



# **Evaluation of the Protocol for Natural Attenuation of Chlorinated Solvents: Case Study at the Twin Cities Army Ammunition Plant**

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## Notice

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## Foreword

The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, EPA's research program is providing data and technical support for solving environmental problems today and building a science knowledge base necessary to manage our ecological resources wisely, understand how pollutants affect our health, and prevent or reduce environmental risks in the future.

The National Risk Management Research Laboratory is the Agency's center for investigation of technological and management approaches for preventing and reducing risks from pollution that threatens human health and the environment. The focus of the Laboratory's research program is on methods and their cost-effectiveness for prevention and control of pollution to air, land, water, and subsurface resources; protection of water quality in public water systems; remediation of contaminated sites, sediments and ground water; prevention and control of indoor air pollution; and restoration of ecosystems. NRMRL collaborates with both public and private sector partners to foster technologies that reduce the cost of compliance and to anticipate emerging problems. NRMRL's research provides solutions to environmental problems by: developing and promoting technologies that protect and improve the environment; advancing scientific and engineering information to support regulatory and policy decisions; and providing the technical support and information transfer to ensure implementation of environmental regulations and strategies at the national, state, and community levels.

The *Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water*, EPA/600/R-98/128, was developed from experiences with relatively small plumes in unconsolidated aquifers. Many EPA enforcement actions involve large plumes in fractured bed rock aquifers. This report is an evaluation of the performance of the *Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water* on a very large plume of chlorinated solvents in a landscape where much of the plume is contained in fractured consolidated rock. This report identifies the successes and some of the shortcomings of the *Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water* when it was applied to a large plume in a fractured consolidated rock aquifer.

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## Abstract

At the request of staff in the EPA Regions, EPA's Office of Research and Development carried out an independent evaluation of the *Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water* (EPA/600/R-98/128). The Protocol was developed around case studies on relatively small plumes in sand aquifers. Staff in the Regions wished to know if the Protocol could be usefully applied to large plumes, or to plumes in aquifers in fractured consolidated rock.

Disposal of waste solvents containing trichloroethylene and 1,1,1-trichloroethane at the Twin Cities Army Ammunition Plant (TCAAP) in Minnesota resulted in the formation of a ground-water contaminant plume over five miles long. As part of the remedial response, the U.S. Army installed an extensive pump-and-treat containment system around the source areas intended to prevent additional loading of contaminants to the downgradient portion of the aquifer.

The site was selected for an independent evaluation of the Protocol for two reasons. First, the ground-water plume was very well characterized and an extensive historical sampling database was available to complement the study. Second, although long-term monitoring indicated that the concentrations of trichloroethylene and 1,1,1-trichloroethane attenuated with distance from the source, natural attenuation did not contain the ground water plume within the site boundary. Thus, the evaluation could determine if an analysis done according to the Protocol would predict a large ground-water plume under existing site conditions.

The results show that the Protocol was successful in predicting the development of the ground-water plume at TCAAP. The screening analysis in the Protocol predicts that the geochemical environment at TCAAP is not favorable to rapid reductive dechlorination. The modeling portion of the study indicated that the current ground-water plume should be expected when the rate of reductive dechlorination is slow.

The study also shows that natural biodegradation complements the on-going efforts to extract contaminated ground water at the source, and should greatly reduce the time required to reduce the concentration of contaminants to U.S. EPA drinking water standards. If the rate of natural biodegradation exhibited in the last ten years continues for the next twenty years, the portion of the aquifer downgradient from TCAAP will be reclaimed.

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## SI Conversion Factors

	Multiply	English (US) Units	by	Factor	to get	Metric (SI) Units
Area:		1 ft <sup>2</sup>		0.0929		m <sup>2</sup>
		1 in <sup>2</sup>		6.452		cm <sup>2</sup>
Flow rate:		1 gal/min		6.31 x 10 <sup>-5</sup>		m <sup>3</sup> /s
		1 gal/min		0.0631		L/s
		1 MGD		43.81		L/s
Length:		1 ft		0.3048		m
		1 in		2.54		cm
Mass:		1 lb		453.59		g
		1 lb		0.45359		kg
Volume:		1 ft <sup>3</sup>		28.316		L
		1 ft <sup>3</sup>		0.028317		m <sup>3</sup>
		1 gal		3.785		L
		1 gal		0.003785		m <sup>3</sup>
Temperature:		°F - 32		0.55556		°C
Concentration:		1 gr/ft <sup>3</sup>		2.2884		g/m <sup>3</sup>
		1 gr/gal		0.0171		g/L
		1 lb/ft <sup>3</sup>		16.03		g/L
Pressure:		1 lb/in <sup>2</sup>		0.07031		kg/cm <sup>2</sup>
		1 lb/in <sup>2</sup>		6894.8		Newton/m <sup>2</sup>
Heating value:		Btu/lb		2326		Joules/kg
		Btu/scf		37260		Joules/scm



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## Background and Goals of the Study

At the request of staff in the EPA Regions, EPA's Office of Research and Development carried out an independent evaluation of the *Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water*, EPA/600/R-98/128 (the Protocol). The Protocol was developed around case studies on relatively small plumes in sand aquifers. Staff in the Regions wished to know if the Protocol could be usefully applied to large plumes, or to plumes in aquifers in fractured consolidated rock.

The U.S. Army, their contractors, and their former contractors at the Twin Cities Army Ammunition Plant (TCAAP) are carrying out a pump-and-treat remedy for ground water contaminated with chlorinated solvents. The ground-water plume at the TCAAP site is over five miles long, and much of the plume is in fractured dolomite and fractured sandstone. The plume was recommended to the Office of Research and Development as a site to conduct a test on the procedures outlined in the Protocol.

A primary purpose of this study was to determine whether the Protocol would accurately predict the behavior of a large plume where natural attenuation is not appropriate as the sole remedy. The ground-water plume at the TCAAP site is well characterized. This offered the opportunity to use the Protocol to predict the effect of natural attenuation on the ground-water plume and compare those predictions with the actual site data.

The second goal was to evaluate the effect of natural attenuation on the time required to restore ground water through the combination of active pumping and natural attenuation. The Protocol was used to evaluate the contribution of biological reductive dechlorination and natural abiotic transformation reactions to the natural attenuation of chlorinated solvents in the ground-water plume at TCAAP. The time required to restore the aquifer through pumping alone was compared to the time expected with a combination of pumping and natural attenuation.

The Protocol is organized around three lines of evidence as identified in the OSWER Directive on Monitored Natural Attenuation (U.S. EPA, 1997). The lines of evidence are (1) historical ground-water data that demonstrate a clear and meaningful trend of decreasing mass or concentration over time; (2) hydrogeologic and geochemical data that can be used to demonstrate indirectly the type(s) of natural attenuation processes active at the site, and the rate at which such processes will reduce contaminant concentrations to required levels; and (3) data from field or microcosm studies which demonstrate the occurrence of a particular natural attenuation process at the site and its ability to degrade the contaminants of concern.

At the TCAAP, the concentrations of trichloroethylene and 1,1,1-trichloroethane at most monitoring wells that are downgradient of the source area have decreased by at least a factor of ten since monitoring began in 1988. A major contribution to the reduction in the size of the plume and concentration of contaminants is the benefit of a pump-and-treat system that has been in operation since 1988. In this evaluation, the first line of evidence was provided by

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comparing the disposition of the plume of trichloroethylene before pumping began in 1988 to the disposition that would be expected if there were no natural biodegradation.

The initial step for natural biodegradation of trichloroethylene was presumed to be reductive dechlorination. To evaluate the second line of evidence for trichloroethylene, the geochemistry of the ground water at the site was surveyed and compared to the geochemistry that is known to be associated with reductive dechlorination. The rate of natural biodegradation of trichloroethylene was estimated by calibrating models to fit the distribution of contamination in the aquifer before pump-and-treat began in 1988. The second line of evidence for natural attenuation of 1,1,1-trichloroethane was evaluated by comparing the observed distribution of 1,1,1-trichloroethane to the distribution that would be produced by the expected rates on abiotic reactions.

To evaluate a third line of evidence for trichloroethylene, the concentration of hydrogen in ground water was determined and compared to the concentration of hydrogen that is known to support reductive dechlorination.

This Technical Brief is not intended to present a full application of the Technical Protocol sufficient for remedy decision-making. At the TCAAP, that decision was already made and the remedies are in place. The remedy for ground-water contamination on the TCAAP is pump-and-treat. This system is designed to extract the contaminant mass and exhaust the plume on the facility. The pumping system has been in continuous operation since 1988. The remedy for contamination in the aquifer downgradient of TCAAP is also pump-and-treat. This system is designed to extract water for water supply.

This Technical Brief does not present information on the identification of receptors, the risk analysis, a discussion of the cleanup goals, or other information that would be required by decision-making authorities to select natural attenuation as a remedy. It focuses on the contribution of natural attenuation to the cleanup of contamination in ground water after the source of contamination has been controlled by an active remedy. It applies those sections of the Protocol that are used to extract rate constants from field data to estimate a rate of natural biodegradation. It then uses those extracted rate constants to forecast the future behavior of the plume of contamination in ground water after source control has been achieved.

At the TCAAP, most of the plume is deep below the water table. Volatilization is not expected to reduce the concentrations of contaminants. The plume has reached its maximum extent, and has started to recede. Sorption is not expected to reduce concentrations. The distribution of chlorinated solvents in the plume is controlled by those processes that degrade or dilute the contaminants.

Under these conditions, an apparent reduction in the concentration of a contaminant as ground water moves downgradient can be caused by at least three phenomena. First, the downgradient concentrations may be lower simply because the contaminant plume has not broken through at that location. Second, the downgradient concentration may be lower as a result of dilution and dispersion along the flow path. Third, the reduction in concentration may be due to biodegradation or abiotic transformation of the contaminant along the flow path.

A major goal was to determine which combination of phenomena best accounted for the observed reductions in contaminant concentrations downgradient. This was done by calibrating two mathematical models, BIOSCREEN and BIOPLUME III, to the site. BIOSCREEN and

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BIOPLUME III were developed to facilitate the modeling of natural attenuation. Both models can be downloaded from the Subsurface Protection and Remediation Division's web site (<http://www.epa.gov/ada/csmos.html>). BIOCREEN is a simple and easy to use model designed to evaluate data collected along a plume centerline. It is essentially a one-dimensional model. It allows estimates of advection, dispersion, sorption, and biodegradation. BIOPLUME III is a two-dimensional model that is better suited to forecasting the future behavior of plumes. It allows separate calibration of the rate of attenuation of the source of contamination, and the rate of attenuation of contamination along the flow path.

Projections of the models based on sorption, dilution and dispersion alone, as well as projections including natural transformations, were compared with the observed concentrations of trichloroethylene along the flow path. Mathematical modeling indicated that sufficient time has passed for the leading edge of the plume to complete the entire flow path from TCAAP to the ultimate receptor of ground-water flow, the Mississippi River. The modeling also indicated that simple dilution and dispersion alone could not account for the existing distribution of trichloroethylene. The actual concentrations were much lower than would be expected, indicating that some process was actively removing the trichloroethylene.

The attenuation of trichloroethylene and 1,1,1-trichloroethane in ground water is often a result of biological transformations carried out under anaerobic conditions in the aquifer. The most important biological process that is capable of transforming trichloroethylene and 1,1,1-trichloroethane is reductive dechlorination. In addition to reductive dechlorination, 1,1,1-trichloroethane undergoes an elimination reaction to form 1,1-dichloroethylene and a hydrolysis reaction to form acetate (McCarty, 1996; Vogel and McCarty, 1987; Vogel et al., 1987; Klecka et al., 1990). The rate of this abiotic reaction is equivalent to the rate of biodegradation.

During reductive dechlorination a chlorine atom in the molecule is replaced with a hydrogen atom. The chlorine atom is released to the environment as a chloride ion. Trichloroethylene is reduced to dichloroethylene (primarily cis-dichloroethylene), which can be further reduced to vinyl chloride, which in turn can be reduced to ethene and ethane (Barrio-Lage et al., 1990; Vogel and McCarty, 1985). Similarly, 1,1,1-trichloroethane is reduced to 1,1-dichloroethane and then to chloroethane. The reduced organic carbon in the dechlorination sequence is conserved. The sum of the molar concentrations of trichloroethylene, the dichloroethylenes, vinyl chloride, ethylene, and ethane does not change as one chemical is dechlorinated to form another.

The plume of trichloroethylene and 1,1,1-trichloroethane has reached its maximum extent and maximum concentrations; sorption should not act to remove contaminant mass. The plume is deep below the water table; volatilization should not be an important removal mechanism. As a consequence, it is reasonable to assume that the difference in concentration between an upgradient and downgradient location is the missing mass that has been destroyed by biodegradation or abiotic reactions. The measured concentration of transformation products in water can be used to calculate the concentration of trichloroethylene or 1,1,1-trichloroethane that must be degraded through reductive dechlorination or removed through abiotic reactions to produce that concentration of transformation products.

There is very little vinyl chloride, ethylene, or ethane in ground water at TCAAP. The amount of trichloroethylene or 1,1,1-trichloroethane that would be destroyed to produce the observed concentration of daughter products is a small fraction of the missing trichloroethylene or

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1,1,1-trichloroethane. If vinyl chloride is formed, it does not accumulate, and it is not further reduced to ethylene and ethane.

The fact that the daughter products of degradation are not present does not necessarily preclude reductive dechlorination. It may be that the rate of degradation of daughter products may be rapid compared to that of the parent compound. It is also possible that the missing trichloroethylene in the plume at TCAAP was initially transformed to cis-dichloroethylene through reductive dechlorination, and that the cis-dichloroethylene was further degraded. In recent years it has been established that bacteria in aquifers can degrade cis-dichloroethylene to carbon dioxide using Iron III, Manganese IV or oxygen as the electron acceptor (Bradley and Chapelle, 1997; Bradley et al., 1998a, 1998b; Klier et al., 1999). They can also degrade any vinyl chloride that might be formed using Iron III, Manganese IV, or oxygen (Bradley and Chapelle, 1996, 1997; Davis and Carpenter, 1990; Hartmans and de Bont, 1992). This would explain why the accumulation of reduced transformation products did not account for the missing trichloroethylene. If this is the situation, then conditions in the ground water at TCAAP must be favorable for reductive dechlorination of trichloroethylene to cis-dichloroethylene. The most direct indicator of conditions favorable for reductive dechlorination of trichloroethylene is the presence of hydrogen in the ground water at concentrations greater than 1 nanomolar (U.S. EPA, 1998).

It is also possible that reductive dechlorination in ground water at TCAAP was weak, and only a minor fraction of the trichloroethylene was transformed to cis-dichloroethylene, which then accumulated only to a limited extent. Under this pattern, conditions would not favor the further reduction of cis-dichloroethylene. Vinyl chloride would never form in the first place. In this situation the apparent attenuation in concentration of the trichloroethylene and 1,1,1-trichloroethane would be caused by sampling monitoring wells that are askew of the centerline of the plume of contamination, or miss the proper depth interval of the plume.

The first pattern that can explain the data is extensive biological degradation of the parent compounds with a combination of reductive dechlorination and anaerobic oxidation of intermediate compounds. The second pattern is limited biological degradation of the parent compounds with minor production of first intermediates, which accumulate. A major goal of this study was to determine which of these two possible patterns of biotransformation best explain the behavior of the chlorinated solvents at TCAAP.

## **Geological and Geographical Context**

The Twin Cities Army Ammunition Plant (TCAAP) is located six miles north of the city of St. Paul, Minnesota. Ground-water flow is toward the southwest to the Mississippi River. Figure 1 presents a geological cross section for the area on and just downgradient of TCAAP. The water table aquifer at TCAAP is an unconsolidated sandy aquifer, the Hillside Sand. Below the Hillside Sand is an aquifer in fractured dolomite, the Prairie du Chien Group. Below the Prairie du Chien is an aquifer in fractured sandstone, the Jordan Sandstone. To the southwest and down the hydraulic gradient from TCAAP, the Hillside Sand and the aquifers below it become confined by non-permeable materials of the Twin Cities Formation.

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A variety of wastes containing chlorinated solvents have been disposed at TCAAP. Near TCAAP, the highest concentrations of solvents are in the Hillside Sand, as pictured in Figure 1. As the plume moves farther downgradient, the plume moves into the Prairie du Chien Group (not shown in Figure 1).

A mathematical model (BIOPLUME III) was used to evaluate the role of natural biodegradation of chlorinated solvents in ground water at TCAAP. Figure 2 presents the areas on TCAAP and the neighborhoods downgradient that were included in the grid of the model. Depicted in Figure 2 are TCAAP, Interstate Highway 694, Interstate Highway 35W, and U.S. Highway 10. To provide a reference, the highways are depicted in subsequent figures of the area considered in this study.

Wells from six locations were selected for this study. It is important to point out that using only six monitoring locations to evaluate a plume that is over five miles long and over 1000 feet wide would be unacceptable to select natural attenuation as a remedy in nearly all cases. The distribution of contamination in three dimensions had been determined from data from over 250 monitoring wells in the site characterization phase of the Superfund RI/FS. These locations were selected from wells that were installed during the site characterization phase of the Superfund RI/FS, and from wells that are installed to monitor the progress of the active pump-and-treat system. To describe the background conditions in the aquifer, a well cluster was selected that was upgradient of the known releases of chlorinated solvents. Two well clusters were selected in known "hot spots" of ground-water contamination on the TCAAP. Pump-and-treat wells in the "hot spots" and at the facility boundary were included. All of the available wells that were downgradient of the TCAAP were evaluated. All of these wells that had shown consistently high concentrations of trichloroethene and 1,1,1-trichloroethane during previous sampling were included in the study.

The locations of monitoring wells on TCAAP are depicted in the Panel A of Figure 3. The locations of wells downgradient of TCAAP are depicted in the Panel B of Figure 3. Table 1 lists construction details on the wells sampled in this study. Wells in the study were sampled in June 1996, December 1996, June 1997, November 1997 and June 1998.

Well 03U113, a shallow well that is not impacted by contamination (see top panel of Figure 3), was sampled in June 1997. Well 03L113, a deep well not impacted by contamination, was sampled in November 1996 and June 1997. Well 03L113 is located in a cluster with Well 03U113.

Monitoring Wells 03U020, 03M020, 03L020, and 04U020 are a cluster of wells. Their location is labeled 03U020 in the top panel of Figure 3. These wells were sampled in November 1996, June 1997, November 1997 and June 1998.

Monitoring Wells 03U002, 03M002, 03L002, and 04U002 are also a cluster of wells. Their location is labeled 03U002 in the top panel of Figure 3. These wells were sampled in December 1996, June 1997 and June 1998.

Monitoring Wells 04U821, 191942, and 04U872 were sampled in June 1997, November 1997 and June 1998 (see bottom panel of Figure 3).

Three of the extraction wells were also sampled. Wells 03U314 (also labeled SC-2) and 03U317 (also labeled SC-5) are located at a hot-spot of contamination near the location of Monitoring Wells 03U020 in Figure 3. Well 03F306 is located at the perimeter of TCAAP near the location



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of Well 03U002 in Figure 3. These wells were sampled in November 1997 and June 1998. The relationship between the extraction wells and the monitoring wells is depicted at a larger scale in Figure 10.

## Geochemical Context

Table 2 presents data on the geochemistry of the waters sampled by the monitoring wells in this study. Data are only presented for sampling conducted in June 1998. There was little variation in the geochemical parameters in a particular well from one sampling date to another. The chemical parameters will be evaluated based on the criteria presented in Table 2.3 of the *Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water* (U.S. EPA, 1998).

With the exception of one sampling date in one well, the oxygen concentrations in the three wells downgradient of TCAAP (19142, 04U821, and 04U872) were below 0.5 mg/liter. The oxygen concentrations in the extraction wells and the deeper wells in the monitoring well clusters on TCAAP were also below 0.5 mg/liter (Extraction Wells 03U314, 03U317, and 03F306, and Monitoring Wells 03M020, 03L020, 04U020, 03M002, 03L002, and 04U002). The most shallow monitoring well in the two clusters on TCAAP has oxygen concentrations above the concentration that is tolerated by dechlorinating microorganisms (Wells 03U020 and 03U002). The oxygen concentrations in the background wells followed the same pattern of oxygen concentrations above 0.5 mg/liter near the water table, and less than 0.5 mg/liter deep below the water table. Oxygen was above 0.5 mg/liter in the shallow well and below 0.5 mg/liter in the deeper well (03U113 compared to 03L113). The concentration of oxygen in the plume of chlorinated solvents does not preclude a contribution of reductive dechlorination to natural attenuation.

The concentrations of Iron II are low in all the wells sampled for this study. The highest concentration was 2.0 mg/liter, in Well 04U020, the deepest well in a cluster of wells on TCAAP. Iron II tends to sorb to or chemically react with aquifer solids. The presence of any measurable concentration of Iron II is good evidence for ongoing Iron III reduction. The highest concentrations in the wells downgradient of TCAAP were 0.7 mg/liter in Well 19142 when sampled in June 1998, and 1.0 mg/liter in Wells 04U821 and 04U872 when sampled in June 1997. Many of the concentrations are below the criterion of 1 mg/liter published in Table 2.3 of the Protocol. The concentrations of Iron II in the monitoring wells do not indicate that there is a highly reduced geochemical environment that is generally associated with reductive dechlorination.

The concentrations of manganese in the plume at TCAAP are generally higher than the concentrations of Iron II, indicating that manganese reduction may be more prevalent than iron reduction in this aquifer. Manganese was measured in the field using a HACH™ Company DR 100 field colorimeter and the Periodate Oxidation Method (APHA, 1975). Because Mn IV is insoluble at neutral pH, the measured concentrations of manganese are probably Manganese II.

In a ground water that is buffered by carbonate minerals in the aquifer matrix, an increase in alkalinity may result from carbon dioxide produced by microbial metabolism. There is very little change in the alkalinity of the ground water in the wells sampled for this study. The wells

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downgradient do not meet the criterion of twice background that is published in Table 2.3 of the Protocol. In fact, there is no significant difference in the alkalinity in the contaminated wells and in the background wells. Because the ground water is hard, substantial increases in alkalinity would be necessary to meet the criterion. In any case, changes in alkalinity in ground water from the wells in this study offer no indication that microbial metabolism has produced carbon dioxide.

The concentrations of sulfate in wells from this study are low, and most are below the criterion of 20 mg/liter published in the Protocol. The same situation applies to concentrations of nitrate. High concentrations of nitrate can inhibit reductive dechlorination. However, the concentrations of nitrate in ground water from the wells in this study are low, and most are below the criterion of 1 mg/liter published in the Protocol. High concentrations of nitrate should not inhibit reductive dechlorination at TCAAP.

Methane can be produced by biological processes under conditions that are strongly associated with reductive dechlorination. None of the ground water sampled for this study had methane concentrations that approached the criterion of 0.5 mg/liter published in the Protocol. Concentrations of methane offer no evidence of the anaerobic metabolic activity that might be associated with reductive dechlorination.

As described in the Protocol, chloride should accumulate from reductive dechlorination, sulfide should be produced from sulfate reduction, and dissolved organic materials may act as a substrate that supports biological reductive dechlorination. The concentrations of chloride, sulfide and total organic carbon (TOC) were determined in water from the monitoring wells. Concentrations of chloride varied from 13.3 to 4.5 mg/liter in the background wells and from 14.9 to 30.7 mg/liter in the pump-and-treat wells on the TCAAP. The concentration of chloride in the wells that were downgradient of TCAAP varied from 10.4 to 13.9 mg/liter. There was no clear evidence of accumulation of chloride over background, and the accumulation did not meet the criterion in the Protocol. The concentration of TOC in all the wells was uniformly low. The maximum concentration determined was 3.8 mg/liter. Most analyses fell in the range of 1.9 to 0.8 mg/liter. There was no evidence that TOC was accumulating in the water. Sulfide was never detected at TCAAP at concentrations exceeding the detection limit of 1.0 mg/liter.

In summary, the ground-water geochemistry at the TCAAP is inconclusive in assessing the role of reductive dechlorination.

## **Distribution of Volatile Organic Contaminants**

Reductive dechlorination requires an electron donor to serve as a source of reducing power and metabolic energy to allow the process to proceed. The petroleum-derived aromatic hydrocarbons (benzene, toluene, ethylbenzene, the xylenes, and the trimethylbenzenes) serve as electron donors to support reductive dechlorination in many contaminated ground waters (Sewell and Gibson, 1991; Clarke, 2000). In the water samples collected for this study, the concentrations of BTEX compounds were very low, less than 5 µg/liter in every case. Their total concentration never approached the criterion of 0.1 mg/liter published in the Protocol. The BTEX compounds are not available to support reductive dechlorination at TCAAP.

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Despite the weak indications of reductive dechlorination at TCAAP, cis-dichloroethylene is present in the ground water from Extraction Wells 03U314, 03U317, and 03F306, TCAAP Monitoring Wells 03U020, 03M020, 03M002, and downgradient Monitoring Well 191942. This compound is most likely produced as the reductive transformation product of trichloroethylene. The distribution of trichloroethylene and cis-dichloroethylene with distance downgradient from the source is presented in Figure 4. The concentration of cis-dichloroethylene was a small fraction of the concentration of trichloroethylene. In general, the concentration of cis-dichloroethylene was approximately 1% of the concentration of trichloroethylene.

The transformation product that is present in highest concentration relative to the potential parent compounds is 1,1-dichloroethylene, which is produced through a spontaneous abiotic reaction from 1,1,1-trichloroethane. Relatively high concentrations of 1,1-dichloroethylene are found in the ground water from Extraction Wells 03U314, 03U317, and 03F306, TCAAP Monitoring Wells 03U020, 03M020, 03U002, 03M002, and 03L002, and downgradient Monitoring Wells 191942, 04U821, and 04U827. The distribution of 1,1,1-trichloroethane and 1,1-dichloroethylene with distance downgradient of the source is presented in Figure 5. In general, the concentration of 1,1-dichloroethylene was a factor of two to a factor of ten lower than the concentration of 1,1,1-trichloroethane.

Another major potential reduction product of trichloroethylene is trans-dichloroethylene. The potential reduction product of the dichloroethylenes is vinyl chloride. In all the ground water sampled for this study, the concentration of trans-dichloroethylene and vinyl chloride was less than 5 µg/liter.

A potential biological reduction product present in ground water from TCAAP is 1,1-dichloroethane, produced from the reductive dechlorination of 1,1,1-trichloroethane (Galli and McCarty, 1989). Figure 6 presents the distribution of 1,1,1-trichloroethane and 1,1-dichloroethane with distance downgradient of the source. The concentration of 1,1-dichloroethane in the downgradient water samples is approximately one-half of the concentration of 1,1,1-trichloroethane.

Although the concentration of the parent compounds was reduced by several orders of magnitude, the combined concentrations of their transformation products never equaled the concentration of the original contaminants that remained after natural biodegradation, much less approached the original concentration of the contaminants.

### **Calibration of BIOPLUME III**

Trichloroethylene was the most persistent contaminant in the plume (compare Figures 4, 5, and 6). The modeling of transport and fate of contaminants emphasized trichloroethylene.

The hydrological and geological parameters in the model used to describe transport and fate were not independently selected from a review of available data. Values for hydraulic conductivity, porosity, retardation due to sorption, and the coefficient of dispersion were taken from a previous model developed for the plume as part of the Superfund Remedial Investigation process (Camp Dresser & McKee Inc., 1991). This was done because the model calibrated for the remedial investigation had been reviewed and approved by the appropriate regulatory authority. The model calibrated for the remedial investigation did not account for biotransforma-

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tion of chlorinated solvents. Because the calibration of BIOPLUME III used the same values for hydraulic conductivity, porosity, retardation due to sorption, and the coefficient of dispersion, the differences between the forecasts of the remedial investigation model and the projections of BIOPLUME III reflect the further contribution of biodegradation. Differences in the models were not an incidental result of differences in the calibration of the flow of water.

### **Calibration of Water Flow**

The natural biodegradation of trichloroethylene and its dechlorination products was described with BIOPLUME III, a two-dimensional transport-and-fate model that is designed to facilitate an understanding of natural biodegradation of organic compounds in ground water. BIOPLUME III is available from the Center for Subsurface Modeling Support (CSMoS) a technical support service located at the Subsurface Protection and Remediation Division, National Risk Management Research Laboratory, Office of Research and Development, U.S. EPA. The web address to download BIOPLUME III and to download instructions to install the model is <http://www.epa.gov/ada/models.html>.

There is a potential for error in using a two-dimensional model to simulate three-dimensional fate and transport processes. Because dispersion is restricted in the two-dimensional model to longitudinal and transverse dispersion, the contribution of vertical dispersion to attenuation is ignored. The two-dimensional model does not account for variations in contaminant concentration with depth, thus the two-dimensional model underestimates natural attenuation through dispersion. The model was calibrated assuming that the entire aquifer at a particular location experienced the highest concentration measured at any depth interval at that location, rather than some average of the actual distribution of contaminant concentrations. The two-dimensional model assumes more contamination is present in the aquifer than is truly present.

The use of trichloroethylene and 1,1,1-trichloroethane at TCAAP began after World War II. The BIOPLUME III simulation of the trichloroethylene plume at TCAAP started with year 0 of the simulation in 1950 and ended with year 70 of the simulation in the year 2020. The first parameters used to calibrate BIOPLUME III were the parameters controlling the ground-water flow properties. The initial conditions for hydraulic heads were imposed by tracing interpreted ground-water contours from a map. BIOPLUME III inputs data on water table elevations by importing a map showing isopleths of the elevation of the water table, then tracing the ground-water contours with a computer mouse. The contours on the map used to calibrate BIOPLUME III (Figure 7) were fit using professional judgment, not a contouring software application. On TCAAP, most of the contamination is in the unconsolidated sand aquifer. Based on pumping tests in the Hillside Sand Aquifer, the horizontal hydraulic conductivity along the southwestern edge of TCAAP was set at 200 feet per day. Downgradient of TCAAP the plume enters the fractured consolidated rock aquifers. Based on pumping tests in the Prairie du Chien group, the horizontal hydraulic conductivity farther downgradient in the New Brighton area was set at 380 feet per day.

The distributed values for horizontal hydraulic conductivity are presented in Figure 8. Each red dot on the figure is a log point where an input value for hydraulic conductivity of either 200 feet per day or 380 feet per day was provided to the model, based on professional judgment and maps of the distribution of contamination in the Hillside Sand aquifer and the Prairie du Chien group. Simple kriging was used to distribute an estimated hydraulic conductivity to the other cells in the grid.

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To be consistent with the Remedial Investigation, the coefficient of longitudinal dispersion was set uniformly at 200 feet. The coefficient of transverse dispersion was set at 40 feet. The effective porosity was set at 0.2; this relatively high value reflects the presence of solution channels in the Prairie du Chien group.

The plume of trichloroethylene in ground water was simulated in BIOPLUME III by calibrating an injection well in Cell 5 and in Cell 8 as depicted in Figure 9, injecting at the rate of 5 gpm. This low rate of injection was selected to avoid errors in the simulation of the flow field. The concentration of trichloroethylene in the injection wells was adjusted empirically until the modeled concentrations matched the real distribution of trichloroethylene in 1988. A modeled injected concentration of 2,500,000 µg/liter produced a simulated concentration in the plume of 27,000 µg/liter. The concentration in the injection wells was held constant until 1988. After 1988 the concentration in the injection wells was lowered according to a schedule that reflected actual reductions in concentrations in monitoring wells in the source.

The plume of chlorinated solvents in ground water at TCAAP is presently being captured by a series of extraction wells. Their effect was simulated by assigning a uniform rate of pumping to the cell in the model grid that contained the well. The allocation of pumping wells in the BIOPLUME III model is depicted in Figure 9. The following two paragraphs describe the calibration of the pumping wells in the BIOPLUME III model.

Cells 1 through 8 are on TCAAP. They were modeled as pumping at a uniform constant rate starting in 1988. Wells in Cell 1 were pumped at 500 gpm, wells in Cell 2 at 610 gpm, wells in Cell 3 at 550 gpm, wells in Cell 4 at 510 gpm, wells in Cell 6 at 155 gpm, and wells in Cell 7 at 115 gpm. The total rate of pumping modeled for the TCAAP Ground Water Recovery System (TGRS) system was 2,440 gpm. Cell 9 contained the pumpout system at New Brighton, also labeled OU1. In the model, wells were pumped at Cell 9 at 1,000 gpm starting in 1950 extending to 1996, then at 2,000 gpm extending to the year 2000, then at 2,700 gpm after the year 2000. Cell 10 contained a pumping system for the OU3 remedy. Wells in Cell 10 were modeled at 1,000 gpm starting in 1992.

The relationship between the actual location of the pumping wells and the cells in the model grid for BIOPLUME III is pictured in Figure 10. Data on the gallons pumped for each well since 1989 was divided by ten to estimate gallons per year, then by 525,600 to convert to gpm. The wells in Cell 1 are B-12 pumping at 240 gpm, B-7 pumping at 248 gpm, and B-10 pumping at 210 gpm for a total of 698 gpm. The wells in or just upgradient of Cell 2 are B-6 pumping at 229 gpm, B-9 pumping at 133 gpm, B-5 pumping at 185 gpm, B-8 pumping at 116 gpm, and B-4 pumping at 170 gpm for a total of 833 gpm. The wells in Cell 3 are B-3 pumping at 209 gpm, B-2 pumping at 109 gpm, and B-1 pumping at 240 gpm for a total of 558 gpm. The wells in Cell 4 are B-11 pumping at 99 gpm, and SC-1 pumping at 29 gpm for a total of 128 gpm. The wells in Cell 6 are SC-3 pumping at 97 gpm and SC-2 pumping at 44 gpm for a total of 141 gpm. The well in Cell 7 is SC-5 pumping at 103 gpm.

Figure 11 presents the simulated heads in 1988, just prior to the initiation of pump-and-treat activities at TCAAP. Figure 12 presents the simulated heads in 2020. The model predicted that the heads came to a steady state within a few years after the initiation of pumping.

The simulated effect of pumping was to lower the water table elevation at the downgradient boundary of TCAAP by a little more than four feet. The steady-state head in Cell 1 was 829.5 feet in 1988 and 825.8 feet in 1990. The steady-state head in Cell 2 was 825.4 feet in

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1988 and 821.2 feet in 1990. The steady-state head in Cell 3 as 825.4 feet in 1988 and 821.1 feet in 1990. The steady-state head in Cell 4 was 825.3 feet in 1988 and 821.5 feet in 1990.

### **Calibration of the Rate of Natural Biodegradation**

At certain times since 1950, large quantities (railroad tankcar loads) of used trichloroethylene and 1,1,1-trichloroethane were released to disposal lagoons on the TCAAP. It is likely that some of this material remains in the aquifer as DNAPL. A source of trichloroethylene and 1,1,1-trichloroethane in ground water near these disposal sites has persisted to the present time.

The rate of natural biodegradation along the flow path at TCAAP was estimated assuming that the plume had come to a steady state before the pump-and-treat activity was initiated in 1988. The screening model BIOSCREEN was used to fit rate constants by curve matching to a simple one-dimensional representation of the flow path. BIOSCREEN is available from the Center for Subsurface Modeling Support (CSMoS), a technical support service located at the Subsurface Protection and Remediation Division, National Risk Management Research Laboratory, Office of Research and Development, U.S. EPA. The web address to download BIOSCREEN and to download instructions to install the model is <http://www.epa.gov/ada/models.html>. The values of hydraulic conductivity selected to calibrate BIOSCREEN were selected after a previous review by a hydrogeologist with the Minnesota Pollution Control Agency.

Figure 13 presents the input screen for BIOSCREEN when the entire flow path was calibrated to conditions appropriate to the Hillside Sand Aquifer. A horizontal hydraulic conductivity of 280 feet per day was input as  $9.9E-02$  cm/sec in Area 1. The hydraulic gradient of 0.002 was extracted from Figure 13. A porosity of 0.22 was assumed. In Area 2 of the input screen, the coefficient of longitudinal dispersion was set to 200 feet, and the coefficient of transverse dispersion was set to 40 feet to be consistent with the assumptions in the models in the remedial investigation. In Area 3, the retardation factor was assumed to be 1.3, to be consistent with the assumptions in models in the remedial investigation. In Area 5, the modeled length was set to 30,000 feet, and the width of the model was set to 6,000 feet. The plume was modeled for forty years, from 1950 to 1990. Area 6 represents the width of the model as a transect perpendicular to ground-water flow along the Southwest margin of TCAAP. The source for the BIOSCREEN simulation is approximately equivalent to Cell 2 and Cell 3 in the BIOPLUME III simulation in Figures 9 and 10.

Field data for comparison to BIOSCREEN are taken from Table 3, which lists the concentration of trichloroethylene and the distance downgradient from the source for selected wells along the centerline of the flow path from TCAAP. These concentrations are the highest that were sampled in each well during routine monitoring over several years in the period prior to the initiation of pumping in 1988. A rate of natural biodegradation was selected that provided the best match of the projections of the model to the actual concentrations in the monitoring wells. The best calibration of BIOSCREEN is presented in Figure 14. The red line is the expected concentrations based on dilution, dispersion, and retardation, but no biodegradation. There was adequate time for the trichloroethylene to move along the flow path, and bring the plume to steady state. This has been confirmed by ground-water contaminant concentration trends observed throughout the TCAAP monitoring network. A first-order rate of natural biodegradation of 0.17 per year (Area 4 in Figure 13) provided adequate calibration to the field data. A first-order rate of 0.17 per year is equivalent to a half life of 4.1 years.

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Figure 15 presents a second calibration of BIOSCREEN to conditions that are more typical of the area near New Brighton, where the plume has moved from the Hillside Sand into aquifers in fractured consolidated rock. The hydraulic conductivity was raised to 480 feet per day ( $1.7E-01$  cm/sec). Under these conditions, an adequate calibration required a first-order rate constant for natural biodegradation of 0.28 per year (compare Figure 16). A first-order rate of 0.28 per year is equivalent to a half-life of 2.8 years.

To determine the uncertainty in the rate constant as determined by curve matching, the data in Table 3 were subjected to log-linear regression. The distance of each monitoring well from the source was divided by the seepage velocity predicted by BIOSCREEN under conditions typical of the area near New Brighton to estimate the travel time for water along the flow path to each well. A linear regression was performed of the natural logarithm of concentration of trichloroethylene against travel time along the flow path. The rate fitted by the regression was equivalent to a rate of natural biodegradation of 0.28 per year. The slower 5% confidence interval corresponds to a rate of at least 0.17 per year. The F statistic for the relationship is very high. The probability that chance alone would give the appearance of degradation, if in fact there was no degradation, is 0.21%.

As an independent evaluation of the rate of natural biodegradation of trichloroethylene that was extracted by this approach, it was applied to the observed attenuation of 1,1,1-trichloroethane in the same wells. The well-established rate of abiotic transformation of 1,1,1-trichloroethane was used as a benchmark to evaluate the overall rate of apparent attenuation. The concentrations of 1,1,1-trichloroethane along the flow path are presented in Table 3. The ground-water temperature at the TCAAP is near 10 °C to 12 °C. McCarty (1996) evaluated the effect of temperature on the rate of abiotic transformation of 1,1,1-trichloroethane. He predicted an average rate of abiotic transformation of 0.14 per year at 15°C. The observed rate of natural attenuation extracted from the data in Table 3, assuming a seepage velocity of 1,600 feet per year, was 0.4 +/- 0.19 per year at 95% confidence. The rate extracted assuming a seepage velocity of 931 feet per year was 0.24 +/- 0.11 per year. This rate would include natural biodegradation as well as the rate of abiotic transformation predicted by the relationships of McCarty (1996) and Klecka et al. (1990). If there were no reductive dechlorination of 1,1,1-trichloroethane and all the attenuation was caused by the abiotic processes, the rate fitted to the field data at the higher estimate of seepage velocity would exceed the published rate by no more than a factor of three. There is no practical or statistical difference between the rate fitted to the field data at the lower estimate of seepage velocity and the published rate of abiotic degradation.

For trichloroethylene, the simple one-dimensional model was best fit with a rate of 0.28 per year when it was calibrated to conditions that predicted a high seepage velocity, and 0.17 per year with a low seepage velocity. A regression through the data under conditions with a high seepage velocity also predicted a rate of 0.28 per year, with a 95% confidence interval of at least 0.17 per year. The BIOPLUME III model was calibrated twice, using both rates to describe biodegradation in the ground water. The "radioactive decay" option under decay parameters was used in BIOPLUME III to simulate reductive dechlorination.

Monitoring data from 1988 to present indicate that the concentrations of trichloroethylene entering the ground water from the residual sources are also attenuating. Most likely, this results from the success of the extraction system. The reduction in the strength of the source

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was simulated by reducing the concentration of trichloroethylene in the hypothetical injection wells in BIOPLUME III that simulate the source area. The concentrations were reduced according to a schedule that produced a first-order reduction in concentration in the simulated plume. Table 4 presents the results of log-linear regressions performed on the concentration of trichloroethylene in twelve monitoring wells and on the TCAAP Ground Water Recovery System (TGRS), over time. The arithmetic average rate of natural biodegradation was near 0.4 per year, with a rate of at least 0.3 per year at 95% confidence. Not all the wells at TCAAP show this marked, downward trend in concentration. To be conservative, BIOPLUME III was calibrated with a simulated rate of attenuation of the source areas of 0.25 per year. The concentrations of the source areas were held constant in the model until 1988 (the year the pump-and-treat system began operation), then declined at a rate of 0.25 per year until the end of the simulation in the year 2020. Under these conditions for attenuation of the source, BIOPLUME III was calibrated for three conditions: for no natural attenuation due to biodegradation, for a degradation rate in the plume of 0.28 per year, and for a degradation rate in the plume of 0.17 per year.

Figure 17 compares the three simulations for 1969. There is effectively little difference in the simulations. Figure 18 compares the simulations in 1988, the year the extraction activities began. Under conditions with no natural bioattenuation, the plume would have reached the Mississippi River at high concentrations. Even with bioattenuation, the plumes would be expected to expand (compare Figures 17 and 18). Figure 19 compares the three simulations in 1998, after ten years of pump-and-treat. The plumes predicted by the simulations with natural attenuation are effectively at steady state (compare Figures 18 and 19). Figure 20 compares the three simulations for the year 2008. The simulation with no natural bioattenuation shows little change from the earlier simulations. In the simulations with bioattenuation, the concentrations in the remaining hot spot are greatly reduced compared to the simulations of the plume before pump-and-treat (compare Figures 20 and 18). In addition, the hot spot in the simulations with bioattenuation has detached from TCAAP and is moving downgradient with the flow of ground water. This illustrates the role of source control in achieving goals for remediation through natural biodegradation. Figure 21 compares the three simulations for the year 2018. In the simulation with no bioattenuation, most of the plume remains in the aquifer. Only the leading edge has been replaced with uncontaminated ground water from upgradient. The simulation with bioattenuation at a rate of 0.28 per year suggests that the plume will have essentially disappeared by 2018. The simulation with bioattenuation at a rate of 0.17 per year predicts that concentrations of trichloroethylene will be very low and approaching MCLs by the year 2018.

## **Role of Hydrogen in Natural Biodegradation at TCAAP**

Conventional geochemical characterization of the ground water at TCAAP indicates that biodegradation through reductive dechlorination is possible, but offers no evidence that it should be expected. Mathematical models that incorporate biodegradation are the best fit to the long-term monitoring data at the site. However, these lines of evidence by themselves do not present compelling evidence that natural bioattenuation is important at TCAAP.

Molecular hydrogen is produced in ground water by fermentation reactions. This hydrogen is an excellent substrate to support reductive dechlorination (Maymo-Gatell et al., 1995; Jakobsen et



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al., 1998). If adequate concentrations of hydrogen are available, reductive dechlorination should occur. The concentration of dissolved hydrogen in ground water is dictated by the dominant microbial processes in the aquifer.

Lovley, Chapelle, and their associates (Lovley et al., 1994) have developed a technique to determine or predict the dominant electron accepting process in ground water by measuring the concentration of dissolved hydrogen. They found that sulfate reduction required a minimum hydrogen concentration of 1 nanomolar, while methanogenesis required a hydrogen concentration of 4 nanomolar. Reductive dechlorination occurs in ground water that is undergoing sulfate reduction or methanogenesis. Following their approach, the U.S. EPA Protocol (U.S. EPA, 1998, see page 41) predicts that reductive dechlorination of solvents will occur if the concentration of hydrogen exceeds 1 nanomolar. Recent experimental evidence has supported this prediction. Yang and McCarty (1998) found that a mixed culture growing on benzoate with cis-dichloroethylene available as an electron acceptor (at 28 °C) poised the hydrogen concentration at 2 nanomolar. They interpreted this concentration as the minimum concentration of hydrogen that would support utilization by organisms carrying out reductive dechlorination. Fennell and Gossett (1998) reported that the lowest hydrogen concentration that would support dechlorination (at 35 °C) was as low as 1.5 nanomolar.

Ground-water samples for the analysis of hydrogen were taken using a pneumatically driven pump according to current EPA guidance (U.S. EPA, 1998). A glass sampling bulb, fitted with a gas-tight septum, was nearly filled with ground water, allowing approximately 50 ml of air to remain in the bulb. Ground water was introduced to the bulb at approximately 400 ml/minute and allowed to escape from the bulb through a second port. Sequential sampling indicated that equilibration between the aqueous phase and the gaseous phase was complete at 30 minutes. Following the equilibration, a 10 ml aliquot of gas was immediately withdrawn from the bulb through the septum using a gas tight syringe. In June 1997, hydrogen was sampled in the field and analyzed in the field within minutes of collection. In June 1998, hydrogen was sampled in the field and sealed in a glass bottle and shipped back to the Subsurface Protection and Remediation Division, Robert S. Kerr Environmental Research Center, Ada, Oklahoma, for analysis within a week of collection. The June 1998 samples are corrected for background concentrations of hydrogen in trip blanks (equivalent to 0.89 +/- 0.18 nanomolar).

The screening process in the Protocol predicts that under the geochemical conditions shown in Table 2, reductive dehalogenation processes are "occurring too slowly to contribute in a meaningful way" to the attenuation of the plume (U.S. EPA, 1998). Hydrogen concentrations are usually in the range of 0.2 to 0.8 nM under iron reducing conditions (Lovley et al., 1994; U.S. EPA, 1998). Much of the ground water in the TCAAP plume contained hydrogen in this concentration range. However, at many locations, hydrogen concentrations were found along the axis of the plume at concentrations that were near or in excess of 1 nanomolar (Table 5).

In their paper on practical considerations for measuring hydrogen in ground water, Chapelle et al. (1997) warn against measuring hydrogen in wells with metal screens (compare Table 1 for construction materials of wells in this study). The background wells, Wells 03U113 and 03L113 are constructed entirely of PVC plastic. Bjerg et al. (1997) demonstrated that PVC, Teflon™, and "probably" stainless steel are suitable materials for wells where samples will be analyzed for dissolved hydrogen. The hydrogen concentrations in water from the deeper background Well (03L113) indicated that the background conditions will support reductive dechlorination. Well

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04U821 is an open borehole. The hydrogen concentration in this well in 1997 indicates that conditions were favorable for reductive transformation of chlorinated solvents as far downgradient as Well 04U821.

Interestingly, high concentrations of hydrogen were also observed in Monitoring Wells 03U020 and 03U002, where ground water also contained oxygen and nitrate. However, ground water at these wells also contained cis-dichloroethylene and concentrations of chloride over five times background level, indicating that degradation of trichloroethylene was occurring in this ground water. It is possible that sampling these wells results in the mixing of ground water that is stratified with respect to redox condition in the upper zones of this aquifer, thus yielding conflicting geochemistry.

Much of the experience base for the range of hydrogen concentrations was built in relatively warm ground water in the southeastern United States, or using laboratory systems maintained at room temperature or above. Ground-water temperature at the TCAAP varied from 9.6 °C to 12.4 °C (see Table 5). Recently the typical range of hydrogen concentrations has been examined for colder ground water more representative of TCAAP. The work of Jakobsen et al. (1998) predicts that the characteristic hydrogen concentration of sulfate reduction at 10 °C would be 0.3 nanomolar, well below the range predicted by Lovley et al. (1994). If temperature has the same effect on the threshold for reductive dechlorination, the criterion of 1 nanomolar in the U.S. EPA Protocol (U.S. EPA, 1998) may be conservative.

## Evaluation of the Protocol

One objective of this study was to assess the accuracy of the EPA natural attenuation protocol in predicting the fate of a ground-water plume at a site where natural attenuation was clearly ineffective at containing ground-water contamination. TCAAP was chosen for this test because the plume extends over five miles from the on-site source area and is very well characterized. The ten years of sampling over 225 monitoring wells, in addition to numerous private and municipal wells, have established not only the extent of the plume but also concentration trends at many locations. Therefore, the results of this natural attenuation study could be verified with an extensive contaminant database and subsurface investigation.

The major conclusions of this evaluation of the EPA Natural Attenuation Protocol are:

**The screening analysis indicated that the geochemistry of the ground water did not favor the reductive dechlorination of solvents and that a natural attenuation remedy at this site was unlikely.** The screening evaluation showed that the ground water was basically manganese and iron reducing, with no evidence of sulfate reducing or methanogenic activity. Under these conditions, the Protocol predicts that the potential for reductive dehalogenation is low. This screening prediction was verified by the magnitude of the ground-water plume. Reductive dehalogenation did not prevent formation of a large plume.

**Application of the Protocol extracted a rate of biodegradation that was slow.** The biodegradation rate at this site was estimated at 0.17 to 0.28 per year for TCE. This rate is slow compared to other sites where natural attenuation appears to be an

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effective remedy. This low rate, coupled with the high ground-water velocity, is consistent with the observed development of the very large solvent plume at the TCAAP site. This biodegradation rate was derived from four sampling events at a limited number of wells along what is considered the longitudinal axis of the plume, consistent with the approach for extracting rate constants that is illustrated in the Protocol.

**The BIOPLUME III modeling accurately predicted the extent and magnitude of the solvent plume at this site.** The model was calibrated with the ground-water data available from previous site investigations consistent with the Protocol's emphasis on natural attenuation verification efforts. Even with a rate for biodegradation rate included, the modeling indicated that a large ground-water plume would develop. Actual ground-water contaminant data from the extensive network of monitoring wells at the site confirm the accuracy of these modeling predictions.

**The relatively high hydrogen concentrations detected in the iron/manganese-reducing ground water environment were not predicted by the Protocol.** More research is needed in manganese reducing ground-water environments to correlate hydrogen concentration to the dominant electron accepting processes. However, it also demonstrated that hydrogen concentrations can, under some circumstances, be a better predictor of the dehalogenation of trichloroethylene to cis-dichloroethylene at a site than the geochemistry alone, underscoring the importance of hydrogen sampling in natural attenuation studies as detailed in the Protocol and supporting literature.

Overall, the study accurately predicted that natural attenuation processes in the ground water at TCAAP would be insufficient to contain the ground-water contaminants within acceptable limits at the site. These results confirm the ability of the Protocol to evaluate and successfully predict the fate of ground-water plumes at similar sites that are not contained through natural attenuation processes.

## **Conclusions Applied to TCAAP**

Based on the concentration of hydrogen in the ground water, there is strong evidence that biological degradation is destroying chlorinated solvents currently present in ground water at TCAAP. Natural attenuation through biodegradation is the most plausible explanation for the apparent reduction in the concentration of chlorinated organic compounds as the plume moves downgradient from the source. Natural biodegradation complements the on-going efforts to extract contaminated ground water at the source, and should greatly reduce the time required to reduce the concentration of contaminants to U.S. EPA drinking water standards. If the rate of natural biodegradation exhibited in the last ten years continues for the next twenty years, the portion of the aquifer downgradient from TCAAP will be reclaimed.

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## Extension to Other Sites

The *Protocol for the Natural Attenuation of Chlorinated Solvents in Ground Water* was originally developed from experiences with chlorinated solvents in unconsolidated sandy aquifers. At these sites, the cost of monitoring wells was relatively cheap, and additional wells could be installed to fill gaps in the monitoring data. In this study, the methods and approaches of the *Protocol for the Natural Attenuation of Chlorinated Solvents in Ground Water* were applied to wells that were available from previous site characterization efforts. The existing wells (several hundred) were originally designed to delineate a plume, and to design a pump-and-treat remedy. The number of wells that were installed to meet these goals were severalfold fewer than would be necessary to justify a selection of natural attenuation as a sole remedy.

The number of wells available for study at the TCAAP was equal to or greater than the number typically available at large and complex sites where plumes of contamination extend several hundred feet deep into consolidated rock. It is unlikely that other large and complex sites will have better infrastructure for monitoring than does the TCAAP. Therefore it is unlikely that the Protocol can be used with existing monitoring wells to justify the selection of natural attenuation as the sole remedy at large and complex sites.

The study shows that the Protocol can be used to evaluate the contribution of natural biodegradation to a cleanup that is achieved through active control of the source of contamination. The information provided can be used to estimate the time required to reach cleanup goals, and to design or optimize strategies for long-term monitoring.

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**Table 1.** Monitoring Wells Selected for an Evaluation of the Natural Attenuation of Chlorinated Solvents in Ground Water at TCAAP

Well	Aquifer Screened	Well Depth (feet)	Screen Length (feet)	Depth Ground Water (feet)	Screen	Riser
Background						
03U113	Lower Hillside Sand	158	20	118	PVC	PVC
03L113	Deep Sands	430	20	118	PVC	PVC
Source Area Pump-out Wells						
03U314 (SC-2)	Upper Hillside Sand	186.5	20	132	SS	S
03U317 (SC-5)	Lower Hillside Sand	430	10	114	SS	S
Source Area Monitoring Wells						
03U020	Upper Hillside Sand	135	20	106	SS	PVC
03M020	Middle Hillside Sand	185	20	106	SS	PVC
03L020	Lower Hillside Sand	229	20	106	SS	PVC
04U020	Jordan Sandstone	260	10	103	SS	PVC
03U002	Upper Hillside Sand	89	20	70	SS	PVC
03M002	Middle Hillside Sand	167	20	73	SS	PVC
03L002	Lower Hillside Sand	238	20	73	SS	PVC
04U002	Prairie du Chien	280	10.5	75	SS	PVC
Perimeter Pump-out Well						
03F306 (B-5)	Prairie du Chien	232	100	82.9	SS	S
Downgradient from TCAAP 4,600 feet						
191942	Prairie du Chien	183	18	47	open hole	S
04U821	Prairie du Chien	147	5	43.6	SS	S
Downgradient from TCAAP 17,000 feet						
04U872	Prairie du Chien	382	30	137.9	open hole	S

SS = Stainless Steel

S = Steel

**Table 2.** Geochemical Indicators of Anaerobic Biotransformation of Chlorinated Solvents in Ground Water at TCAAP (Reported are Values for the June 1998 Round of Sampling)

Well	Oxyge mg/liter	Mangane mg/liter	Iron (II) mg/liter	Alkalinity mg/liter	Sulfate mg/liter	Methane mg/liter	Nitrate mg/liter
Background							
03U113	1.8	0.02	0.0	247	13.3	0.001	0.59
03L113	0.1	0.33	0.0	224	4.5	0.018	<0.1
Source Area Pump-out Wells							
03U314 (SC-2)	0.4	0.65	0.25	236	17.2	0.011	0.44
03U317 (SC-5)	1.0	0.37	0.0	234	17.2	0.001	0.59
Source Area Monitoring Wells							
03U020	6.7	0.70	0.0	291	32.6	0.001	2.35
03M020	0.1	0.80	0.0	231	2.9	0.035	0.11
03L020	0.5	6.0	0.25	227	4.2	0.015	<0.1
04U020	0.1	0.8	0.65	231	5.9	0.007	<0.1
03U002	3.3	0.1	0.0	274	14.2	0.001	0.62
03M002	0.2	1.1	0.0	284	10.7	0.001	0.57
03L002	0.0	0.34	0.25	230	6.2	0.008	<0.1
04U002	0.0		0.15	237	2.8	0.011	<0.1
Perimeter Pump-out Wells							
03F306 (B-5)	0.5	0.66	0.0	242	7.4	0.004	0.17
Downgradient from TCAAP 4,600 feet							
191942	0.1	<0.1	0.7	260	12.4	0.005	<0.1
04U821	0.2	<0.1	0.1	220	10.4	0.001	0.25
Downgradient from TCAAP 17,000 feet							
04U872	0.3	<0.5	0.25	269	25.1	0.017	<0.1

*The ground water is depleted of oxygen, but there is little evidence of intense anaerobic microbial activity, such as the accumulation of methane. There is accumulation of Iron (II) and Manganese (II), but their concentrations are low.*



**Table 3.** Apparent Attenuation of Concentrations of TCE and 1,1,1-TCA in Selected Monitoring Wells with Distance Downgradient of Source Area D on TCAAP (The Concentrations are the Highest Detected in the Years Prior to Initiation of Pump-and-treat)

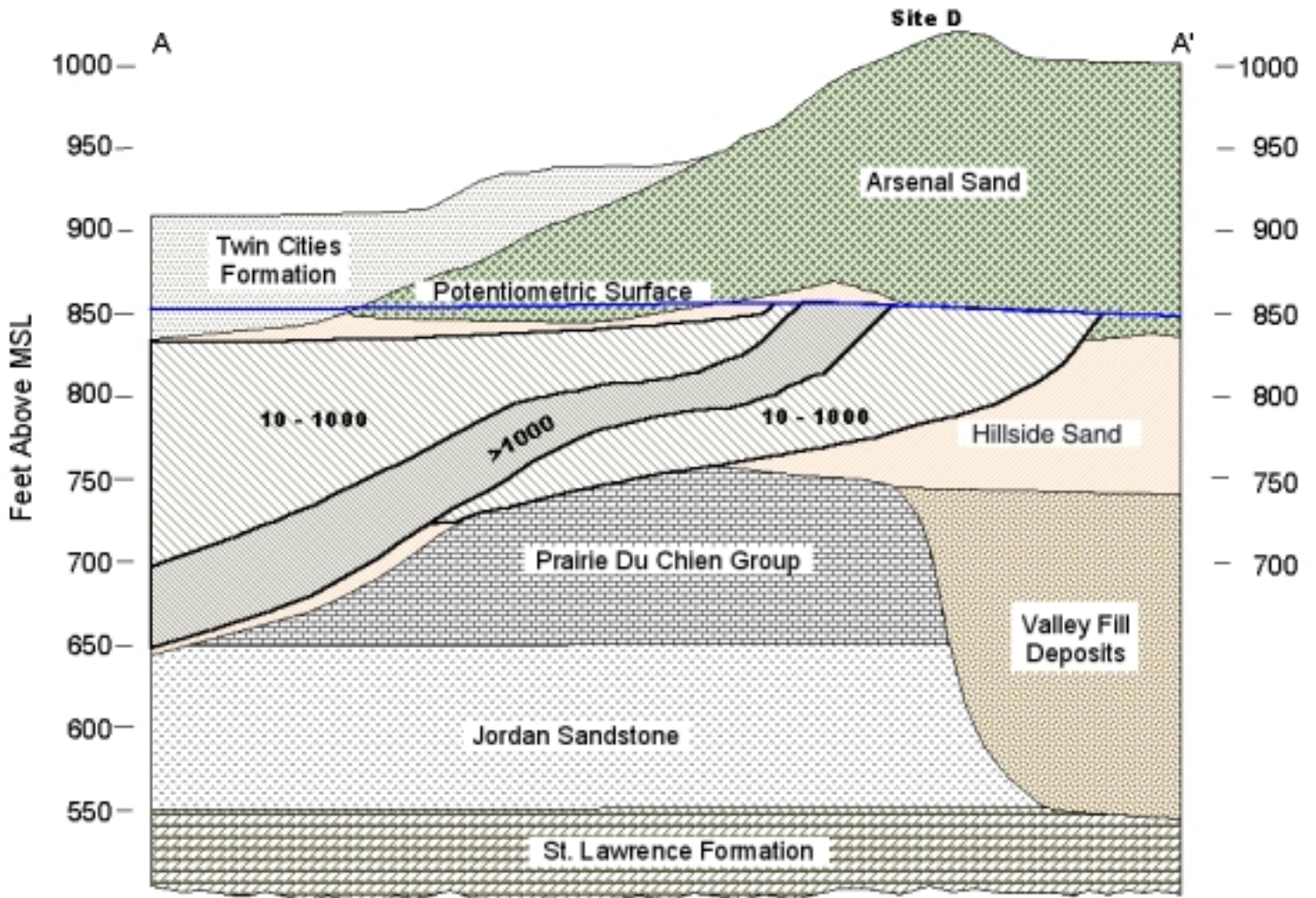
Well	Distance Downgradient (feet)	Highest TCE Concentration (µg/liter)	Highest 1,1,1-TCA Concentration (µg/liter)	Estimated Travel Time (years)
03U020	2,000	11,000	6,000	1.25
03L002	3,500	2,700	4,200	2.20
04U821	7,800	950	170	4.9
04U850	13,200	910	71	8.30
04U872	22,800	168	19	14.3
04U882	27,000	67	7.7	17.0

**Table 4.** Apparent Rate of Attenuation in Concentration of TCE in Selected Monitoring Wells at TCAAP

Well	Time Interval in Regression (years)	Number of Samples in Regression	First-Order Rate of Attenuation (per year)	95% Confidence Interval on the Rate of Attenuation (per year)
03U096	10	10	0.365	0.202
03U094	9	9	0.359	0.245
03U003	21	21	0.278	0.206
03U079	16	16	0.353	0.277
03U093	27	27	0.691	0.574
03U094	9	9	0.359	0.245
03L002	14	14	0.383	0.296
03L020	4	4	0.430	0.218
03L883	13	13	0.376	0.239
04U002	13	13	0.348	0.283
04U020	15	15	0.556	0.457
04U848	18	18	0.574	0.486
TGRS	8	8	0.229	0.185
MEAN			0.41	0.30

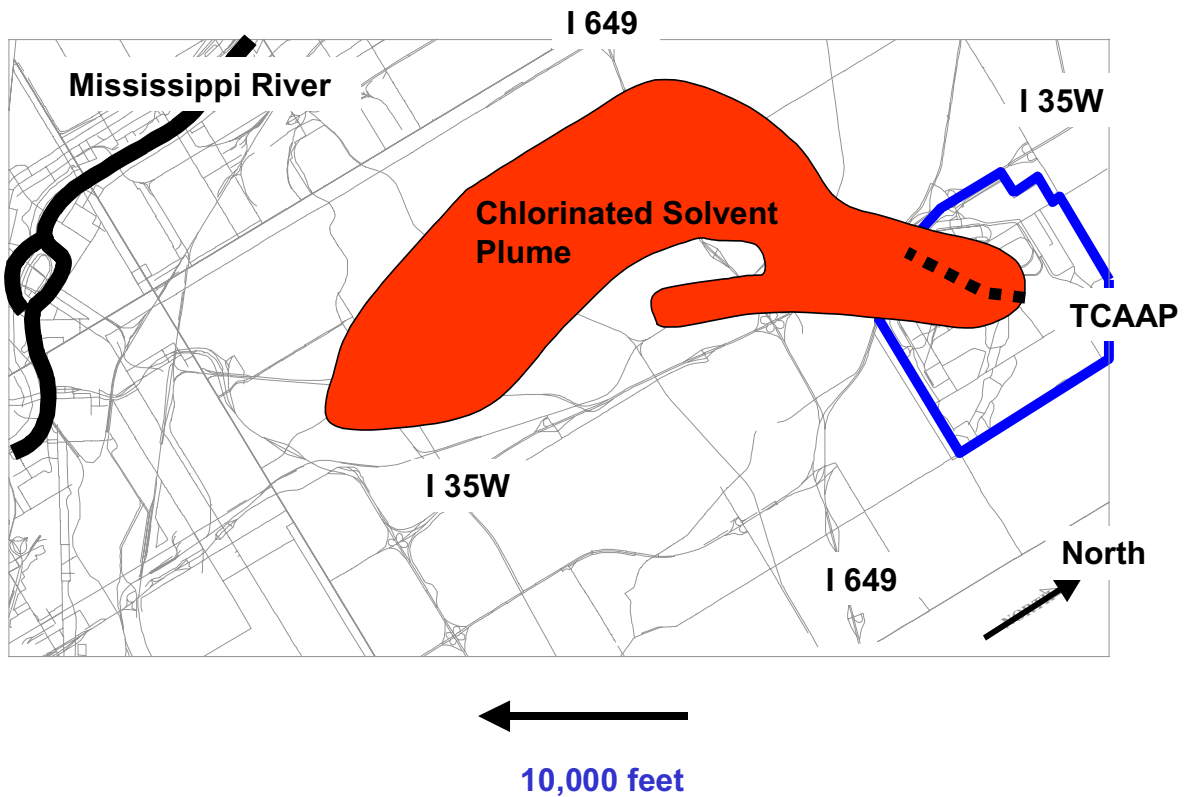
**Table 5.** Concentration of Hydrogen, Oxidation/Reduction Electrode Potential Against an Ag/AgCl Reference Electrode, and Temperature of Ground Water Sampled from TCAAP

Well	Order Shallow to Deep	Hydrogen nanomolar		Redox millivolts		Temp. °C	
		6/1997	6/1998	6/1997	6/1998	6/1997	6/1998
Date of Background							
03U113	1.0	0.84	0.8	-113	93.8	11.3	10.8
03L113	2.0	12.9	1.16	-123	-52.0	10.6	10.5
Source Area Monitoring Wells							
03U020	1.0	3.05	3.2	126	97.0	12.4	11.0
03M020	2.0	1.41	7.5	104	-175.1	9.57	11.8
03L020	3.0	0.79	13.6	-133	-115.0	10.8	11.0
04U020	4.0	0.38	5.5	-171	-166.6	10.8	10.6
Source Area farther downgradient							
03U002	1.0	0.76	1.4	94	106.0	11.6	11.4
03M002	2.0	0.36	1.3	97	2.0	11.0	11.7
03L002	3.0	1.07	0.2	45	-5.1	11.3	10.6
04U002	4.0	1.5	36	-74	-79.6	11	10.5
Downgradient 4,600 feet from TCAAP							
191942		0.97	0.86	-117	-162.0	11.3	11.2
04U821		1.16	0.18	-78	-122.0	10.9	10.7
Downgradient 17,000 feet from TCAAP							
04U872		0.90	0.44	-140	-114.0	10.9	10.0



**Cross Section A-A' near Site D**

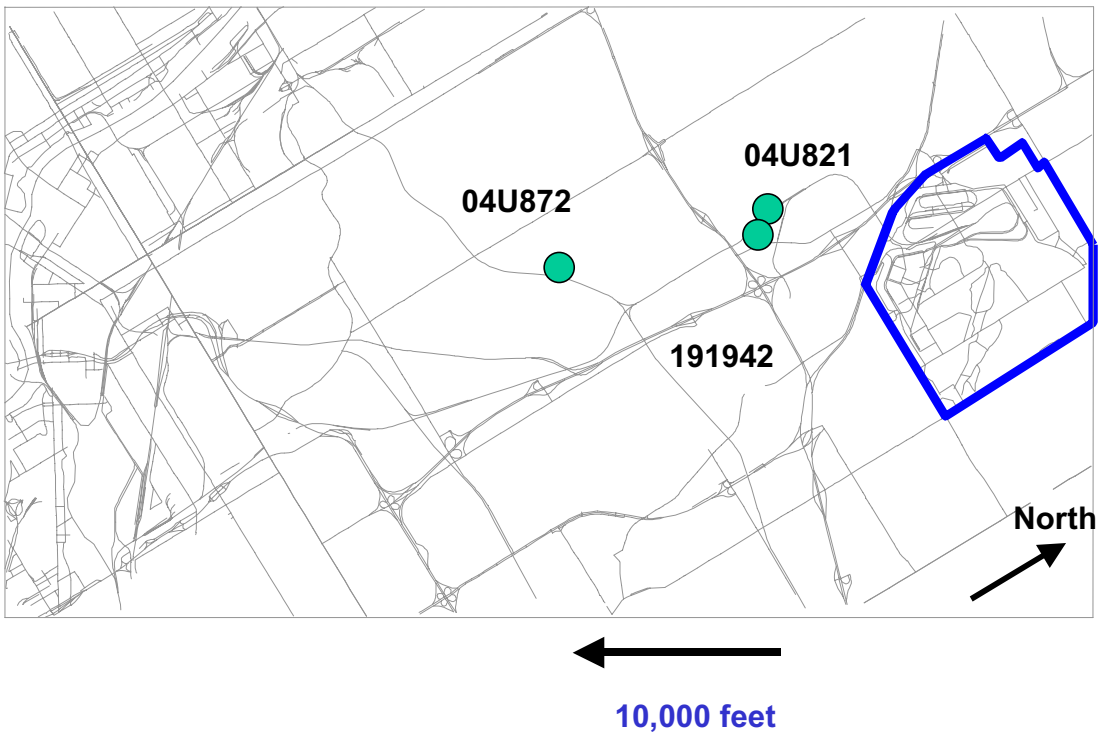
**Figure 1.** Geological cross section at the Twin Cities Army Ammunition Plant, showing the origin of the chlorinated solvent plume in ground water. The section A' to A extends from Northeast to Southwest in the direction of ground-water flow (from right to left in the figure). The distance along the section from A' to A is 4,500 feet. Site D is the most important source of chlorinated solvents in ground water. Presented are the concentrations of trichloroethylene in mg/liter. The vertical distribution of chlorinated solvents is determined by the distribution of solvents in vertical clusters of monitoring wells.



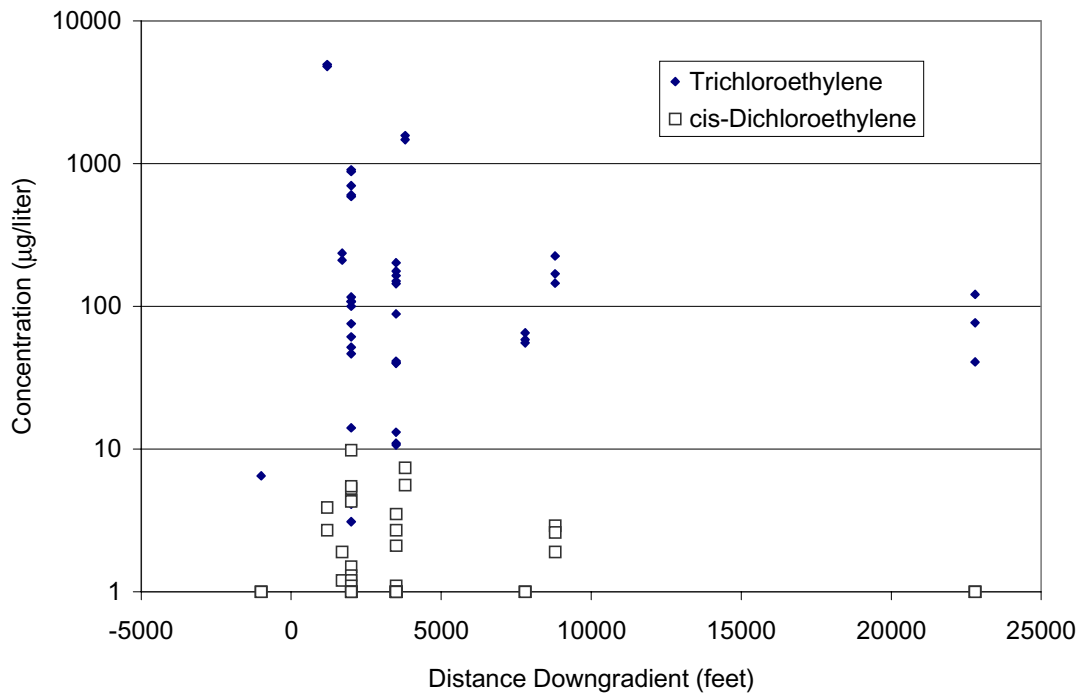
**Figure 2.** Location of the Twin Cities Army Ammunition Plant (TCAAP) and the associated plume of chlorinated solvents in ground water with respect to the Mississippi River, to Interstate 35W, and to Interstate 694. The heavy dotted line at the head of the plume is the location of the vertical cross section presented in Figure 1.



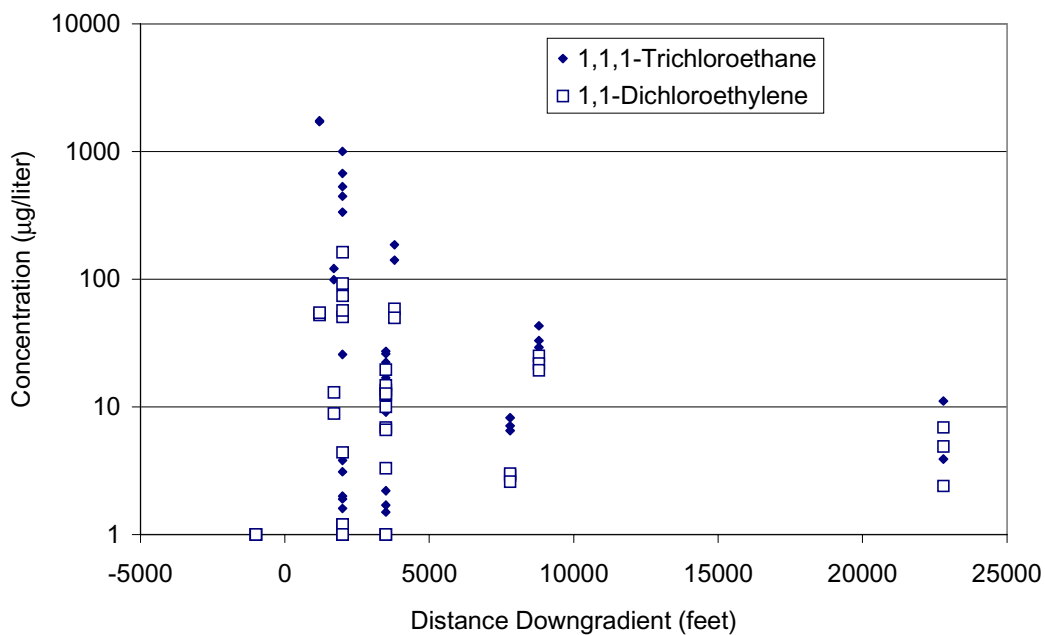
**Figure 3. Panel A.** Locations of monitoring wells or monitoring well clusters on the TCAAP that were involved in the geochemical study to evaluate monitored natural attenuation. Ground-water flow from right to left in the figure.



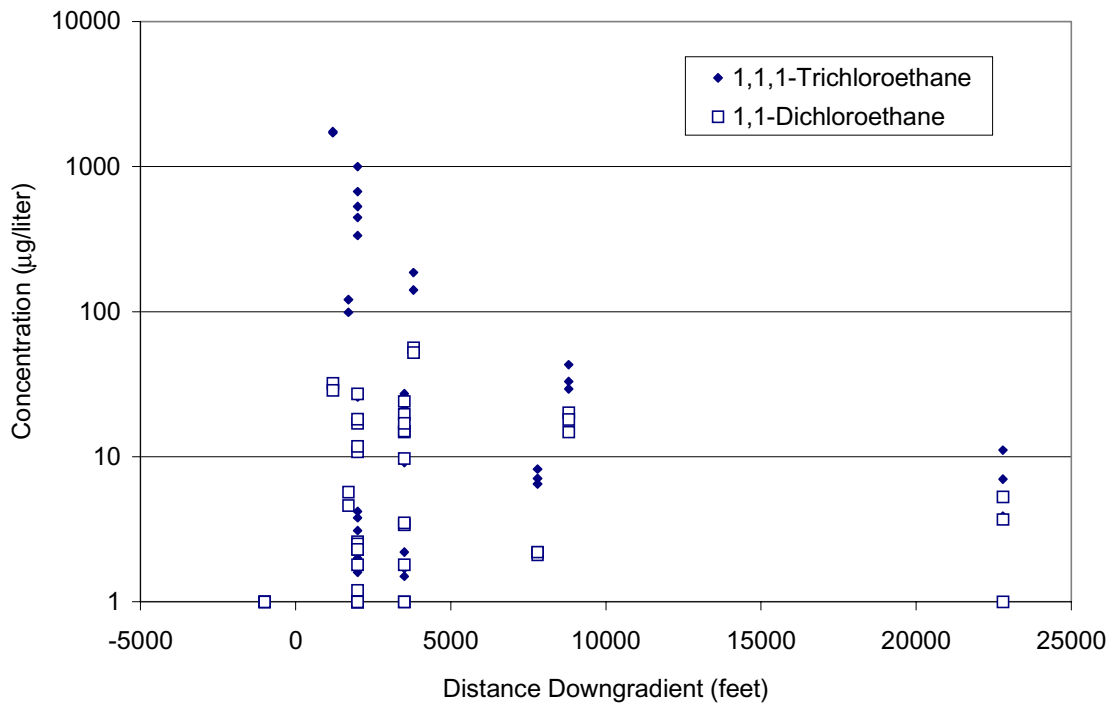
**Figure 3. Panel B.** Locations of monitoring wells or monitoring well clusters that are downgradient of the TCAAP that were involved in the geochemical study to evaluate monitored natural attenuation. Ground-water flow from right to left in the figure.



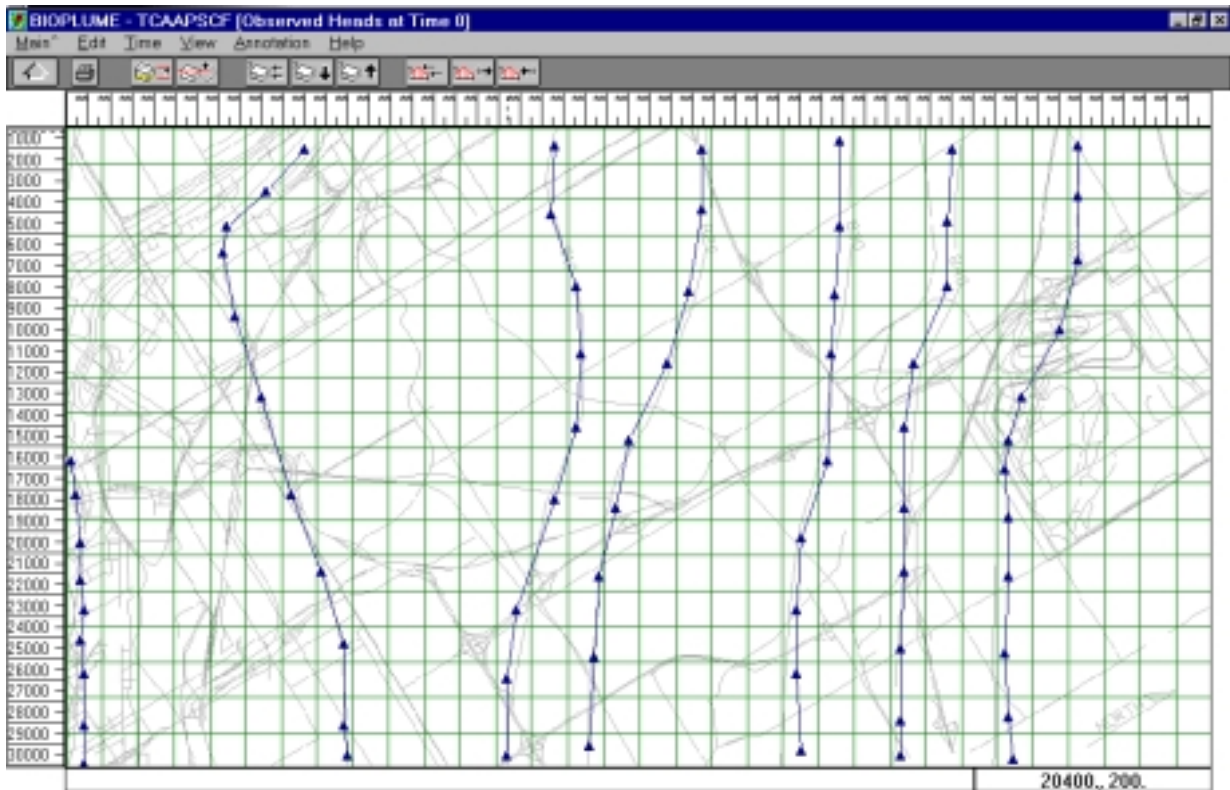
**Figure 4.** Relative concentration of trichloroethylene and its biological reduction product cis-dichloroethylene in ground water from TCAAP. Wells in the study were sampled in June 1996, December 1996, June 1997, November 1997 and June 1998.



**Figure 5.** Relative concentration of 1,1,1-trichloroethane and its abiotic transformation product 1,1-dichloroethylene in ground water from TCAAP. Wells in the study were sampled in June 1996, December 1996, June 1997, November 1997 and June 1998.

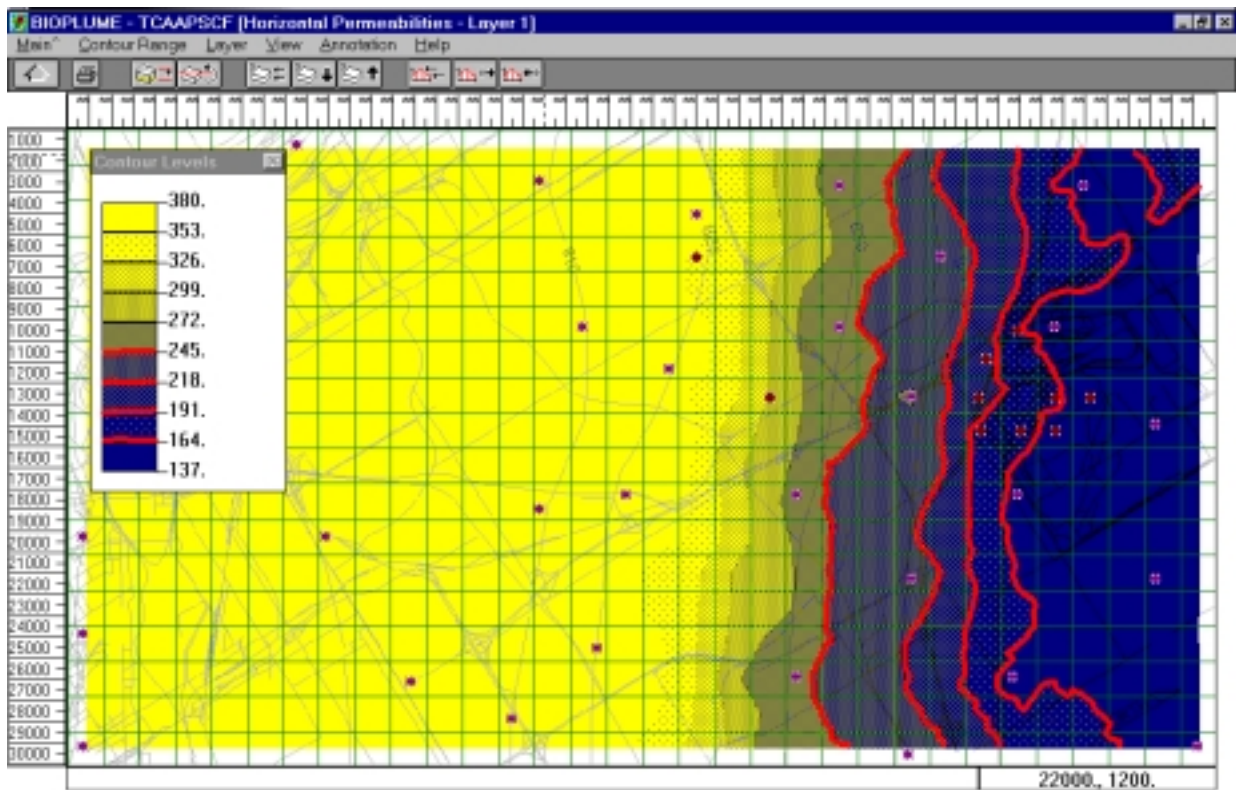


**Figure 6.** Relative concentration of 1,1,1-trichloroethane and its biological reduction product 1,1-dichloroethane in ground water from TCAAP. Wells in the study were sampled in June 1996, December 1996, June 1997, November 1997 and June 1998.

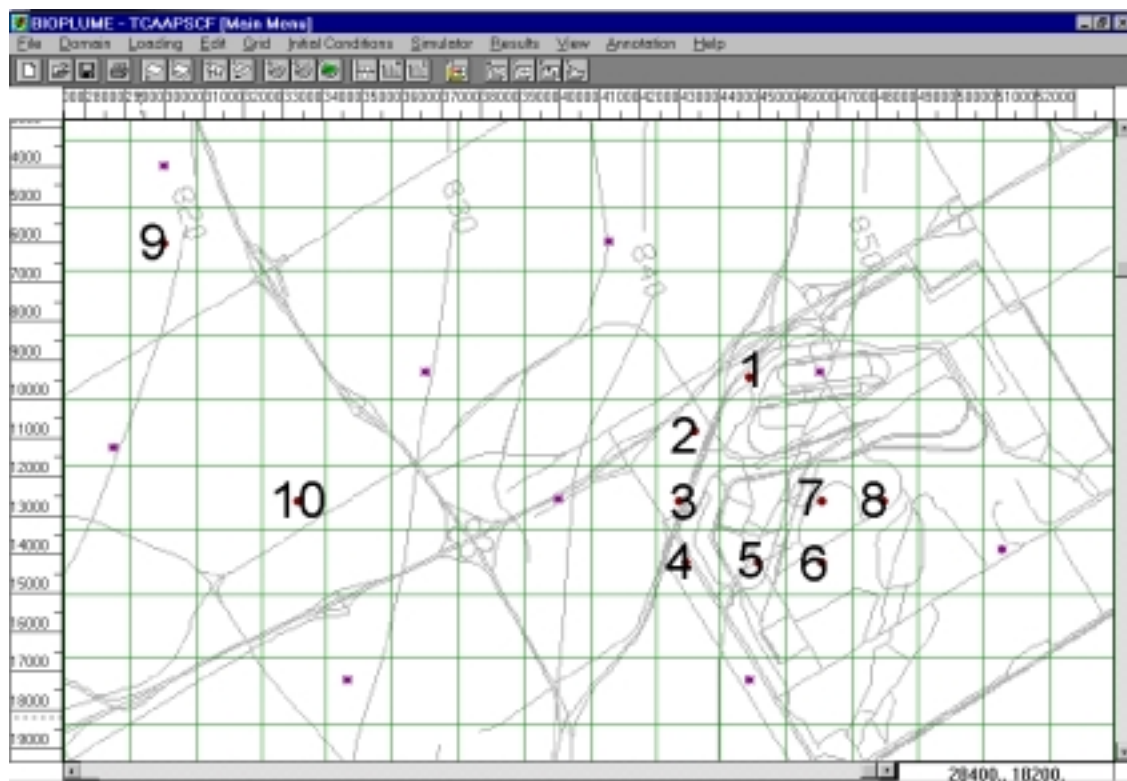


**Figure 7.** The triangles connected by lines are the water table elevations used to calibrate the initial conditions in BIOPLUME III. Ground-water flow is from right to left; the interpreted contours provided on the map used to calibrate water elevations have a difference in elevation of ten feet.



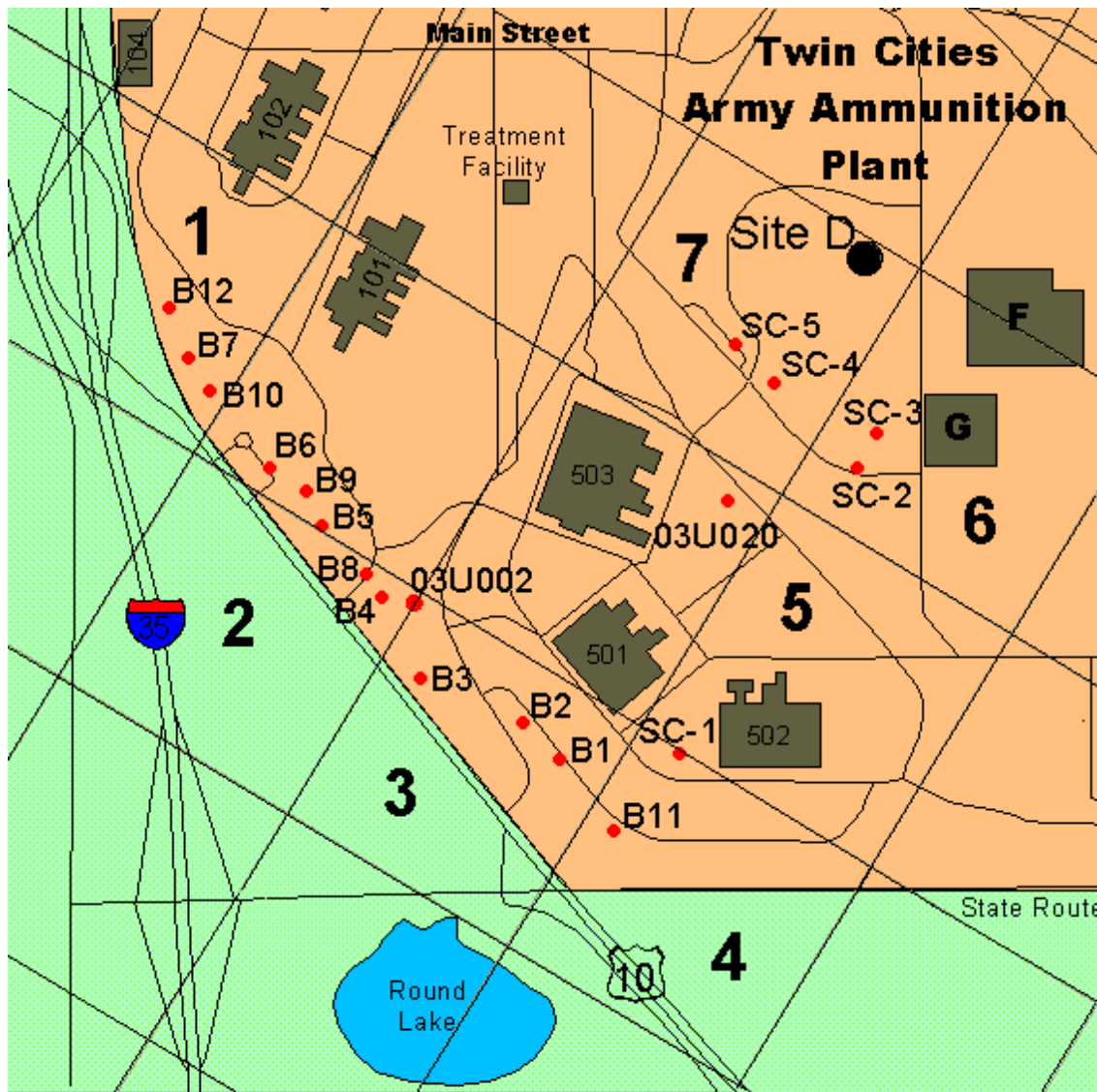


**Figure 8.** Kriged values for horizontal hydraulic conductivity used to calibrate BIOPLUME III. Values are in feet per day.

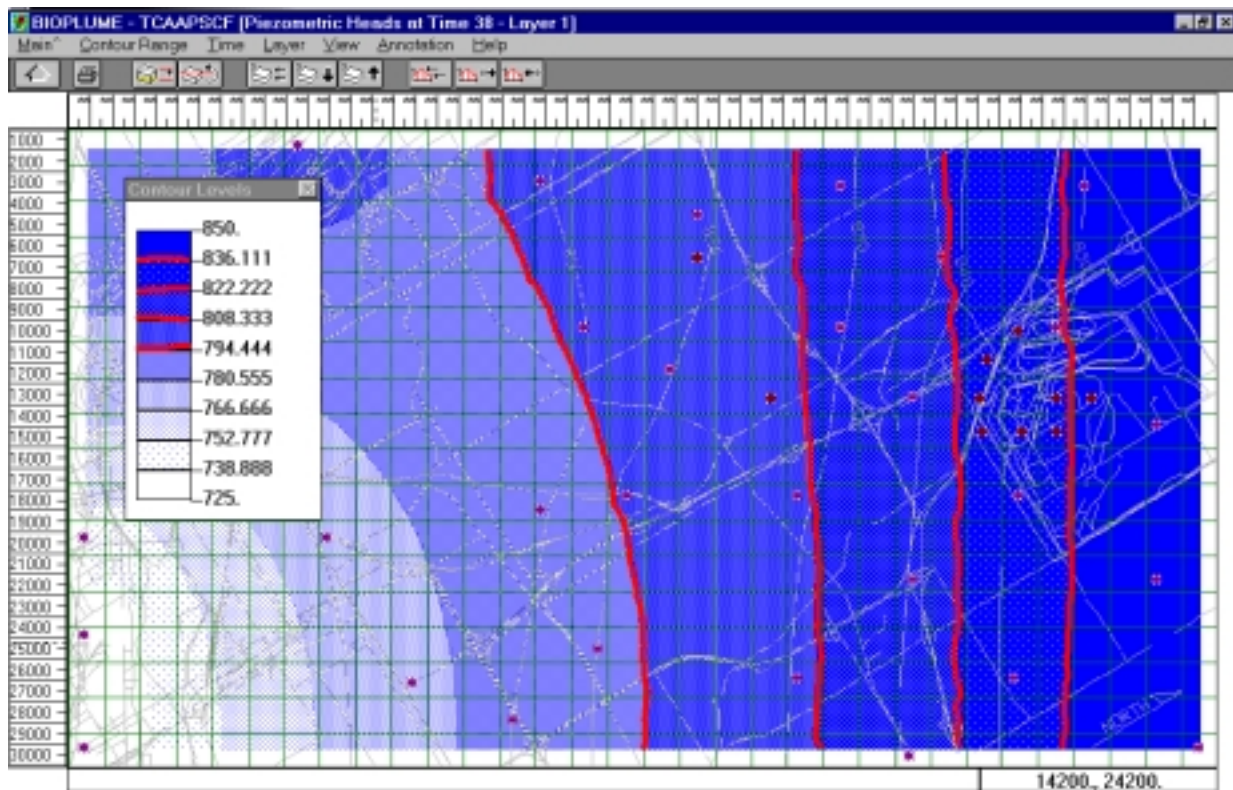


**Figure 9.** Cells used to calibrate BIOPLUME III. The cells labeled with a number are modeled with either an injection well or an extraction well as described in the text. The cells with an \* are log points used to calibrate the distributed parameters in BIOPLUME III.

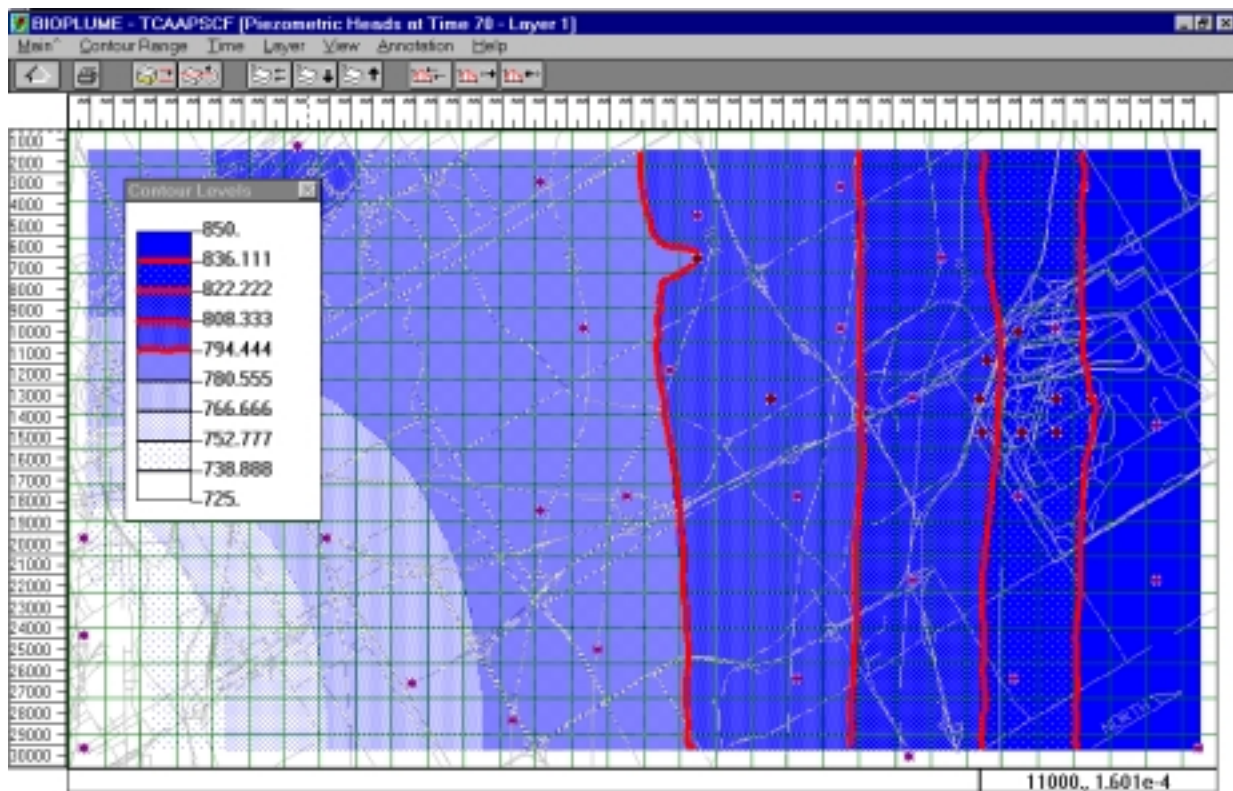




**Figure 10.** The grid used to calibrate BIOPLUME III superimposed on surface features at TCAAP. The locations labeled BP or SC are pump-and-treat wells at TCAAP. The model only allows one extraction or injection well per cell in the grid. The cells labeled 1 through 7 are modeled with an extraction or injection well as described in the text and Figure 9. Well B-5 is also labeled 03F306, Well SC-2 is also labeled 03U317 and Well SC-5 is also labeled 03U314.



**Figure 11.** Heads modeled by BIOPLUME III just prior to beginning pump-and-treat activities in 1988.



**Figure 12.** Steady-state heads modeled by BIOPLUME III for the year 2020, after initiation of pump-and-treat starting in 1988.

Air Force Center for Environmental Excellence  
Version 1.3  
TCAAP  
K = 280 ft/d  
Run Name

**1. HYDROGEOLOGY**  
Seepage Velocity\* Vs 931.2 (ft/yr)  
or  
Hydraulic Conductivity K 9.9E-02 (cm/sec)  
Hydraulic Gradient i 0.002 (ft/ft)  
Porosity n 0.22 (-)

**2. DISPERSION**  
Longitudinal Dispersivity\* alpha x 200.0 (ft)  
Transverse Dispersivity\* 40.0 (ft)  
Vertical Dispersivity\* alpha z 0.0 (ft)  
or  
Estimated Plume Length Lp (ft)

**3. ADSORPTION**  
Retardation Factor\* R 1.3 (-)  
or  
Soil Bulk Density rho (kg/ft<sup>3</sup>)  
Partition Coefficient Koc (L/kg)  
Fraction Organic Carbon foc (-)

**4. BIODEGRADATION**  
1st Order Decay Coeff\* lambda 1.7E-1 (per yr)  
or  
Solute Half-Life t-hal 0 (year)  
or Instantaneous Reaction Model  
Delta Oxygen\* DO 0 (mg/L)  
Delta Nitrate\* NO3 0 (mg/L)  
Observed Ferrous Iron\* Fe2+ 0 (mg/L)  
Delta Sulfate\* SO4 0 (mg/L)  
Observed Methane\* CH4 0 (mg/L)

**5. GENERAL**  
Modeled Area Length\* 30000 (ft)  
Modeled Area Width\* 6000 (ft)  
Simulation Time\* 40 (yr)

**6. SOURCE DATA**  
Source Thickness in Sat. Zone\* 100 (ft)  
Source Zones:  
Width\* (ft) Conc. (mg/L)\*  
1000 0.3  
1000 1  
1700 11  
1000 1  
1000 0.3  
Source Decay (see Help)  
Source Half-life\* infinite (yr)  
Soluble Mass in NAPL, Soil infinite (Kg)

**7. FIELD DATA FOR COMPARISON**  
Concentration (mg/L) 11.0 2.7 .95 .91 .168 .067  
Dist. from Source (ft) 0 3000 6000 9000 12000 15000 18000 21000 24000 27000 30000

**8. CHOOSE TYPE OF OUTPUT TO SEE:**  
RUN CENTERLINE View Output  
RUN ARRAY View Output  
Help Recalculate This Sheet  
Paste Example Dataset  
Restore Formulas for Vs, Dispersivities, R, lambda, other

Figure 13. Set-up screen for BIOSCREEN when calibrated to conditions in the Hillside Sand Aquifer, hydraulic conductivity at 280 feet per day, calibrated rate of bioattenuation 0.17 per year.

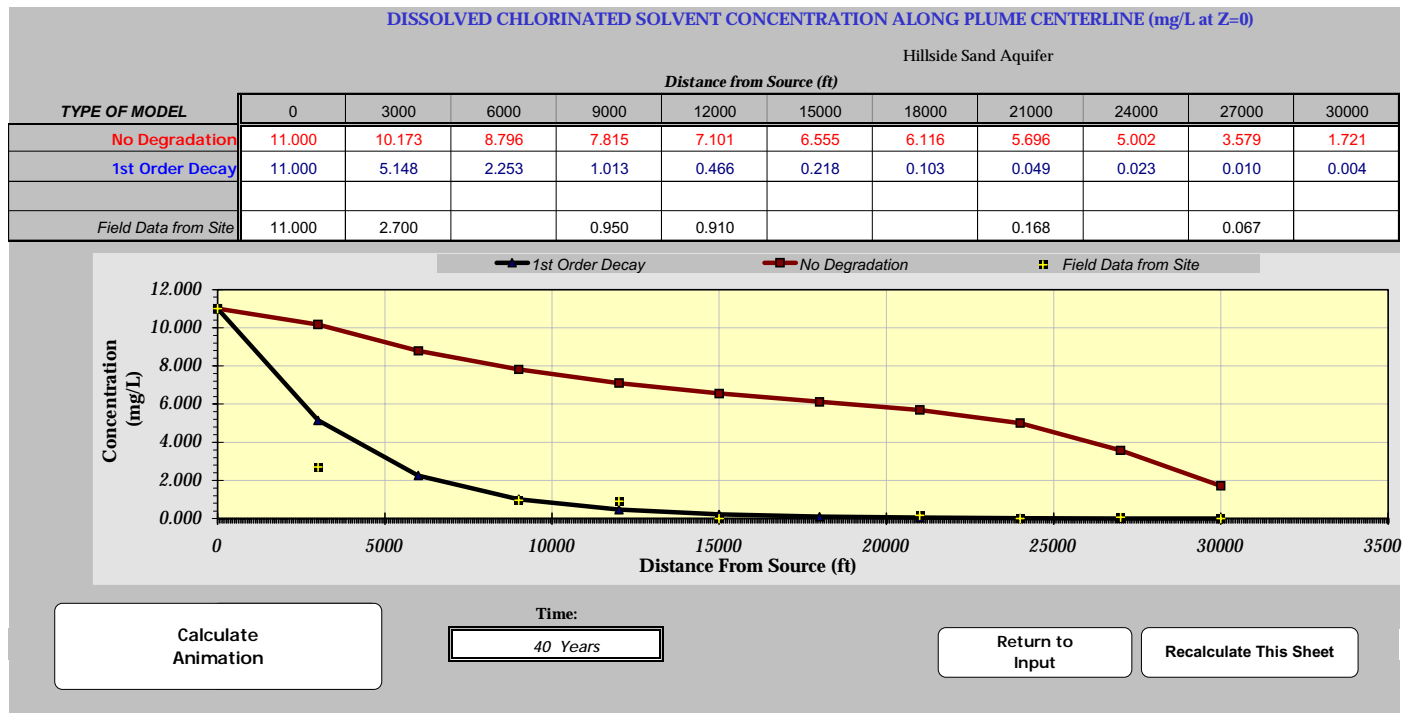


Figure 14. Centerline output of BIOSCREEN under conditions in the Hillside Sand Aquifer. Hydraulic conductivity is 280 feet per day, and the calibrated rate of natural biodegradation is 0.17 per year.



Air Force Center for Environmental Excellence  
Version 1.3

**1. HYDROGEOLOGY**  
 Seepage Velocity\*  $V_s$  1589.6 (ft/yr) or  $\uparrow$  or  
 Hydraulic Conductivity  $K$  1.7E-01 (cm/sec)  
 Hydraulic Gradient  $i$  0.002 (ft/ft)  
 Porosity  $n$  0.22 (-)

**2. DISPERSION**  
 Longitudinal Dispersivity\*  $\alpha_{Lx}$  200.0 (ft)  
 Transverse Dispersivity\* 40.0 (ft)  
 Vertical Dispersivity\*  $\alpha_{Lz}$  0.0 (ft) or  $\uparrow$  or  
 Estimated Plume Length  $L_p$  (ft)

**3. ADSORPTION**  
 Retardation Factor\*  $R$  1.3 (-) or  $\uparrow$  or  
 Soil Bulk Density  $\rho_b$  (kg/ft<sup>3</sup>)  
 Partition Coefficient  $K_{oc}$  (L/kg)  
 Fraction Organic Carbon  $f_{oc}$  (-)

**4. BIODEGRADATION**  
 1st Order Decay Coeff\*  $\lambda$  2.8E-1 (per yr) or  $\uparrow$  or  
 Solute Half-Life  $t_{1/2}$  (year)  
**or Instantaneous Reaction Model**  
 Delta Oxygen\*  $DO$  0 (mg/L)  
 Delta Nitrate\*  $NO_3$  0 (mg/L)  
 Observed Ferrous Iron\*  $Fe^{2+}$  0 (mg/L)  
 Delta Sulfate\*  $SO_4$  0 (mg/L)  
 Observed Methane\*  $CH_4$  0 (mg/L)

**5. GENERAL**  
 Modeled Area Length\* 30000 (ft)  $L$   
 Modeled Area Width\* 6000 (ft)  $W$   
 Simulation Time\* 40 (yr)

**6. SOURCE DATA**  
 Source Thickness in Sat. Zone\* 100 (ft)  
 Source Zones:  

Width* (ft)	Conc. (mg/L)*
1000	0.3
1000	1
1700	11
1000	1
1000	0.3

 Source Decay (see Help)  
 Source Half-Life\* Infinite (yr)  
 Soluble Mass  $\uparrow$   
 In NAPL, Soil Infinite (Kg)

**7. FIELD DATA FOR COMPARISON**  

Concentration (mg/L)	11.0	2.7	.95	.91		.168	.067				
Dist. from Source (ft)	0	3000	6000	9000	12000	15000	18000	21000	24000	27000	30000

**8. CHOOSE TYPE OF OUTPUT TO SEE:**  
 RUN CENTERLINE View Output  
 RUN ARRAY View Output  
 Help or Recalculate This Sheet  
 Paste Example Dataset  
 Restore Formulas for  $V_s$ , Dispersivities,  $R$ ,  $\lambda$ , other

Figure 15. Set-up screen for BIOSCREEN under conditions near New Brighton. Hydraulic conductivity is near 480 feet per day and the rate of bioattenuation is 0.28 per year.

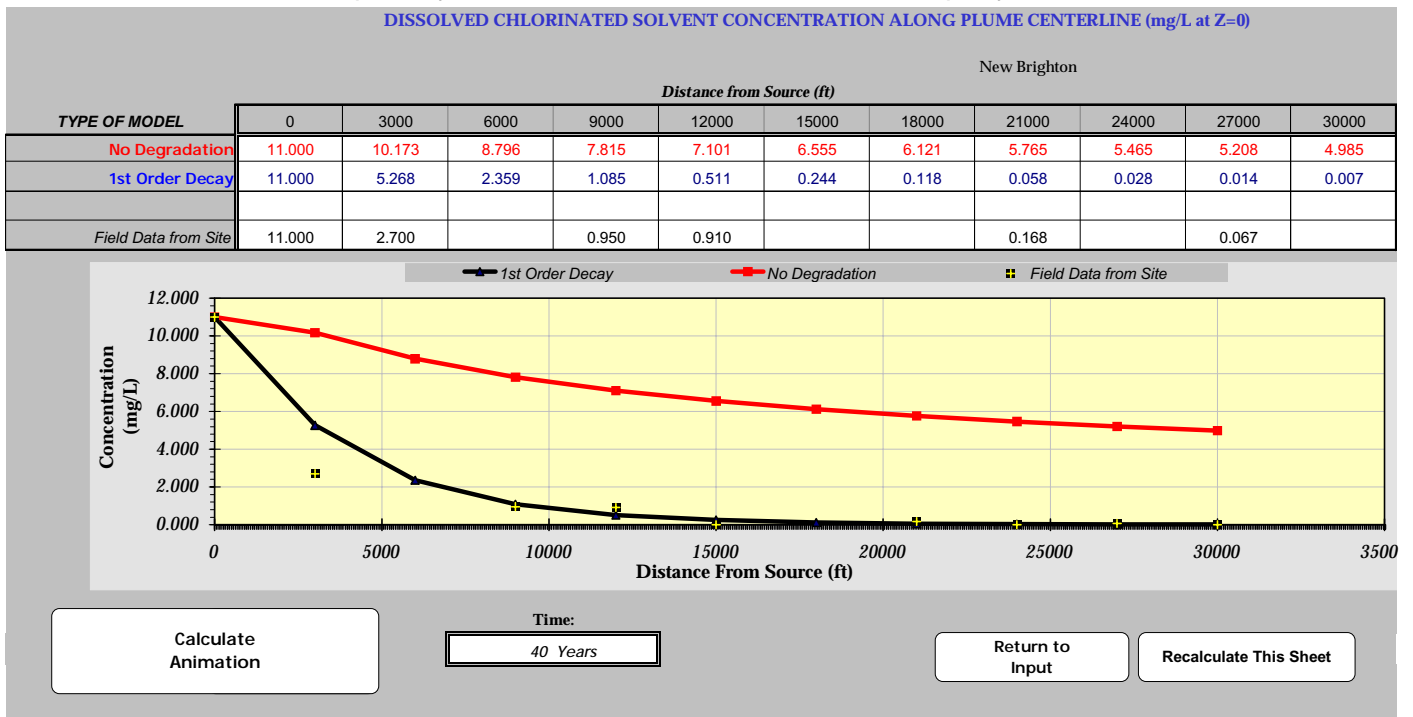
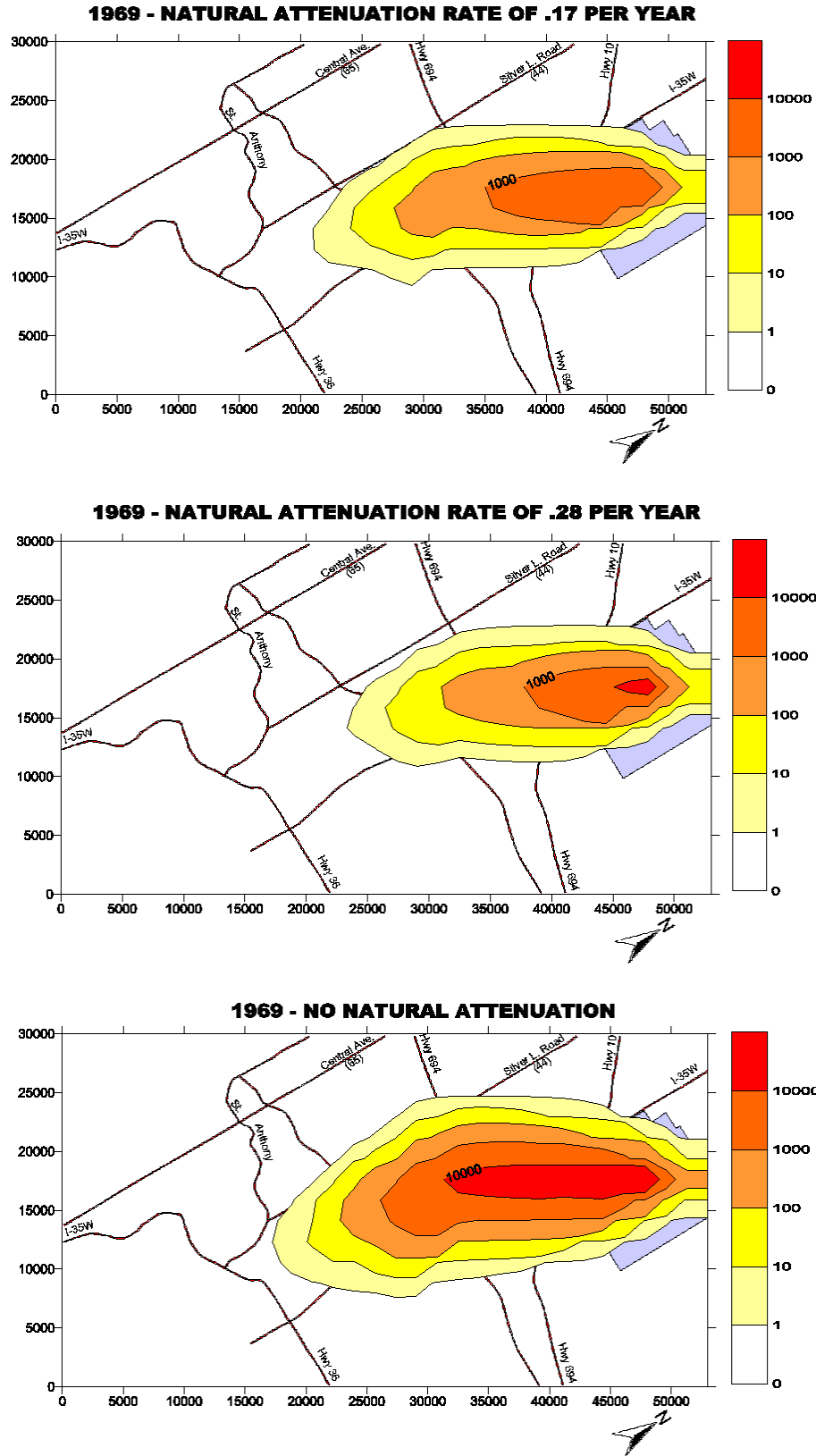
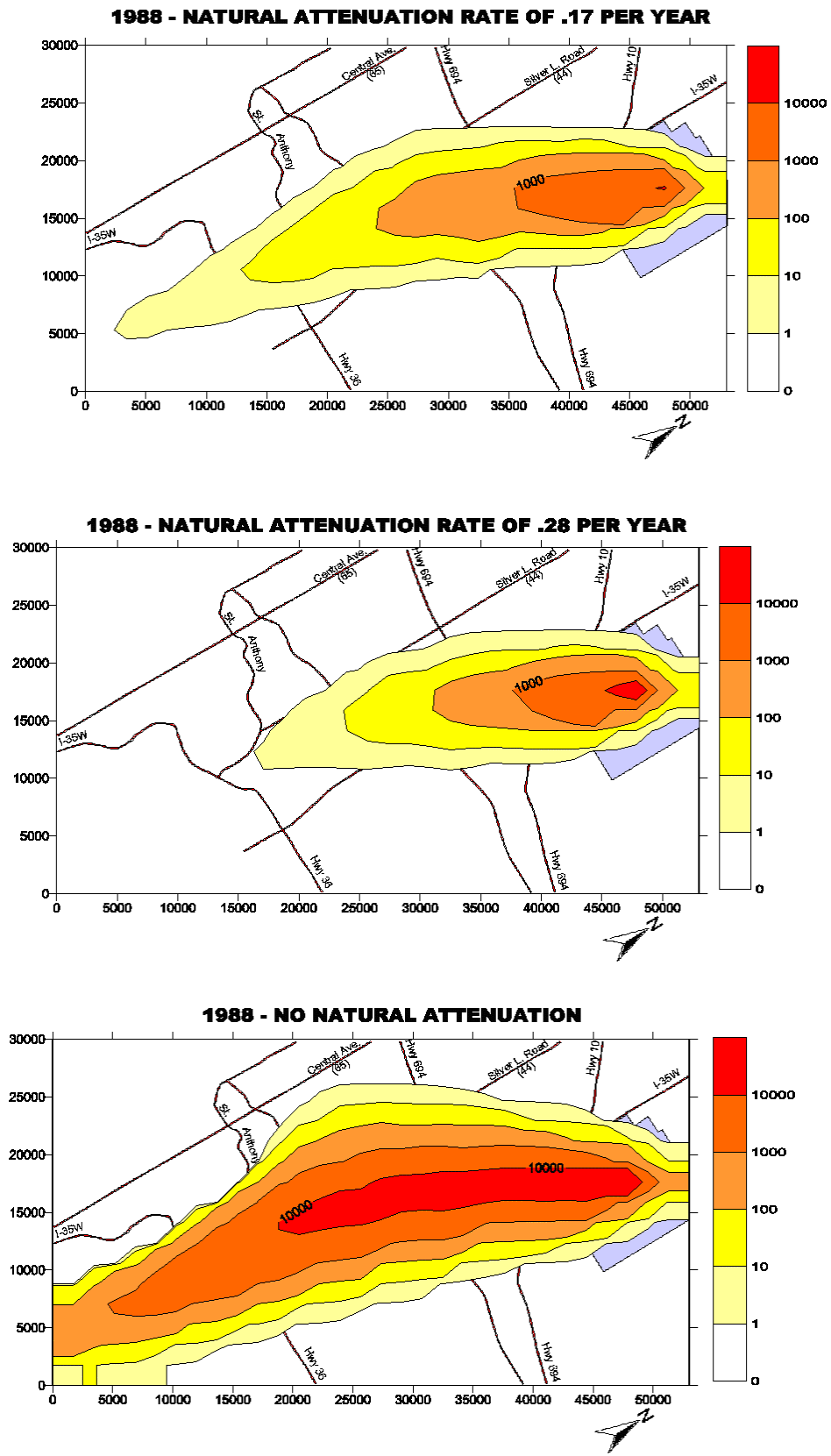


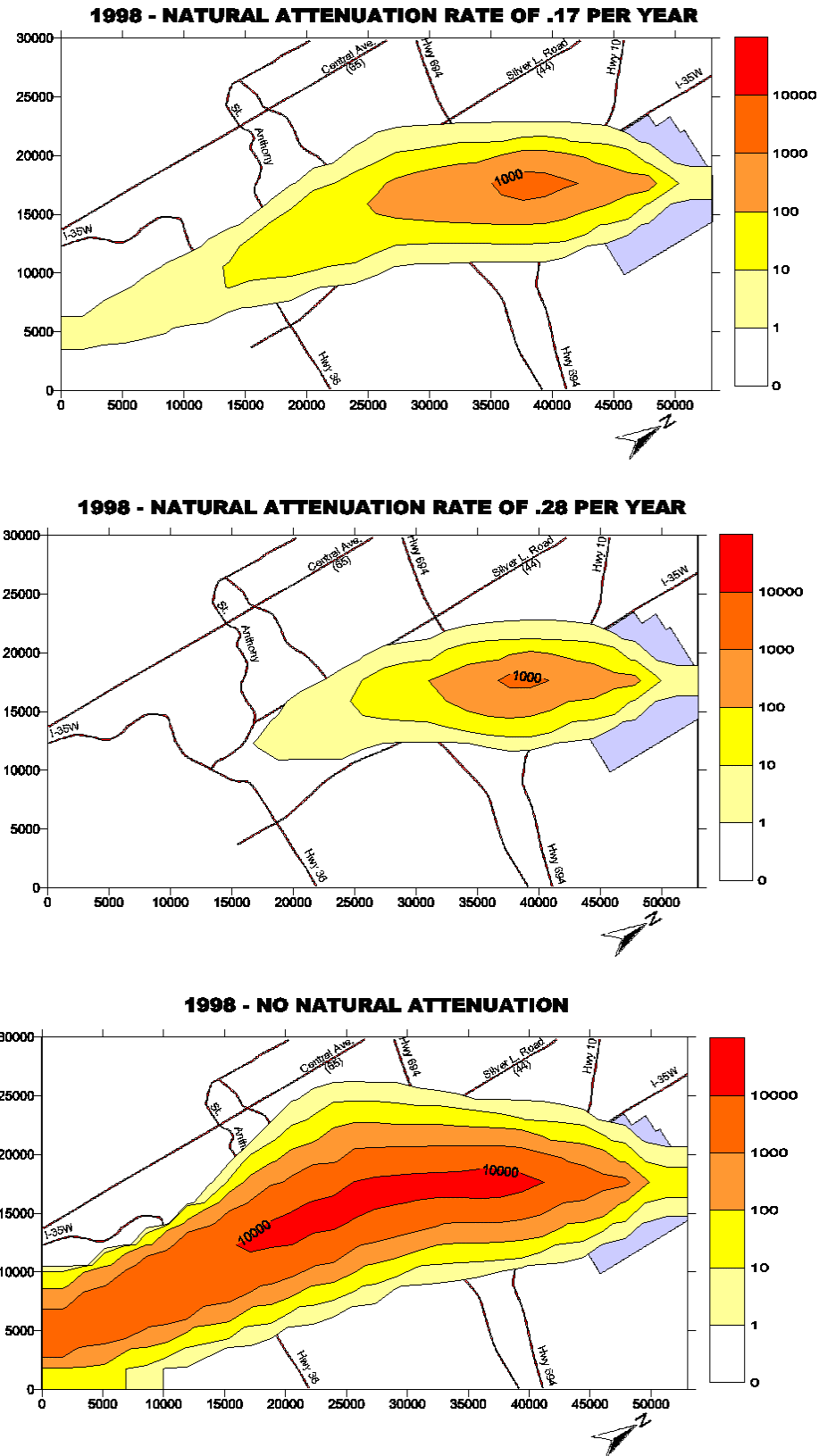
Figure 16. Centerline output of BIOSCREEN calibrated to the conditions at New Brighton, hydraulic conductivity is 480 feet per day, and the calibrated rate of natural biodegradation is 0.28 per year.



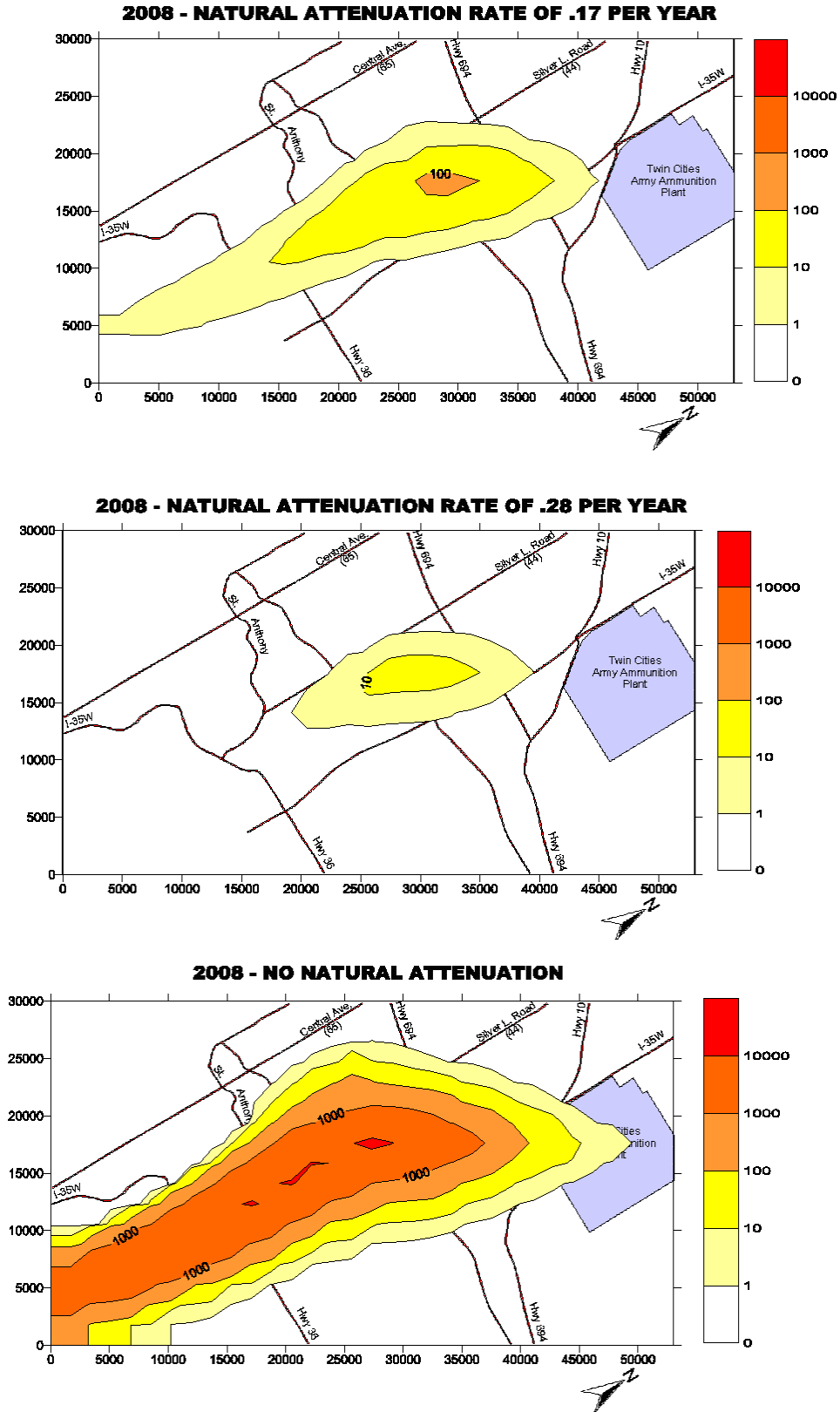
**Figure 17.** Projections of concentrations of TCE at TCAAP with and without bioattenuation in 1969. Distances are in feet, concentrations are in µg/liter.



**Figure 18.** Projections of concentrations of TCE at TCAAP with and without bioattenuation in 1988. Distances are in feet, concentrations are in µg/liter. Pump-and-treat began in 1988.

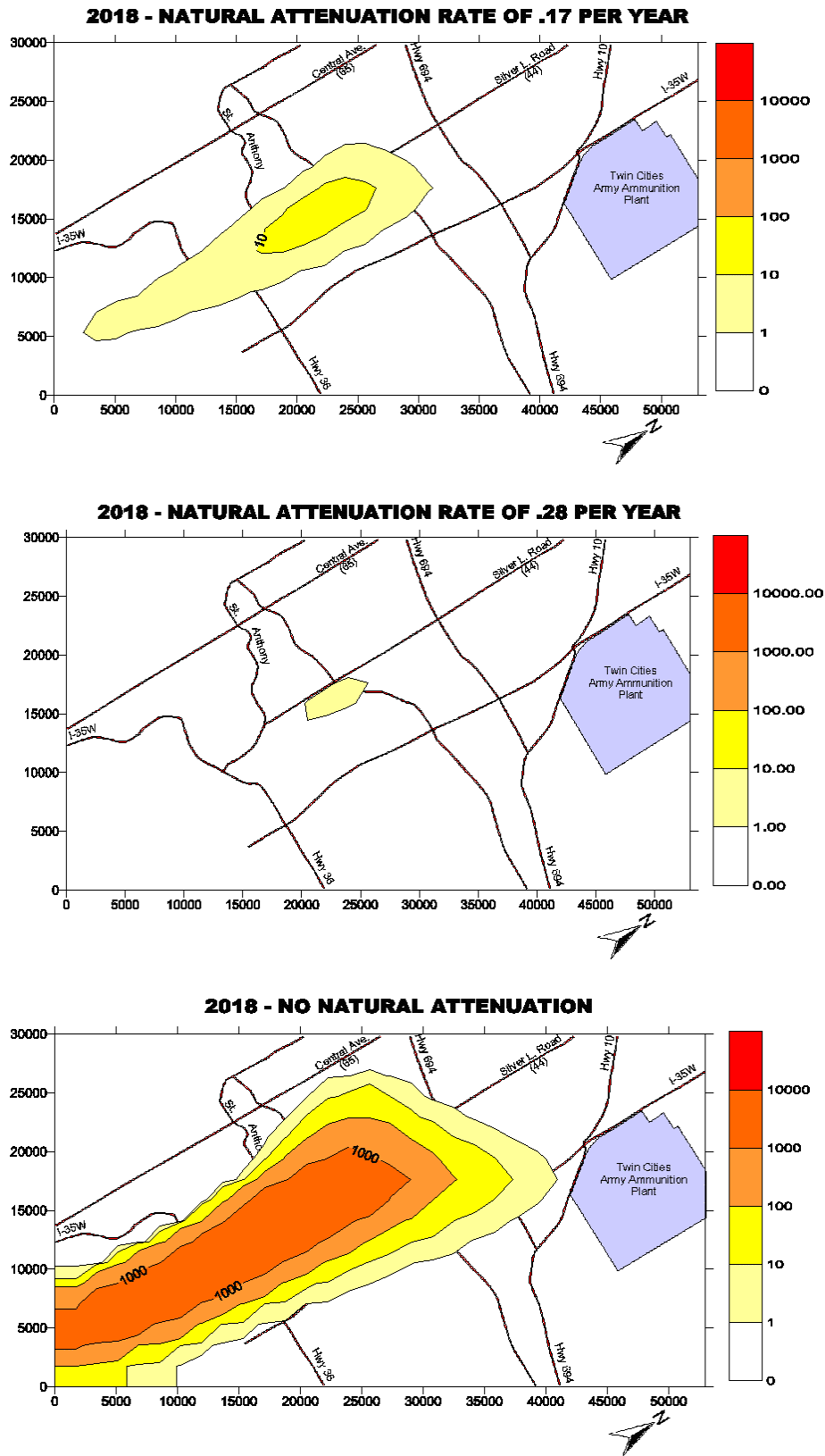


**Figure 19.** Projections of concentrations of TCE at TCAAP with and without bioattenuation in 1998. Distances are in feet, concentrations are in  $\mu\text{g/liter}$ . A pump-and-treat remedy in the source began in 1988.



**Figure 20.** Projections of concentrations of TCE at TCAAP with and without bioattenuation in the year 2008. Distances are in feet, concentrations are in µg/liter.





**Figure 21.** Projection of concentrations of TCE at TCAAP with and without bioattenuation in the year 2018. Distances are in feet, concentrations are in  $\mu\text{g}/\text{liter}$ .