



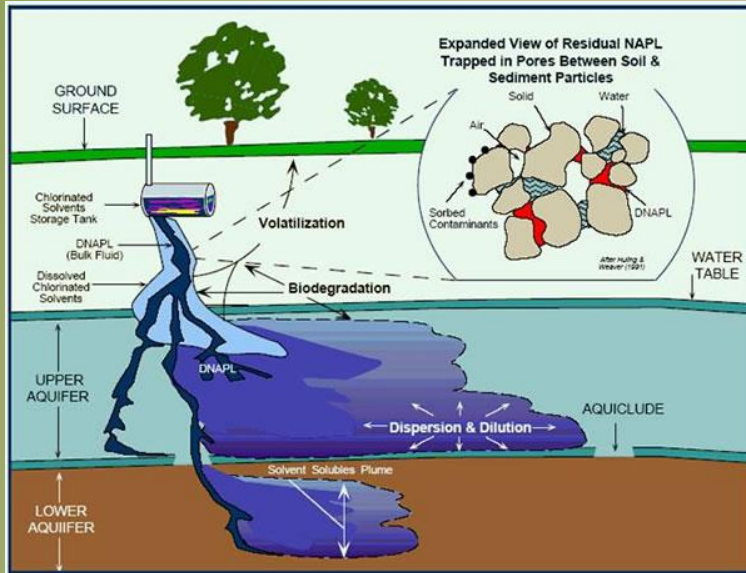
Chlorinated DNAPL Identification using the Membrane Interface Probe (MIP)

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Chlorinated DNAPL Identification



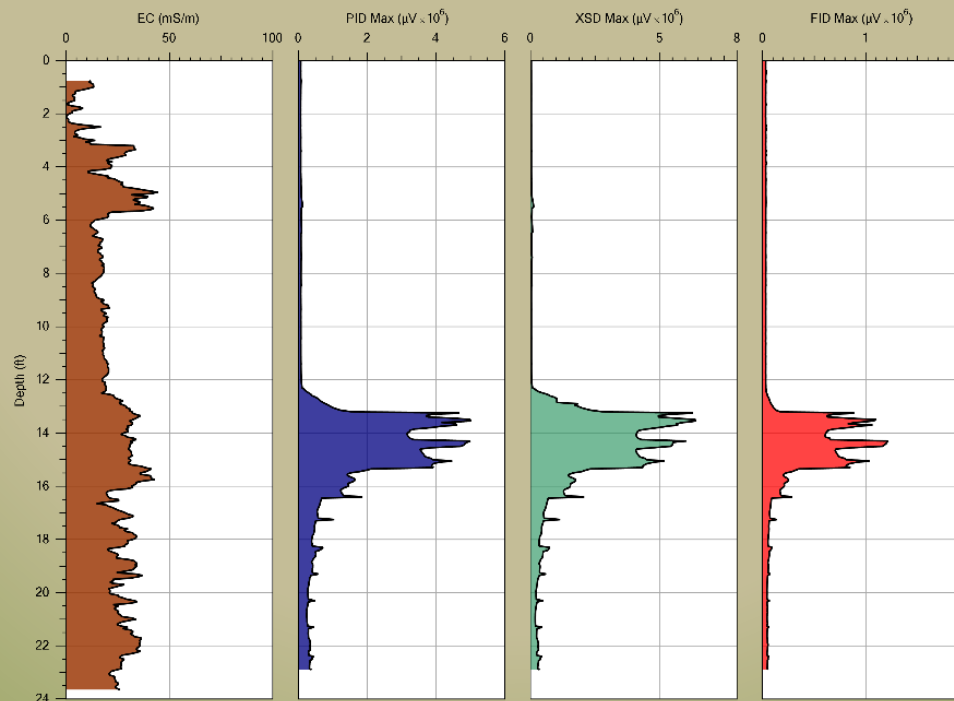
Chlorinated VOC (CVOC) contamination is a big problem in the subsurface environment and can result in major health risks when located private or municipal wells or surface water receptors.

The membrane interface probe (MIP) has been used for years to map CVOC plumes to determine magnitude and extent of contamination. Logging in dissolved phase

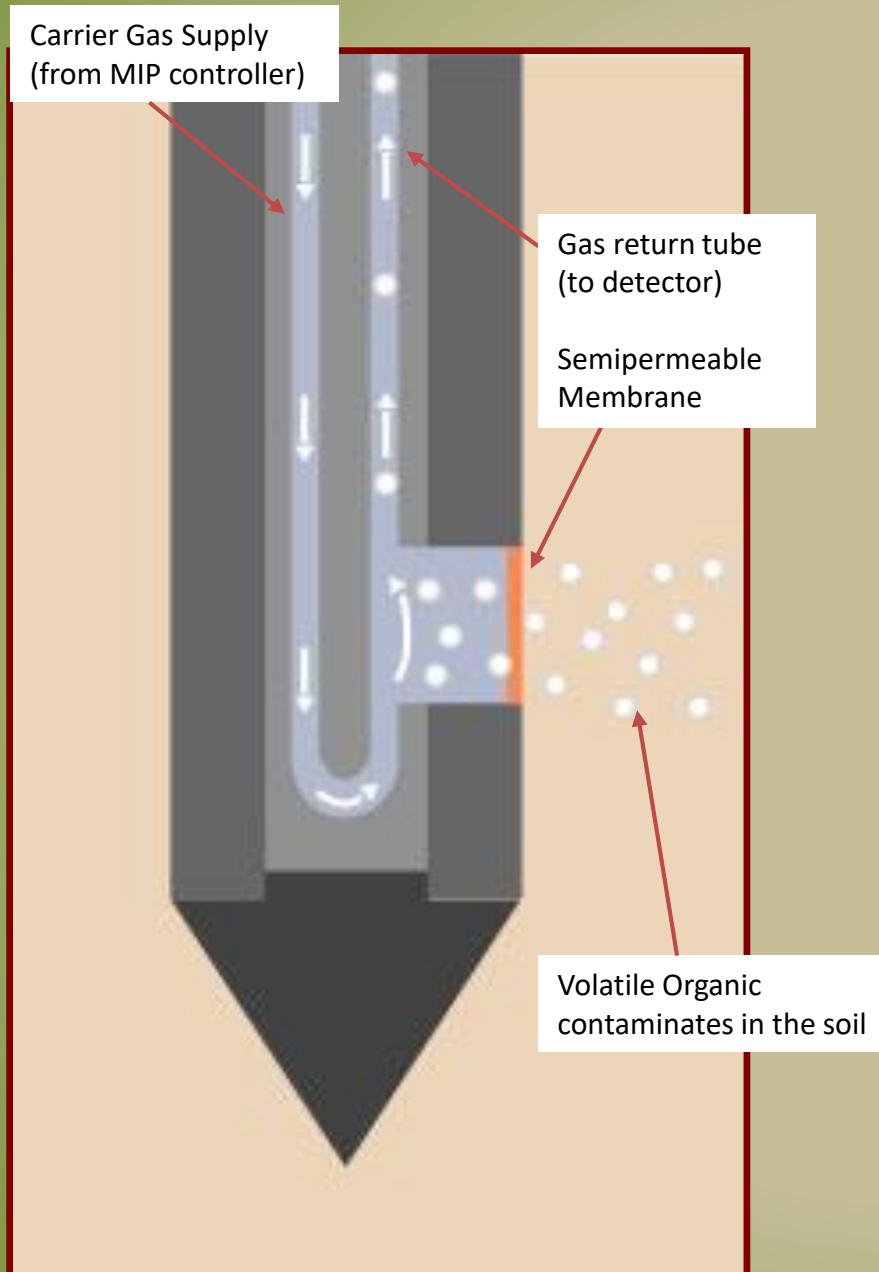
plumes is fairly straightforward, when there is a possibility of intersecting a DNAPL zone, identifying that from MIP logs has been anything but straightforward. While MIP contaminant detection is semi-quantitative, recent changes to the common MIP detectors used, as well as, a better understanding of the detectors themselves can help to discern from MIP logs when the plume changes from dissolved phase to having DNAPL present.

Chlorinated DNAPL Identification

This study was undertaken to show that identifying zones of chlorinated DNAPLs can be successfully pinpointed using the Membrane Interface Probe (MIP) system. We have designed an operational protocol for the MIP system when expecting to encounter high dissolved phase CVOC plumes and/or DNAPL zones. This will give MIP operators and data reviewers the knowledge needed to help identify DNAPL zones as well as determine their vertical extent from the results obtained in the MIP logs.



MIP Theory of Operation



Left: A continuous carrier gas flow (nitrogen) sweeps past a heated semipermeable membrane. VOCs, in the subsurface, diffuse across the membrane into the carrier gas stream where they are carried to gas phase detectors at the surface.

The MIP system consists of the membraned probe, trunkline and the gas phase detectors. This systems allows the contaminants in the subsurface to be mapped by the detectors versus depth in real time.

MIP Detectors

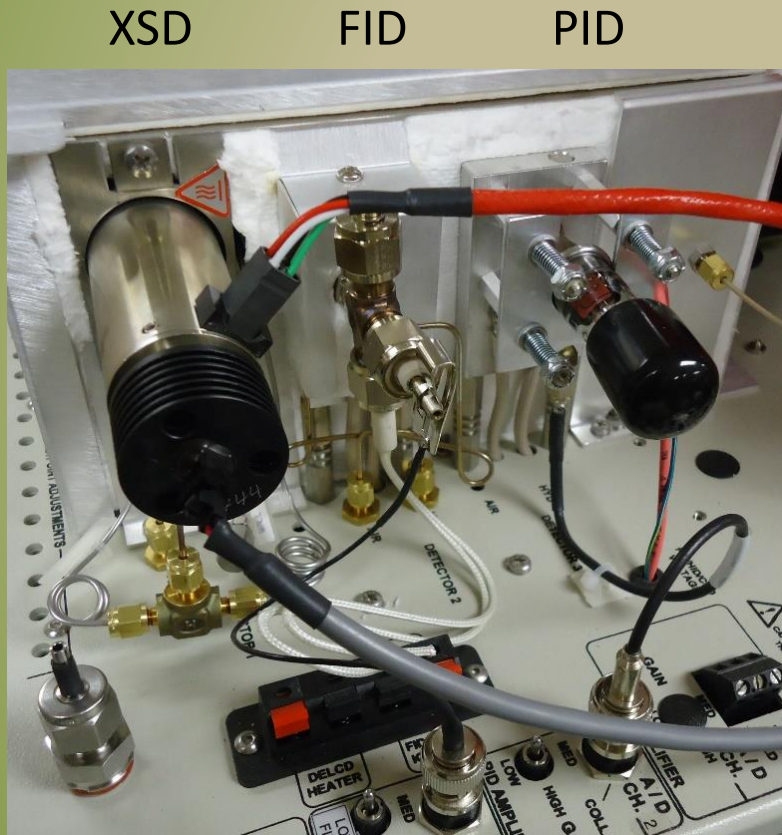


Photo Ionization Detector (PID)

Responds to all molecules whose ionization potential is below 10.6eV. This includes aromatic hydrocarbons and molecules with carbon double bonds (PCE, TCE). Most common PID lamp = 10.6eV.

Flame Ionization Detector (FID)

Responds to any molecule with a carbon-hydrogen bond which includes most VOCs which combust in the H₂-Air flame. The FID is mass not concentration sensitive.

Halogen Specific Detector (XSD)

Responds only to halogenated (F⁻, Cl⁻, Br⁻) VOC compounds.

MIP Detectors

Lower Detection Limits

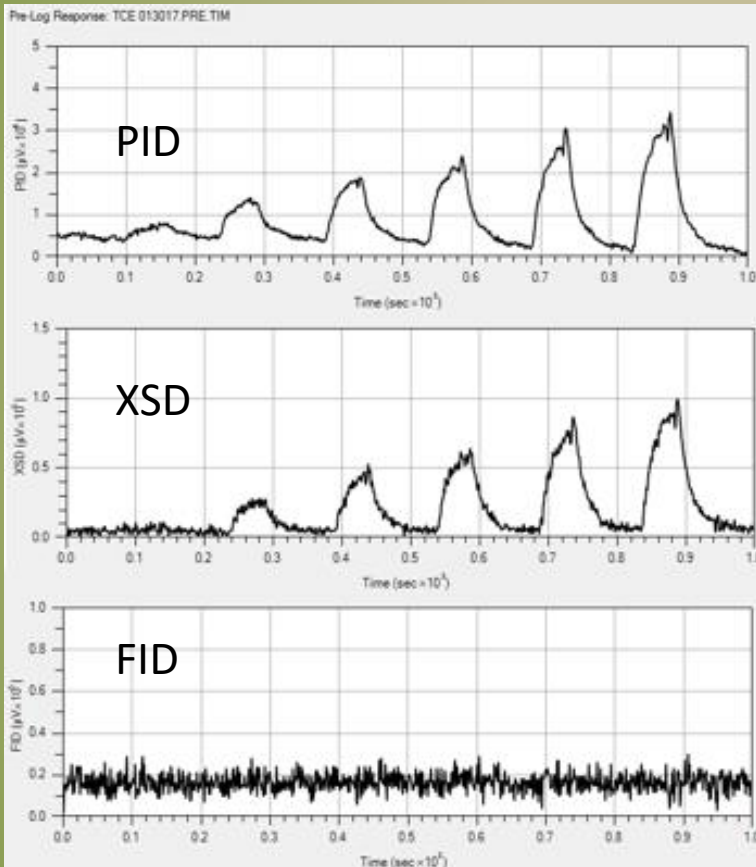
PID, XSD 0.10-0.50ppm TCE
FID ~10-15x higher than PID

The FID is not as sensitive as the PID and XSD at lower concentrations.

A MIP system detection limit should be determined by system specific MIP chemical response tests

- Based upon MIP operation with a 150' standard trunkline (TL) using a 40ml/min carrier gas flow rate
- Lower detection limit and detector response are influenced by MIP setup and detector maintenance.

MIP detector response to TCE from 0-0.5ppm



MIP Detectors

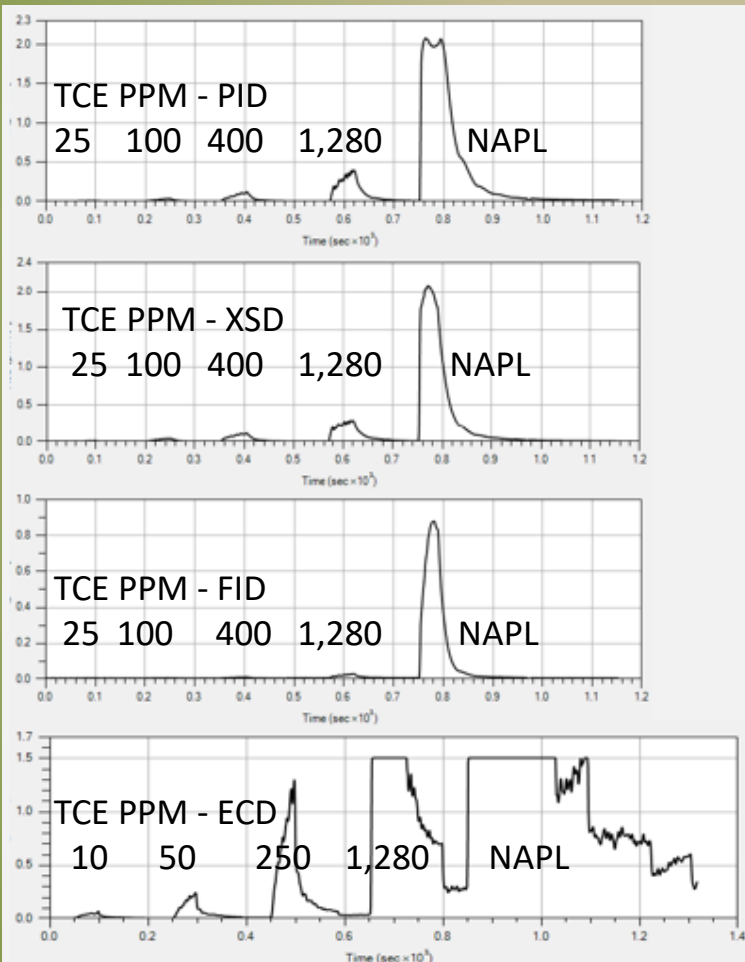
Upper Detection Limits

PID, XSD Both detectors displays similar response magnitudes for TCE. Response extends beyond the TCE solubility point of water.

The FID displays far greater response contrast of high dissolved phase and DNAPL than the PID and XSD.

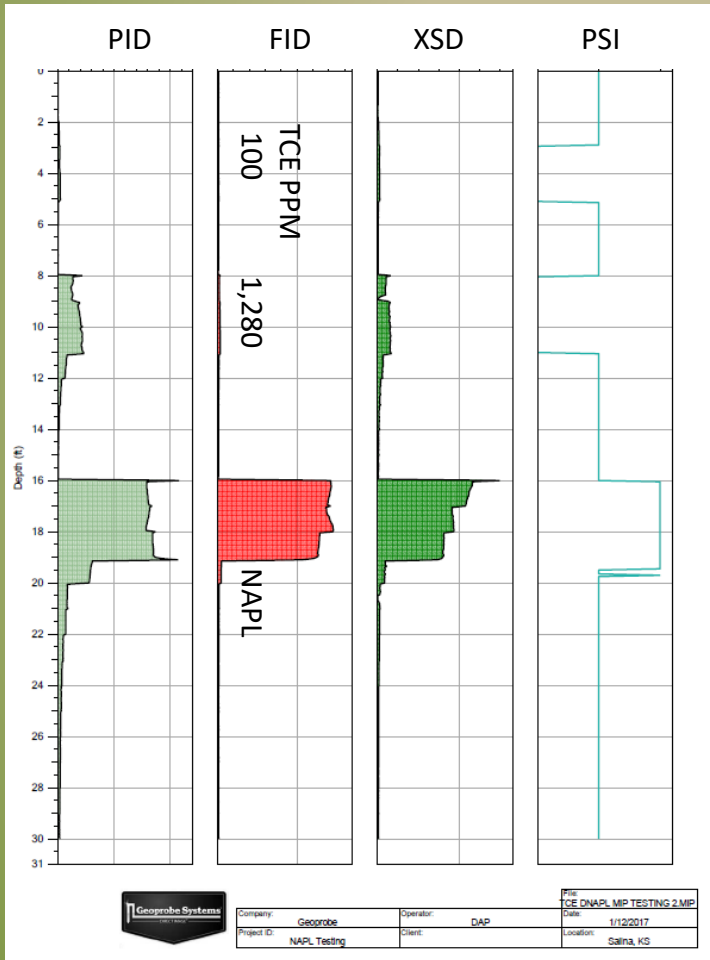
PID, XSD and FID all exhibit good response beyond the water solubility point of TCE.

An ECD's response is variable to the number of chlorine atoms on the molecule and chemical structure. An ECD does not differentiate between high dissolved phase and DNAPL.



Vertical Definition of DNAPL

How the Detector Response Affects Contaminant Carryover

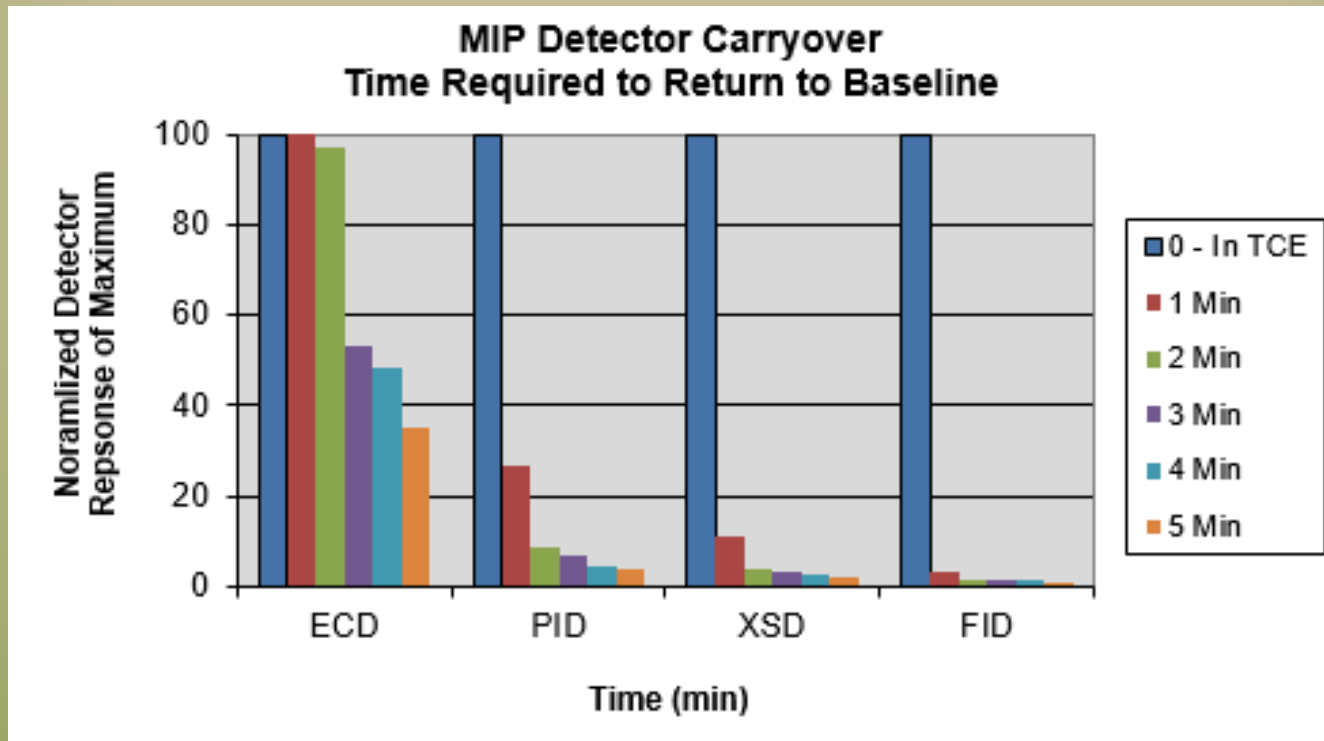


The vertical position of DNAPL is clear based upon the FID drop in response even though the PID and XSD are slower to return to baseline. The FID's insensitivity at lower concentrations will help define the bottom of the DNAPL plume with minimal carryover.

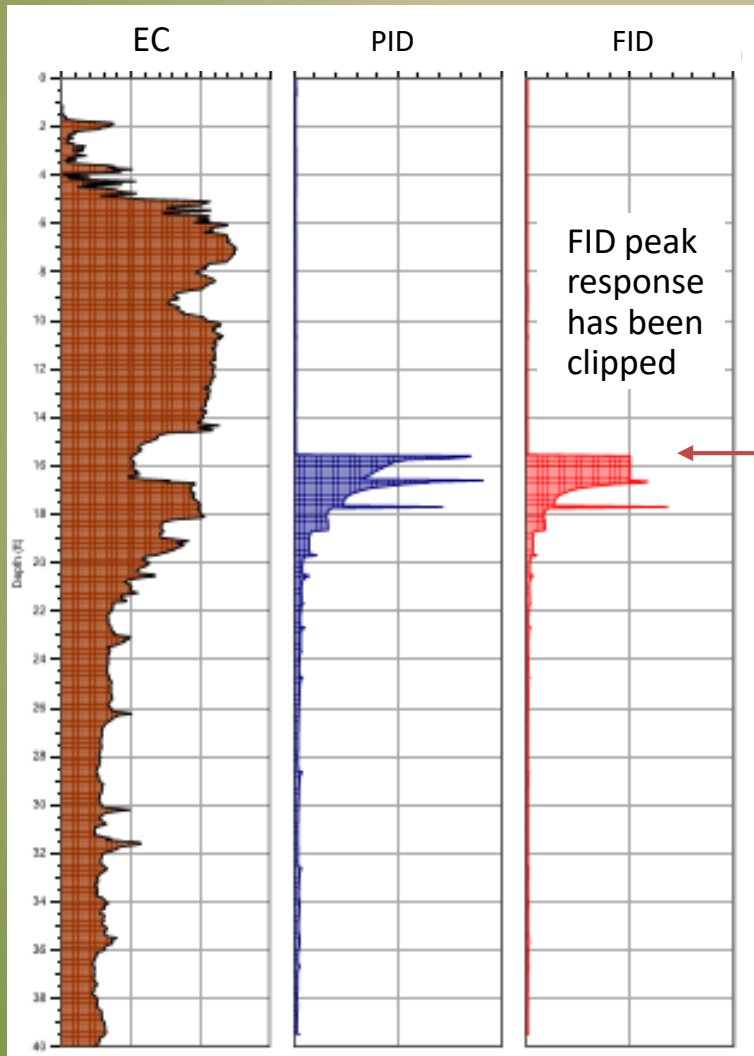
Vertical Definition of DNAPL

How the Detector Response Affects Contaminant Carryover

The laboratory tests reveal that when TCE NAPL was removed from the membrane, after 3 feet of exposure, the FID would reach 2% of the max detector signal within 2 minutes, providing the clearest picture of the DNAPL zone vertical thickness.

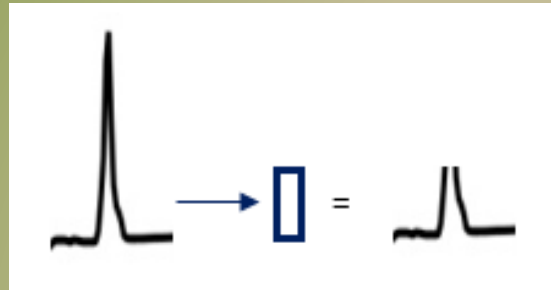


MIP Detector Gain Adjustments

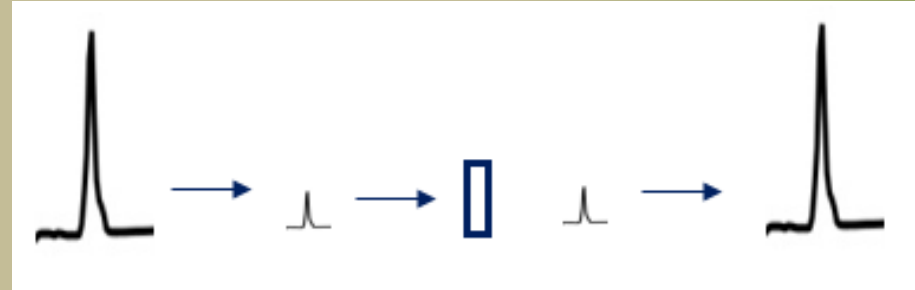


The FID in the log below to the left shows the problem that can occur when detector gain settings are not adjusted properly when the MIP system encounters high dissolved phase or DNAPL concentrations. The tops of the detector response peaks will get clipped. This is a critical step when mapping high concentration VOC plumes.

MIP Detector Gain Adjustments



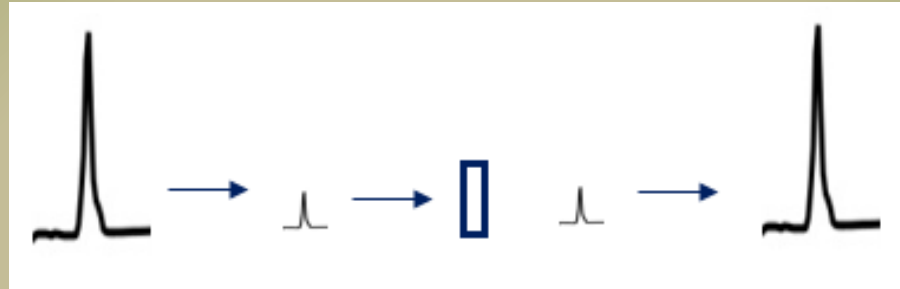
Peak Size Signal Output Window Clipped Peak



Peak Size Gain Adjusted Signal Output Window Peak Out Peak Attenuation Readjustment

Peak clipping occurs due to the Gas Chromatograph having a maximum signal output limit which on some instruments is 5,000mV. The signal can go higher than this however the instrument cannot output that signal without getting it clipped at the limit (above left). Peak “clipping” can be avoided with proper adjustments by the operator which can be made either during the logs as needed or prior to beginning a log in anticipation of the high responses seen in high dissolved phase or NAPL plumes.

MIP Detector Gain Adjustments



Peak Size → Gain Adjusted → Signal Output Window → Peak Out → Peak Attenuation Readjustment

Gain/Attenuation Settings on the GC detectors and the DI Acquisition software

HP GC Range*	DI Acq. Attenuation* Factor	SRI Gain PID & FID	DI Acq. Attenuation Factor	XSD Gain	DI Acq. Attenuation Factor
0	1	High	PID/FID = 1	High (100)	1
1	2	Medium	PID=10/FID=20	Medium (10)	10
2	4	Low	PID=100/FID=200	Low (1)	100
3	8				

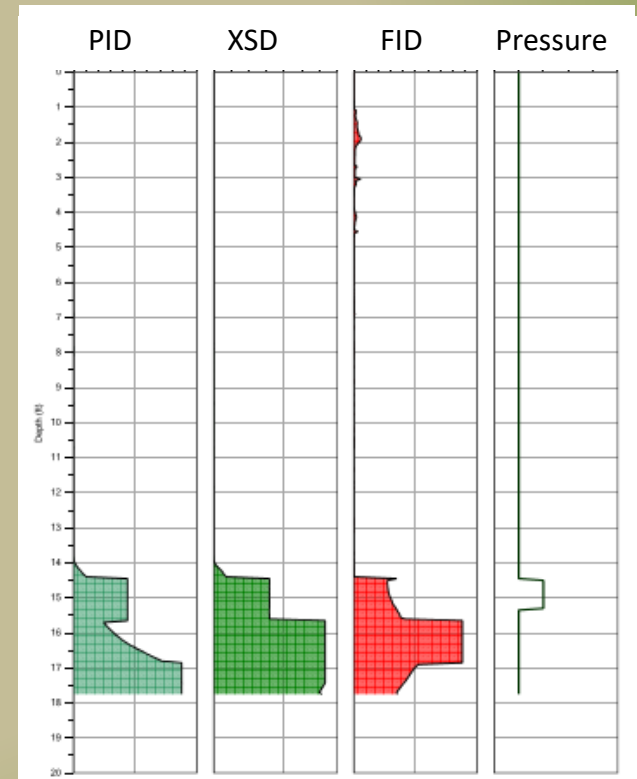
GC Gain/Range settings and associated software multipliers.

*The detectors on the HP GC can have up to a range of 7 on the GC corresponding to an acquisition software attenuation factor of 128.

MIP Operational Protocol

For Mapping High Dissolved Phase to DNAPL CVOCs

1. Preset the detector gain adjustment to a low setting along with the proper software attenuation adjustments to avoid peak “clipping”.
2. Use the information from all 3 detectors to best determine DNAPL vertical thickness. The FID shows the greatest response contrast between high dissolved phase and DNAPL.
3. Chlorinated contaminants will be confirmed with the use of the XSD.



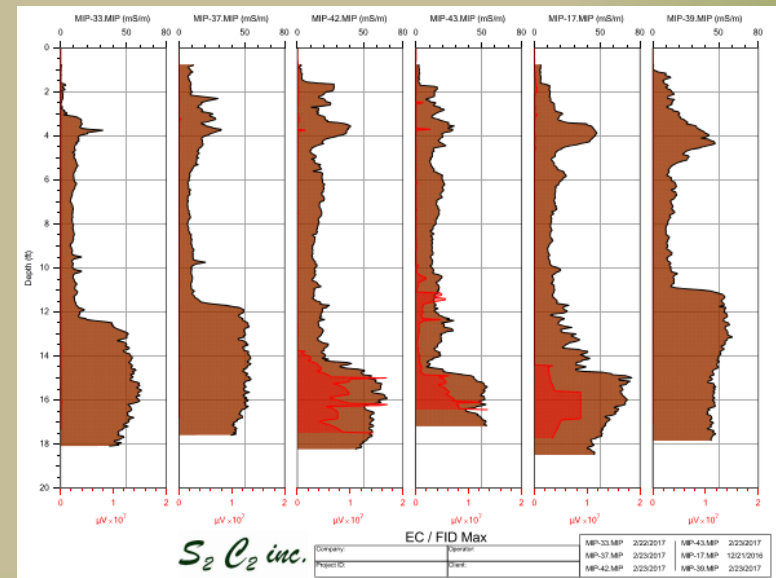
MIP Operational Protocol

For Mapping High Dissolved Phase to DNAPL CVOCs

4. Display the logs in cross section format at a common detector scale to pick out locations where detector response magnitudes are indicative of where DNAPL would be present.
5. Do not use or pay attention to ECD responses in these locations.

These procedures would be effective for all chlorinated VOC DNAPLs and could also be useful when encountering LNAPL gasoline plumes.

EC and FID Responses



Field Site – DNAPL Identification



The site was a former industrial facility in northern New Jersey that used chlorinated solvents in their processes. The consultant found a 1950's aerial photo of a former stream channel that came onto the property from an adjacent site. The goal of the Investigation was to determine the origin of the DNAPL.

Field Site – DNAPL Identification

MIP Setup Operating Conditions

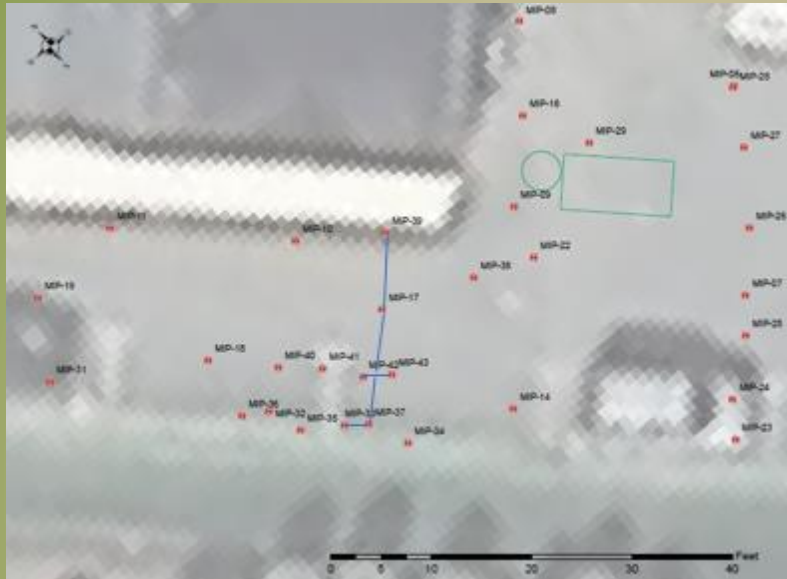
MIP Operators: S2C2

100' (30m) heated trunkline set to 100°C, probe temp 121°C

Carrier gas flow rate 37ml/min, MIP pressure – 5PSI.

HP5890 GC with PID, FID and XSD detectors. Detector gain settings in a low position for the highest response at the start of the log along with appropriate attenuation factors in the software.

Field Site – DNAPL Identification

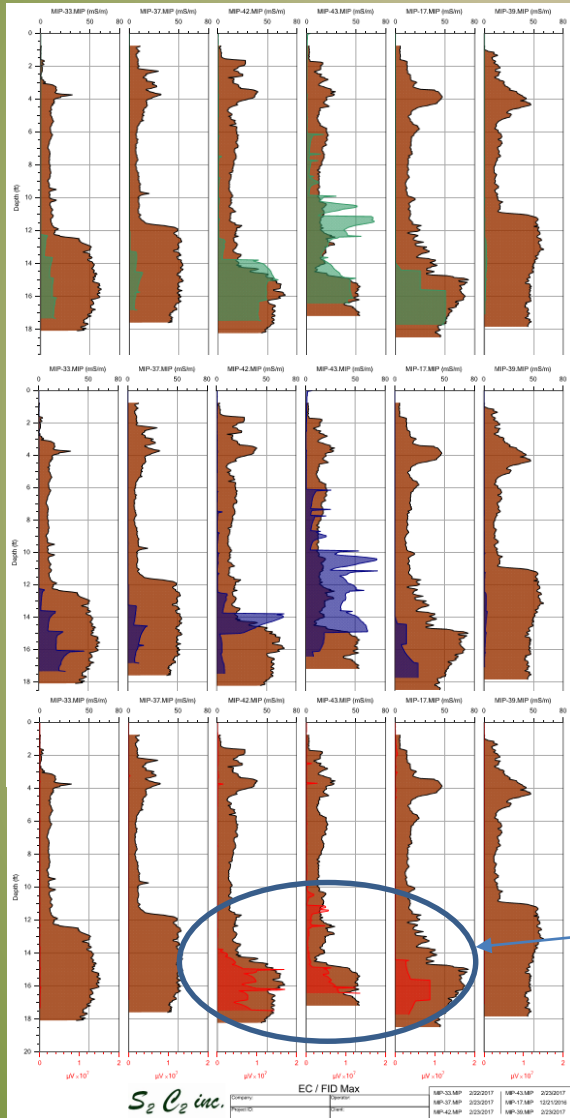


Left: The Site map below shows where MIP logs have been performed on this site. The blue line shows the logs included in the cross section MIP graphs which show electrical conductivity (EC) along with each detector response.

Right: The field crew is preparing to advance the MIP probe with the heated trunkline.



Field Site – DNAPL Identification



The MIP log cross-sections show where the contaminants are present.

The XSD lets us know it is halogenated (likely chlorinated) contaminant.

The PID displaying a similar pattern to the XSD tells us that the response is to a double bonded CVOC. Ionization potential <10.6eV.

The FID displays the greatest contrast in response magnitude between high dissolved phase and DNAPL. The FID's insensitivity at lower concentrations help us to focus on MIP logs 42, 43, and 17 as the most likely to contain DNAPL.

Field Site – DNAPL Identification

After completing MIP log 17 a discrete groundwater sample was taken. The bucket below shows the water and DNAPL coming from the tubing showing that DNAPL was present. Samples were sent to a lab for analysis.



Field Site – DNAPL Identification

Discrete groundwater samples were taken from a boring adjacent to MIP log 17 and were sent to a fixed lab for analysis. The lab report confirms the presence of DNAPL (TCE = 22%) in the sample taken from the DNAPL zone as well as a number of other contaminants including a high concentration of Toluene.

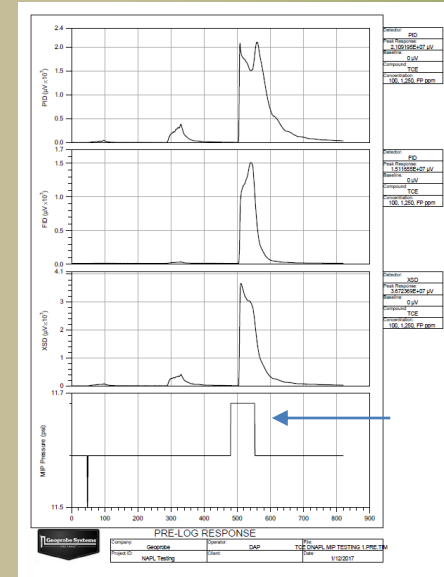
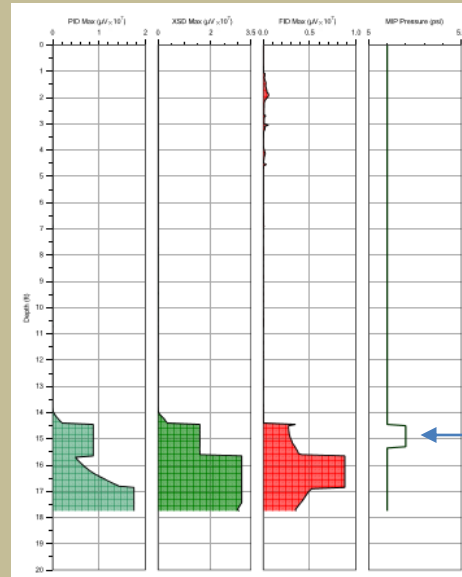
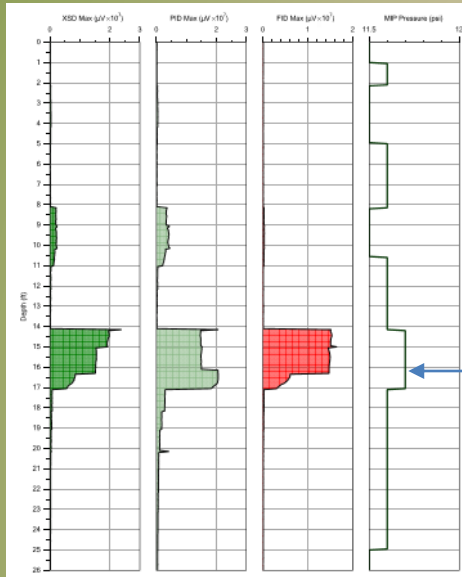


DNAPL Sample Lab results by SGS Accutest LabLink

Compound	Result	RL	Units
Chloroform	64,000	50,000	µg/L
Cis-1,2-Dichloroethylene	58,000	50,000	µg/L
Methylcyclohexane	352,000	250,000	µg/L
Tetrachloroethylene	582,000	50,000	µg/L
Toluene	3,090,000	50,000	µg/L
1,1,1-Trichloroethane	53,700	50,000	µg/L
Trichloroethene	221,000,000	5,000,000	µg/L
Total Xylenes	63,600	50,000	µg/L

Other Indicators of DNAPL revealed by the MIP Logs

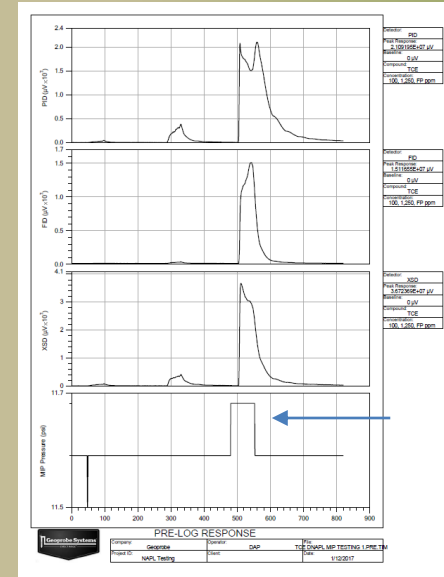
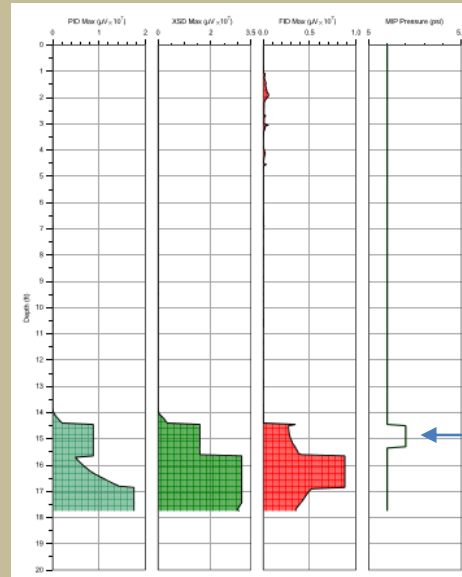
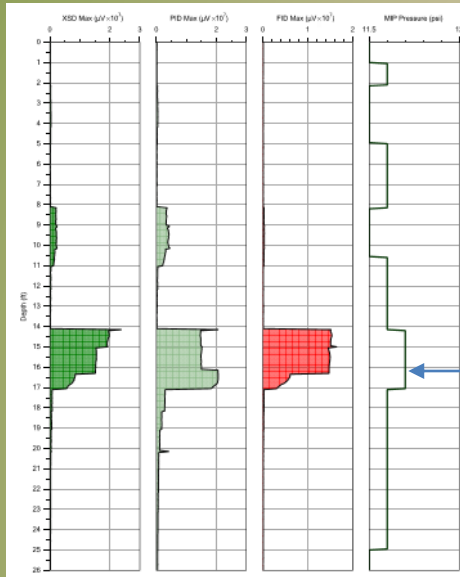
MIP Pressure Increases



Throughout this study on DNAPL detection using MIP instrumentation we observed slight pressure increases in the MIP trunkline. These pressure increases would occur when DNAPL had been exposed to the membrane and would be traveling in the MIP carrier gas line on its way to the detectors.

Other Indicators of DNAPL revealed by the MIP Logs

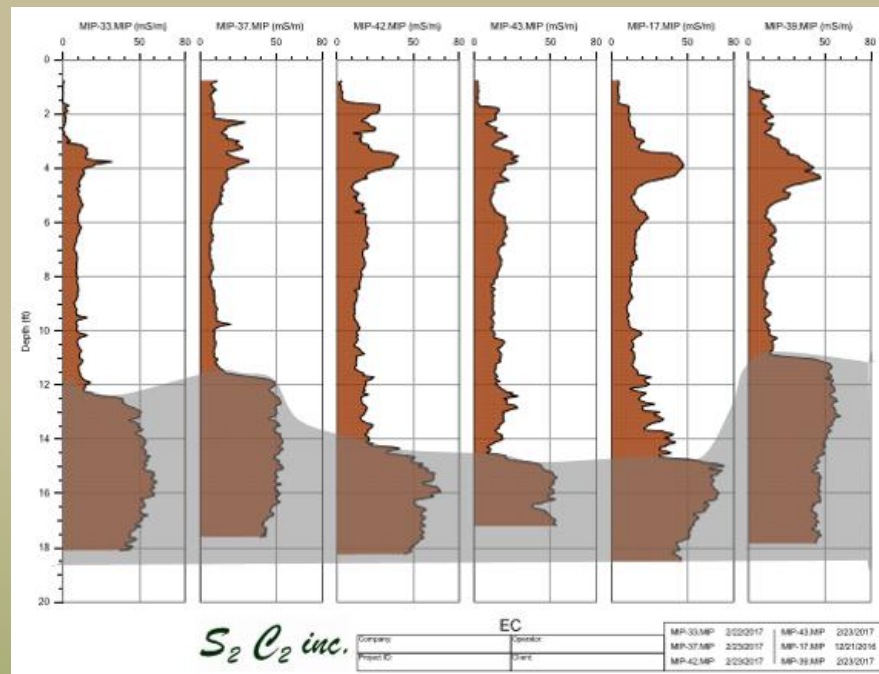
MIP Pressure Increases



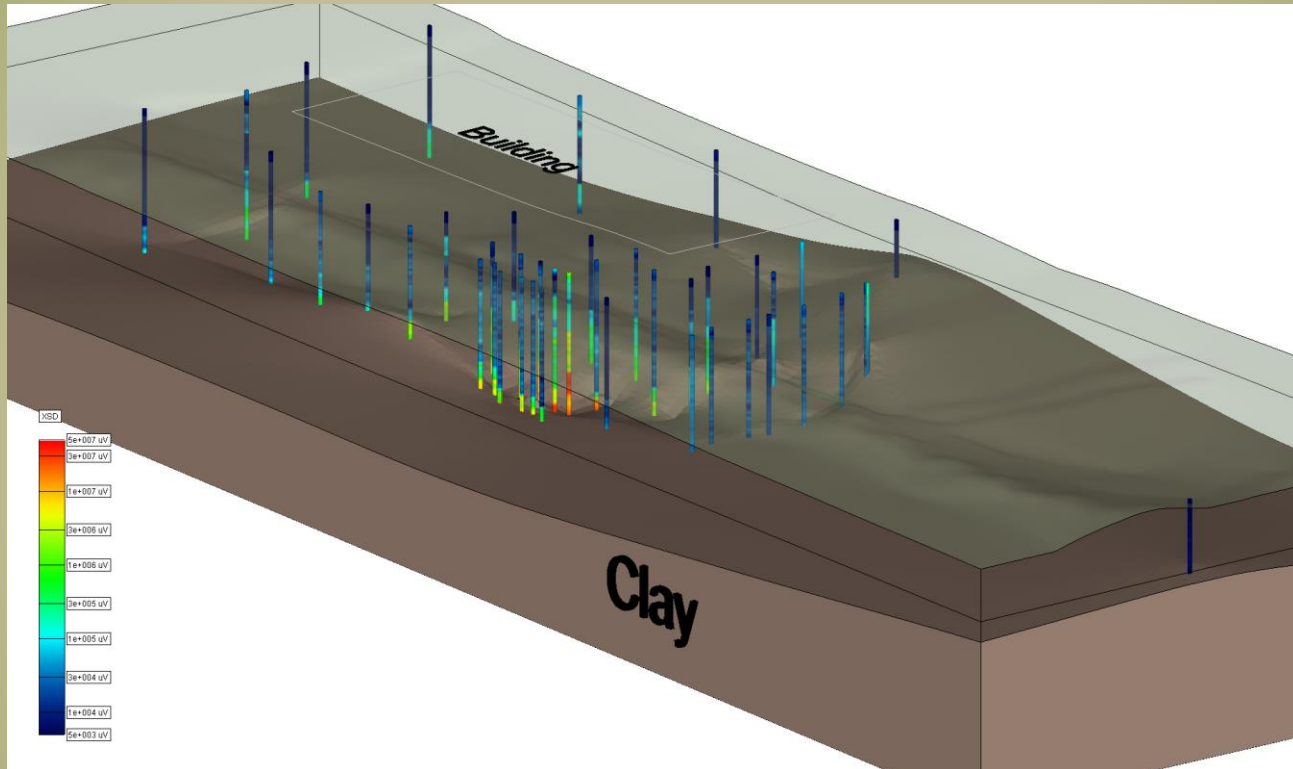
These pressure increases are not large and may not be completely reliable in their occurrence, however they serve as a possible indicator of the presence of DNAPL in the carrier gas stream. This pressure increase is likely due to an increased vapor density within the gas line which slightly increases the MIP gas line pressure needed to maintain the same carrier gas flow rate in the system.

Other Indicators of DNAPL revealed by the MIP Logs Permeability Traps in an Aquitard

Review EC and/or HPT pressure graphs in cross-section using the DI Viewer software. This can help to pinpoint any permeable depressions in an aquitard that can form a pool for the DNAPL to reside. If depressions do exist in the clay, logs displayed in cross sections or a 3D map of EC or HPT pressure may reveal subsurface features that are holding or carrying them either on or off site in the case of a buried stream channel.



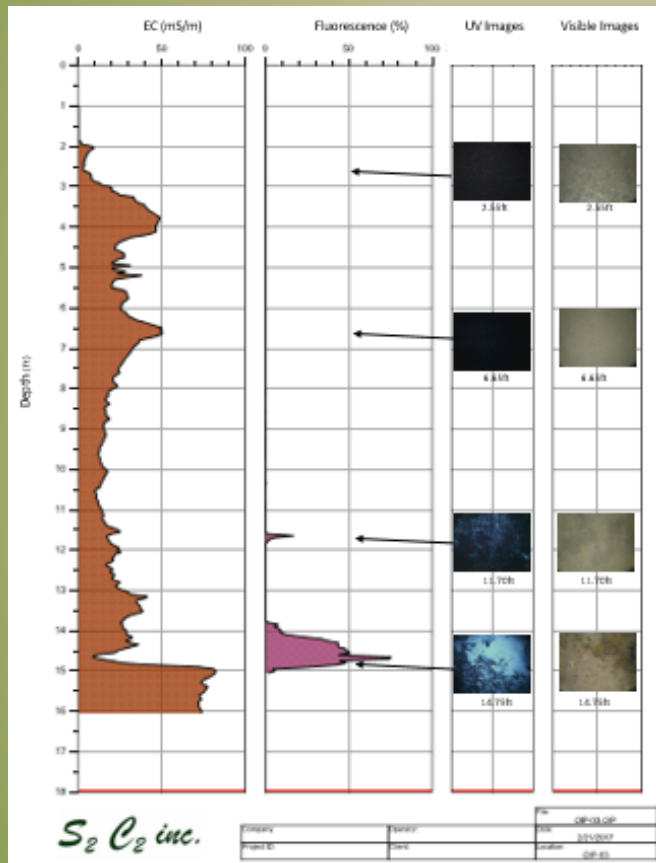
Other Indicators of DNAPL revealed by the MIP Logs Permeability Traps in an Aquitard



This image shows the top of the clay unit with its surface depressions near the center of the image. Each MIP-XSD log response is also positioned on the map with the highest XSD responses located at the low spots in the clay surface. This is where chlorinated DNAPL has been recovered.

Other Indicators of DNAPL

DNAPL Confirmation using OIP Fluorescence

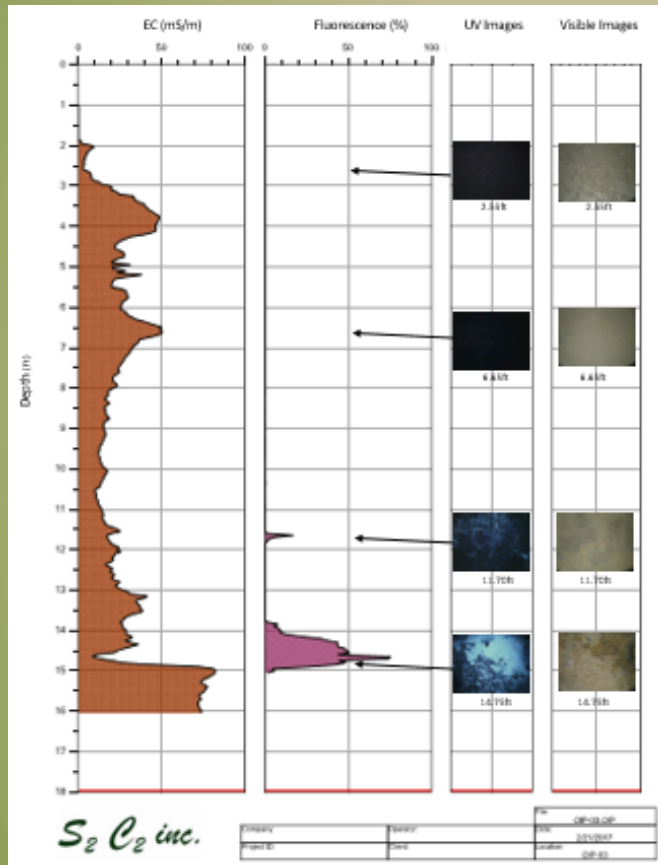


Multiple Optical Image Profiler (OIP) logs were performed to map the fluorescence of hydrocarbons present in the DNAPL. The OIP system utilizes a 275nm UV LED and an onboard camera to take images of the fluorescence which are analyzed for their color.

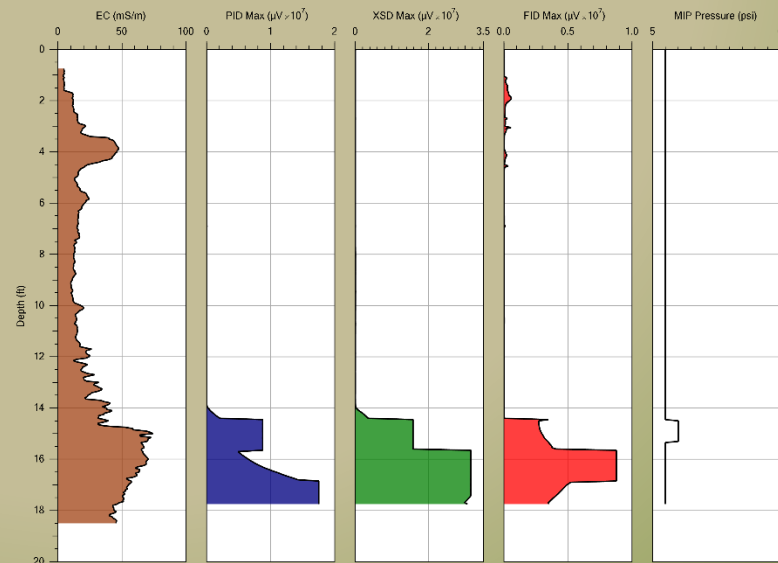
DNAPL TCE by itself will not fluoresce, however with the presence of enough PAHs in the form of oil and/or grease the DNAPL will fluoresce when introduced to the 275nm UV light source.

Other Indicators of DNAPL

DNAPL Confirmation using OIP Fluorescence



The OIP log (performed within 1' of MIP-17) confirms the DNAPL is located in a 1' band sitting on top of the clay from 14'-15'. This fluorescence of the DNAPL using OIP confirms the MIP detector readings. The PID, XSD and FID all begin large magnitude responses in that same interval as well as an increased MIP pressure spike seen in the log.



DNAPL Determination using MIP Detectors

Conclusions

- If expecting extremely high responses pre set the detector gain to its lowest adjustment and make the appropriate software attenuation adjustment.
- Use the information provided by all detectors
- The FID may provide the best indication of the area where CVOC DNAPLs are located when viewed in cross section because of the greater response magnitude.
- Watch for physical features such as permeability traps or buried stream channels. These may be revealed in log cross section by EC or HPT pressure.
- Be observant of potential MIP pressure spikes in zones where DNAPL is likely.
- Do not rely on an ECD to give any useful information in high concentration TCE or PCE site mapping.
- Confirmation of MIP indication of CVOC DNAPL by an OIP fluorescence investigation is not reliable. CVOC DNAPLs do not fluoresce on their own.
- Groundwater or soil sampling will confirm the findings.

Chlorinated DNAPL Identification using the Membrane Interface Probe (MIP)

We would like to thank S2C2 and Betts for participating with us in this study and allowing us to share information from their site.

The logo for S2C2 inc. is written in a black, cursive script font on a white rectangular background.The logo for BETTS features a stylized flame icon on the left, composed of a blue base and a yellow-to-green gradient top, followed by the word "BETTS" in a bold, blue, sans-serif font on a white rectangular background.The logo for Genuine Geoprobe is enclosed in a black oval border. The word "Genuine" is in a small, black, sans-serif font above the word "Geoprobe", which is in a larger, orange, sans-serif font. A registered trademark symbol (®) is located to the upper right of "Geoprobe".