE 11.** HRC injection diagram with hydrogen concentration at day 149.

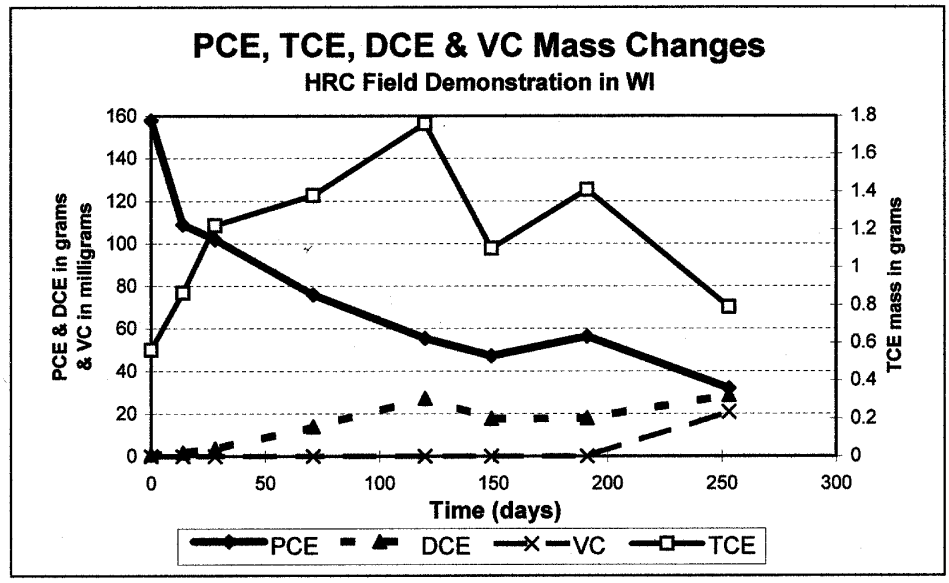


**FIGURE 12.** Field demonstration with Montgomery Watson results.

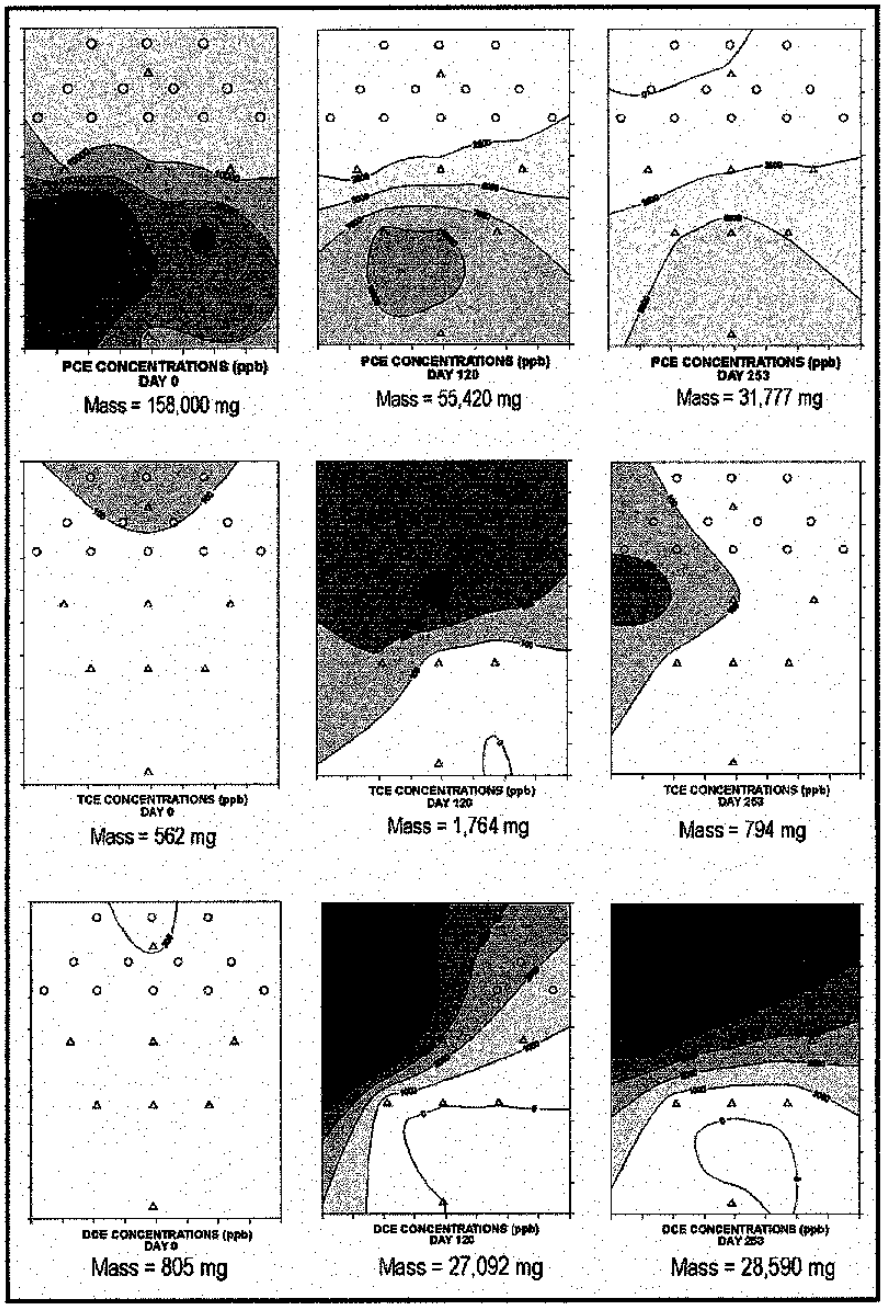


**FIGURE 13.** PCE, TCE, and cis-1,2-DCE concentration contour maps at days 0, 120, and 253.