













This is an example of a standard MIP log run in a fine grained soil with overlaid lab analytical data for soil TCE concentrations. The soil concentrations from this location reached to just below  $500\mu$ g/kg in the soil. In this particular location the standard MIP provided good signal to the TCE concentrations present.





This standard MIP-XSD log shows only a very slight response in the 17'-22' range of this log while the groundwater samples from this course sand and gravel aquifer show lab results of 1-4mg/L at these depths. We knew we needed to find a way to improve our detector signal especially for areas like this.



A closer look at the XSD baseline shows very marginal signal for these concentrations.



Back in 1999, Geoprobe performed a study on how detector responses varied to MIP trunkline flow rates. It was clear that reducing the trunkline flow would provide an increased detector signal. A major problem that was seen was when trunkline flow rates dropped below 5ml/min the detector signal dropped off rapidly. Also the slower the flow rates in the trunkline the longer it takes to reach the detectors.



A main reason for the increased detector signal response with lower flow rates is because the contaminant that diffuses across the membrane is now being carried in increasing lower volumes of gas thus concentrating that contaminant.



If we look back at the graph of how flow rate affect response levels we can see that if we follow the trend line to a flow of zero our detector response should theoretically continue its upward trend until it reaches a point close to an order of magnitude higher detector response than standard MIP flow rates provide. The question was how can we achieve that without having our response fall off?



We thought we would try to stop the carrier flow behind the membrane (in the trunkline) and then after a period of time restart the flow at a higher rate to bring the sample quickly to the detectors.





The first feasibility test was performed by running a comparison of a standard MIP response test using the continuous flow rate of 40ml/min and then stopping the flow and restarting again. The results showed a 10x increase in signal response for the same contaminant concentration and membrane exposure time.



This is the basic flow circuit that contained inside the low level controller box that allows us to start and stop the trunkline flow having no flow at the membrane during sample collection and a high flow rate to bring the sample to the detectors.



The low level MIP controller handles all of the low level cycling of the trunkline flow and the valve switching which allows either clean carrier gas or the trunkline carrier gas to enter the sample loop. This is all handled in conjunction with the DI acquisition low level software addition.



When the low level MIP controller is added to the current FI based MIP system the different gas lines of the system are all plumbed through this controller. The supply gas for the trunkline coming from the MIP Controller, both the supply and return trunkline gas lines, a transfer line over to the detectors and a detector gas supply line (this one needs to be created from the gas chromatograph).





This shows the 2 independent gas flows created by the valve system in the LL control box. Specific timed events entered in the software by the operator will determine how long trunkline flow will be stopped as well as when the valve is switched to send the sample from the trunkline to the sample loop creating the point of the sample hand-off. The most important aspect of this configuration is the constant flow that the detectors see maintains a stable baseline. If the detectors saw all of the carrier gas flow cycling their baselines would be terrible showing massive amounts of noise greatly reducing the improvement of the method.



Example offset MIP-XSD logs (1m) in fine grained soils show the difference that the stoppage of trunkline flow can make in detector response magnitude. One may suspect there could be some contaminant response on the standard MIP-XSD log on the left but the LL MIP-XSD log on the right leaves no doubt where the contaminant is located.





These are images of the newly added control panel in the DI acquisition software for the automated operation of the LL cycling. The input screen is where the operator enters the cycle specific timed events. The top portion of the input screen determines how frequently to run the LL cycle as the log is advanced. In this case it will begin the LL cycle every 1ft when the probe stops forward advancement for 2sec inside of a 0.4ft window around each ft interval. The lower section of the input panel is how long the operator chooses to collect the sample at the membrane with no trunkline carrier flow, the transfer loop is loaded from the trunkline for 10seconds and after the trunkline flow is restarted the contents of the sample loop will be injected or directed over to the detectors. The output screen where the software is in the LL cycle, what the next sample interval is and what specific flow rates are within the system.

LL MIP Acquisition Software					
LL MIP Cycle Parameters:					
<ul> <li>Test Standard:</li> <li>Detectors:</li> <li>Detector Flow Rate:</li> </ul>	500ppb TCE XSD/PID/FID ~20ml/min				
<ul> <li>TL Flow Rate:</li> <li>TL – No Flow:</li> <li>Inject Time:</li> <li>Load Loop Time:</li> </ul>	~60ml/min 45sec 51sec 10sec				
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These are the parameters that were used in the next LL MIP response tests. A 500ppb TCE standard was used and the detectors had a 20ml/min constant flow rate. The trunkline flow rate was approximately 60ml/min but was shut off for 45seconds to collect the sample at the membrane. The trunkline carrier gas will be redirected to the transfer loop for 10seconds, the final 10seconds of the inject time which is when the contents of the transfer loop get sent over to the detectors.





This is a picture of the completion of an LL MIP response test of 500ppb TCE including the response test screen and LL MIP control panel. The detector peaks seen here show the PID and XSD having very similar responses while the FID, a much less sensitive detector, has only a very slight response at this concentration.



Low level MIP response test shows a 10x increase in the detector response magnitude over the standard MIP method.





This is a detection limit study done to determine the lower limit of the LL MIP system. Here a blank was run shown at ~125seconds and then TCE in ppb concentrations of 25, 50 and 100. Each of these levels shows the a good response and increases in magnitude proportionally to the previous concentration. Detection limits are determined by signal vs. noise you must have adequate detector signal many times over baseline noise. In this case the baseline noise would be what is seen in our blank however it is possible that we would not see that signal response in clean soil zones. Also just having a LL MIP controller does not mean that an operators system can see <100ppb, that is ultimately still determined by the condition of the detector system and how well maintained the detectors are. The LL controller will improve specific detector system signal by approximately an order of magnitude over whatever that system is capable of detecting by standard MIP.







Here is an overlay of a standard MIP log (black) and a LL MIP log (red) that were performed within 1m of each other. The reproducibility on the EC gives us confidence that these logs were performed in very close proximity. In the next couple of slides we will take a closer look at the comparison of the PID and FID graphs of these two logs.



These are MIP-PID log graphs from a standard MIP log compared with a LL MIP log performed within 1m of each other on the edge of a hydrocarbon plume. Both sets contain the same two PID graphs, the standard MIP Log on the left and LL on the right are autoscaled to focus on the specific detector baseline. The baseline on the standard run log shows some contaminants from 14'-19' the rest of the standard MIP-PID baseline is marginal as far as providing discernible signal over the baseline noise. The graph set on the right are the same PID graphs with the scales set at the same level which is scaled for the LL MIP log. This shows how much more robust the PID detector signal is during the LL MIP operation resulting in much greater signal to noise ratios.



These are MIP-FID log graphs from a standard MIP log compared with a LL MIP log performed within 1m of each other on the edge of a hydrocarbon plume. Both sets contain the same two FID graphs, the standard MIP Log on the left and LL on the right are autoscaled to focus on the specific detector baseline. The baseline on the standard run log shows some contaminants from 14'-19' the rest of the standard MIP-PID baseline is marginal as far as providing discernible signal over the baseline noise. The graph set on the right are the same PID graphs with the scales set at the same level which is scaled for the LL MIP log. This shows how much more robust the PID detector signal is during the LL MIP operation resulting in much greater signal to noise ratios.



Geoprobe Systems						
LL MIP Logs						
<ul> <li>I L MIP Log in mixed hydrocarbon – xVOC plume</li> <li>Graphs L-R: EC, PID, FID, XSD</li> <li>Hydrocarbons to 20' xVOCs 20-30'</li> <li>Fine grained lithology</li> </ul>						
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This is a standard run MIP-XSD log with overlaid xVOC lab soil results up to 500ug/kg. Good correlation between the XSD responses and the soil lab results. This log was performed in 2011 when validating the performance of the combined MiHpt probe.

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0001	3 Analyt		suits nom	
Denth	CCI 4	Chlrfm	TCF	Total X-VOC
(ft bgs)	(µg/kg)	(µg/kg)	(µg/kg)	(µg/kg)
4	28 ND	28 ND	28 ND	28 ND
6	22 ND	22 ND	22 ND	22 ND
8	26 ND	26 ND	26 ND	26 ND
9	24 ND	24 ND	24 ND	24 ND
10	24 ND	24 ND	24	24
11	24 ND	24 ND	28	28
12	24 ND	24 ND	25	25
13	25 ND	25 ND	33	33
14	25 ND	25 ND	31	31
16	26 ND	26 ND	33	33
17	23 ND	23 ND	31	31
18	21 ND	21 ND	21 ND	21 ND
20	30 ND	30 ND	39	39
22	25 ND	25 ND	140	140
24	27 ND	27 ND	<b>30</b> QC	<b>30</b> QC
25	26 ND	26 ND	190	190
26	25	19 ND	420	445
26.1 DUP	26	17 ND	450	476
27	30 ND	30 ND	410	410
28	18 ND	18 ND	300	300
29	24 ND	24 ND	230	230
30	23 ND	23 ND	91	91
31	26 ND	26 ND	90	90



When looking for comparison data for the LL MIP system we went back in 2012 to the WS19 location and performed a replicate standard run MIP log. These graphs show the EC reproducibility is good especially in the lower half of the log. The XSD also shows very good reproducibility confirming that the XSD was responding similarly as it had at this location the previous year.



Standard log 1 was the original WS19 location, standard log 2 was the replicate log the following year and the LL MIP XSD graph performed on the same day as standard log #2 shows the greater magnitude of the LL MIP XSD response. All three logs are scaled equally at the scale needed for the LL XSD graph. All logs have the analytical data overlaid on each XSD graph. The 30ug/kg TCE hits from 10'-20' are much clearer to detect over the baseline noise with the LL MIP XSD.

Geoprobe Systems LL MIP Logs						
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These are offset standard MIP and LL MIP logs where the EC shows a high level of reproducibility confirming these logs were performed in the same area of the site.



Here again we are showing and standard run MIP log on the left next to a LL MIP log performed within 1m. The data set on the left is a close up view of the XSD baseline which shows marginal signal that is difficult to determine contaminant signal versus baseline noise. We might suspect there is contaminants in the bottom half of the log but it is difficult to be certain. The LL log shows very robust signal over the baseline when we are in the contaminant zone. The graph set on the right has both the standard MIP and LL MIP log scaled to the same value to show the magnitude of improved detector signal.



The study site is located in Salina, KS near the intersection of  $5^{th}$  and North streets. Previous investigation by KDHE revealed an extensive 1,2-DCA plume along with smaller concentric plumes of carbon tetrachloride & chloroform. The 1,2-DCA has been impacting two local municipal wells. For our test of the HPT-GW sampler we ran a log transect across the plume (red x's). Remediation was started at the site about 3 years before our study and the plume extent appears to be changing.





These EC and HPT graphs in these logs show a coarse grain lithology with fairly high permeability.

This is an overlay comparison of Standard MIP Log (black) and LL MIP Logs (red) with left to right: EC, HPT PSI & XSD. The EC and HPT PSI display a high level of reproducibility confirming that both sets of the standard MIP and LL MIP comparison locations were performed in the same location of the site.



Here is a cross section of the LL MIP logs run at the site. Most of the contaminants were seen on the north end of the cross section. This is where the groundwater sampling was taken from for lab analytical comparison.



This is an overlay of 2 logs obtained with the recently developed combination MIP & HPT probe operated with the new Low Level detection procedure. The EC log and HPT pressure log are interpreted as discussed above. On the right is a log from the MIP halogen specific detector (XSD). This detector is sensitive to chlorinated VOCs like PCE, TCE, carbon tetrachloride, chloroform and 1,2-DCA. Above 35ft the XSD displays a baseline response, indicating essentially no contamination. However, below 35ft the detector response clearly indicates the presence of chlorinated VOC contamination. We selected preliminary sampling intervals based on the XSD response to get a range of contaminant concentrations. Of course the EC and HPT pressure logs were reviewed as well ... no groundwater samples between ~37-40ft due to high pressure/low permeability.



This is the HPT-GWS log run at the N5 location about 3ft from the LL-MiHpt log reviewed above. The EC and HPT pressure logs look very much like the LL-MiHpt log data. On the right here is the **corrected** HPT pressure log. This log is generated by subtracting the atmospheric & hydrostatic pressure (blue wedge, center graph) from the raw hpt pressure log, and shows the actual pressure required to inject water into the formation matrix. (This removes the "baseline rise" caused by hydrostaic pressure). Indicated here are the depths where we stopped and collected water samples, very close to the proposed depths based on the LL-MiHpt log.





The samples for VOCs were sent to Continental Analytical Services lab for analysis. CAS is fully accredited. (www.cas-lab.com)



Just a reminder of where we are relative to the groundwater plume. Location N5 is at the north end of the transect. Next we will review the groundwater sample results for each HPT-GWS log location. Then we will look at a cross section of the three MiHpt logs run at the locations, across the plume.



This is a simple plot of the sample results for the three primary analytes at the site overlaying the MIP-XSD detector response at the N5 location. Notice that 1,2-DCA concentrations are elevated between ~35-45ft while C-CL4 and CH-CL3 concentrations are elevated from about 47-57ft.



This is another plot of the analytical results over the XSD detector response at the N5 location. This view emphasizes the presence of an upper plume of 1,2-DCA and a lower plume of C-CL4 and CH-CL3. Duplicates for each depth interval are plotted here. Only one set of duplicates (51ft) resulted in a significant RPD. Next we'll look at plots of the analytical results for the other two HPT-GWS sample logs.



While there is only one sample from the lower plume of C-CL4 and CH-CL3 it demonstrates that the contaminants in the upper and lower plume are distinct.



Because of an unexpected clay layer at 55ft (not seen on this log but is visible on the HPT-GW log) we missed getting a hot sample in the lower plume. But the XSD response demonstrates that the lower C-CL4/CH-CL3 plume is present at this south location.



This is a cross section displaying the HPT pressure log and XSD log for each of the 3 locations investigated. This view is facing west with north to the right. Note how the concentrations in both the upper 1,2-DCA plume and the lower C-CL4 & CH-CL3 plume decrease to the south. Also the upper and lower plumes become more distinct. Also, at the north most log there is a good bit of detector response in the sandy portion of the aquifer. Conversely as you progress south the detector response (and contaminant concentrations) are more focused around the fine grained/high pressure layers in the formation. This suggests residual contaminants are backdiffusing out of the fine grained materials.











