GROUND WATER AND CONTAMINANT TRANSPORT MODELING FOR THE CEDARVILLE AQUIFER

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OHD 004 243 002

Project No. 0292.11.37

December 20, 2004

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TABLE OF CONTENTS

1.0 INTRODUCTION 1

2.0 MODELING OBJECTIVES AND OVERALL APPROACH 1
2.1 Steps Required in Creating the Transport Model 2

3.0 CONCEPTUAL MODEL 3

4.0 COMPUTER CODE SELECTION 5

5.0 MODEL CONSTRUCTION 5
5.1 Finite Difference Grid Development 5
5.2 Boundary and Initial Conditions 6
5.3 Stratigraphy and Model Parameterization 7

6.0 MODEL CALIBRATION 9

7.0 SUMMARY AND CONCLUSIONS 14

8.0 REFERENCES 15

List of Text Tables

5.1: Calibrated Model Input Parameters 11

List of Figures

5-1. Finite Difference Grid
5-2. Transport Calibration Results for PCE
5-3. Transport Calibration Results for TCE
6-1. cis-1,2-DCE Concentrations in the Upper Cedarville Aquifer
6-2. Vinyl Chloride Concentrations in the Upper Cedarville Aquifer

Table of Contents (cont.)

List of Attachments

1. Raw Data and Files Used in the Vernay Facility Contaminant Transport Modeling for the Cedarville Aquifer (provided on a DVD in Appendix VIII to the RFI Phase II report)

1.0 INTRODUCTION

In June 2004, the Payne Firm, Inc. (Payne Firm) submitted a Phase I Resource Conservation and Recovery Act (RCRA) Facility Investigation (RFI) report (Payne Firm et al., 2004) for the Vernay Laboratories, Inc. (Vernay) Facility located at 875 Dayton Street, Yellow Springs, Ohio (Facility). As part of the Phase I RFI report, a ground water flow model was constructed and calibrated to understand and depict the ground water flow field beneath and in the vicinity of the Vernay Facility; and, to confirm that two operating ground water capture wells located along the eastern property boundary of the Facility are effectively controlling the migration of volatile organic compounds (VOCs) from the Facility. Details of the ground water flow model were presented as Appendix VII to the Phase I RFI report (Payne Firm et al., 2004).

Since the submittal of the Phase I RFI report, ground water modeling efforts have focused on completing a contaminant transport model for the site. The ground water flow model was used to form the basis the contaminant transport model, which is needed to define the temporal behavior of the tetrachloroethylene (PCE) and trichloroethylene (TCE) contaminant concentrations in the Cedarville Aquifer beneath the Facility and the surrounding area, and to confirm that the existing monitoring well network is sufficient to meet the data quality objectives and data needs of the RCRA Corrective Action, including the CA750 contaminant migration under control demonstration. Contaminant transport analyses were conducted using MODFLOW and MT3D. The results of these analyses indicate that both the PCE and TCE plumes are stable and well contained within the existing monitoring well network. This contention is also supported by the existing field data.

This report is divided into seven sections. Following this introduction, Section 2 presents the modeling objectives and overall approach; Section 3 identifies the major components of the conceptual model; Section 4 addresses the computer code selection; Section 5 presents the construction of the numerical model; Section 6 discusses the activities undertaken for the model calibration; and the report is closed with Section 7, which presents the summary and conclusions of the ground water flow and contaminant transport modeling.

2.0 MODELING OBJECTIVES AND OVERALL APPROACH

It is vital to establish why the model is being created, and to properly design the model simulations to sufficiently address the data needs that the modeling effort is intend to satisfy. The objectives of this

current exercise were to: 1) define the temporal behavior of PCE and TCE contaminant concentrations in the Cedarville Aquifer beneath the Facility and the surrounding area since these are the only two VOCs that have been detected above a level of concern off the Facility; 2) determine the effect that two operating pump and treat extraction wells have had on the migration and distribution of PCE and TCE downgradient of the Facility; 3) determine if PCE and TCE concentrations detected in wells at the fringe of the contaminant plume downgradient of the Facility are stable if detected above a level of concern; and, 4) confirm that the existing monitoring well network is sufficient to establish future behavior of the contaminant plume(s). These objectives were satisfied using the following model simulations:

1. A three-dimensional ground water model that generated a flow field (array of head values) representing average conditions in the Vernay area.
2. A 'plume development' (chemical transport) model that evaluated how the average flow field, along with other transport parameters, affected chemical movement in ground water and plume development from past sources at the Vernay Site.

As indicated above, a three-dimensional computer model for analyzing ground water flow was constructed, calibrated and used as the basis for the transport model (Payne Firm et al., 2004). The plume development model couples the expansion of the plume, prior to the installation of the two extraction wells, and the stabilization of the plume (after the installation of the wells) into a continuous simulation. The following discussion describes the procedures used in creating the plume development model.

2.1 Steps Required in Creating the Transport Model

Steps completed in creating the numerical transport model include the following:

1. Adopting a conceptual model to guide the creation of a model.
2. Choosing appropriate computer code(s) for the analysis.
3. Establishing the time period represented by the model and the duration of subdivisions of this period (time steps) required for modeling.
4. Selecting a suitable model domain, including determining the dimensional (horizontal and vertical) limits of the analysis.
5. Establishing the model structure, including determining the number of model layers and the grid spacing requirements.
6. Assigning the characteristics of chemical sources, consisting of dimensions, locations, concentrations and time dependency.
7. Assigning transport parameters, including the distribution coefficient (defines contaminant adsorption to soil and affects transport by retarding the rate of contaminant movement) and the degradation coefficient for the modeled chemical species (relates to the rate of chemical decay or 'half life' in the ground water system).
8. Selecting chemical calibration targets.

9. Evaluating and assigning appropriate model computational characteristics, for example, solution method, iteration limits and convergence criteria, to enhance model stability, computational efficiency, and solution accuracy.
10. Running the model and adjusting assigned model parameters within predetermined limits to achieve the closest fit between model results and calibration targets.

Completion of these steps is necessary to create a model representing field conditions as accurately as possible within the constraints of practicality and data availability. A more detailed discussion of the modeling process is summarized in the sections that follow.

3.0 CONCEPTUAL MODEL

A conceptual model was developed to serve as the basis for the construction of the transport model. A conceptual model generally summarizes the theoretical understanding of the primary conditions that affect ground water flow and chemical transport and fate.

Contaminant plumes in ground water develop when contaminants such as PCE and TCE are released to the environment. Over time the contaminants are carried downward by precipitation through the unsaturated soils to the underlying ground water table. As the contaminants dissolve slowly into the ground water they are carried downgradient. When they migrate to ground water, TCE and PCE may volatilize, adsorb to rock matrix or carbon particles in the aquifer, and/or degrade chemically or biologically. Thus, movement of these chemicals downgradient is often retarded in comparison to the rate of ground water flow.

As contaminant plumes move downgradient from the source area they tend to spread laterally and vertically, thereby lowering the average contaminant concentration as the plume expands. The shape taken by an individual plume varies depending primarily on the nature of the geologic materials making up the aquifer, but also secondarily on the rate of ground water flow. In fine-grained unconsolidated sediments such as sands and silts, plumes tend to spread out laterally in a fan shape as they move downgradient. This process is called dispersion. Plumes generated in extremely coarse-grained materials such as cobbles assume a more cigar-shaped signature. Vertical flow also occurs and is controlled by the uniformity of the sediments as well as the vertical hydraulic gradient. When all the aquifer materials are of essentially the same size and are well-rounded, vertical flow can easily take place assuming a vertical hydraulic gradient exists. Fine-grained layers of sediments such as clays and silts in an otherwise coarse-grained aquifer prevent or retard downward (or upward) vertical flow. Finally, ground water flowing at a moderate to fast rate tends to minimize both horizontal and vertical dispersion, while slower flow (normally in fine-grained materials) allows greater dispersion.

Contaminant plumes extend downgradient from the source area over time until a steady state condition is reached based on the rate of contaminant flux to the ground water and the degree of chemical degradation taking place in the aquifer. Contaminant concentrations decline as downgradient flow occurs because processes such as dispersion, volatilization, adsorption, and chemical transformation and biodegradation

are constantly taking place in the aquifer. The length of a plume will depend on: 1) how rapidly these processes work; 2) the rate of ground water flow; 3) the rate of chemical releases to the aquifer; and, 4) other environmental factors such as temperature and the basic chemistry of the ground water. Ultimately, even with a constant source of contamination to the aquifer, any plume will reach a point beyond which it can no longer expand and will more or less stabilize. This stabilization, or steady state condition, occurs when degradation processes in the aquifer remove as much contaminant mass as is being released to the aquifer in the source area.

If the source of contamination is cut off, for example by pump and treat extraction wells, a reduction in chemical concentrations will occur downgradient of the source area and will be especially noticeable along the axis of the plume. Over time the reduction in plume concentrations will be propagated farther downgradient consistent with the hydraulic conductivity of the aquifer. Subsequently the plume will begin to contract in areal extent.

The most significant elements of this conceptual model that are particularly relevant to the construction of the transport model for the Vernay Facility and surrounding area are presented below:

- Ground water flow in the Cedarville Aquifer controls the direction of contaminants migrating in ground water.
- As demonstrated in the Phase I RFI report (Payne Firm et al., 2004), the Cedarville Aquifer can be represented as an equivalent porous medium at the scale of the facility and vicinity. This is supported by the following: 1) the results of an aquifer pumping test performed on CW01-01 shows little evidence of anisotropy or delayed yield characteristics typical of discrete fracture systems; 2) there is very little vertical hydraulic head present in wells screened in the upper, middle and lower portions of the aquifer; 3) the potentiometric surfaces of the Cedarville Aquifer exhibit a smooth and continuous surface without areas of rapidly changing or anomalous hydraulic head values; 4) the measurement of natural ground water geochemical parameters such as temperature, pH, and specific conductivity are relatively constant on a quarterly basis; and, 5) site specific geophysical and rock core inspection indicates that ground water flow is predominantly controlled by horizontal bedding plane partings.
- Sources of chemicals in ground water beneath the Vernay Facility are defined by direct-push soil and ground water sampling data collected at the Facility. Concentrations measured at direct-push sampling locations at or near sources are assumed to represent average conditions near the specific location to a depth of about 3 to5 feet below the water table of the Cedarville Aquifer. These sources continue to contribute chemicals to ground water at a steady rate; the properties of the glacial till deposits that comprise the vadose zone beneath the Facility control the movement of contaminants above the water table of the Cedarville Aquifer.
- Analytical data collected from ground water monitoring wells screened in the Cedarville Aquifer indicate that no chemical ‘slugs’ are moving through the ground water system.

4.0 COMPUTER CODE SELECTION

The computer codes that were used for this analysis are MODFLOW, MT3D and MODPATH. MODFLOW, the United States Geological Survey finite-difference ground water flow model, is a popular, publicly available and widely used computer code. Ground water flow within the Cedarville Aquifer is simulated using a block-centered finite-difference approach. Layers can be simulated as confined, unconfined, or a combination of confined and unconfined. Flow associated with external stresses, such as wells, areal recharge, evapotranspiration, drains, and streams can also be simulated.

The modular three-dimensional (3-D) transport model referred to as MT3D was originally developed by Zheng (1990) at S. S. Papadopulos & Associates, Inc., and subsequently documented for the Robert S. Kerr Environmental Research Laboratory of the U.S. Environmental Protection Agency. In the past several years, various versions of the MT3D code have been commonly used in contaminant transport modeling and remediation assessment studies.

MODPATH is a particle tracking post-processing package that was developed to compute three-dimensional flow paths using output from steady-state or transient ground water flow simulations by MODFLOW. MODPATH is described in USGS Open-File Reports 89-381 and 89-622. MODPATH uses a semi-analytical particle tracking scheme that allows an analytical expression of the particle's flow path to be obtained within each finite-difference grid cell. Particle paths are computed by tracking particles from one cell to the next until the particle reaches a boundary, an internal sink/source, or satisfies some other termination criterion.

5.0 MODEL CONSTRUCTION

One primary goal of mathematical modeling is to synthesize the conceptual model into numerical terms from which flow and transport processes may be investigated under specified conditions. This process entails several discrete steps: (1) partitioning the conceptual model into units of time and space; (2) assignment of boundary conditions; and (3) specification of the values for the parameters. The following sections briefly discuss the approach taken and the relevance of each of these topics to the modeling process. The electronic files and raw data used in the modeling are included as Attachment I on the DVD provided in Appendix VIII of the RFI Phase II report.

5.1 Finite Difference Grid Development

The determination as to what area should be included in the model is typically based on the presence of natural hydrogeologic boundaries. Ideally, the modeled area would be completely surrounded by streams, ground water divides and/or rocks of very low permeability. These types of features greatly assist in defining the boundaries of the system. The source term boundaries used for the model are discussed below in Section 5.2.

In a numerical model, the region of interest is partitioned into a series of grid blocks (i.e., elements), which are arranged in layers. This practice, termed discretization, effectively replaces the continuous

problem domain with an array of blocks. The basic concept involves dividing up the area as realistically as practical. When possible, geologic logs and other information typically are used to identify geologic unit contacts. One of the critical steps in applying a ground water model is selecting the size of the grid blocks. Smaller grid blocks lead to more accurate numerical solutions. The desire for accuracy, however, must be balanced against the impracticality of solving for large numbers of nodes and the long computer run times that may be involved. For this modeling exercise, a finite difference grid (i.e., squares and rectangles) was adopted with 693,720 active cells that range in length from 12.5 feet, in the vicinity of particularly relevant features (e.g., contaminant source), to 50 feet at the model boundaries (Figure 5-1).

5.2 Boundary and Initial Conditions

To obtain a solution for the governing equation of ground water flow and contaminant transport, information is required about the physical state of the ground water system. This information is described by boundary and initial conditions. Boundary conditions are the conditions the modeler specifies as known values to solve for the unknowns in the problem. These values may be associated with either ground water flow or contaminant transport. Boundaries generally are quantified in terms of the volume of ground water and contamination moving through the system. The physical boundaries are then translated into mathematical terms and input into the computer model. For example, if the concentration of a contaminant source is known to be 5,000 µg/L in ground water this knowledge can easily be translated into the model as a constant-concentration boundary; that is, a constant-concentration which is set to 5,000 µg/L. All of the ground water flow boundary conditions (e.g., recharge, constant heads, pumping wells) are described in the Phase I RFI report (Payne Firm et al., 2004). The flow boundaries are used as the basis for the contaminant transport model. The two Facility extraction wells that affect ground water flow in the modeled area, withdraw water from the model at an average rate of 7 gallons per minute.

As presented in Section 4.0 of the RFI Phase I report (Payne Firm et al., 2004), there are numerous potential PCE and TCE sources at the Facility where solvent usage dated back to the late 1950's, which is consistent with the general industrial usage of chlorinated solvents in America at that time period (Doherty, 2000a,b; Pankow and Cherry, 1995). Based upon monitoring well and geoprobe data collected during the RFI, the most significant sources of PCE and TCE contributing to ground water contamination are located beneath the western side of Plant 3. PCE and TCE released in this area are most likely associated with the vapor degreasers that were used to clean metal parts with solvents throughout the Facility beginning in the late 1960s. To account for incidental releases prior to the installation of the vapor degreasers in the late 1960's, the PCE and TCE release times are each set to 1965 in the model. It should also be kept in mind that the use of PCE and TCE in the general operations at the Vernay Facility would have lead to contamination in different areas of the Facility and over different time frames, as described in the RFI Phase I report. The modeling, however, is focused on those sources that are the most significant contributors to ground water contamination as directly indicated by VOCs detected in ground water samples collected from the Facility.

In estimating the PCE source strength, the following considerations were taken into account: (1) the highest PCE concentrations detected in the ground water are located on the western side of Plant 3 and range from 3,000 to 160,000 µg/L; (2) the solubility of PCE in water is approximately 150,000 µg/L. Therefore, the detection of PCE at 160,000 µg/L in the ground water suggests that "free product" was also in the water sample; (3) with the exception of two samples (i.e., 160,000 and 26,000 µg/L) all of the geoprobe and monitoring well data indicate that PCE concentrations are less than 5000 µg/L in ground water; and (4) the area defined by the geoprobe and monitoring well data indicates that the highest concentrations of PCE cover a very limited area near Plants 2 and 3.

To accommodate these characteristics, the PCE source in the modeling was set to a concentration of 10,000 µg/L and was distributed over an area of 3125 ft^2 (Figure 5-2). Although this PCE concentration of 10,000 µg/L is less than the highest concentrations detected, it is a reasonable assumption because the model assumes that concentrations are uniformly averaged over the entire grid block. The size of the source term area has also been conservatively estimated to ensure that the mass of PCE being transported by the ground water has not been underestimated.

A similar type of approach was used to estimate the source concentrations of TCE. The highest concentration of TCE detected in the geoprobes or monitoring wells is 4,700 µg/L. To take into account, however, that TCE may be present at higher concentrations, the TCE source concentration in the modeling was set to 8,000 µg/L and assigned to an area approximately 300 ft^2 (Figure 5-3).

5.3 Stratigraphy and Model Parameterization

The determination of how many model layers to include depends on both the conceptual model and the objectives of modeling. Multiple layers are used when it is necessary to accommodate the vertical variation of hydrologic parameters that represent the hydrogeologic units within the modeled region. In the Vernay Facility modeled area, however, there is very little evidence that vertical variations in the lithology are controlling ground water flow. Therefore, for the flow simulations a single model layer that is approximately 75 feet thick was used to simulate ground water flow through the upper, middle and lower Cedarville Aquifer (Payne Firm et al., 2004). For the transport simulations, this conceptualization was changed and the model was divided into 15 vertical layers, each approximately 5 feet thick. This fine vertical discretization is necessary to reduce the effects of artificial dispersion that tends to unrealistically spread the plume too deep vertically.

<u>Transport Parameters</u>

Estimates for most of the model inputs affecting contaminant transport were based on field data collected during the RFI. In a few instances regional data or literature values representing similar hydrogeologic conditions were used if local data were unavailable. Transport parameters for the transient (time-dependent) transport analysis were constant with time and, with the exception of source concentrations, were constant throughout the model area. The model input parameters specific to contaminant transport are the following:

- Effective Porosity
- Dispersivity
  - Longitudinal
  - Transverse
  - Vertical
- Retardation Factor
- Half-Life
  - PCE
  - TCE

With the exception of the retardation factor (no retardation was assumed), all of the transport parameters were adjusted during the model calibration as discussed in Section 6. A brief description of each of these parameters is presented below.

Effective Porosity. The effective porosity is the ratio of the volume of interconnected pore spaces available for transport to the total system volume. It is used to estimate the velocity at which ground water and contaminants travel through a porous medium. The smaller the effective porosity, the higher the ground water velocity and the more rapidly contaminants will be transported.

Dispersivity. The equations of solute transport that are solved in contaminant-transport codes are derived assuming that the solute migration is due to advection and hydrodynamic dispersion. Advection describes the bulk movement of ground water flow where hydrodynamic dispersion is caused by the tendency of the solute to spread out from the path that it would be expected to follow if transported only by advection. This spreading of the contamination over an ever-increasing area is called hydrodynamic dispersion and has two components: mechanical dispersion and diffusion. Hydrodynamic dispersion causes dilution of the solute and occurs because of spatial variations in ground-water flow velocities and mechanical mixing during fluid advection. Molecular diffusion, the other component of hydrodynamic dispersion, is due to the thermal kinetic energy of solute molecules and also contributes to the dispersion process. Thus, if hydrodynamic dispersion is factored into the solute transport processes, ground-water contamination will cover a much larger region than in the case of pure advection, with a corresponding reduction in the maximum and average concentrations of the contaminant. Dispersion also increases the velocity of the contaminants because it considers the fact that some contaminants will travel through faster pathways (and some slower) than if only pure advection was assumed.

Because hydrodynamic dispersion is the sum of mechanical dispersion and diffusion, it is possible to divide the hydrodynamic dispersion term into the two components and have two separate terms in the equation. Under most conditions of ground-water flow, diffusion is insignificant and is frequently neglected in many of the contaminant transport codes.

Representing dispersion adequately in computer codes is difficult, because dispersion is related to spatial scale and variations in aquifer properties that are generally not explicitly simulated in the code. Furthermore, dispersion coefficients are very difficult to measure in the field and have been shown

generally to increase with scale of observation. These difficulties are generally addressed by using dispersivity values from the published literature and refining these estimates during the model calibration process.

Retardation Factor

The rate at which contaminants migrate relative to ground water is termed the Retardation Factor and is determined by the effective porosity (see definition above), bulk density and distribution coefficient described below.

Bulk Density. The bulk density is the ratio of the mass of the solid phase of rock (i.e, dry rock) to its total volume (solid and pore volumes together). Rock cores obtained from the Cedarville Aquifer during the Phase I RFI (Payne Firm et al., 2004) indicate that the bulk density of the Cedarville Aquifer ranges from 2.41 – 2.59 gr/cm^3.

Distribution Coefficient. A distribution or partitioning coefficient (designated K_d), which describes the degree of sorption, is used to calculate the partitioning of contaminants such as PCE and TCE between the ground water and aquifer and, thereby, strongly influences the sorption capacity or retardation.

6.0 MODEL CALIBRATION

In March 2000, a ground water extraction interim remedial measure commenced at the southeastern portion of the Facility with the operation of an extraction well (CW01-01) that was constructed in the Cedarville Aquifer (Payne Firm et al., 2004). This well was supplemented by a second extraction well that was installed near the northeast corner of the Facility in January 2003 during the Phase I RFI. Normally, as remediation reduces source concentrations, the length and width of the existing plume geometry will, at first, remain more or less constant while the chemical concentrations within the plume decline. Thereafter, the plume length and width will decrease. The decreases in plume size and chemical concentrations are expected to occur at a slow rate in the facility area because of slow ground water flow velocities caused by the relatively low hydraulic conductivities of the Cedarville Aquifer. Although remediation times may be extended in lower permeability aquifers, the slower transport velocities allow more time for natural degradation processes to occur.

The contaminant transport model was constructed to incorporate all of the relevant properties of the ground water system and the specific properties of PCE and TCE. Generally, the hydraulic, physical and chemical parameters used in a contaminant transport model will not change in the future. Thus, those parameters apply for an analysis of future conditions. The steady state flow conditions in the model represent average conditions in the recent past and, because flow conditions in the Vernay area change little over time, these average conditions apply to the near future represented by the model.

Once a contaminant plume stabilizes, degradation of the contaminants will cause the plume to contract until the contaminants can no longer be detected. The time required for the plume to stabilize and

ultimately to contract can be predicted by evaluating how specific environmental factors control contaminant movement and mass reduction. The major environmental factors affecting the development and stabilization/contraction of the PCE and TCE plumes originating from the Vernay Facility are as follows:

- *Velocity of ground water flow*, which is directly dependent on hydraulic conductivity, aquifer porosity, and hydraulic gradient, and indirectly dependent on the rate of recharge to the aquifer and water levels in local lakes and streams.
- *Dispersion characteristics of the ground water system*, which depend primarily on the directness (or indirectness) of the path ground water takes as it flows downgradient.
- *Magnitude of PCE and TCE adsorption to aquifer materials*, as expressed by the coefficient of adsorption (K_d), which is controlled primarily by the bulk density and organic carbon content of the aquifer materials and adsorption characteristics of PCE and TCE.
- *Bulk degradation rate of sorbed and mobile PCE and TCE mass* (incorporating the effects of physical, chemical and biological action), which reduces concentrations through actions that include dilution, volatilization, reductive dechlorination (loss of chlorine by chemically reducing conditions), or complexation (chemical reaction and combination with other compounds present in the environment).
- *Human influences*, such as disruption of ambient ground water flow or contaminant removal by extraction wells.

With respect to model calibration targets, the PCE and TCE plumes are most extensive within the upper and middle portion of the Cedarville Aquifer Furthermore, the most recent PCE and TCE concentration data available (at the time of the model calibration) was April 2004 (Second Quarter 2004 ground water sampling event; Payne Firm, 2004). Therefore, in order to ensure that the calibration did not underestimate the size of the plumes, values of PCE and TCE sampled in April 2004 from the upper, middle and lower portions of the Cedarville Aquifer were used as calibration targets.

Composite isoconcentration contours of PCE concentrations for this time period over the upper and middle intervals are presented in Figure 5-2. A similar depiction of TCE concentrations is provided in Figure 5-3. VOCs were not detected above a laboratory reporting limit from the lower portion of the Cedarville Aquifer.

The goal of this phase of model calibration was to achieve the best possible match to the PCE and TCE plume concentration contours. Model calibration was achieved by adjusting the model input parameters provided in Table 5.1. The final values that were obtained by matching the model predictions to the field data are also shown in the table. Although it is possible that both PCE and TCE do experience retardation, in order to ensure that the model does not underestimate transport velocities, no retardation was assumed to occur.

Table 5.1: Calibrated Model Input Parameters

Model Input Parameter	Calibrated Value	Potential Range of Values	References	
[1]Effective Porosity (%)	0.25	0.05 – 0.50	Freeze and Cherry (1979)	
Dispersivity (ft) Longitudinal Transverse [1]Vertical	250 25 0.05	14-323 ft 25 -82.5 ft.	$\forall_L$ = 0.1(plume length) $\forall_T$= 0.1($\forall_L$)	Gelhar et. al. 1992
			$\forall_L$ = 14-323 ft. $\forall_T$ = 0.33($\forall_L$)	U.S. EPA (1996)
			$\forall_L$ = 0.33-328 ft. $\forall_T$ = 0.1($\forall_L$)	AT123D
Retardation Factor (dimensionless)	1 (no retardation)	1-1.25	Although there is probably very little total organic carbon in the Cedarville Aquifer, some retardation will most likely occur. To be conservative, however, no retardation is assumed.	
Half-Life (years) PCE TCE	5 8	2 hours – 8 years 30 days – 10 years	Aronson, et. al. (1997) Alleman, et. al., (1999) Wiedemeier et. al., (1999)	

[1]The value for effective porosity accounts for the interaction between the matrix and fracture porosities.
[2]Vertical dispersivity is set to the lowest possible value in which numerical stability is maintained.
$\forall_L$ = Longitudinal Dispersivity
$\forall_T$ = Transverse Dispersivity

A comparison of the model output with actual field monitoring data show a relatively good match over most of the plume (Figures 5-2 and 5-3). A close comparison, however, reveals a few differences as discussed below.

PCE

In order to demonstrate the consistency of the modeled predicted plume migration directions with those observed in the field, a particle tracking analysis was performed with MODPATH. The particle trace shown in Figures 5-2 and 5-3 predicts the path that ground water\contaminants would take from the source to its farthest predicted extent if advection alone is considered in the absence of pumping. As discussed previously, however, dispersion will significantly affect the width of the plume along this flow path.

When dispersion is considered, the model provides a good prediction of the extent of the plume (>1 µg/L), although the model overestimates the distance between the 1 and 5 µg/L contour lines, particularly in the northeast portion of the plume. As discussed in Section 5.3, the amount of spreading experienced by the plume is controlled by the dispersivity. As part of the model calibration, the dispersivity values were decreased to determine whether a better match to the sharp concentration fronts within the northeast portion of the plume could be achieved. Although not as much spreading occurred with lower dispersivity values, the relative positions of the 1 and 5 µg/L contours remained about the

same. The contaminant velocities were significantly underestimated with the lower dispersivities, however. Therefore, the dispersivity values were set to those presented in Table 5.1, which are consistent with the site-specific geology as well as the overall size of the plume.

The primary reason that the very sharp concentration front exhibited by the data is difficult for the model to match is that all numerical models experience a certain amount of "numerical dispersion" that is inherent to the solution techniques used to solve the differential equations. This artificial dispersion typically presents a problem only at fairly low concentrations. Since the primary objective of the modeling is to estimate the temporal behavior of the plume (as defined by detection limits), greater emphasis was placed on obtaining a better fit to the measured data at the 1 µg/L contour than matching the interior concentration contours of the plume.

The modeled plume also tends to be wider than the measured plume along the central axis of the plume. These differences occur because the band of higher hydraulic conductivity assumed in the model appears to be wider than that which is probably present in the field. These differences are minor (and conservative), however, when they are considered in context of the overall objectives of the modeling.

With respect to the vertical distribution of the contaminant plume, the model predicts that that the plume would migrate somewhat deeper vertically than actually observed by the monitoring well data. Since the model is very finely discretized in the vertical dimension (i.e. 15 model layers) and the vertical dispersivity is relatively low (0.05 feet) it appears that the specified areal recharge rate (6 in\yr) may be slightly higher than is actually present. During the flow calibration, however, it was important not to underestimate the areal recharge because this would lead to larger capture zones resulting in overly optimistic projections. This over prediction of the vertical extent of the plume suggests that the extraction wells are somewhat more effective in capturing contamination than is predicted by the model.

Since the temporal nature of the plume is most sensitive to the value assigned to the contaminant half life (or degradation rate), a brief discussion of the processes that control the degradation of the contaminants is provided below.

Transformation (or degradation) of organic chemicals in the subsurface environment can occur through the action of microorganisms that may be attached to the rock matrix or contained in the void space. Bacteria have been found in subsurface environments throughout extensive depths. Active microbial populations are found in most typical subsurface conditions. In many cases, significant populations exist at depth. Even in low numbers, subsurface microbes possess adequate metabolic activity to reduce the levels of organic compounds migrating through the subsurface soil profiles. Biodegradation of organic chemicals by microorganisms ultimately produces microbial cells, water, and carbon dioxide (i.e., complete "mineralization"). The enzymes produced by the microorganisms are essentially responsible for the innocuous byproducts, like carbon dioxide and water, via biologically mediated oxidation/reduction reactions without intervention or introduction of any substance.

The basis for intrinsic bioremediation is the ability for microorganisms to use organic contaminants as a source of carbon and energy for respiration and survival. Not all organic contaminants can be used as carbon and energy, however. In the environment, microorganisms transform available electron donors into forms useful for cellular energy and growth by facilitating the transfer of electrons from donors to acceptors. For biodegradable compounds, this results in oxidation of the organic donor and reduction of the electron acceptor. For thermodynamic reasons, microorganisms preferentially utilize those electron acceptors that provide the greatest amount of free energy during respiration (in order: oxygen, nitrate, ferric iron, sulfate, carbon dioxide). The energy produced by these reactions is quantified by the Gibb's free energy of the reaction, a measure of the maximum useful energy released by a chemical reaction at a constant temperature and pressure. During biodegradation, microorganisms will facilitate only those redox reactions that yield energy. These redox reactions are facilitated via microorganisms.

None of the detected contaminants of concern at the Vernay Facility can be used as a carbon source for either aerobic or anaerobic biodegradation. They can, however, be cometabolically transformed through oxidation or reductive dechlorination. The anaerobic biotransformation of PCE and TCE occurs through a microbially mediated, sequential dehalogenation process depicted below:

PCE → TCE → *cis*-1, 2-DCE → VC → ethene → ethane

The degree to which this sequence proceeds depends on three factors:

- The presence of dechlorinating microorganisms
- The presence of suitable electron donors
- The presence of competing electron acceptors

Evidence that dechlorination of PCE and TCE is occurring includes the presence of cis-DCE and VC as shown in Figures 6-1 and 6-2, respectively. Both cis-DCE and VC are highly mobile and the fact that they are not more widespread suggests that they are being completely mineralized. Otherwise, cis-DCE and VC would be expected to be detected farther downgradient than both PCE and TCE.

During the model calibration process, it was observed that the farthest reaches of the PCE plume would begin to recede if a half life of 5 years or less was assigned to PCE. To assess whether this half life is within the range observed at other sites, a literature review was conducted (see Section 8.0). The following references provide case history summaries at numerous sites where chlorinated solvents are the primary contaminants of concern. Aronson, et. al. (1997), present a mean half-life value (for all the field studies reviewed) for PCE of 238 days. Alleman, et. al., (1999) indicate a range of 2 hours to 4 months, and data presented by Wiedemeier et. al., (1999) show a PCE half life ranging from 13-1019 days. Based upon this information, the modeling assumption that the PCE half life is no longer than 5 years appears to be conservative and it is very possible that PCE is degrading at a faster rate in the Cedarville Aquifer. It should also be kept in mind that if PCE is experiencing retardation, half lives longer than the 5 years would also be sufficient to contract the plume. Actual field monitoring data further substantiate that the

outer reaches of the plume are stable with respect to a level of concern, as presented in Section 3.0 of the RFI Phase II report.

TCE

The calibration of the model to the TCE measured in the monitoring wells is complicated by the fact that not only was TCE used at the Facility, but TCE can also be created by the degradation of PCE. Therefore, TCE has both an areal source (e.g., extent of PCE plume) and a point source located at the Facility (Figure 5-3). For the purposes of model calibration, it is assumed that the degradation of PCE does not provide an additional source for TCE. This conservative assumption effectively overestimates the migration rates of TCE because all of the TCE is assumed to have migrated from the source on the Facility. The transformation of PCE into TCE is qualitatively considered, however, since the overall shape of the TCE plume mimics that of PCE relatively well, and the TCE plume is almost fully contained within the PCE plume.

With respect to the model predictions, the TCE source at the Facility has produced a plume that is similar in dimensions to the PCE plume, but is characterized by lower chemical concentrations. The TCE plume based on April 2004 values in the shallow and intermediate Cedarville Aquifer is shown in Figure 5-3. Although the model provides a good prediction of the extent of the plume (>1 µg/L), the model conservatively overestimates the distance between the 1 and 5 µg/L contour lines, particularly in the northeast portion of the plume. As discussed previously, this phenomenon was also observed with the PCE concentrations and is caused primarily by artificial dispersion and does not adversely affect the overall projections of the model. Again, as was observed for the PCE, the model over predicts the vertical distance that the plume would migrate which is probably due to an overestimate of the recharge values as discussed previously.

During the model calibration process, it was determined that the farthest reaches of the TCE plume would begin to recede if a half life of 8 years or less was assigned to TCE. To assess the validity of this assumption, a literature review similar to that conducted for PCE was performed (see Section 8.0). The referenced studies show a mean TCE half life of approximately 2.5 years. These published values suggest that the assumption of an 8 year TCE half-life is conservative. More importantly, however, the monitoring well data indicate a stable plume as presented in Section 3.0 of the RFI Phase II report.

7.0 SUMMARY AND CONCLUSIONS

The hydrologic conceptual site model was developed to collect and process information on the subsurface water flow and contaminant transport in order to establish the temporal characteristics of the PCE and TCE contaminant plumes. A properly calibrated numerical model that simulates ground water flow and contaminant transport can be used to meet the following objectives: 1) define the temporal behavior of PCE and TCE contaminant concentrations in the Cedarville Aquifer beneath the Facility and the surrounding area since these are the only two VOCs that have been detected above a level of concern off the Facility; 2) determine the effect that two operating pump and treat extraction wells have had on the

migration and distribution of PCE and TCE downgradient of the Facility; 3) determine if PCE and TCE concentrations detected in wells at the fringe of the contaminant plume downgradient of the Facility are stable above a level of concern; and 4) confirm that the existing monitoring well network is sufficient. To accomplish these objectives, the ground water flow model that was constructed and calibrated during the Phase I RFI (Payne Firm et al., 2004) was used as the basis for a contaminant transport model.

MODFLOW, MT3D and MODPATH were the computer codes selected to conduct the flow and transport analysis. The major aspect of the site conceptual model that was taken into consideration in selecting a computer code to use for the transport analysis was that the Cedarville Aquifer can be represented as an equivalent porous medium at the scale of the facility and vicinity. The output from MODFLOW is a ground water velocity field which is used by MT3D, in conjunction with fate and transport parameters, to simulate the migration of PCE and TCE. A particle tracking analysis was also conducted with MODPATH to illustrate the ground water flow direction from the contaminant source areas. All of these computer codes are widely used, well documented, and in the public domain.

With respect to the construction of the model, a finite difference grid was utilized that incorporated 693,720 active cells ranging in length from 12.5 in the vicinity of the contaminant source(s) to 50 feet at the model boundaries. Although the model was discretized vertically into 15 layers, this fine discretization was primarily to reduce vertical dispersion, rather than to simulate vertical inhomogeneities within the model layers.

PCE and TCE source concentrations were determined based upon ground water data obtained from geoprobes and monitoring wells (Payne Firm et al., 2004; Payne Firm, 2004). Release times were established from a historical review of PCE and TCE use at the Facility. Fate and transport parameters were estimated based on field data, literature reviews and model calibration. Ground water data collected during April 2004 were used as the calibration targets.

The results of the transport analyses indicate that both the PCE and TCE plumes are stable and well contained within the existing monitoring well network. This contention is also supported by the existing field monitoring data.

8.0 REFERENCES

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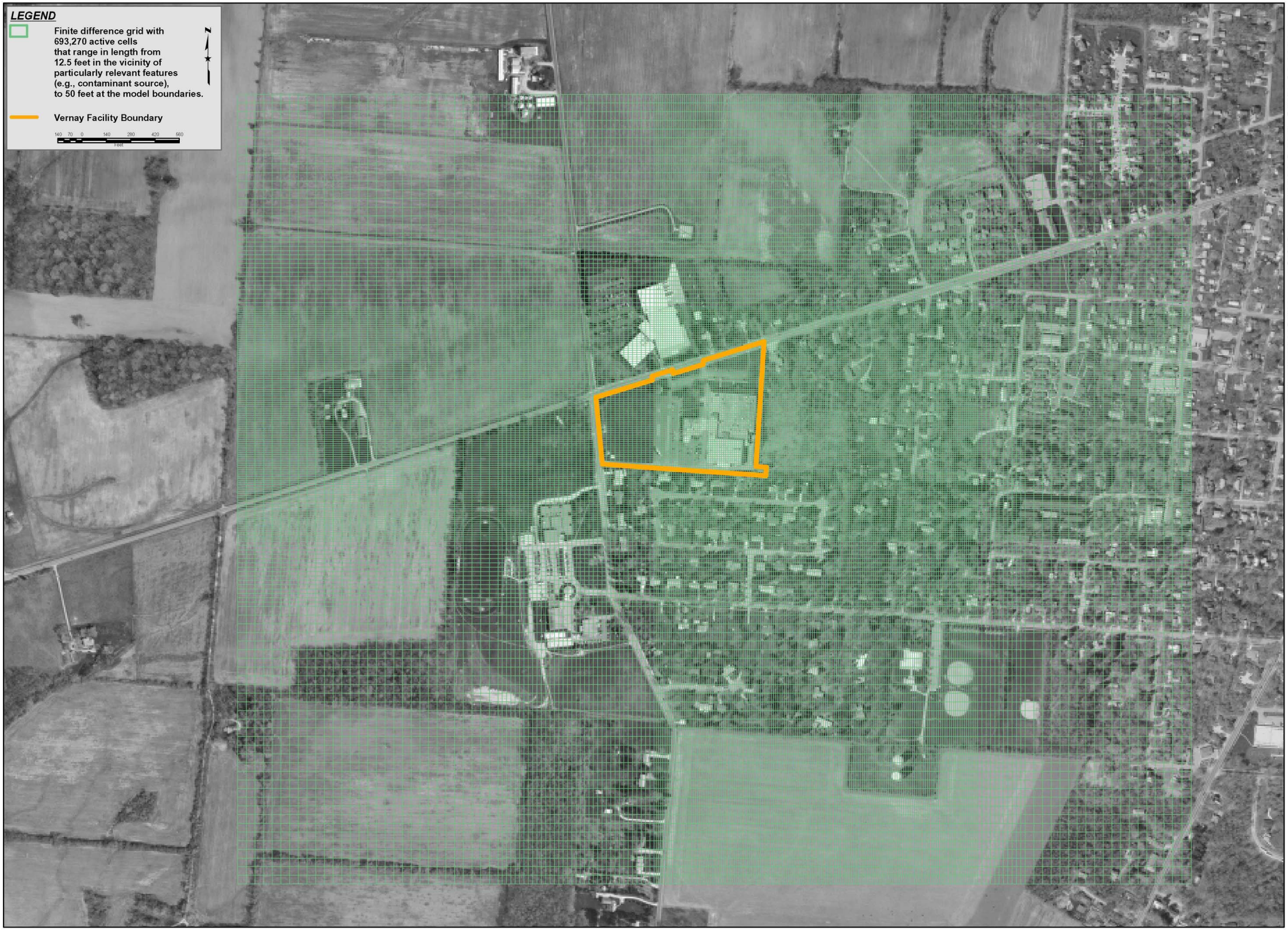

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Cincinnati, Ohio

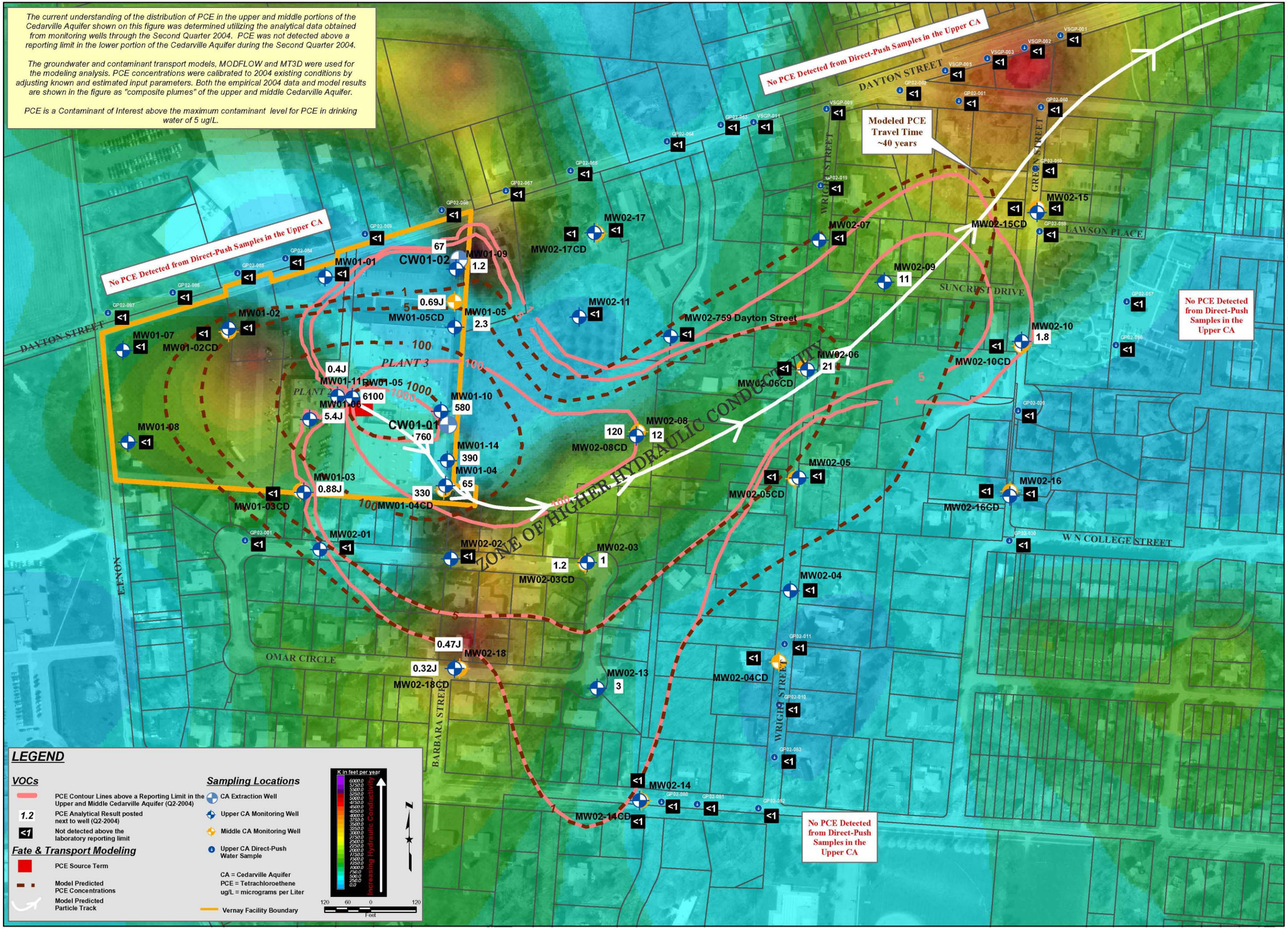
CLIENT	VERNAY LABORATORIES, INC.	FIGURE NO. 5-1	DATE 11/16/04
TITLE	FINITE DIFFERENCE GRID	DRAWN BY ALH	APPROVED BY DAVID BACK, P.G.
		PROJECT NO. 292.11.37	

REFERENCE Greene County Auditors, Orthophotograph (2003); State Plane Coordinates from Woolpert Surveying, LLP, Dayton, Ohio (NAD83/NAVD88)

The current understanding of the distribution of PCE in the upper and middle portions of the Cedarville Aquifer shown on this figure was determined utilizing the analytical data obtained from monitoring wells through the Second Quarter 2004. PCE was not detected above a reporting limit in the lower portion of the Cedarville Aquifer during the Second Quarter 2004.

The groundwater and contaminant transport models, MODFLOW and MT3D were used for the modeling analysis. PCE concentrations were calibrated to 2004 existing conditions by adjusting known and estimated input parameters. Both the empirical 2004 data and model results are shown in the figure as "composite plumes" of the upper and middle Cedarville Aquifer.

PCE is a Contaminant of Interest above the maximum contaminant level for PCE in drinking water of 5 ug/L.



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Cincinnati, Ohio

CLIENT	VERNAY LABORATORIES, INC.
TITLE	TRANSPORT CALIBRATION RESULTS FOR PCE
FIGURE NO.	5-2
DATE	12/20/04
DRAWN BY	ALH
APPROVED BY	DAVID BACK, P.G.
PROJECT NO.	292.11.37

REFERENCE Greene County Auditors, Orthophotograph (2003); State Plane Coordinates from Woolpert Surveying, LLP, Dayton, Ohio (NAD83/NAVD88)

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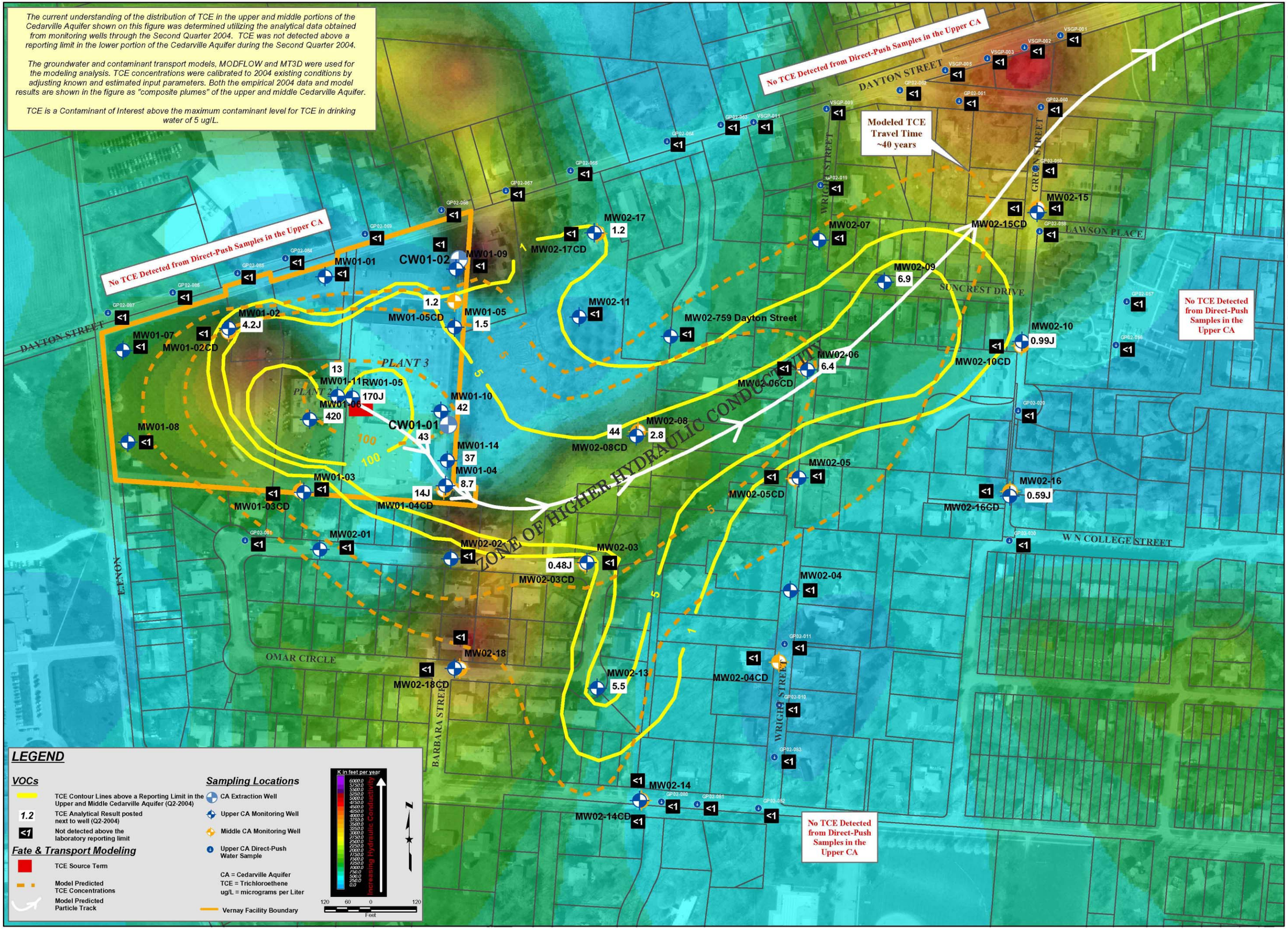
The current understanding of the distribution of TCE in the upper and middle portions of the Cedarville Aquifer shown on this figure was determined utilizing the analytical data obtained from monitoring wells through the Second Quarter 2004. TCE was not detected above a reporting limit in the lower portion of the Cedarville Aquifer during the Second Quarter 2004.

The groundwater and contaminant transport models, MODFLOW and MT3D were used for the modeling analysis. TCE concentrations were calibrated to 2004 existing conditions by adjusting known and estimated input parameters. Both the empirical 2004 data and model results are shown in the figure as "composite plumes" of the upper and middle Cedarville Aquifer.

TCE is a Contaminant of Interest above the maximum contaminant level for TCE in drinking water of 5 ug/L.



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CLIENT	VERNAY LABORATORIES, INC.
TITLE	TRANSPORT CALIBRATION RESULTS FOR TCE
FIGURE NO.	5-3
DATE	12/20/04
DRAWN BY	ALH
APPROVED BY	DAVID BACK, P.G.
PROJECT NO.	292.11.37

REFERENCE Greene County Auditors, Orthophotograph (2003); State Plane Coordinates from Woolpert Surveying, LLP, Dayton, Ohio (NAD83/NAVD88)

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The current understanding of the distribution of cis-1,2-DCE in the upper portion of the Cedarville Aquifer shown on this figure was determined utilizing the analytical data obtained from monitoring wells through the Second Quarter 2004. cis-1,2-DCE was not detected above a reporting limit in the middle and lower portions of the Cedarville Aquifer during the Second Quarter 2004.

cis-1,2-DCE is a Contaminant of Interest above the maximum contaminant level for cis-1,2-DCE in drinking water of 70 ug/L.

No cis-1,2-DCE Detected from Direct-Push Samples in the Upper CA

No cis-1,2-DCE Detected from Direct-Push Samples in the Upper CA

No cis-1,2-DCE Detected from Direct-Push Samples in the Upper CA

No cis-1,2-DCE Detected from Direct-Push Samples in the Upper CA

DAYTON STREET

ELENON

OMAR CIRCLE

BARBARA STREET

WRIGHT STREET

GREEN STREET

LAWSON PLACE

SUNCREST DRIVE

W N COLLEGE STREET

PLANT 3

PLANT 2

ZONE OF HIGHER HYDRAULIC CONDUCTIVITY

CW01-01

CW01-02

MW01-01 <0.5

MW01-02 6.1

MW01-03 <0.5

MW01-04 4.8

MW01-05 <0.5

MW01-06 11

MW01-07 <0.5

MW01-08 <0.5

MW01-09 0.27J

MW01-10 95

MW01-11 4.9

MW01-14 110

RW01-05 <0.5

MW02-01 <0.5

MW02-02 <0.5

MW02-03 <0.5

MW02-04 <0.5

MW02-05 <0.5

MW02-06 2.2

MW02-07 <0.5

MW02-08 1.2

MW02-09 1.9

MW02-10 <0.5

MW02-11 <0.5

MW02-13 3.1

MW02-14 0.37J

MW02-15 <0.5

MW02-16 <0.5

MW02-17 1.4

MW02-18 <0.5

MW02-759 Dayton Street <0.5

0.30J

<0.5

LEGEND

VOCs

- cis-1,2-DCE Contour Lines above a Reporting Limit in the Upper Cedarville Aquifer (Q2-2004)
- 1.2 — cis-1,2-DCE Analytical Result posted next to well (Q2-2004)
- <1 — Not detected above the laboratory reporting limit

120 60 0 120 Feet

Sampling Locations

- CA Extraction Well
- Upper CA Monitoring Well
- Upper CA Direct-Push Water Sample

CA = Cedarville Aquifer

cis-1,2-DCE = cis-1,2-Dichloroethene

ug/L = micrograms per Liter

Vernay Facility Boundary

K in feet per year

6000.0 5750.0 5500.0 5250.0 5000.0 4750.0 4500.0 4250.0 4000.0 3750.0 3500.0 3250.0 3000.0 2750.0 2500.0 2250.0 2000.0 1750.0 1500.0 1250.0 1000.0 750.0 500.0 250.0 0.0

Increasing Hydraulic Conductivity

N

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Cincinnati, Ohio

DATE	12/20/04
APPROVED BY	DAVID BACK, P.G.
FIGURE NO.	6-1
DRAWN BY	ALH
PROJECT NO.	292.11.37

CLIENT: VERNAY LABORATORIES, INC.

TITLE: cis-1,2-DCE CONCENTRATIONS IN THE UPPER CEDARVILLE AQUIFER

REFERENCE: Greene County Auditors, Orthophotograph (2003); State Plane Coordinates from Woolpert Surveying, LLP, Dayton, Ohio (NAD83/NAVD88)

The current understanding of the distribution of VC in the upper portion of the Cedarville Aquifer shown on this figure was determined utilizing the analytical data obtained from monitoring wells through the Second Quarter 2004. VC was not detected above a reporting limit in the middle and lower portions of the Cedarville Aquifer during the Second Quarter 2004.

VC is a Contaminant of Interest above the maximum contaminant level for VC in drinking water of 2 ug/L.

No VC Detected from Direct-Push Samples in the Upper CA

No VC Detected from Direct-Push Samples in the Upper CA

No VC Detected from Direct-Push Samples in the Upper CA

No VC Detected from Direct-Push Samples in the Upper CA

DAYTON STREET

DAYTON STREET

WRIGHT STREET

GREEN STREET

LAWSON PLACE

SUNCREST DRIVE

W N COLLEGE STREET

ELENON

OMAR CIRCLE

BARBARA STREET

PLANT 3

PLANT 2

ZONE OF HIGHER HYDRAULIC CONDUCTIVITY

MW01-01 <1
MW01-02 <1
MW01-03 <1
MW01-04 <2
MW01-05 <1
MW01-06 <14
MW01-07 <1
MW01-08 <1
MW01-09 <1
MW01-10 23
MW01-11 <1
RW01-05 <250
MW01-14 3.5 J
CW01-01 <5
CW01-02 <5
MW02-01 <1
MW02-02 <1
MW02-03 <1
MW02-04 <1
MW02-05 <1
MW02-06 <2
MW02-07 <1
MW02-08 <1
MW02-09 <1
MW02-10 <1
MW02-11 <1
MW02-13 <1
MW02-14 <1
MW02-15 <1
MW02-16 <1
MW02-17 <1
MW02-18 <1
MW02-759 Dayton Street <1

LEGEND

VOCs

- VC Contour Lines above a Reporting Limit in the Upper Cedarville Aquifer (Q2-2004)
- 1.2 — VC Analytical Result posted next to well (Q2-2004)
- <1 — Not detected above the laboratory reporting limit

120 60 0 120
Feet

Sampling Locations

- CA Extraction Well
- Upper CA Monitoring Well
- Upper CA Direct-Push Water Sample

CA = Cedarville Aquifer

VC= Vinyl Chloride

ug/L = micrograms per Liter

Vernay Facility Boundary

K in feet per year
6000.0
5750.0
5500.0
5250.0
5000.0
4750.0
4500.0
4250.0
4000.0
3750.0
3500.0
3250.0
3000.0
2750.0
2500.0
2250.0
2000.0
1750.0
1500.0
1250.0
1000.0
750.0
500.0
250.0
0.0
Increasing Hydraulic Conductivity

N

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Cincinnati, Ohio

DATE	12/20/04
APPROVED BY	DAVID BACK, P.G.
FIGURE NO.	6-2
DRAWN BY	ALH
PROJECT NO.	292.11.37

CLIENT: VERNAY LABORATORIES, INC.

TITLE: VC CONCENTRATIONS IN THE UPPER CEDARVILLE AQUIFER

REFERENCE: Greene County Auditors, Orthophotograph (2003); State Plane Coordinates from Woolpert Surveying, LLP, Dayton, Ohio (NAD83/NAVD88)