

## Improving the Accuracy and Usefulness of the MIP Using Carbon-Traps<sup>1</sup>

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**ABSTRACT:** Chlorinated solvents are prevalent groundwater contaminants throughout the United States. These volatile compounds present major risks to human health and the environment and are often difficult to delineate in the subsurface due to their high mobility. Currently, the Membrane Interface Probe (MIP) is used as a screening tool with semi-quantitative capabilities for the detection of chlorinated solvent compounds in the subsurface. The MIP is a tool driven into the ground that heats the soil and groundwater adjacent to the probe, increasing the volatility of the compounds present. The vapor phase produced diffuses across a membrane into a closed, inert gas loop that carries these vapors to a photoionization (PID), flame ionization (FID), or electron capture (ECD) detector at the ground surface. However, because these detectors are not compound specific and have a relatively high detection limit, use of the MIP tool is limited to delineate source areas rather than the extent of subsurface impact from chlorinated solvents.

To improve the capability of the MIP, GeoTrans applied the use of carbon-trap tubes to the carrier gas from the MIP at the site of a tetrachloroethylene (PCE) release in Bradford, Pennsylvania. The PCE release was from a dry cleaner where a dense non-aqueous phase layer was identified in the subsurface. The MIP was used at this site to identify the vertical and horizontal extent of the down-gradient groundwater plume resulting from this release. The carbon-trap tubes were used to identify individual compounds and the relative concentrations of these compounds in the MIP carrier gas at continuous intervals in the subsurface. Each carbon-trap tube was desorbed and analyzed in the field using an onsite mobile laboratory. In addition, individual subsurface samples were obtained for comparison to MIP and carbon-trap results. The results and analysis of the vapor phase gas produced by the MIP resulted in the delineation of the down-gradient PCE and degradation by-product plume in real-time eliminating the need for costly additional investigation.

### **MIP DESCRIPTION AND LIMITATIONS**

The MIPS heats soil and groundwater adjacent to the probe (target temperature is 120 degrees Celsius [ $^{\circ}$ C]) as it is driven through the subsurface using direct push (Geoprobe<sup>®</sup>) drilling equipment. Heating increases the volatility of compounds of interest and the vapor phase produced diffuses across a membrane into a closed, inert gas loop that carries these vapors to the ground surface. Common detectors used to identify volatile organic compound (VOC) vapors in the inert return carrier gas include a PID (used for the detection of aromatic hydrocarbons), FID (used to detect straight chained hydrocarbons), and ECD (used as an indicator of chlorinated solvents) for “real time” identification of VOCs. These detectors are sensitive to a group or type of compound and cannot identify individual compounds. Also commonly used on the MIP is an electrical conductivity sensor to identify subsurface lithology simultaneously with VOCs. The signals generated

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by these instruments are commonly recorded along with the temperature of the MIP and the speed and depth of MIP advance through the subsurface in increments of 0.05 feet.

Proper use of the MIP is described in the American Society of Testing and Materials (ASTM) Standard D-7352-07. However, this standard provides no indication of the accuracy, precision or bias associated with MIP use. Comparison of MIP results in the saturated zone to actual groundwater sample results have indicated that the MIP is capable of detecting the presence of chlorinated compounds beginning at 100 parts per billion (ppb) of total chlorinated compounds and degradation by-products. A survey of contractors that offer MIP services indicated that chlorinated compounds in-situ detection limits were in the range from 200 to 500 ppb total VOCs (United States Environmental Protection Agency [USEPA], 2005). As such, the MIP is currently deemed useful as a qualitative field screening tool when total chlorinated compound concentrations in the subsurface are known to be greater than the stated limits of detection.

The factors that reportedly prevent the use of the MIP as a more quantitative investigative tool are numerous and there is little or no quantitative guidance available to predict the effectiveness of the MIP in detecting a specific compound in a specific stratum or condition. The actual mass or volume of soil and/or groundwater that is extracted (or heated) by the MIP is unknown and potentially varies depending upon the type of soil in the subsurface, the amount of time the MIP is in contact with the soil and/or groundwater, the compounds in the soil, the actual temperature of the MIP, and possibly other factors. ASTM Standard D-7352-07 indicates the MIP should be driven at a rate which allows the MIP temperature to remain constant which may vary in the vadose and saturated zones and with depth. Furthermore, advancement of the MIP by direct push is controlled by the ability of the direct push drilling equipment to penetrate the subsurface.

In an attempt to produce more quantitative results from the MIP, GeoTrans conducted a subsurface investigation of a known PCE release using carbon-traps to retain compounds brought to the surface in the MIP return gas flow for onsite analysis using a Gas Chromatograph (GC).

## **SITE BACKGROUND AND GEOLOGY**

The former Bradford Mall Cleaners in Bradford, PA (Site) was the source a PCE release in 1995. Spent PCE was discharged into the local sanitary sewer where it entered the subsurface through a crack in a 4-inch diameter sanitary sewer lateral. GeoTrans began investigation in 2000 and identified a dense non-aqueous phase liquid (DNAPL) in purge water from the second monitoring well installed (MW-2).

Both unconsolidated and consolidated geologic materials underlie the Site with bedrock mapped as the Chemung Group (Fettke, 1938) which consists of a series of interbedded shales and sandy shales, and fine-grained sandstones. The total thickness of the Chemung unit is approximately 2,100 feet. The oil and gas-bearing sands of the Bradford Oil Field occupy a little over 1,000 feet in the middle of this group. Overlying the bedrock is Quaternary alluvium which was deposited in the Tunungwant Creek Valley during the time glaciers were present to the north. This alluvium consists of unconsolidated deposits of gravel, sand, and silt, which can attain a thickness of several hundred feet towards the middle of the valley. With the Site located in the approximate middle of this valley, the alluvium attains a thickness of nearly 250 feet. The materials comprising the alluvium are of local origin, being weathered from bedrock outcropping

in the area. Above the alluvium, fill was placed on wetlands and a culvert was installed for a major stream to allow development of the Site as a shopping mall.

Four (4) previous subsurface investigations were conducted concerning the release of PCE at the Site prior to the MIP investigation. A poorly documented investigation was conducted in 1995 which included four (4) borings, collection of eight (8) soil samples and three (3) groundwater samples. This investigation identified two (2) soil and one (1) groundwater sample containing PCE at concentrations that exceeded Pennsylvania Department of Environmental Protection (PADEP) cleanup criteria.

On October 24 and 25, 2000 GeoTrans conducted a review of PADEP files followed by soil gas sampling at twelve (12) locations, subsurface soil sampling and well installation at four (4) locations, and groundwater sampling at the four (4) monitoring wells (MW-1 through 4). Samples obtained were analyzed for PCE and its degradation by-products using both an onsite mobile laboratory and an offsite PADEP Certified laboratory. This investigation identified soil gas PCE concentrations up to 260 micrograms per liter ( $\mu\text{g/L}$ ), soil concentrations at one (1) location that exceeded PADEP non-residential soil to groundwater standards, and PCE and its degradation by-products were identified in groundwater (contaminant plumes) at concentrations that were significantly greater than PADEP standards.

From May 29, 2001 to June 1, 2001 GeoTrans conducted an investigation of the stream in the center of the Site, a sanitary sewer investigation to locate the point of the release, and further soil and groundwater investigation. From this investigation, the majority of the groundwater plume limits and the exact location of the subsurface release point were identified. The groundwater plume was found to be hydraulically isolated from, and did not discharge to the stream in the center of the Site.

On November 12 and 13, 2003 GeoTrans conducted a groundwater investigation to delineate the down-gradient portion of the groundwater contaminant plumes. This investigation indicated that the release to groundwater was undergoing sequential degradation (natural attenuation) from PCE at the release point through trichloroethene (TCE) in the direction of groundwater flow with accumulation of cis-1,2 dichloroethene (DCE) and vinyl chloride (VC) down-gradient of the PCE plume.

## **MIP INVESTIGATION**

GeoTrans utilized the MIP at four (4) locations to identify stratigraphy and the PCE and degradation by-product plumes at depth. To calibrate the soil conductivity results from the MIP, GeoTrans advanced the MIP next to four (4) soil borings (SB-2, 12, 23 and 25) to compare the results obtained from these continuously logged borings to the MIPS response before proceeding to depth at each location. Based on MIP soil conductivity measurements and known shallow stratigraphy, subsurface stratigraphy deeper than 20 feet below ground surface (BGS) was identified as sand and gravel which is consistent with geologic references.

The MIP was driven into the ground at the Site using a using a small, track mounted, hydraulically operated piston-type direct push drilling system (Geoprobe<sup>®</sup> Model 6610DT). A PID, FID and ECD were used in series to identify aromatic hydrocarbons, straight chained hydrocarbons, and chlorinated solvents in the inert gas from the MIP with results in units of micro-volts ( $\mu\text{V}$ ). In addition, the depth of the MIP in feet BGS, the speed of MIP advance in feet per minute (ft/min), soil conductivity in

micro Siemens per meter ( $\mu\text{S}/\text{m}$ ), temperature of the probe in degrees Celsius ( $^{\circ}\text{C}$ ), and the pressure of the inert carrier gas in pounds per square inch (psi) were provided by the MIP controller and recorded along with the PID, FID, and ECD results every 0.05 feet of MIP advance.

To identify the presence of specific compound in the subsurface, the inert gas flow from the MIP was split to flow through a Tenax<sup>®</sup> (carbon) trap. Each trap was installed in the MIP gas flow for a distance that ranged from 2 to 10 feet of MIP drive BGS. The length of time the trap was subject to the MIP gas flow was dependent upon the PID, FID, and ECD signal strength (indicating high or low loading to the trap so the trap is not overloaded) balanced with the need to control the limit of detection of each compound in the MIP gas flow (less gas flow through the trap raises the detection limit and vice versa).

The traps were then heated in the field to  $125^{\circ}\text{C}$  and the contents flushed into an SRI 8610 Environmental GC using a 60 meter capillary column. The GC was temperature programmed to separate the individual compounds of interest which included PCE, trichloroethylene (TCE), DCE, 1,1-dichloroethylene, trans-1,2-dichloroethylene, 1,2-dichloroethane, 1,1,1-trichloroethane, chlorobenzene and VC. The response for each compound was reported as the area of the peak for each compound on the GC plot. One (1) blank carbon-trap was also analyzed in the field with no compounds of concerns identified.

The field GC and MIP were calibrated each day (looking primarily for retention time windows for each compound) by running an aqueous performance test for all of the compounds of concern. A performance test involved immersing the MIP probe into a solution of known concentration for 45 seconds to emulate the process by which the MIP data is produced during subsurface exploration (Geoprobe Systems<sup>®</sup> 2006). The recommended speed of MIP probe advance into the subsurface is roughly 1 ft/min. The model used for the calibration test would be a 15 second push from stopping point to the next followed by a 45 second residence time at the stopping point for a total ideal drive of 1 foot. However, as previously indicated, the actual speed of the drive is dependent upon the Geoprobe<sup>®</sup> operator and actual subsurface conditions. The gases exiting the MIP system during the calibration test were also captured in carbon-trap which was desorbed (heated) to the GC to confirm or re-set the retention time windows for each compound and identify the standard concentration area reported by the GC.

Calibration of the MIP – GC system is critical since the permeability of the MIP membrane to compounds of concern changes (decreases) with membrane wear. The MIP investigation started with a new membrane and daily calibration confirmed that the MIP membrane transmitted less of each compound of concern after the initial day of use. GeoTrans used the results of these performance tests to calculate the mass of each compound in the MIP return gas flow over the “trapped” interval. The area response of the GC was set equal to known calibration solution concentration for each compound during one foot of MIP drive. During subsurface investigation, a gas flow rate of 40 milliliter per minute was used. The mass of each compound in the MIP return gas flow was calculated using the total time the trap is receiving gas flow from the MIP, the gas flow rate (to obtain the total MIP return gas flow through the trap), and the response area/concentration relationship from the calibration testing. This approach resulted in the calculation of the mass of each compound of concern per foot of MIP drive (mg/foot).

## **GROUNDWATER ELEVATIONS AND SAMPLING**

For comparison purposes, GeoTrans obtained depth to groundwater measurements and groundwater samples from monitoring wells adjacent to MIP borings and from all Site monitoring wells during the MIP investigation. GeoTrans conducted groundwater monitoring from June 15 through 18, 2004 and submitted all groundwater samples to a PADEP-Certified laboratory for analysis of PCE and degradation by-products.

GeoTrans also obtained discrete groundwater samples at two (2) “deep” selected intervals based on MIPS information through installation of a decontaminated groundwater sampler. The sampler consisted of an expendable drive point, the drive head rod, a protective sheath, an inner stainless steel screen, and an O-ring seal. Decontaminated drive rods were added to the top of the sampler as it was driven to the selected interval using a Geoprobe<sup>®</sup>. Once the desired depth was achieved, extension rods were placed down the center of the drive rods to knock the expendable point loose and to hold the screen in position as the rods were retracted 4-feet exposing the stainless steel screen which filled with groundwater. Once in place, groundwater was sampled in the same manner as a monitoring well. To identify vertical gradients, the groundwater sampler was left in-place after sampling to allow groundwater to equilibrate. An elevation survey was conducted to establish the top elevation of the sampling rod and the depth to groundwater was measured to identify the groundwater elevations. These measurements indicated a vertical groundwater gradient of -0.0236 at the center of the plumes and -0.0065 at the down-gradient edge of the plumes.

## **RESULTS**

MIP results are commonly portrayed in a series of graphs showing the soil conductivity in mS/M, the speed of MIP advance in ft/min, PID, FID and ECD signals in  $\mu$ V, and MIP temperature versus depth BGS. Higher soil conductivities are commonly associated with finer grained, lower permeability soil and higher ECD response is commonly associated with the impact from chlorinated solvents. Review of these graphs can provide a general understanding of where the potential impact is located relative to a potentially lower permeability zone. As stated previously, borings, soil and/or groundwater sampling and laboratory analysis of soil and/or groundwater samples is the only method to confirm these findings and identify the actual compounds present and their concentration.

The carbon-trap results from the four (4) MIP borings and groundwater monitoring results are shown in Figure 1 for PCE and Figure 2 for DCE and VC. These figures show a scaled cross section of the center line of the PCE plume which includes the mall buildings, ground surface, well and well screen locations, subsurface release location, stream culvert location, the location of the groundwater table during the MIP investigation, location of the MIP borings and discrete groundwater sample locations. Ground water flow in these figures is from the release location to stream location. As shown, the results from carbon trapping are expressed in grams of each compound in the MIP return gas flow per foot of MIP advance. As presented earlier, the total mass of each compound identified in the carbon-trap of a selected MIP advance interval was determined and then divided by the length of MIP advance.

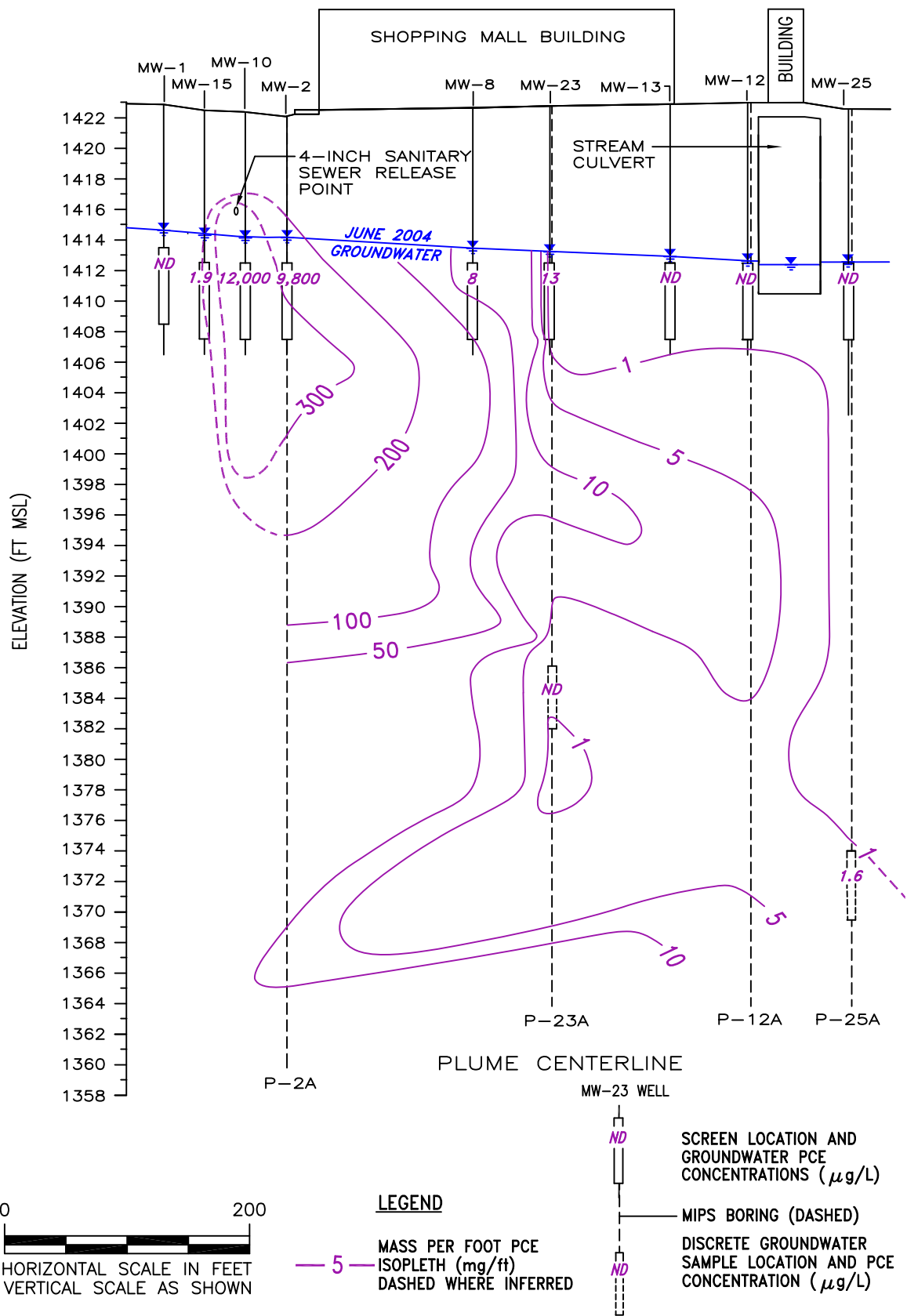


Figure 1. June 2004 PCE mass isopleths (mg/ft) and groundwater concentrations ( $\mu\text{g/L}$ ).

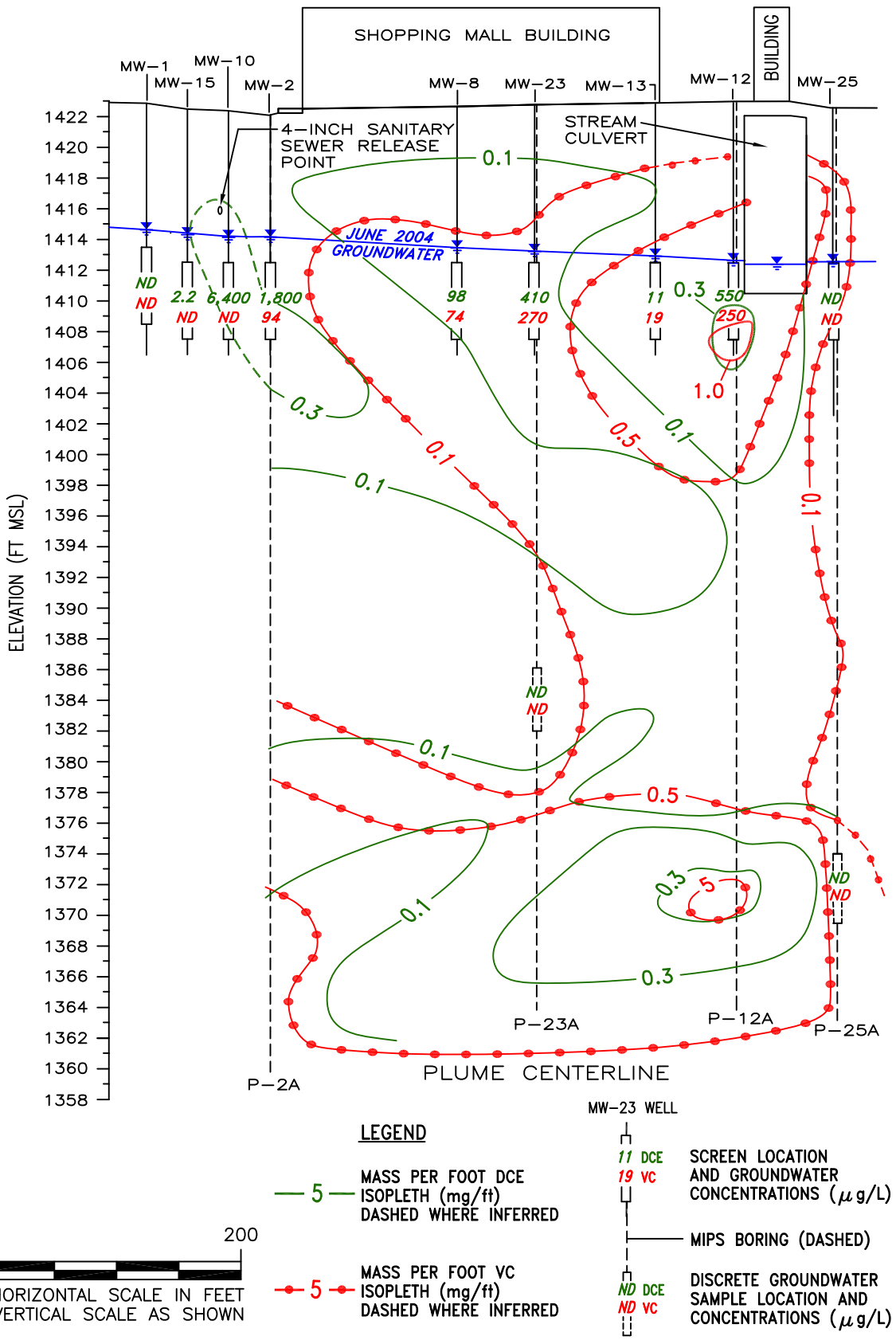


Figure 2. June 2004 DCE and VC mass isopleths (mg/ft) and groundwater concentrations ( $\mu\text{g/L}$ ).

Both Figure 1 and 2 show the details of subsurface compound distribution as isopleths of mg/foot. These isopleths portray the subsurface distribution of each compound with detail not normally obtained from normal MIP use. As shown in Figure 1, the PCE plume has an area of higher mass near the point of PCE release with a higher mass extending directly downward indicating a probable DNAPL advanced through the groundwater table. As the DNAPL is diluted and impact transitions to the dissolved phase, the PCE mass isopleths shows a change in direction to an approximate 45 degrees downward (as a result of a negative vertical gradient) in the direction of groundwater flow. As shown, PCE was identified in the vadose zone only near the area of the release.

The PCE mass isopleths also show good correlation with the PCE groundwater monitoring results below the groundwater table with the exception of the discrete groundwater sample result below MW-23. This result shows that the MIP identified a PCE mass while no PCE was identified in the discrete groundwater sample. This difference may be due more to the fact that the MIP is a down-hole onsite analysis versus normal groundwater monitoring which introduces the opportunity of volatile loss during sample acquisition, containerization, shipment and storage prior to offsite analysis.

Review of the DCE (intermediate degradation by-product of PCE) mass isopleths in Figure 2 reveals a distribution pattern more consistent with the dissolved phase and similarities to the PCE pattern near the release with a higher mass identified further down-gradient. The MIP mass DCE isopleths results show an order of magnitude greater mass at depth and down-gradient of the release which is consistent with the presence of DCE as a by-product of PCE. Interestingly, the down gradient mass increase appears to have occurred at two (2) locations; one near the water table surface and a second at depth. The mass distribution pattern for VC (degradation by-product of DCE) is similar to the DCE mass distribution pattern with the exception of the vicinity of the release. This is consistent with the longer times required to degrade PCE to DCE and then to VC.

The MIP results also show a significant detection of VC and DCE in the vadose zone above the down-gradient portion of the VC and DCE plume where no releases of these compound were known to occur. Therefore, this result may be from the MIP carbon-trap detection of soil vapor trapped beneath the mall building and associated structures and indicates the potential versatility of the carbon-trap approach in which compound impacts to three different media can be detected (soil, groundwater and soil vapor impact).

As shown in Figure 2, the DCE and VC mass isopleths also show good correlation with the DCE and VC groundwater monitoring results below the groundwater table with the exception of the discrete groundwater sample result below MW-23 and MW-25. These results show that the MIP identified DCE and VC mass at both locations while no DCE or VC was identified in the discrete groundwater samples. Both DCE and VC were identified in the MIP return gas flow at the discrete groundwater sample location below MW-25 at 0.16 and 0.48 mg/foot, respectively. This result indicates that in-situ and in-field analysis of the MIP return gas flow is potentially more sensitive in detecting groundwater impacts from VC and DCE than conventional groundwater monitoring techniques.

## **CONCLUSIONS**

The results of this investigation indicate that the use of carbon-traps to identify individual compounds in the MIP return gas flow is effective in identifying the distribution of PCE and degradation by-products in the subsurface. The MIP carbon-trap approach appears to be capable of identifying impacts to soil vapor, soil and groundwater in the field in near “real time” and is potentially more sensitive to detecting these compounds in the saturated zone than conventional groundwater monitoring techniques. Future investigations conducted with MIP carbon traps should focus on identification of variables affecting the MIP detection and recovery of subsurface impacts and how they can be controlled to further improve the quantitative capabilities of the MIP.

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## **REFERENCES**

- Christy, T.M. 1996 “A Permeable Membrane Sensor For the Detection of Volatile Compounds in Soil.” Presented at the National Ground Water Association Outdoor Conference, Las Vegas, NV, May 1996.
- Fettke, Charles R., 1938, “The Bradford Oil Field, Pennsylvania and New York, Pennsylvania Geological Survey, Fourth Series, Bulletin M21.
- USEPA, Office of Superfund Remediation and Technology Innovation 2005 “Sensor Technologies Used During Site Remediation Activities – Selected Experiences.” Appendix 1, EPA 542-R-05-007.
- Geoprobe Systems® 2006, “Geoprobe® Membrane Interface Probe (MIP) Standard Operating Procedure”, Technical Bulletin MK3010.
- ASTM 2007, “Standard Practice for Direct Push Technology for Volatile Contaminant Logging with the Membrane Interface Probe (MIP)”. Standard D-7352-07.