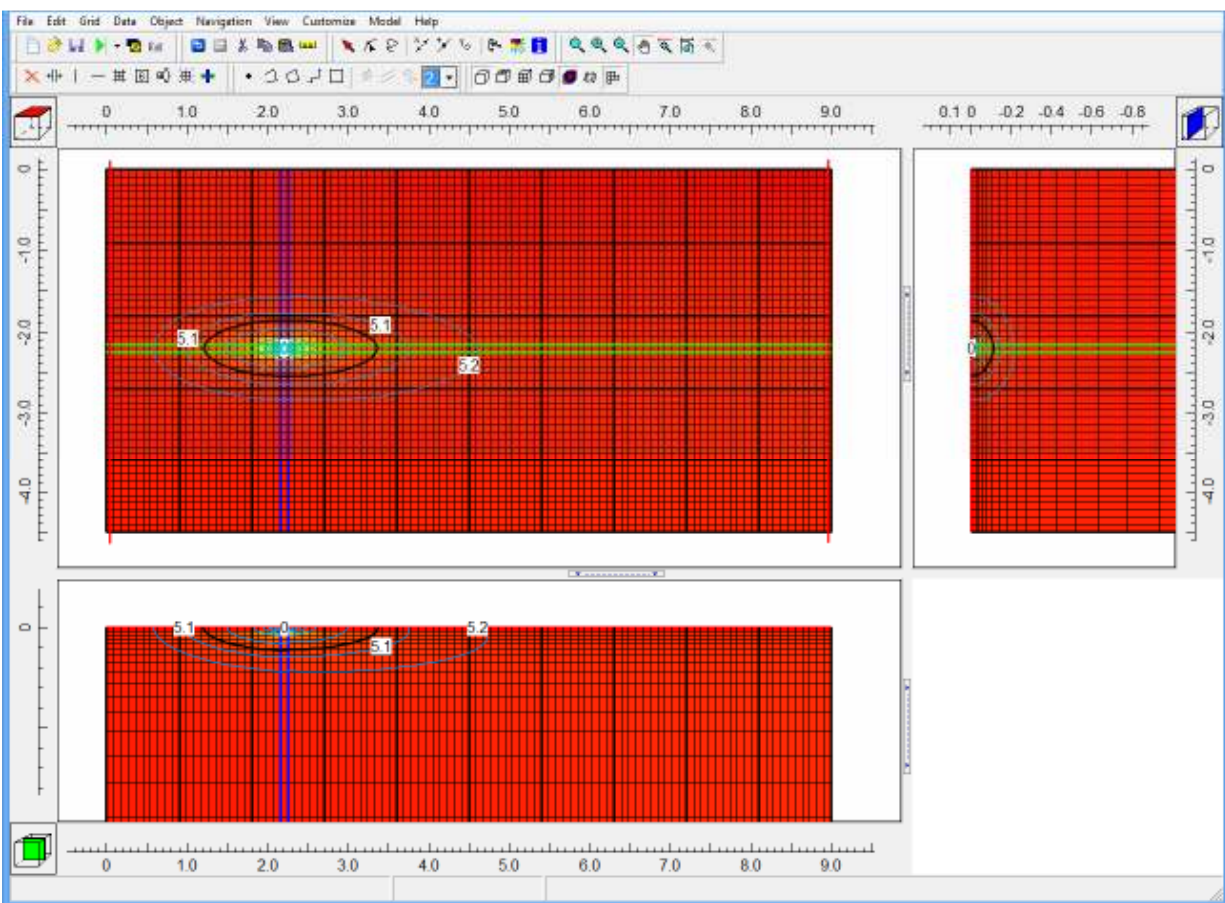# Zone of Influence Model for the $CO_2$ Sampling Technique Developed to Quantify the Attenuation Rate of Chlorinated Solvent Contamination



Prepared by:

Yutaka Hagimoto and Richard H. Cuenca

Hydrologic Engineering, Inc.

September 30, 2013

**Abstract**

The objective of this project is to develop a zone of influence (ZOI) model for the proposed technology that is to study attenuation of contaminated groundwater using stable carbon isotope in solute $CO_2$ (Boyd et al., 2013). The technology is designed to sample $CO_2$ from a well head and perform on-site analysis for degradation rate of chlorinated solvents which are common dense non-aqueous phase liquids (DNAPL). Carbon dioxide is the terminal product of the chain dechlorination (degradation) of chlorinated solvents; therefore, the amount of $CO_2$ that originated from the chlorinated solvents can be used to estimate the attenuation rate of contaminated groundwater. Thus, this modeling project focuses on $CO_2$ in the aquifer as the target solute and develops a ZOI model using parameters available from Naval Air Station North Island located at the north end of the Coronado Peninsula on San Diego Bay. Four models have been developed, one areal model to study hydrology around the study site and three ZOI models to study the $CO_2$ collection under different conditions (e.g., hydraulic gradient and background $CO_2$ concentration). The simulation results indicated that the size of ZOI is significantly influenced by the groundwater hydrology and the background $CO_2$ concentration.

**Section 1: Technical Background**

Microbial dechlorination of chlorinated solvents can be illustrated as:

$$PCE \rightarrow TCE \rightarrow DCE \rightarrow VC$$
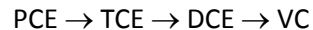
where PCE is tetrachloroethene ($C_2Cl_4$), TCE is trichloroethene ($C_2HCl_3$), DCE is dichloroethylene ($C_2H_2Cl_2$) and VC is vinyl chloride ($C_2H_3Cl$). Both PCE and TCE are typically considered as dense non aqueous phase liquids (DNAPL) and are more dense (1,100 to 1,600 $kg/m^3$, respectively) and less viscous (0.57 to 1.0 cP, respectively) than water. This can result in rapid rates of subsurface migration of the solvents. Typically, chlorinated solvents are no longer moving at sites where they were introduced to the subsurface even as recently as two or three years ago (Kueper et al., 2004). Therefore, simulating their migration requires information on the exact location and timing of the release as well as details of the aquifer hydraulics and hydrology (e.g., distribution of aquitard, topography of aquifer bottom, etc.).

The above chain reaction continues further as:

$$VC \rightarrow CO_2 + H_2O + salts \ : mineralization$$

$$VC \rightarrow Ethylene \ (C_2H_4) \quad : dechlorination$$
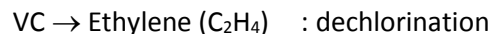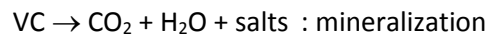
Mineralization is a microbial process and can be significant even under hypoxic conditions (Bradley, 2012). By detecting and quantifying $CO_2$ produced via mineralization, the proposed technology is designed to study the attenuation rate of chlorinated solvents in groundwater. The technology circulates air in a well head as it strips and collects $CO_2$. The depleted $CO_2$ stimulates the release of $CO_2$ from water in the well, which creates a $CO_2$ concentration gradient around the well and allows solute $CO_2$ to migrate towards the well. The objective of this project is to estimate the zone of influence (ZOI) associated with this $CO_2$ collection.

## Section 2: Simulation Models

**Modeling Environment**

The ZOI model was developed using MT3DMS (Zheng and Wang, 1999) and MODFLOW-2005 (Harbaugh, 2005). MT3DMS is the biodegradation model capable of simulating multi-solute transport and reaction, and used to simulate $CO_2$ solute transport as a part of the ZOI model. MODFLOW-2005 is the hydrogeological model considered as the reference code to simulate groundwater dynamics and is used to simulate groundwater flow in the unconfined aquifer at the study site. The two models have been used together as the standard package for multi-species contaminant transport simulations (Prommer et al., 2003). This project uses ModelMuse (Winston, 2009) to link and interface the two models.

The target $CO_2$ of the technique is produced from chlorinated solvents (e.g., DCE and VC). However, $CO_2$ derived from soil gas and calcium carbonate (limestone) is also considered significant in the in-situ unconfined aquifer of the site. These $CO_2$ with different origins have unique stable isotope ratios. Among different biodegradation models studied (e.g., MT3DMS, RT3D, Biosereen, Biochlor, and SEAM3D), there is no model that is capable of coupling a groundwater simulation model and simulating this complex $CO_2$ system while tracking individual $CO_2$ solutes. Therefore, this project treats $CO_2$ with different origins together.

**Parameterization for Site Groundwater Flow**

Table 1 summarizes the groundwater hydraulic and $CO_2$ solute properties of the study site used for the ZOI models. The study site is located within IR Site 5 Unit 2 which is located between golf holes of the Sea and Air Golf Course (Fig. 2-1). Twelve observation wells used in the 2013 field test are distributed around the center of the study site (Fig. 2-2). All hydraulic properties used for the ZOI model were obtained from previous reports (Battelle and Geosyntec Consultants, 2012; Accord Engineering, Inc., 2011).

Table 2-1. Parameter summary for the ZOI model.

| Parameter | Units | Value |
|---|---|---|
| Hydrology | | |
| Hydraulic Conductivity | (m/hr) | 0.44 (aquifer), 10 (well) |
| Porosity (aquifer) | | 0.48 (aquifer), 0.99 (well) |
| Bulk Density | (g/cm$^3$) | 1.4 |
| Specific Yield | (cm$^3$/cm$^3$) | 0.2 |
| Hydraulic Gradient | (m/m) | 0.015 |
| | | |
| $CO_2$ Solute Transport | | |
| Diffusion Coefficient ($CO_2$) | (m$^2$/hr) | 6.77E-6 |
| Longitudinal Dispersivity | (m) | 6.1 |
| Horizontal Transverse Dispersivity | (m) | 0.61 |
| Vertical Transverse Dispersivity | (m) | 0.061 |
| Soil Gas $CO_2$ | (%) | 0.56 |

The hydraulic gradient at the study site was estimated as 0.015 m/m based on the groundwater elevation map (Battelle and Geosyntec Consultants, 2012) created for June of 2011 (Fig. 2-1). The

constant hydraulic gradient was assumed for the ZOI model during the 2-week collection period because the groundwater flow at the site is considered steady during the summer (discussed later) and mainly controlled by the surrounding ponds and creek in the golf course (Fig. 2-1).
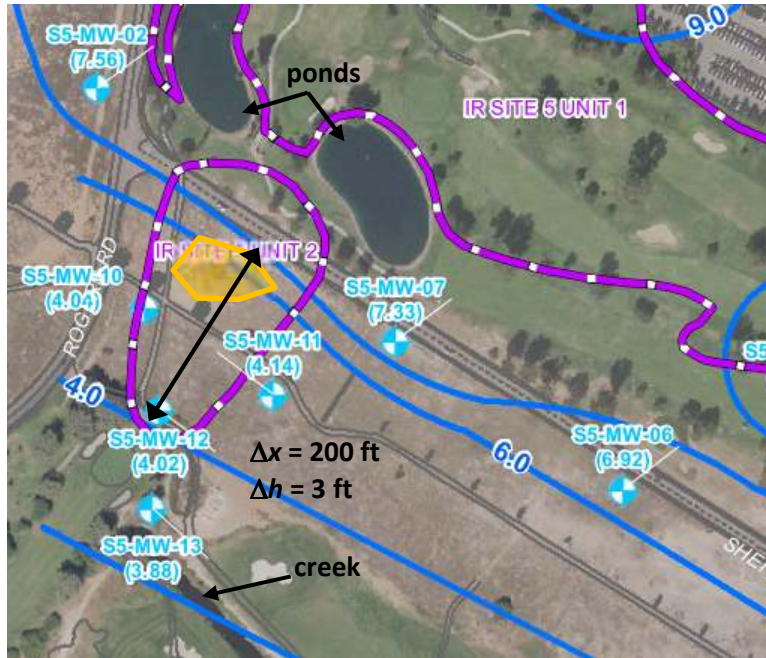


Figure 2-1. Approximate location of the study site (yellow polygon) with groundwater contour lines in June 2011 (left), and locations of the land marks. Values in the map are in feet.
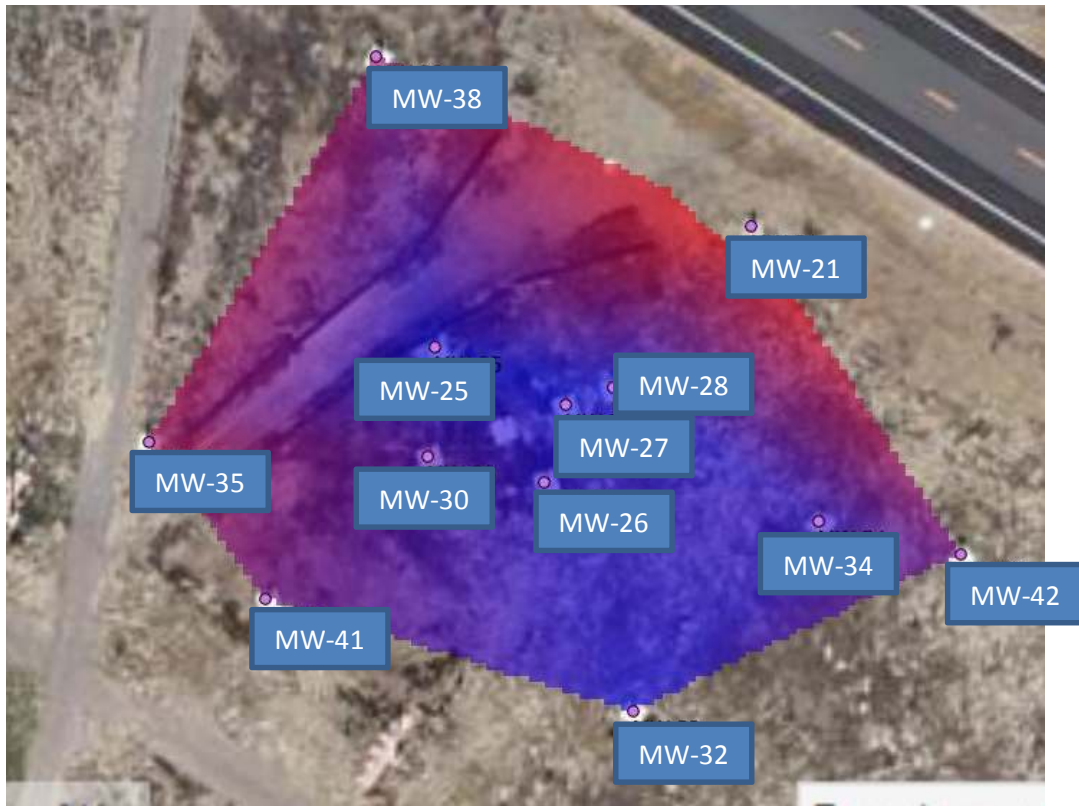
Hydrologic Engineering, Inc.

Figure 2-2.  Location of the 12 sampling wells at the study site (personal communication, September, 2013).

The areal model (Fig. 2-3) was developed as a preparatory study.  Three years of weather data (2007, 2011 and 2012) were obtained from the CIMIS San Diego station (Station ID 184) to estimate the recharge rate of the aquifer.  Also, tidal data for the same three years were obtained from the NOAA San Diego Station (Station ID: 9410170) to define boundary conditions.  From the aerial photo, surface water pools (e.g., ponds and creeks) were identified on the eastern side of the area (in the golf course and park).  A constant head equal to the elevation of these surface water bodies was assigned to the boundary.

The areal model indicated that the effects of short term (e.g., daily and weekly periods) changes in sea level around the peninsula on groundwater flow at the study site were not significant (Fig. 2-4).  This result agrees with the previous report from Wiedemeier and Associates (personal communication, April, 2013).  Fig. 2-4 indicates that the groundwater hydrology at the study site is usually steady between late summer and fall.  Therefore, the groundwater flow during the $CO_2$ collection periods (August and September in 2013) is assumed steady (i.e., constant hydraulic gradient).  The hydraulic gradient estimated by the areal model was 0.009 m/m that is smaller, but reasonably close to the value estimated from the groundwater elevation map in June 2011.

Figure 2-3.  Domain of the areal model to simulate the hydrology of the study site (in the orange square) and the surrounding area.  Elevation of the observed sea level was imposed along the solid blue line to simulate the tidal effect.  No flux boundary condition was set for the eastern boundary (black line).
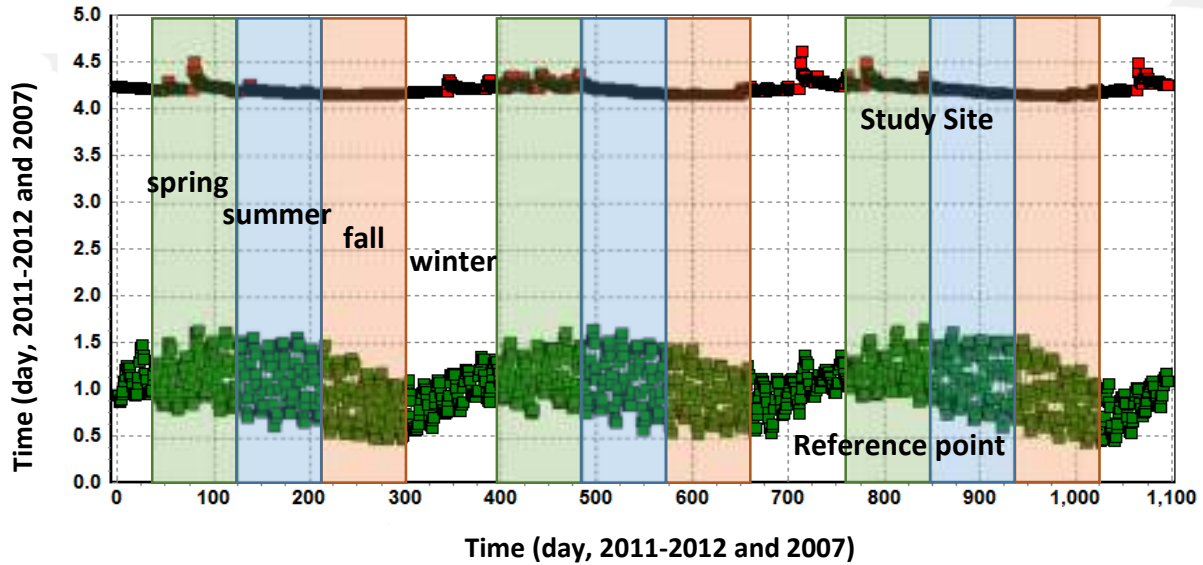
Figure 2-4. Simulated groundwater table at the study site (red squares) and the reference point near the coast (green squares). The distance from the coast to the study site and the reference point was 490 m and 40 m, respectively.

**Parameterization for Site Solute Transport**

Mineralization of chlorinated solvents was not simulated in the ZOI model because estimated $CO_2$ production during the collection period via mineralization was considered negligible (Appendix A). According to the progress report for Operable Unit 24 (Battelle and Geosyntec Consultants, 2012), the average $CO_2$ concentration of the soil gas was 0.56 % which is approximately 14 times higher than that of atmospheric gas ($\approx$ 0.04 %). Using Henry's law, the equilibrium concentration of dissolved $CO_2$ at the groundwater table with the $CO_2$ rich soil gas is estimated as 8.4 g $CO_2/m^3$. Also, the observed $CO_2$ collection rate at the site ranged from 0.012 g/day to 0.314 g/day. Compared to these values, the $CO_2$ production rate via mineralization is considered negligibly small (< 0.001 $g/m^3$ per day with the maximum reported concentration of DCE and VC). Because the $CO_2$ production rate is significantly smaller than the other $CO_2$ fluxes, the ZOI model would not be affected by not accounting for mineralization. However, mineralization has accumulated $CO_2$ in the aquifer over time. According to the field observation at IR Site 5 in 2011, approximately 40% of observed $CO_2$ in the groundwater was from a fossil source.

All $CO_2$ collection periods in 2013 were 2 weeks. Prior to the $CO_2$ sampling, the initial distribution of solute $CO_2$ in the aquifer around the sampling well was assumed in equilibrium with the $CO_2$ supplied from the overlying soil gas and mineralization; therefore, the $CO_2$ distribution was assumed uniform. With this assumption, the project can assume any $CO_2$ gradient observed at the end of the 2-week simulation period is caused by the $CO_2$ collection in the collection well. With the uniform $CO_2$ distribution, the ZOI associated with the $CO_2$ collection was defined as the volume of aquifer that has a $CO_2$ concentration of 95% or less of the initial concentration.

Hydrologic Engineering, Inc.

## Section 3: ZOI simulation in a static aquifer

This section describes the scenario designed to estimate the size of ZOI under static aquifer conditions; therefore, it only accounts for diffusion of $CO_2$ through the aquifer. The entire domain for this ZOI model is 1.0 m x 1.0 m x 0.25 m deep. The horizontal spatial resolution is 0.01 m x 0.01 m (Fig. 3-1 left), and the vertical resolution varies from 0.005 m at the surface to 0.05 m at the bottom (Fig. 3-1 right). The 4-inch diameter sampling well is represented as the 0.0081 $m^2$ circle at the center of the domain (red area in Fig. 3-1). After a one-day spin-up period, the model was run for 2 weeks to simulate the $CO_2$ collection from the well head by imposing a $CO_2$ concentration of 0.0 $g/m^3$ at the groundwater surface within the well. This simulates the behavior of the $CO_2$ filter in the well head.
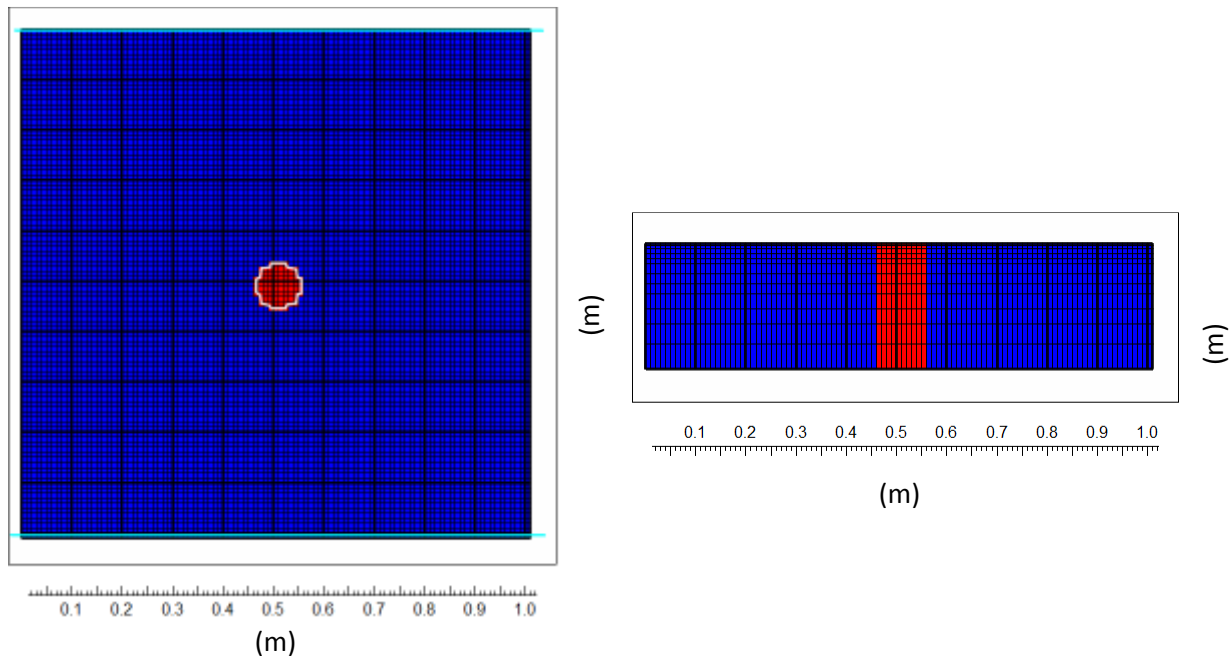


Figure 3-1. Top (left) and side (right) views of the ZOI model domain and the sampling well location. The 4-inch diameter well is located at the center of the domain and penetrates through the entire aquifer depth.

The result of the simulation is described in Fig. 3-2. The boundary of the ZOI (solid black line) is the contour line for 8.0 $g/m^3$. The simulated ZOI has a smooth half-sphere shape (0.28 m diameter and 0.13 m depth) that extends approximately 0.09 m beyond the well wall. The volume of the ZOI was estimated as 0.005 $m^3$. Appendix C describes method used to estimate the volume of the ZOI using the simulation results.
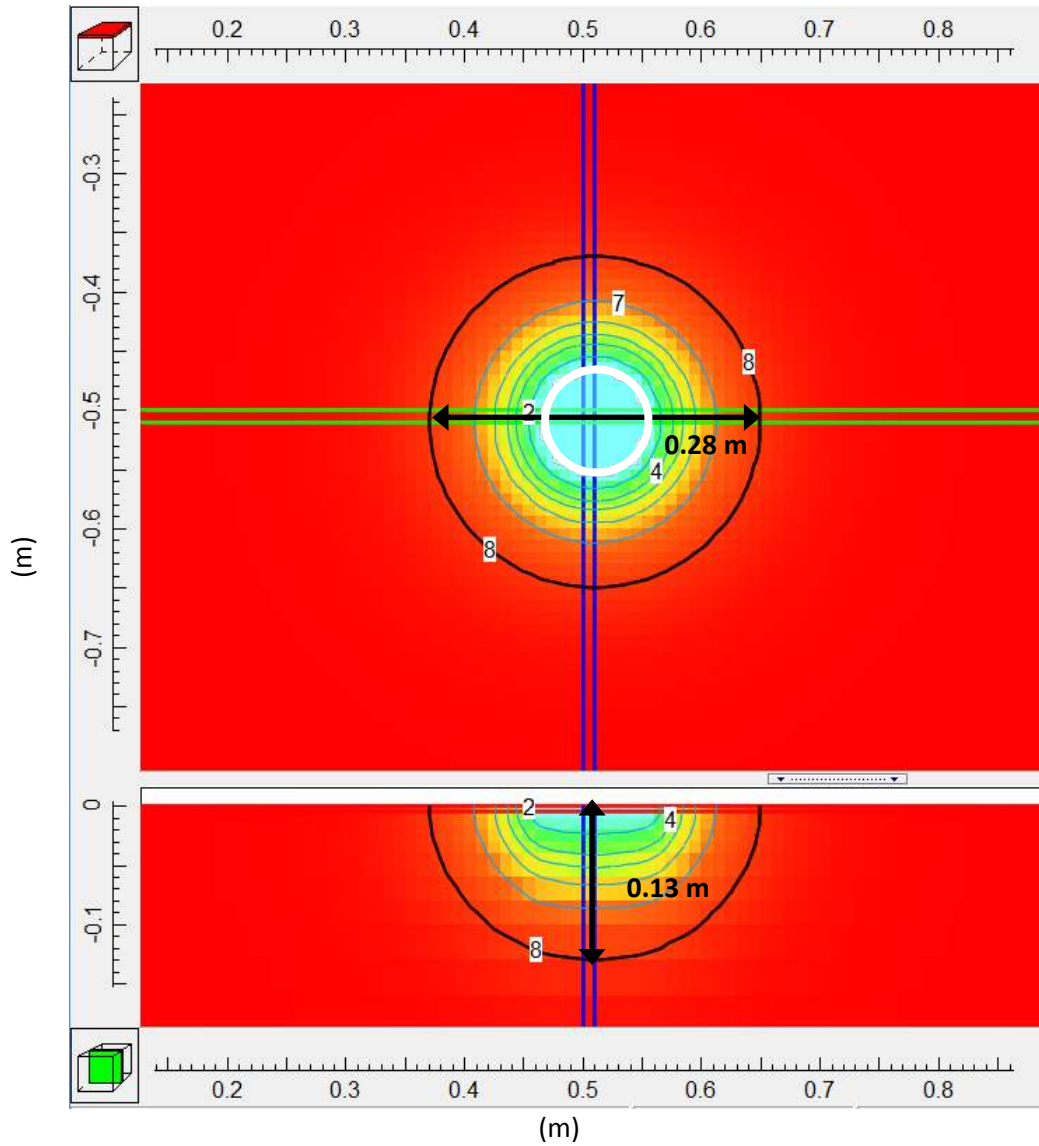
Figure 3-2. Top (top) and front (bottom) views of the $CO_2$ distribution after 2-week $CO_2$ collection under the static aquifer condition. The sampling well is indicated by the white circle, and the ZOI is indicated by the black contour line representing $CO_2$ concentration of 8.0 $g/m^3$.

Hydrologic Engineering, Inc.

**Section 4: ZOI simulation in a steady state aquifer with reported average hydraulic gradient**

This section describes the scenario designed to evaluate effect of groundwater flow on the ZOI. The ZOI model was run with the estimated hydraulic gradient (0.015 m/m) and hypothetical background $CO_2$ concentration (8.4 g $CO_2$/m$^3$). The entire model domain for this scenario was 9.0 m x 4.5 m x 10.0 m deep (Fig. 4-1). The horizontal spatial resolution is set to 0.09 m x 0.09 m, which makes one grid area equal to 0.0081 m$^2$: the same as the well area (light blue grid in Fig. 4-1). The vertical spatial resolution varies from 0.05 m at the surface to 1.7 m at the bottom. The hydraulic gradient was applied to the ZOI model by setting the constant head condition along the two boundaries (red solid lines in Fig. 4-1), which allows groundwater to flow in the west to east direction.
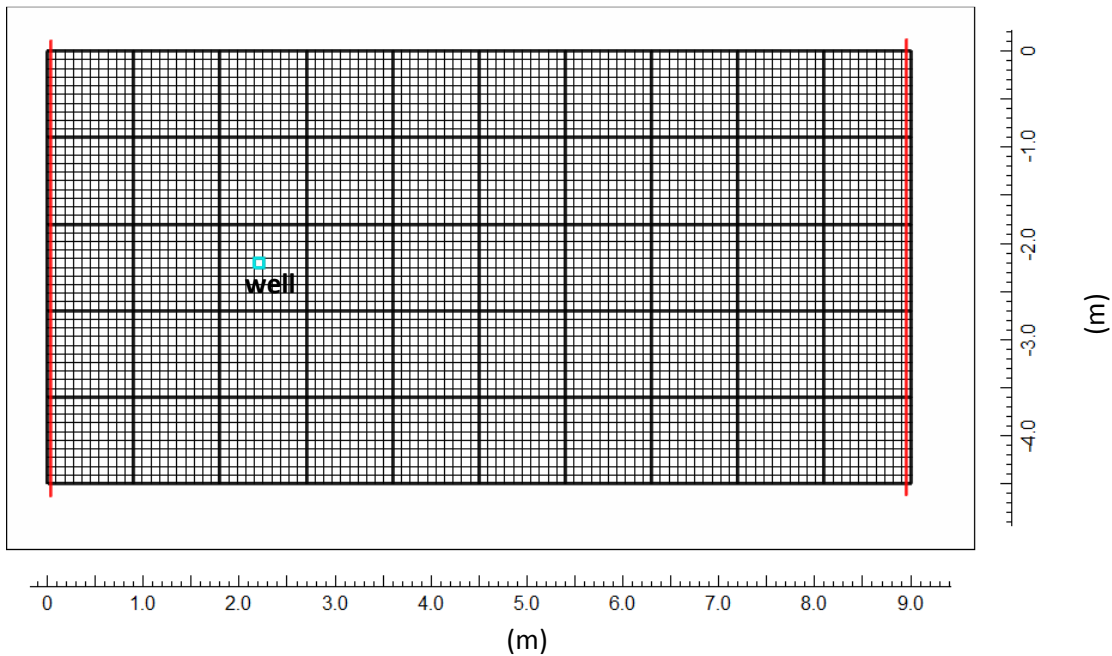


Figure 4-1. Top view of the ZOI model for Scenario 2. The constant head boundary condition was assigned along both ends of the model which creates a hydraulic gradient of 0.015 m/m over the model domain. The sampling well is indicated as the light blue grid.

Figure 4-2 shows the simulated $CO_2$ distribution at the end of the 2-week sampling period. Because of truncation errors caused from solving the partial differential equations, simulated groundwater and $CO_2$ movements are not perfectly symmetric. Also, the shape of the ZOI is not circular due to groundwater flow. The boundary of the ZOI (solid black line) is represented by the contour line for 8.0 g/m$_3$ (95 % of the background $CO_2$ concentration). It is obvious that the effect of the slight hydraulic gradient on the ZOI is significant. The volume of the ZOI was estimated as 0.191 m$^3$. The ZOI is extended to 2.36 m and 0.74 m in the longitudinal and transverse directions, respectively. However, the depth of the ZOI is 0.12 m that is slightly shallower than the ZOI depth in the static aquifer described in the previous section.

Overall, the expansion of the ZOI is significant, and considered mainly caused by dispersion, which indicates the importance of groundwater hydrology to the ZOI modeling.
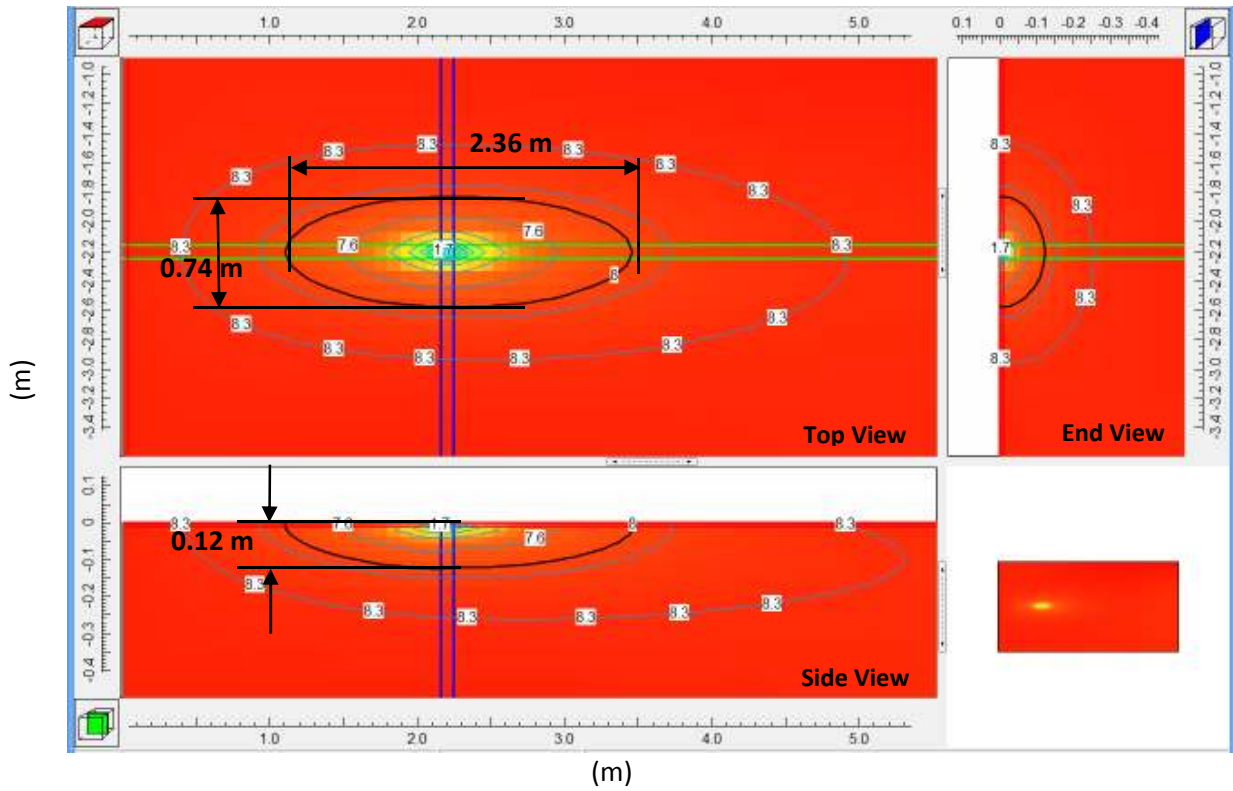


Figure 4-2. Top (top) and side (bottom) views of simulated $CO_2$ distribution assuming the hydraulic gradient of 0.015 (m/m). The side view is exaggerated by 2.5 times in vertical direction to show the $CO_2$ concentration gradient.

## Section 5: Estimation of ZOI using calibrated model

This section describes the process to estimate background $CO_2$ concentration using the ZOI model described in the previous section and the observed $CO_2$ collocation rates. In summer of 2013, $CO_2$ was collected from 12 observation wells (Fig. 2-2) for the 2-week collection period. The average hourly collection rate was 0.0052 g $CO_2$/m$^3$, and varied from 0.0005 g/hr to 0.0131 g/hr. This project calibrated the background $CO_2$ concentration of the ZOI model for these collection rates. The calibration assumed that the collection rate was constant during the collection period. The calibration also assumed the equilibrium between the $CO_2$ output (i.e., collection) and supply (i.e., diffusion) at the water table in the well at the end of the collection period. In other words, the $CO_2$ concentration of the water surface in the well was assumed to be decreased to 0.0 g $CO_2$/m$^3$ by the end of the simulation.

Fig. 5-1 shows the $CO_2$ distribution of the calibrated ZOI model for the average collection rate. The results of the ZOI calibration for the three collection rates are summarized in Table 5-1. The calibration result indicates a strong linear correlation between the observed collection rate and the calibrated background $CO_2$ concentration (Fig. 5-2). Also, estimated ZOI volume indicates a strong linear correlation with background $CO_2$ concentration, therefore, $CO_2$ collection rate.
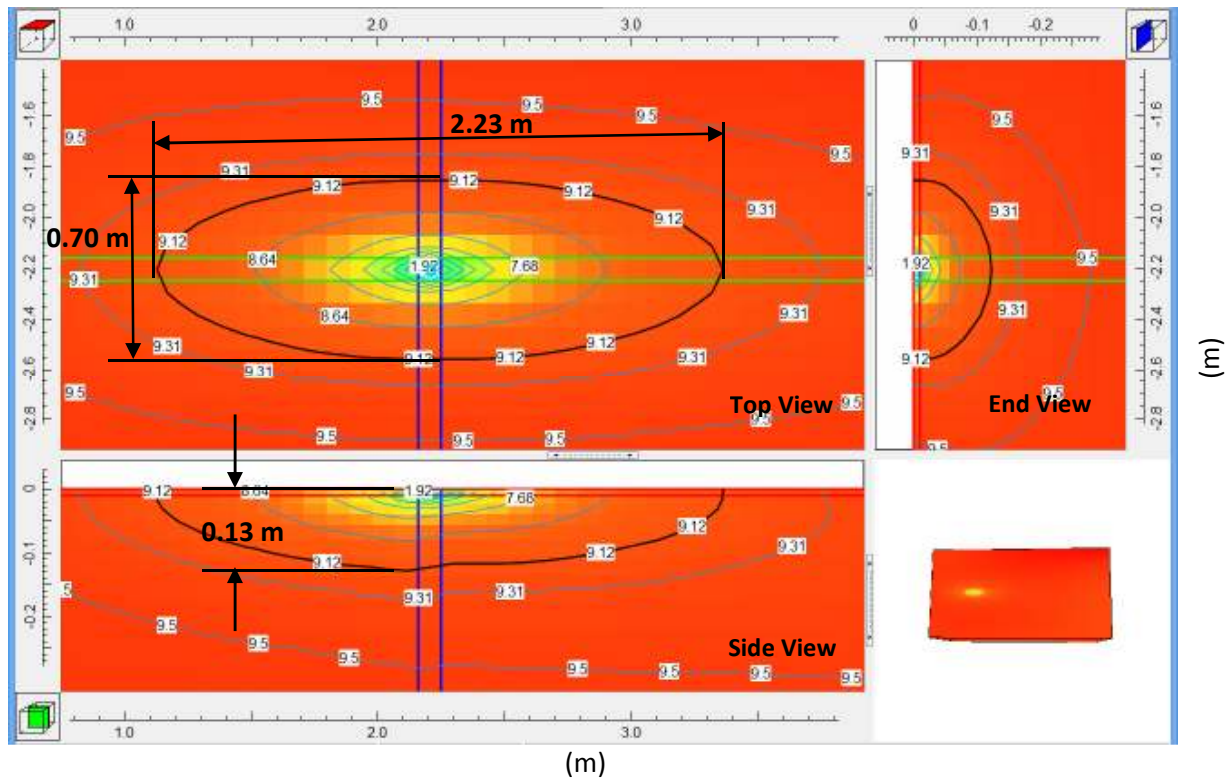


Figure 5-1. Calibrated ZOI model for the average $CO_2$ collection rate (0.0052 g/m$^3$). The calibrated background $CO_2$ concentration was 9.6 g/m$^3$, and the ZOI threshold concentration was 9.12 g/m$^3$ (solid black line). Longitudinal and transverse diameters of the ZOI were 2.23 m and 0.70 m, respectively. Depth of the ZOI was 0.13 m.

Hydrologic Engineering, Inc.

Table 5-1. Estimated background $CO_2$ concentrations and simulated ZOI sizes with different $CO_2$ collection rates.

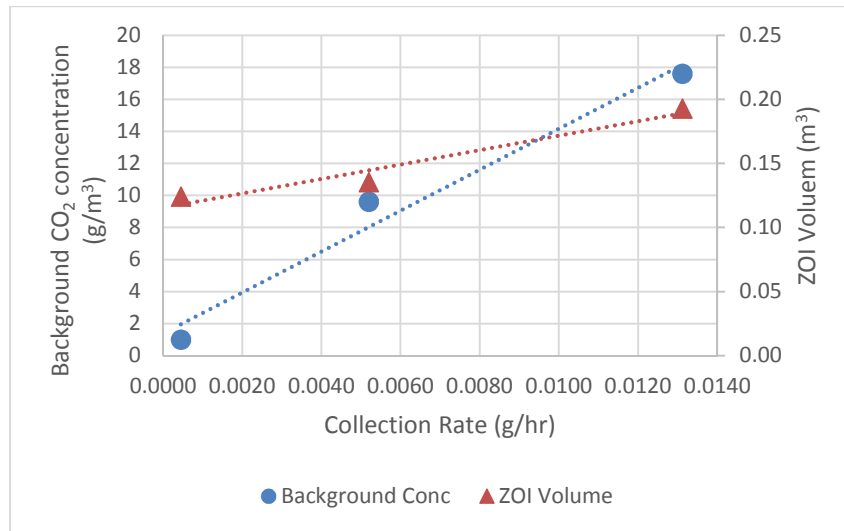| Collection Rate Level | Collection Rate | Background Concentration | ZOI Size | | | |
| --- | --- | --- | --- | --- | --- | --- |
| | | | Longitudinal | Transverse | Depth | Volume |
| | (g/hr) | (g/m$^3$) | (m) | | | (m$^3$) |
| Maximum | 0.0131 | 17.6 | 2.47 | 0.77 | 0.13 | 0.193 |
| Average | 0.0052 | 9.6 | 2.23 | 0.70 | 0.13 | 0.135 |
| Minimum | 0.0005 | 1.0 | 2.08 | 0.66 | 0.12 | 0.124 |



Figure 5-2. Estimated background CO2 concentration and ZOI volume versus collection rate.

Assuming the partial pressure of the atmospheric $CO_2$ is 0.04 %, the equilibrium $CO_2$ concentration of non-contaminated aquifer exposed to the atmosphere is 0.60 g/m$^3$ (Appendix B). The estimated background $CO_2$ concentration for all collection rates are higher than this value. Because $CO_2$ concentration of soil gas is generally considered higher than that of atmospheric gas due to microbial respiration (Bohn et al., 2002); therefore, equilibrium $CO_2$ concentration of confined aquifer can be higher than 0.60 g/m$^3$. However, the wide range of the estimated background $CO_2$ at the study site suggests additional and highly localized $CO_2$ sources, possibly chlorinated solvents (e.g., DCE and VC) and the their ongoing mineralization, existing in the aquifer. In fact, the isotope analysis for the collected $CO_2$ indicated that average 24% (varying from 0.7% to 60.4%) of collected carbon from the study site was derived from petroleum sources (Appendix D), which supports our argument.

The calibration described in this section was done assuming the steady hydraulic gradient and constant collection rates over the collection period. To evaluate the significance of these assumption, two

Hydrologic Engineering, Inc.

supplemental simulation were done.  One supplemental simulation to test the sensitivity to the hydraulic gradient indicated approximately 50 % increase in the estimated background $CO_2$ concentration (i.e., increased from 6.5 $g/m^3$ to 9.7 $g/m^3$) with 10 % increase in hydraulic gradient (i.e., increased from 0.0150 m/m to 0.0165 m/m).  Also, the other supplemental simulation to test the sensitivity to the constant $CO_2$ collection rate indicated approximately 46 % increase in the estimated background $CO_2$ concentration (i.e., increased 6.5 $g/m^3$ to 9.5 $g/m^3$) if the collection rate changes from 0.00530 g/hr (+10 %) at the beginning to 0.00434 $g/m^3$ (-10 %) at the end of the 2-week collection period.  These significant change in the estimated background $CO_2$ concentrations indicates importance for ZOI estimation to collect and account for these aquifer and operation parameters for its accuracy and reliability.

**Section 6: Summary**

In this project, the ZOI models associated with the new technique were developed, and the size of the ZOI was estimated for different aquifer conditions (static vs. steady-state) and background $CO_2$ concentrations.  Our results suggest the ZOI size can be significantly influenced by groundwater flow and background $CO_2$ concentration.  The estimated ZOI size was increased with groundwater flow.  It appears that dispersion of $CO_2$ caused by groundwater flow increases $CO_2$ supply toward the well.  Therefore, it is suggested that collection of information about the aquifer for accurate ZOI estimation.  Also, the estimated ZOI size (e.g., extension and volume) was increased with an increase in the background $CO_2$ concentration.  This project only calibrated 3 collection levels, but the results indicate a strong linear relationship among the ZOI size, the background $CO_2$ concentration and the $CO_2$ collection rate.  The wide range of the estimated background $CO_2$ concentration within the study area suggests additional localized and active $CO_2$ source.  Additional isotope analysis for the collected $CO_2$ also indicated that significant fraction of the collected $CO_2$ was derived from petroleum.  It was also realized that the ZOI model could become more accurate and reliable by collecting and accounting for operation parameters such as changing $CO_2$ collection rate over the collection period.

**APPENDIX A: Estimation of daily production rate of $CO_2$ from DCE and VC**

To make a conservative estimate of $CO_2$ production rate, all decayed DCE and VC were assumed converted into $CO_2$. Whelan et al. (2007) describes a case study for the dechlorination reaction and solute transport of the chlorinated solvents using solute transport and reaction models. In their example, the half-life of DCE and VC are given as 3.8 years and 9.5 years, respectively.

The exponential decay model used to estimate decay rate of these solvents is expressed as:

$$N_{t+1} = N_t \left(\frac{1}{2}\right)^{\frac{t_p}{t_{0.5}}}$$

where $N_t$ and $N_{t+1}$ are the quantity of the substance at time $t$ and $t+1$, $t_p$ is the period (= 1 day), and $t_{0.5}$ is the half-life (in days). Using this equation, the daily $CO_2$ production rate equivalent to the solvent ($\Delta N$) can be expressed as:

$$\Delta N = N_1 - N_2 = N_1 - N_1 \left(\frac{1}{2}\right)^{\frac{1}{t_{0.5}}}$$

where $N_1$ and $N_2$ are the quantity of the substance in day 1 and day 2. Using the half-life and observed concentrations in Table A1, the daily production rate of $CO_2$ from DCE and VC is estimated as 5.4 E-6 ($g/m^3$) which is considered not significant for the $CO_2$ fluxes of the ZOI models (e.g. collection rate and dissolving rate).

**Table A1. Summary of daily $CO_2$ production estimation using the exponential decay model.**

| Parameters | DCE | Date | VC | Date |
|---|---|---|---|---|
| Half-life | 1387 (days) | | 3467.5 (days) | |
| *Max. Concentration | 0.0099 ($g/m^3$) | 16 Jun 2010 | 0.0022 ($g/m^3$) | 30 Nov 2010 |
| Daily Production Rate | 4.0 E-6 ($g/m^3$) | | 4.4 E-7 ($g/m^3$) | |
| Total Daily Production Rate | 5.4 E-6 ($g/m^3$) | | | |

* These measurements were made at IR Site 5 (Accord Engineering, Inc., 2011).

Hydrologic Engineering, Inc.

**APPENDIX B: Calculation of equilibrium $CO_2$ concentration in the unconfined aquifer facing $CO_2$ rich soil gas**

Soil gas was sampled at Operable Unit 24 in March 2011 (Battelle and Geosyntec Consultants, 2012). Although this sampling location is different from our study site (Installation Restoration Site 5), the sample result was used to estimate possible surface $CO_2$ concentration of the unconfined aquifer and for the hypothetical ZOI models.

Equilibrium $CO_2$ concentration at the groundwater surface ($C_{water}$ in mol/L) can be calculated using the Henry's law:

$$C_{water} = \frac{P_{CO2}}{K_H}$$

where $K_H$ is the Henry's constant (L·atm/mol), and $P_{CO2}$ is the partial pressure of $CO_2$ in soil gas (atm). According to the report, the average partial pressure of $CO_2$ in the soil gas was 0.56% (0.0056 atm) in 2011. Assuming Henry's constant for $CO_2$ is 29.4 L·atm/mol (Fitts, 2002), the equilibrium concentration of $CO_2$ in the aquifer surface is 1.9 E-4 mol/L that is equal to 8.4 g $CO_2$/m$^3$. Also, assuming the partial pressure of $CO_2$ in the atmosphere is 0.04% (4.0 E-4 atm or 400 ppm), the equilibrium concentration of $CO_2$ in non-contaminated aquifer surface is 0.60 g $CO_2$/m$^3$.

Hydrologic Engineering, Inc.

**APPENDIX C:  Estimating ZOI Volume from the Simulation Results**

In this project, the volume of the ZOI was estimated using the integration technique described here (Fig C1).  The shape of the ZOI was assumed smooth and continuous.
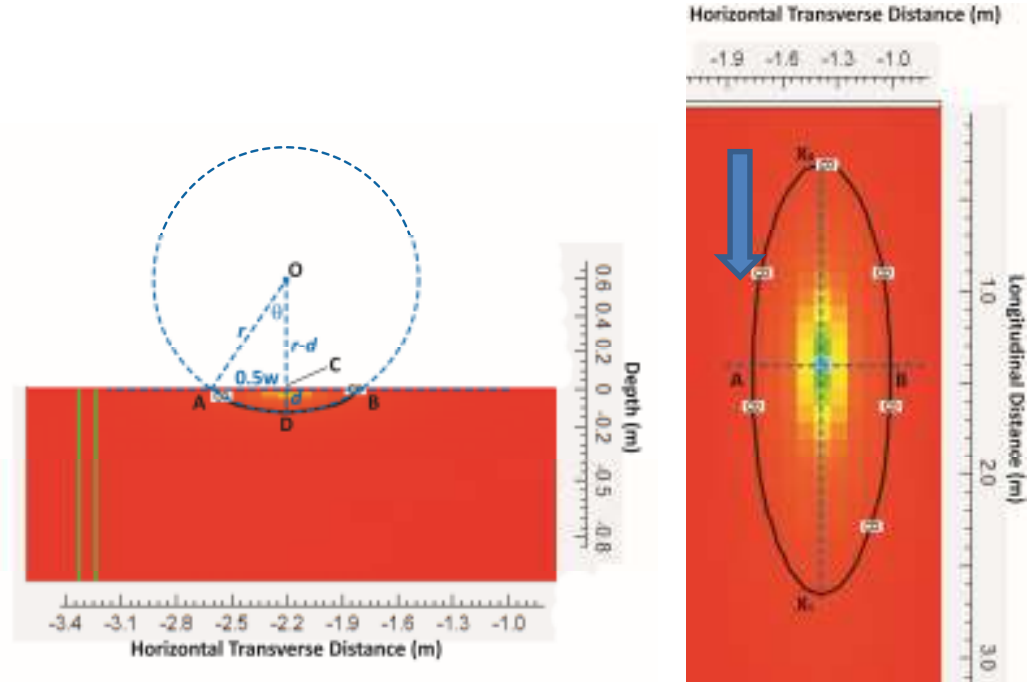


**Figure C1.  Estimation of cross-sectional area of a ZOI segment (area ABC in left) over the longitudinal length ($X_0$-$X_1$ in right).**

Cross sectional area of ZOI (area ABD in Fig. C1 left) was approximated as a difference between Pie-OADB and Triangle-OAB.  Radius of the imaginary circle can be determined by applying the Pythagorean theorem as:

$$r = \frac{1}{2d}\left(d^2 + \frac{1}{4}w^2\right)$$

where $r$ is the radius of the circle, $w$ is the width of the ZOI, and $d$ is the depth of the ZOI (m).  Also, the angle at O for the pie-OADB can be determined as:

$$\cos\theta = \frac{r-d}{r}$$

Triangle-OAB and Pie-OADB can be calculated as:

$$\text{Triangle} - \text{OAB} = \frac{1}{2}w(r-d)$$

$$\text{Pie} - \text{OADB} = \frac{\theta}{180}\pi r^2$$

The volume of the ZOI ($V_{ZOI}$) was estimated as:

$$V_{ZOI} = \sum \left( \text{Pie} - \text{OADB}_i - \text{Triangle} - \text{OAB}_i \right) \times \Delta x$$

where, $\Delta x$ is 0.09 m in this project and $i$ varies from 0 to N (= $X_1 - X_0/\Delta x$).

Hydrologic Engineering, Inc.

**APPENDIX D:  Summary of Observed CO$_2$ Collection Rate and Isotope Analysis**

The following values were provided by Thomas Boyd who ran the field and laboratory works for the 12 observation wells in 2013.

**Table D.  Summary of CO$_2$ collection and isotope analysis results at the study site within IR Site 5 Unit 2 in 2013**

| Observation Well | CO2 Collection Rate | Modern Carbon | Petroleum Carbon | Contaminant Carbon Collection Rate |
|---|---|---|---|---|
| | (g/hr) | (%) | (%) | (g/d) |
| MW-01 | 0.01312 | | | |
| MW-21 | 0.01275 | 33.7 | 60.4 | 0.184914 |
| MW-25 | 0.00045 | 84.7 | 0.7 | 0.000074 |
| MW-26 | 0.00162 | 70.2 | 17.7 | 0.006853 |
| MW-28 | 0.00052 | 81.0 | 5.0 | 0.000625 |
| MW-30 | 0.00419 | 74.6 | 12.5 | 0.012530 |
| MW-32 | 0.00057 | | | |
| MW-34 | 0.00130 | 71.7 | 15.9 | 0.004950 |
| MW-35 | 0.00927 | 40.2 | 52.9 | 0.117544 |
| MW-38 | 0.00745 | 64.6 | 24.3 | 0.043380 |
| MW-41 | 0.00603 | 76.8 | 10.0 | 0.014429 |
| MW-42 | 0.00518 | 64.7 | 39.2 | 0.048740 |
| | | | | |
| Minimum | 0.00045 | 33.7 | 0.7 | 0.000074 |
| Average | 0.00520 | 66.2 | 23.9 | 0.043404 |
| Maximum | 0.01312 | 84.7 | 60.4 | 0.184914 |

**Modern Carbon**: the fraction of the collected CO$_2$ derived from a contemporary end member (carbon delivered from living biomass, atmosphere, and soil organic matters).

**Petroleum Carbon**: the fraction of the collected CO$_2$ derived from a fossil end member.

**Contaminant Carbon Collection Rate**: daily collection rate of g carbon as a fraction from petroleum.

Hydrologic Engineering, Inc.

# References

Accord Engineering, Inc. 2011. Semi-Annual Post-Closure Maintenance Report for Calendar Year 2011 Installation Restoration (IR) Program Site 2 (Old Spanish Bight Landfill), Site 4 (Public Works Salvage Yard), and Site 5, Unit 1 (Golf Course Landfill).

Battelle, and Geosyntec Consultants. 2012. Annual Progress Report October 2010 to December 2011, Operable Unit 24.

Bohn, H.L., B.L. McNeal, R.A. Myer, and G.A. O'Connor. 2002. Soil Chemistry. Wiley.

Boyd, T.J., M.J. Pound, D. Lohr, and R.B. Coffin. 2013. Radiocarbon-depleted $CO_2$ evidence for fuel biodegradation at the Naval Air Station North Island (USA) fuel farm site. Environ. Sci. Process. Impacts 15(5): 912–918.

Bradley, P.M. 2012. Microbial Mineralization of cis-Dichloroethene and Vinyl Chloride as a Component of Natural Attenuation of Chloroethene Contaminants under Conditions Identified in the Field as Anoxic.

Fitts, C.R. 2002. Groundwater Science. Academic Press.

Harbaugh, A.W. 2005. MODFLOW-2005, the US Geological Survey modular ground-water model: The ground-water flow process. US Department of the Interior, US Geological Survey.

Kueper, B.H., G.P. Wealthall, J.W. Smith, S.A. Leharne, and D.N. Lerner. 2004. An illustrated handbook of DNAPL transport and fate in the subsurface. Environment Agency, United Kingdom.

Prommer, H., D.A. Barry, and C. Zheng. 2003. MODFLOW/MT3DMS-based reactive multicomponent transport modeling. Ground Water 41(2): 247–257.

Whelan, G., K.J. Castleton, and M.A. Pelton. 2007. FRAMES-2.0 Software System: Linking to the Groundwater Modeling System (GMS) RT3D and MT3DMS Models. Pacific Northwest National Laboratory.

Winston, R.B. 2009. ModelMuse: A Graphical User Interface for MODFLOW-2005 and PHAST. US Geological Survey.

Zheng, C., and P.P. Wang. 1999. MT3DMS: A modular three-dimensional multi-species transport model for simulation of advection, dispersion, and chemical reactions of contaminants in ground-water systems. Documentation and user's guide. Tuscaloosa, AL.