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Rapid Site Characterisation Using MIP integrated with a GC-MS - Field Trial

Environment & Health Programme

Internal Report OR/08/005



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ENVIRONMENT & HEALTH PROGRAMME

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Rapid Site Characterisation Using MIP integrated with a GC-MS - Field Trial

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Hapiste GC-MS integrated with MIP.

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Summary

This report describes the integration of a portable Gas Chromatograph-Mass Spectrometer (GC-MS) with a Membrane Interface Probe (MIP) site survey system in order to provide on-site qualitative and quantitative Volatile Organic Compound (VOC) data at the SABRE research cell in Derbyshire.

The first part of the report gives an introduction to both technologies and a background to the site conditions. Methodologies and limitations are discussed.

The second part of the report discusses and compares the results obtained from the MIP pushes, GC-MS analysis of the gas stream and soil samples collected from boreholes drilled adjacent to the MIP wells. An attempt is made to calibrate the MIP voltage responses using data from the GC-MS, results are presented both in the text and in the appendices.

A comparison of on-site and off-site soil analysis data is made, highlighting the potential for loss of volatiles when samples are sent away for analysis. Soil data is also compared to the on-site down hole gas data.

1 Introduction

1.1 BACKGROUND

The Membrane Interface Probe (MIP) system is a dynamic, intrusive investigation tool ideally suited to the investigation and characterisation of subsurface Volatile Organic Compounds (VOC's). Subsurface contaminants are volatilised in-situ and brought to the surface via a carrier gas and analysed using a variety of detectors. The limitations of this system are that the detectors only identify *areas* of contamination and do not identify or quantify the compounds present. By integrating a portable Gas Chromatograph Mass Spectrometer with the MIP system it should be possible to provide qualitative and quantitative data in the field.

1.2 OBJECTIVES

The aim of the project was to

1. Establish a practical method of analysing the gas stream from a Membrane Interface Probe (MIP) using a HAPSITE Portable GC-MS to provide real time on-site characterisation and contaminant speciation.
2. Evaluate the performance of the portable GC-MS for on-site analysis of soils contaminated with Volatile Organic Compounds (VOCs)
3. Compare soil contaminant concentrations with MIP response data

1.3 SITE DETAILS

The study was undertaken at the Source Area BioREmediation (SABRE) project site located in River Derwent valley, approximately 5 km east south east of Derby city centre. The SABRE Research Site (SRS) is located in an area (c. 100 x 25 m) of solvent impacted ground, which is contained within a larger chemical plant owned by Celanese Ltd.

The subsurface profile at the SRS comprises made ground, alluvium, river terrace deposits and mudstone. The made ground ranges in thickness from 0.60 m to 2.80 m and contains a mix of sand and gravel of brick, clinker, ash and concrete with soft to firm slightly sandy clay. The alluvium is between 0.40 m to 2.10 m thick and is characterised by slightly sandy gravelly clay. At some locations the alluvium has been removed and replaced with fill. The river terrace deposits range in thickness from 2.10 m to 5.50 m and consist of gravels or sandy gravels, occasionally becoming sandy with depth. The mudstone comprises stiff clay with mudstone lithorelicts, is highly weathered and has a variable surface topography. The unweathered mudstone contains thinly bedded silty mudstones with some gypsum horizons (Lelliott et al 2004)

Trichloroethylene (TCE) and associated reductive dechlorination products have been identified in groundwater samples from boreholes at the the SABRE Research Site (SRS). Maximum TCE concentration is associated with the former MCA plant area, whereas cis-1,2-dichloroethene (cDCE) and vinyl chloride (VC) concentrations are observed to increase immediately downgradient of the MCA plant area towards the south and southeast. Previous Membrane Interface Probe (MIP) profiling within the SRS identified a trend of increasing TCE concentration towards the contact between the river terrace deposits and the mudstone. Conversely, cDCE concentration decrease with depth, suggesting that degradative activity is currently higher in the near surface superficial deposits. (Lelliott et al 2004).

2 Scope of work

2.1 MEMBRANE INTERFACE PROBE (MIP)

The scope of work comprised two days MIP drilling at two locations, however, progress during the time period enabled a third location to be drilled as detailed below:

- Drilling two locations to refusal (6.5-7.0 m below ground level (bgl)) to provide continuous MIP data;
- Re-drilling of two locations for collection of MIP gas stream samples;
- Drilling one location with combined MIP data acquisition and gas stream sampling;
- Collection of gas stream samples from identified horizons for GC-MS analysis.

2.2 SONIC DRILLING FOR CORE RECOVERY

Two validation boreholes were drilled as close to the MIP boreholes as possible using a 'sonic' drilling method. Core was collected at 0.5 m intervals and sub-samples of the core taken that correspond to the depth of the gas samples. These samples were further subdivided and preserved on-site. One split of the sample was sent to an off-site analytical laboratory whilst the second split was analysed on-site using the GC-MS coupled to a headspace analyser attachment.

2.3 MIP SITE INVESTIGATION STRATEGY

Two locations were drilled by standard advancement of the MIP to provide a full profile of conductivity and contaminants as a base line. A second MIP borehole at each location was then advanced adjacent to the first MIP borehole and gas stream sampling conducted in addition to MIP operation. Sufficient time was available that a third location was drilled, enabling a drive of combined MIP acquisition and sampling to be undertaken without knowing the impact zones to be encountered and sampled (MIP3A).

2.3.1 Membrane Interface Probe Description

The Membrane Interface Probe (MIP) system is a dynamic, intrusive investigation tool ideally suited to the investigation and characterisation of subsurface volatile organic contaminants (VOC's). The 32mm diameter MIP probe is advanced into the ground using a Geoprobe® dynamic-push drilling unit. A carrier gas is used through a cable in the down-hole rods to deliver a continuous sample stream from the probe to a Gas Chromatograph (GC) for whole stream gas analysis with the column removed. Geoprobe systems consider the MIP to be a semi-quantitative tool. The membrane interface portion of the MIP consists of a small hydrophobic polymer port that is permeable to gas. The permeable port is a stainless steel screen with an area of 37.42 mm² and a thickness of approximately 0.76 mm, which is impregnated with a thin film of Teflon® (TFE). The membrane is screwed onto a steel housing (sub) that contains a resistive heater coil and a thermocouple allowing the temperature of the membrane to be controlled and monitored. Increasing the heater temperature increases the rate of adsorption into the membrane, diffusion through the membrane, and evaporation from the membrane surface into ultra pure grade nitrogen carrier gas. This carrier gas is circulated over the back of the membrane and then through a transfer line via a nafion dryer to a GC.

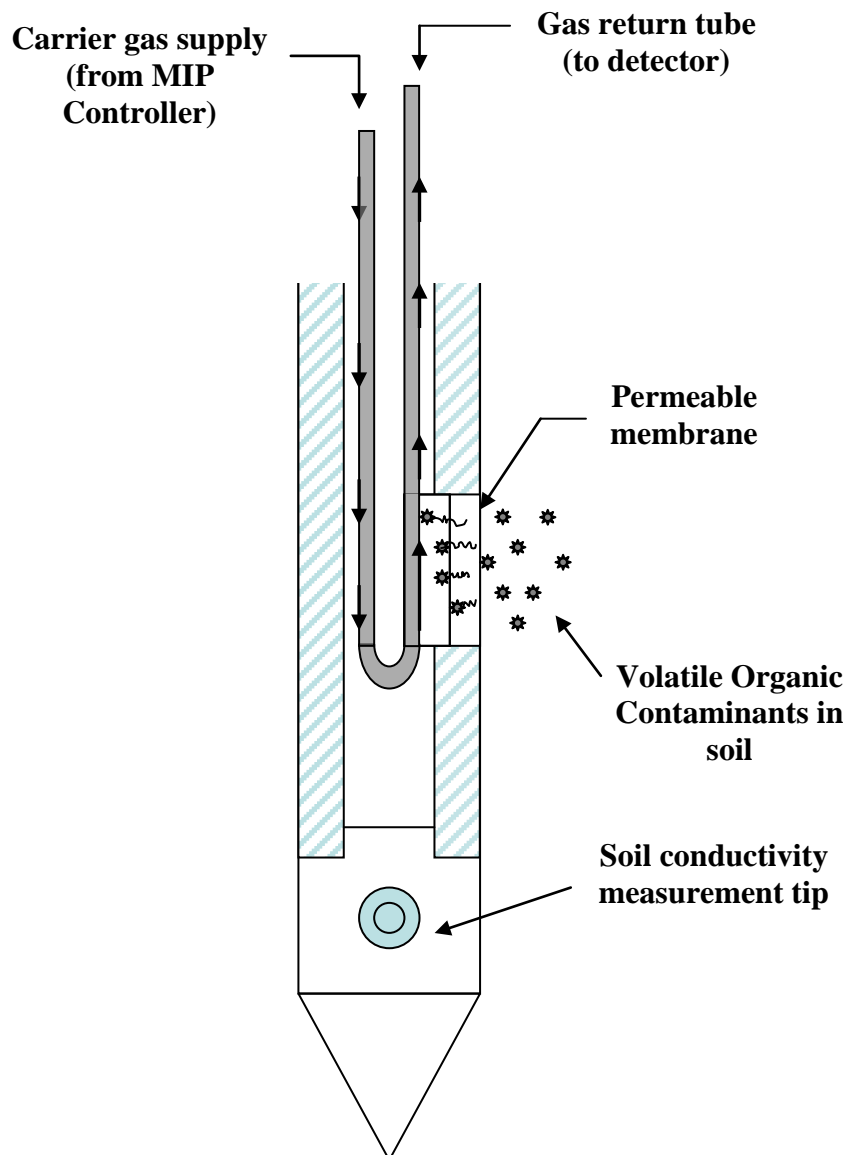


Figure 1 Schematic of Membrane Interface Probe

The GC was fitted with three detectors in series. These detectors were Photo Ionisation Detector (PID), Flame Ionisation Detector (FID) and Dry Electrolytic Conductivity Detector (DELCD).

The PID is non-destructive and is sensitive to aromatic / unsaturated compounds e.g. BTEX and benzene. The out-flow gas from the PID is split and passed to a FID that responds to most organic compounds and to a DELCD that is sensitive to chlorinated compounds e.g. trichloroethene (TCE) and chlorobenzene. The varying responses in the detectors (in millivolts) with depth defines the location of contaminants within the total depth profile. The results are considered qualitative rather than quantitative although the magnitude of response is indicative of concentration within the same contaminant plume.

The MIP sub incorporates a soil conductivity dipole enabling logging of the geology (subject to soil sample correlation). The soil conductivity can distinguish between high and low permeability media, for example between sands and clays respectively.

The temperature of the probe is preset and monitored from the surface. The actual temperature at any point is dependant on ground conditions and drive rate. Changes in the probe temperature can often be used as an indication of groundwater presence.



Figure 2 MIP tools and dynamic push system

2.3.2 Membrane Interface Probe Methodology

2.3.2.1 SENSITIVITY AND QA

Prior to progression of each MIP borehole a system test using butane gas is conducted to validate correct function of the PID and FID (TCE vapour can be used for the DELCD). The delay of response to the GC is recorded and entered into the software to give a travel time for the carrier gas. A standard solution is made of a compound of interest i.e. 1ppm in 0.5 litres of distilled water. The sensitivity test validates the ability of the setup to detect the contaminant of interest at low concentrations. MIP data, both soil conductivity and detector response, is correlated by logging and sampling for laboratory analysis at selected locations across a site.

2.3.2.2 DRILLING

The probe is advanced at a constant speed to cover 300mm in 45 seconds, it is then held at that position for 1 minute to increase contaminant exposure and recover to set temperature. Subject to site conditions the probe may be held at each horizon (300mm progression) until the minimum temperature is achieved i.e. a compound of interest may require 130°C to be detected. Purging of high contaminant levels or wicking of temperature may also require longer residual times to maintain sensitivity. The cycle is repeated to depth with rods added every 1.2m.

On completion of the drive the MIP is again immersed in the prepared standard to validate that sensitivity has not declined unacceptably and that the data acquired is valid.

2.3.3 Membrane Interface Probe Limitations

The MIP samples VOCs, and to a certain extent Semi Volatile Organic Compounds (SVOCs), in direct contact with its heated membrane. The sample size or area influenced by the heated membrane has not been studied; but is affected by temperature of the membrane, the type of subsurface media (vadose zone soil or saturated soil), and contact time between membrane and

soil. Because the sample mass and volume are not known, the MIP data is considered to be estimates that are a function of depth and lateral distribution. However, there are other limiting factors to take into account when using the MIP:

1. Sensitivity - the maximum achievable detector limits indicated by Geoprobe are in the range of 1ppm Benzene or BTEX (PID and FID). 250ppb chlorinated VOC's (DELCD) and 5ppm chlorinate compounds (PID). Sensitivity is dependant on several factors including the compound, probe temperature and residence time of the carrier gas behind the membrane and the delivery flow rate to the detectors.
2. The MIP system cannot identify individual chemicals.
3. The MIP data appears to be biased toward detection of VOCs in the saturated zone.
4. Detector response is non linear and is a total of all liquid, solid and vapour phases encountered at any depth horizon.
5. The thin Teflon membrane coating on the MIP is subject to damage in aggressive geology e.g. gravel or made ground rubble. The sensitivity of a new membrane will decrease in the first few metres of use, when the sensitivity of a membrane drops below the level of sensitivity required then the membrane is replaced.

The variables that may influence the detector responses are tabulated below:

Table 1 Controllable variables associated with using the MIP

Controllable Variables	Control	Reason
Air pressure and quality	Maintain moisture and hydrocarbon traps	Moisture and pressure affects detectors
Nitrogen pressure and quality	Only use recommended gas types from a reliable source	Operator check for holes, pinches, blockages and loose connections
Hydrogen pressure and quality		
Detector temperatures	The temperature is adjusted, set and displayed on the GC. Each detector has an optimum working temperature.	Affects the FID flame and therefore the sensitivity and reliability.
Oven temperature		If the temperature is too low some compounds can stick to the detectors allowing them to become saturated.
Clean detectors	Follow the method described for each detector in the GC manual.	The copper wires, if too cool, can condense the compounds prior to reaching the detectors. Decreasing sensitivity and creating false peaks.
		Ensure the detectors are clean, check the responses by using standards for each drive.

Table 2 Indication of the limitations of the MIP

Variables	Affects	Reason	Limitations and adverse effects
Geology - clay, silt, sand and gravel	Speed of penetration.	Different densities, particle size and distribution and levels of compaction.	Drive rates vary instead of being constant (300mm/45 sec)
	The sensitivity of the membrane.	Abrasive nature of the ground.	Sand and gravel can damage the membrane
Chemicals	Sensitivity and accuracy	Saturation of the membrane, detectors and lines by high concentrations of SVOC's or heavy end hydrocarbons	Contamination carryover in gas lines or detectors. Purging and bake-out required between drives.
		Precipitation of contaminant in carrier gas lines due to temperature drop	Contamination carryover indicating a greater zone of impact than present.
		Volatility	The more volatile a chemical is the greater the concentration that will pass across the membrane.
		Mixes of chemicals	The MIP system cannot distinguish between a chemical and a mixture. Although indication of plume differentiation may be gained from response and recovery times and comparison between detectors.
		Concentrations	The response is non linear, only an approximation of the contamination can be made. The system is semi-quantitative for similar contaminant mix on any site..
		Affinity	If the chemical has a high affinity with water it will not, or only very slowly, pass across the membrane. Even if present in high concentrations e.g. MTBE.
Water	Temperature	Heater cannot maintain a constant temperature while being driven through groundwater	In ground with a high hydraulic conductivity maintaining a high temperature (140°C) can be almost impossible.
Speed of penetration	Contact time with contaminant & temperature	Geology/operator	Variable time for diffusion through the membrane and residence time affects response to contaminant.
Membrane quality	Sensitivity and absorption rate	The thickness of the Teflon coating and the membrane varies. Each membrane is unique in it's response	Each membrane will give a slightly different response to the next one. The response will also decline with wear.

2.4 HAPSITE PORTABLE GC-MS METHODOLOGY

2.4.1 HAPSITE ® Portable Gas Chromatograph Mass Spectrometer Description

The HAPSITE portable Gas Chromatograph Mass Spectrometer (GC-MS) was developed by Inficon Inc for on-site measurement of volatile organic compounds in air, water, soil and gas samples. This technology is based on the principle of quadrupole GC-MS for compound identification and quantification. The sample components are separated by a GC column and passed into the mass spectrometer (MS) through a membrane interface. The interface between the GC and the MS is a 70% dimethyl silicone/30% polycarbonate membrane that provides the permeability for VOCs to the MS, but excludes inorganic constituents, such as nitrogen carrier gas, from the MS. As each compound emerges from the GC column, it passes through the selected membrane into the MS where the sample is fragmented by high-energy electron impact ionization. The mass fragments are then detected through a quadrupole filter. Compound identifications are achieved by matching ion spectra in the National Institute of Standards and Technology (NIST) library (Cal/EPA Evaluation Report)

The HAPSITE is capable of measuring volatile organic compounds with molecular weight typically 45 to 300 amu, boiling point approximately from -50°C to +180°C. The internal standard gas is used as a mass calibrator for compound identification and quantitation (www.HAPSITE.com).

2.5 GAS SAMPLING METHOD

The BGS HAPSITE instrument does not currently have a calibrated method for the analysis of air (calibration is not in the scope of this project) so a standard GC-MS 15 minute air loop method was used. This is a general purpose method used for identification of unknowns in the low ppm to high ppb range. Atmospheric samples are passed through the GC column for separation of individual components prior to detection by mass spectrometer. This method can be calibrated for quantitative analysis of selected compounds or semi quantitative analysis can be determined using internal standards. Runs last 15 minutes followed by a few minutes for the column temperature to decrease prior to the next run. Data was quantified using peak normalisation based on internal standard peak areas.

An alternative method that is only qualitative is the Survey method – Used to quickly screen a location for volatile compounds, atmospheric samples are drawn directly into the mass spectrometer, bypassing the GC column. Survey methods can provide tentative identification of compounds by using either target mass spectra (i.e. compounds of interest) or by searching the total mass spectra response against an in-built library (AMDIS). Sensitivities range from 500ppb to 2 ppm for selective ion monitoring or 1ppm to 10ppm for a full scan run. Sample runs are two to three minutes and the instrument provides a real time plot of response versus sampling time, the mass spectrum or a list of detected compounds. Compound identification is hindered by complex mixtures.

2.5.1 Hand Control Unit/Inlet Line

The Hand Control Unit/Inlet line (Figure 3) is an external sampling probe for the Analytical module with an LCD display and keypad. The probe provides an inert heated conduit for conduction of a sample flow into the HAPSITE. The inlet line is temperature controlled and usually maintained at 85° to 95°F.



Figure 3 HAPSITE probe connected to Tedlar® bag

Gas samples can be introduced to the HAPSITE in two ways:

1. The gas sample is collected in a 1.0 litre Tedlar® bag (Figure 3). The Tedlar® bag is attached to the GC/MS sampling probe using a short piece of Teflon tubing. On demand, the internal pump pulls the sample through the sample loop for a predetermined amount of time, usually 30 to 60 seconds. Internal standards are drawn into the instrument from the onboard internal standard cylinder at a ratio of 1:10 to the sample. After the sampling is complete, the valve is automatically switched to the inject position which sweeps the sample and internal standards onto the pre-column. After 100 seconds any heavier compounds, such as diesel, are back-flushed out of the system. To ensure that representative samples are analysed, the sample line and loop are completely flushed with sample for 30 to 60 seconds before sample injection onto the GC column. The GC column is a 30m long Supelco SPB 1 (100% methyl silicone phase, 0.32 mm i.d. coated with 1.0 mm film).
2. Air and other gas samples may also be drawn directly from the source, through the sampling probe and into the HAPSITE without using a Tedlar® bag as a collection device. This is a major advantage of the HAPSITE in that direct sampling will better preserve the integrity of the sample and allow for faster turn around time.

2.5.2 Integration with the MIP Gas Stream

An attempt was made to split the gas flow to couple the MIP GC with the GC-MS. However, the optimum gas flow for MIP detection is a return flow around 40 ml/min and the GC-MS required a sample delivery of 100ml/min. Increasing the return flow to meet the GC-MS requirement desensitised the MIP to an unworkable level. Reduction of the GC-MS in-flow was not attempted so as to protect the intake pump from damage. Gas stream samples were collected by removing the gas return line from the MIP GC and attaching to a Tedlar® bag at horizons of interest. Gas was diverted for approximately 6 minutes at the 40 ml/m rate to collect enough sample to run a GC-MS analysis and a duplicate if required. Tedlar® bags were marked with location, MIP file number and depth.

This system also had the additional benefit of allowing the MIP push to continue whilst the analysis was underway.



Figure 4 MIP detectors integrated with GC-MS

2.5.3 Headspace Sampling System

In conjunction with a headspace equilibrium sampling accessory the instrument has the capability to analyse water and soil samples. Headspace analysis involves heating water or a mixture of VOC contaminated soil and water to a known temperature in a sealed sample container. The heat forces the volatile compounds to partition between the liquid and the headspace in the sealed container. After allowing sufficient time for equilibrium (approximately 20 minutes), the headspace containing VOCs from the sample is introduced to the HAPSITE as a gas sample through a heated sample line.



Figure 5 HAPSITE Field-Portable Headspace Sampling System

The oven accommodates four standard 40-ml vials. A sampling needle can be easily inserted into the vial for withdrawal of the headspace for the analysis.

Samples were analysed using a calibrated method based on the EPA 8260B method used in fixed laboratories. Calibration details are presented in Appendix 1.

2.6 SONIC BORING RIG SITE INVESTIGATION

2.6.1 Sonic drilling

'Sonic' drilling uses high frequency vibrations (0 - 150 Hertz) generated in the drillhead by two out of balance rollers that cause the drill pipe to vibrate. The rollers are synchronised to ensure that the vibrations are transmitted vertically down the drill string to the bit. Aided by these vibrations, even a small machine can exert many times its own weight to the cutting edge of the bit. When the drillhead is in sonic mode, the soil particles that come into contact with the drilling tools are fluidised reducing friction and allowing rapid penetration without the need for a flushing medium. This fluidisation only occurs within a few millimetres of the drilling tools and therefore does not distort the samples in any way. Even in very soft estuarine deposits layered sections of sand and silt can be recovered undisturbed and logged by the site engineer. Core recovery is normally near 100% and as there is no flushing medium, the core is not contaminated by drilling activities.

Two fully cored boreholes were drilled as close to MIP2 and MIP3A as possible so that comparative soil samples could be collected from the same depths that the gas samples were collected. Samples were split for analysis on-site using the HAPSITE connected to the headspace analyser and for analysis at Scientifics laboratory, Derbyshire.

2.6.2 On-site soil analysis methodology

Ten grams of soil were weighed and placed into a 40-ml VOA screw cap vial. The soil is weighed on a wet basis. Twenty ml of deionised water was added to the VOA vial. The vial is then sealed with a PTFE coated septum and internal standards and surrogates are added to the sample. The sample vials are then placed in a heated chamber and maintained at 60°C for 20 minutes prior to headspace analysis. A calibrated Selective Ion Monitoring (SIM) method was used to analyse the headspace. This method only looks at selected masses and not the entire range thereby increasing sensitivity and providing quantitative and qualitative data.

2.6.3 Off-site soil analysis methodology

Samples were supplied to the laboratory in 22ml crimp top vials spiked with internal standards and recovery standards. Ten millilitres of deionised water was added to one gram of soil and one gram of sodium chloride. The spiked sample vials are heated with shaking for 15 minutes at 70°C in a headspace autosampler. A portion of the equilibrated headspace formed above the sample is then injected into a gas chromatograph equipped with a capillary column and mass spectrometer to identify and quantify VOCs.

3 Field investigation data

Three locations were drilled at the SABRE Research Site at positions reflecting the hydraulic gradient (Figure 6). The following table lists for reference the file numbers used at each location.

Table 3 MIP Identifiers and file numbers

Location	MIP File No.	GC File No
MIP1	SAB01	SAB01
Gas splitting trial		SAB02
		SAB03
MIP2 (source zone)	SAB02	SAB04
MIP2B	SAB03	SAB05
	SAB04	
	SAB05	SAB06
MIP3A (down-gradient)	SAB06	SAB07
	SAB07	SAB08

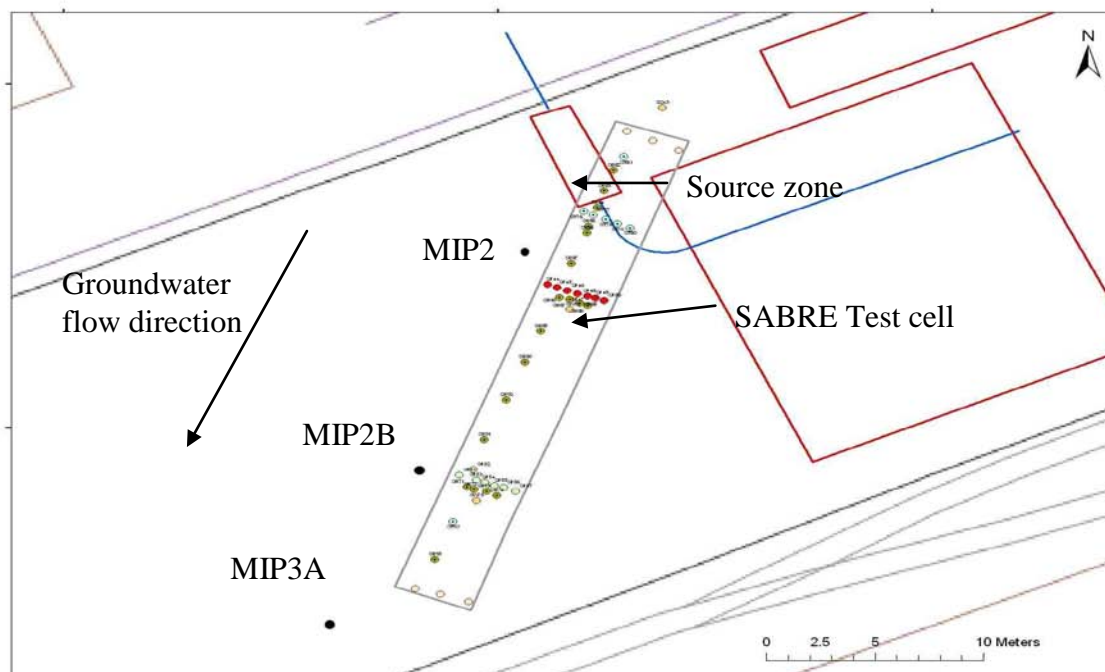


Figure 6 Location of MIP and cored boreholes at the SABRE test cell

3.1.1 Soil Conductivity

The downhole sequence indicated by the soil conductivity values was, high value (made ground) to approximately 3.0 m bgl, low value horizon (sand and gravel) and a high value horizon (clay/weathered mudstone). MIP borehole refusal occurred at 7.5 m bgl at location MIP1, at 7.6 m bgl at location MIP2 and at 8.8 m bgl in location MIP3. Soil Conductivity is presented on MIP logs in Appendix 2.

3.1.2 Probe Temperature

The probe temperature varied with penetration rate and hydraulic conductivity of the geology encountered. The low conductivity horizon was found to wick the temperature significantly

during driving and temperature recovery was slow between drives. The sensitivity and the detector response to contaminants was observed to increase with increasing temperature however, while the probe was stationary collecting samples and once optimum temperature was achieved, the detector response declined as the contaminant was baked out of the limited area in contact with the membrane.

3.1.3 Membrane Interface Probe Detector Responses

Responses were recorded on all detectors in each drive. Non chlorinated response was recorded in the made ground mainly on the FID between 0.7 and 2.0 m bgl. Responses increased significantly on PID and DELCD below 4 m bgl with the highest responses on all detectors occurring near the base of the drives between 6.5 to 7.5 m bgl.

The MIP detector responses are presented on the MIP logs in Appendix 2.

3.1.4 Gas Stream Sample Collection

Samples were collected for GC-MS analysis in MIP holes MIP2 and MIP2B when the MIP detectors showed a positive response. The MIP probe was held at depth and the sample line detached from the MIP GC and connected to the Tedlar® bag for five to six minutes. For MIP push 3A, samples were collected every 60cm throughout the hole depth.

Table 4 shows the MIP sample depths and soil sample depths taken in the cored boreholes..

Table 4 MIP and core sample horizons

Location	Soil File No	Depth (m)	Soil sample
MIP2	SAB02	1.95	
		4.40	x
		5.10	x
		5.98	x
		6.78	x
MIP2B	SAB05	1.53	
		3.00	
		4.20	
		5.37	
		6.59	
		7.16	
MIP3A	SAB07	1.21	X
		1.82	X
		2.43	X
		3.04	X
		3.65	X
		4.26	X
		4.87	X
		5.48	X
		6.09	X
		6.70	One sample
		7.31	
		7.92	
8.53			



Figure 7 Contaminated core material at 5.5 m bgl in MIP3A (SAB07)



Figure 8 River Terrace Gravels in MIP3A (SAB07)

4 RESULTS

4.1 MIP GAS STREAM RESULTS

Gas samples were collected and analysed from three MIP pushes; MIP2, MIP2A and MIP3A. MIP2 and MIP2A samples were collected when the detectors registered an increased voltage. MIP3A was sampled every 60cm (length of each MIP push). MIP data logs are given in Appendix 2, and GC-MS data plots in Appendix 3.

Trichloroethylene (TCE) and cis 1,2-dichloroethene (cDCE) were the only compounds identified in the gas samples, Vinyl chloride (VC) was not detected in gas samples. Figure 9 gives an example of the MIP detector output compared with GC-MS analysis.

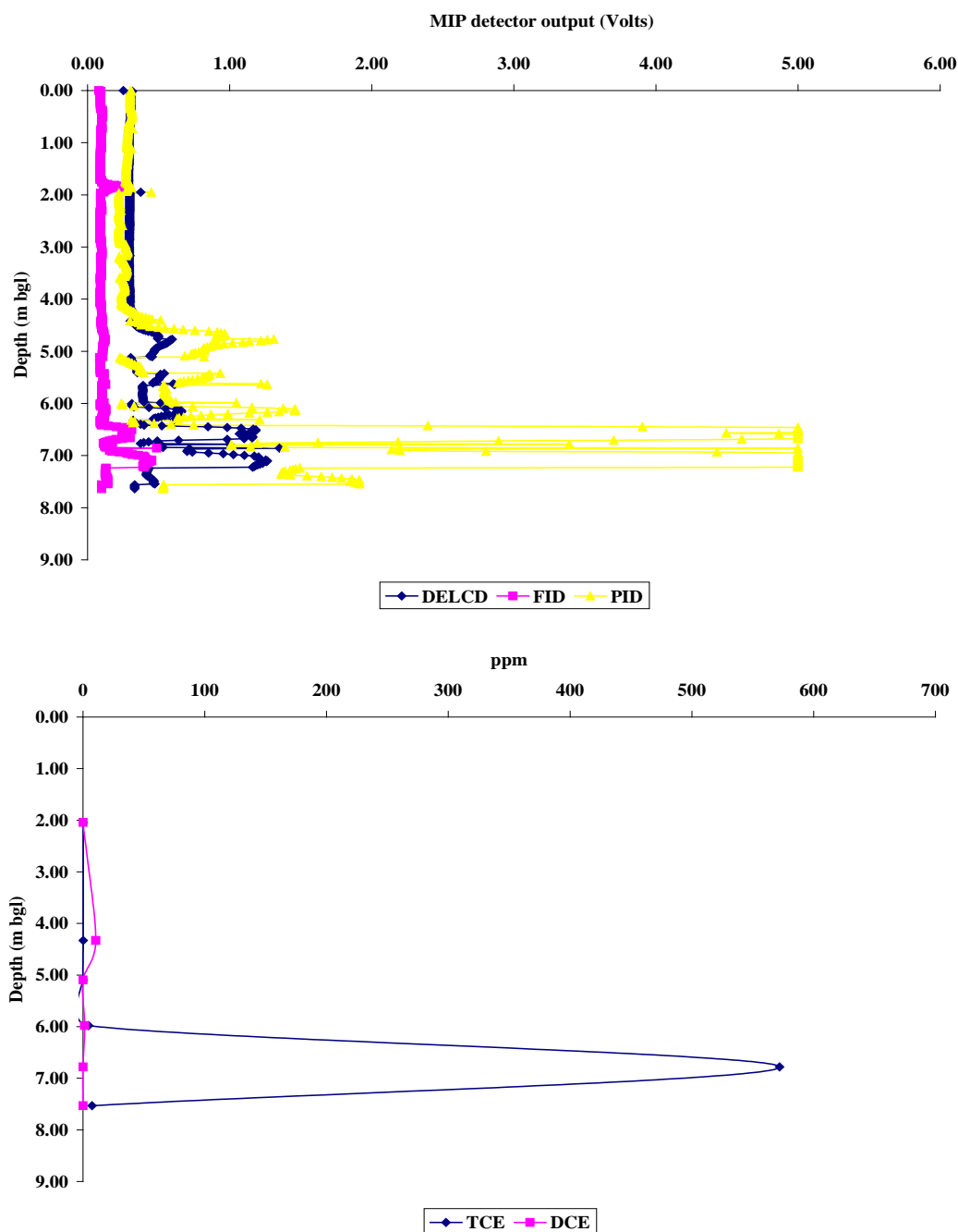


Figure 9 MIP detector output (volts) for MIP2 compared to GC-MS analysis

The MIP DECLD detector is most sensitive to chlorinated compounds e.g. TCE and its breakdown products; however the PID detector gave the biggest responses at this site. The PID and DECLD have clear peaks at 2.0, 4.3-5.0, 6.0 and 6.9 m bgl. The maximum achievable detector limits indicated by Geoprobe are 0.25 ppm chlorinated VOC's (by DECLD) and 5ppm chlorinate compounds (by PID). Corresponding GC-MS analysis identifies these peaks as TCE and cDCE at concentrations ranging from 0.11 ppm to 572 ppm suggesting that greater sensitivity than quoted is achievable. The high concentration of TCE (Figure 9.) masks the detection of cDCE at shallower depths (~4.5 and 6 m bgl) in the plume (Figure 10). It is also apparent that the PID response of ~1V is equivalent to approximately 10 ppm cDCE.

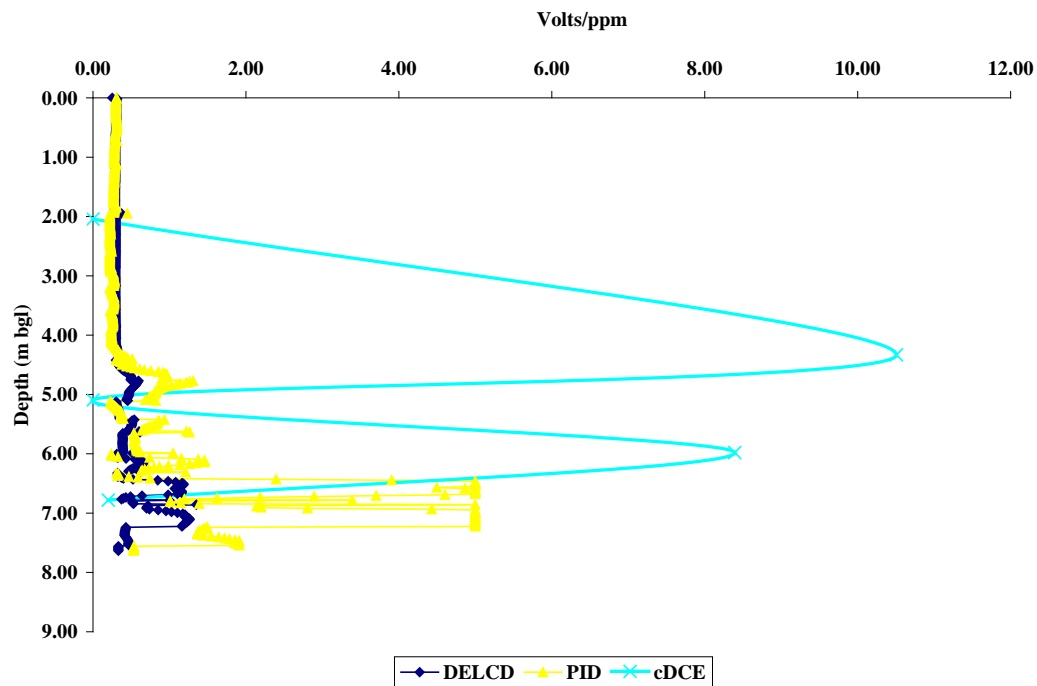


Figure 10 cDCE concentrations corresponding to PID peaks at 4.5 and 6 m bgl in MIP2

The MIP system is considered by its manufacturers as semi-quantitative because the sphere of influence of the heated membrane and thus sample mass and volume in contact with the membrane is not known. However, the magnitude of response is indicative of concentration within the same contaminant plume although the detectors do not identify or quantify the compounds in the gas stream. By using the GC-MS as the detector, quantifiable results can be attributed to MIP peak areas. In this way it may be possible to calibrate the MIP to site conditions by plotting TCE concentration against voltage. Figure 11 shows combined data from each of the MIP pushes for TCE concentration against PID voltages. The slope of the curve is used to calculate TCE concentrations from PID voltages.

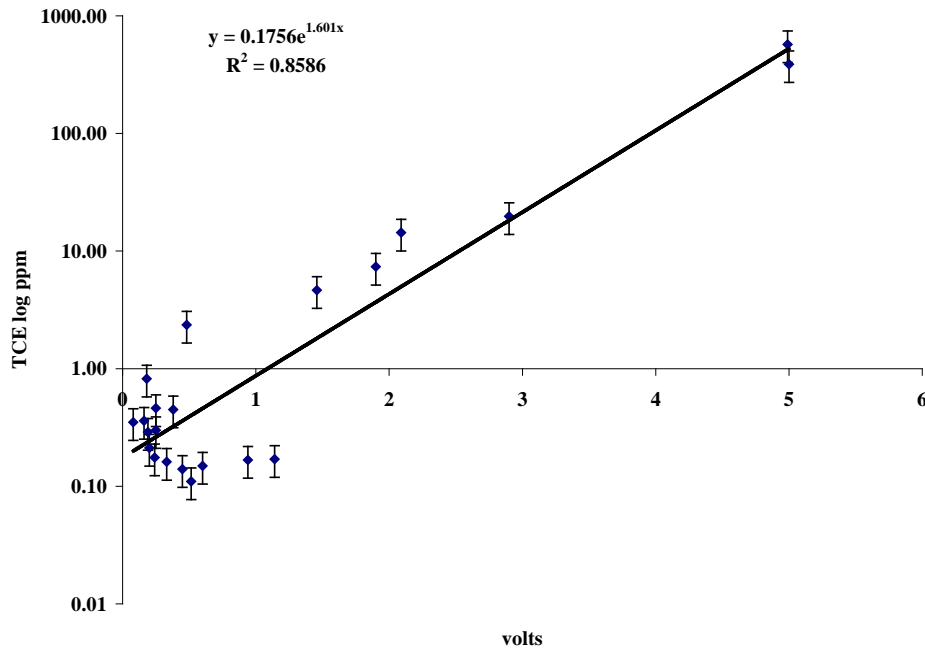


Figure 11 Calibration curve using TCE and PID detector

Measured and calculated results for each MIP push are tabulated below:

Table 5 MIP2 measured and calculated results

Depth (m bgl)	cDCE ppm	TCE ppm	Calculated TCE	Difference
2.04	0.00	0.14	0.36	0.22
4.33	10.51	0.11	0.40	0.29
5.09	0.07	0.17	1.09	0.92
5.98	8.39	4.65	1.81	-2.84
6.78	0.00	572	518	-9.28
7.53	0.00	7.35	3.68	-3.67

Table 6 MIP2B measured and calculated results

Depth (m bgl)	cDCE ppm	TCE ppm	Calculated TCE	Difference
1.73	0.00	0.21	0.24	0.03
3.00	0.00	0.18	0.26	0.08
4.19	0.00	0.17	0.79	0.62
6.01	1.84	0.16	0.30	0.14
6.59	2.20	0.15	0.46	0.31
7.16	2.23	388	526	139

Table 7 MIP3A measured and calculated results

Depth (m bgl)	cDCE ppm	TCE ppm	Calculated TCE	Difference
1.22	0.00	0.82	0.23	-0.59
1.83	0.00	0.36	0.23	-0.13
2.44	0.00	0.35	0.20	-0.15
3.06	0.00	0.30	0.26	-0.04
3.66	0.00	0.29	0.24	-0.05
4.29	5.46	0.46	0.26	-0.20
4.87	7.45	0.45	0.32	-0.13
5.48	5.04	2.36	0.38	-1.98
6.10	13.68	14.33	4.99	-9.34
7.32	9.11	19.76	18.24	-1.52

Overall, bearing in mind the semi-quantitative nature of the sampling method, data calculated using the calibration curve compare relatively favourably with the measured concentrations particularly at between 1 and 5 volts response from the MIP detectors (Figure 12).

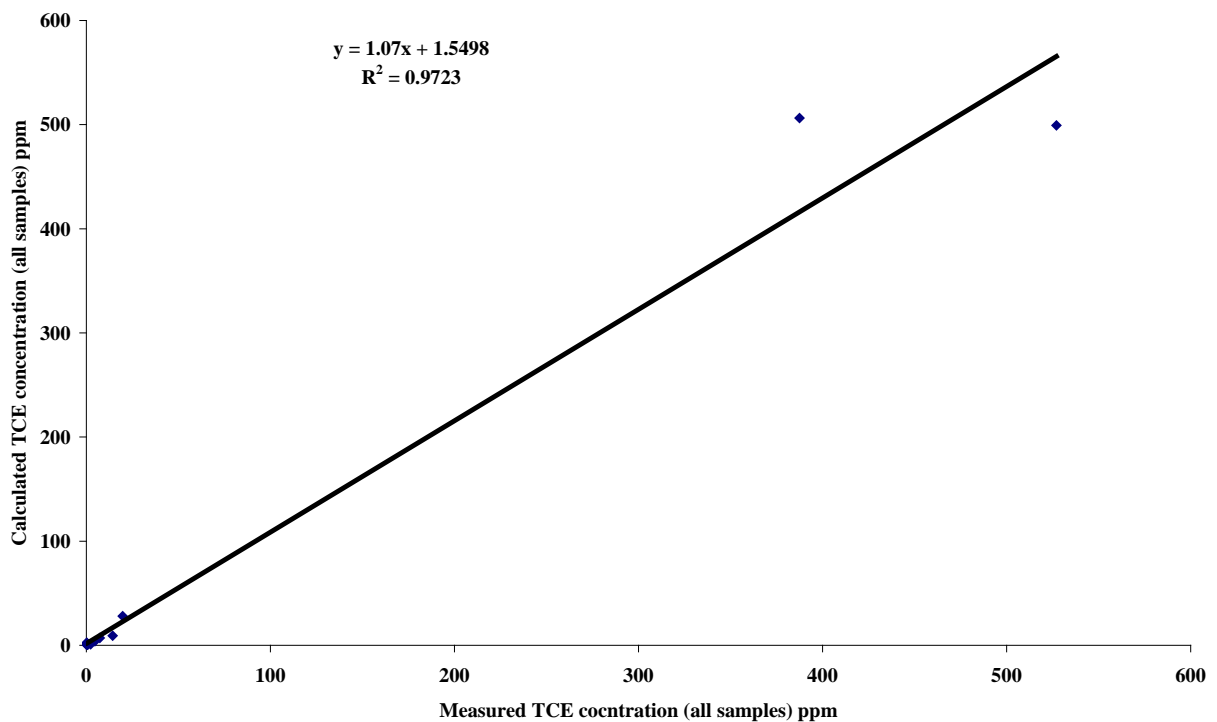


Figure 12 Results calculated for TCE using site determined calibration curve against measured concentrations.

4.2 SAMPLING FREQUENCY

Clearly, greater sample density provides a better understanding of the subsurface conditions; however one of the benefits of MIP technology is the speed at which a site can be characterised. Integrating a GC-MS detection system with the MIP increases the run time of each hole by at least five minutes per sample whilst sufficient sample is collected into Tedlar® bags ready for analysis. Turnaround time for analysis by GC-MS is 20 minutes, however samples may be stored to prevent further delay to the MIP push. For MIP3A samples were collected every 60cm (every 2 horizons) regardless of the MIP detector responses

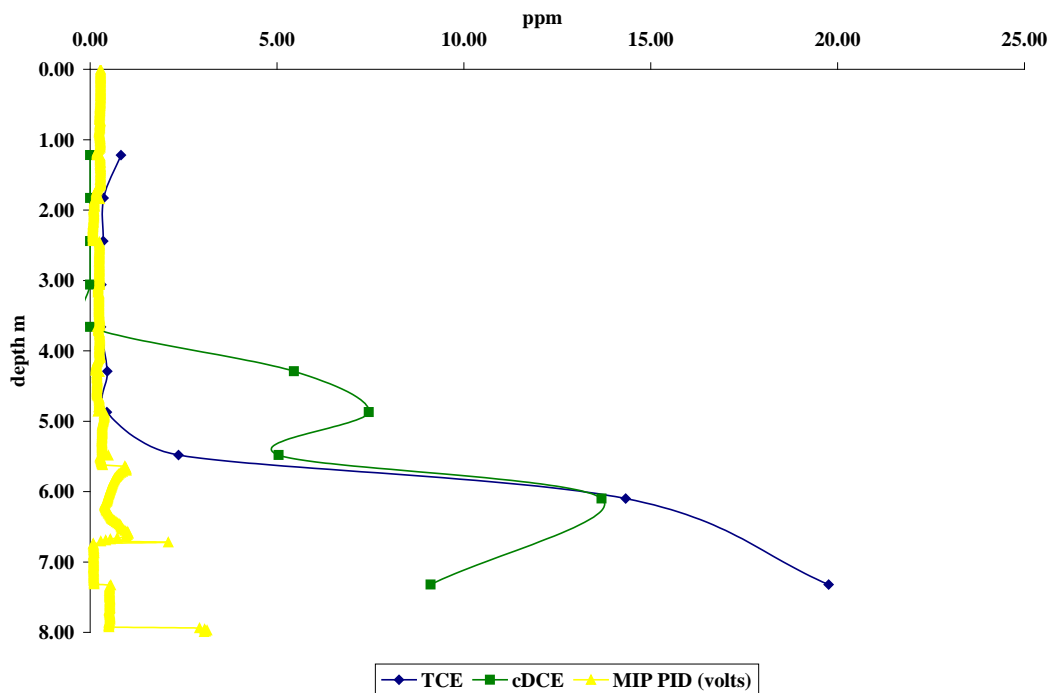


Figure 13 MIP3A – TCE, cDCE and PID data (high sampling frequency)

The MIP detectors do not seem to be particularly sensitive to cDCE (Figure 13) and a sampling regime based on MIP voltages would have missed the peak of cDCE at between 4-5 m bgl.

4.3 SOIL ANALYSIS RESULTS

Two boreholes were drilled as close to MIP pushes MIP2 and MIP3A as possible. Samples were collected from core at depths corresponding to the gas analysis as a direct comparison (Table 4). Samples were accurately weighed and split upon collection for on-site analysis by the HAPSITE GC-MS and off-site analysis by Scientifics laboratories. Results are tabulated below:

Table 8 MIP2 (SAB02) on-site and off-site soil data comparison

Depth (m bgl)	VC-BGS	VC-Scientific	cDCE - BGS	cDCE Scientific	TCE - BGS	TCE - Scientific	PCE - BGS	PCE - Scientific
	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g
2.04	2.62	1.50	9.18	3.60	0.16	0.00	0.00	0.00
4.39	55.10	5.10	475	90.0	19.6	4.60	0.64	0.00
5.09	2.01	0.00	794	486	143.	104.	3.32	2.60
5.97	0.50	0.00	5.44	0.00	227.	69.0	0.50	0.00
6.78	0.00	0.00	0.76	0.00	34.1	35.0	0.10	0.00

Table 9 MIP 3A (SAB07) on-site and off-site soil data comparison

Depth (m bgl)	VC-BGS	VC-Scientific	cDCE - BGS	cDCE Scientific	TCE - BGS	TCE - Scientific	PCE - BGS	PCE - Scientific
	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g
1.22	0.00	0.00	1.28	0.00	0.71	2.20	0.00	0.00
1.83	0.00	0.00	0.82	0.00	0.17	0.00	0.00	0.00
2.4	0.00	0.00	0.00	0.00	0.06	0.00	0.00	0.00
3.06	2.93	0.00	0.98	0.00	0.37	0.00	0.00	0.00
3.66	13.9	2.60	1.72	4.80	0.04	0.00	0.00	0.00
4.55	0.00	6.90	2.12	57.0	0.00	3.60	0.00	0.00
4.90	27.6	5.10	280	67.0	27.3	16.0	0.12	0.00
5.50	70.7	52.0	990	757	0.99	1.80	0.21	0.00
7.50	10.9	4.90	435	195	50.7	39.0	0.06	0.00

On-site soil data compare favourably with off-site. In almost all cases on-site data have higher concentrations than off-site data which may be explained by volatile loss during transportation and time before analysis in the off-site laboratory. Comparison plots of VC, DCE and TCE concentrations in MIP2 and MIP3A are presented in Appendix 4.

4.4 SOIL DATA COMPARISON WITH MIP PROFILES

Soil data identifies the main contaminant in MIP3A as cDCE rather than TCE seen in the on-site gas samples. Figures 14 and 15 show a scaled MIP voltage response plotted against cDCE and TCE soil data from both on-site and off-site laboratories. The soil data correlate with the PID peaks and show an increase in cDCE that corresponds with a decrease in TCE concentrations at around 5.5 m bgl that is also seen in the gas analysis.

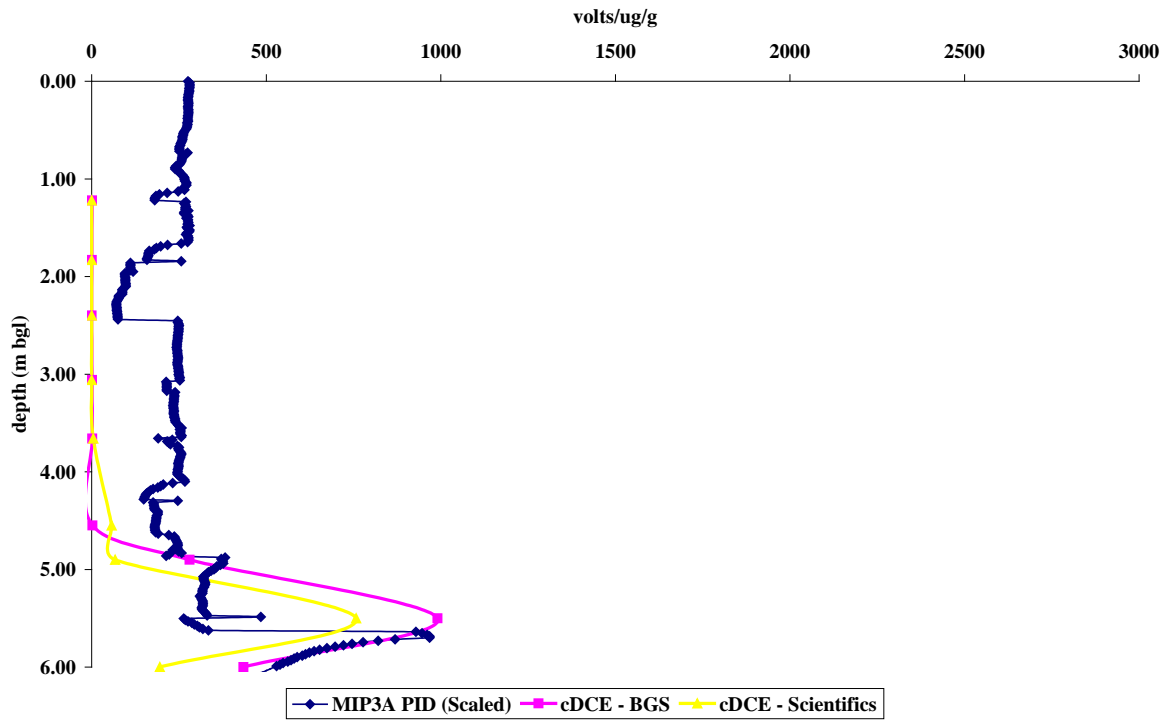


Figure 14 MIP-PID response compared with soil data for DCE in MIP3A

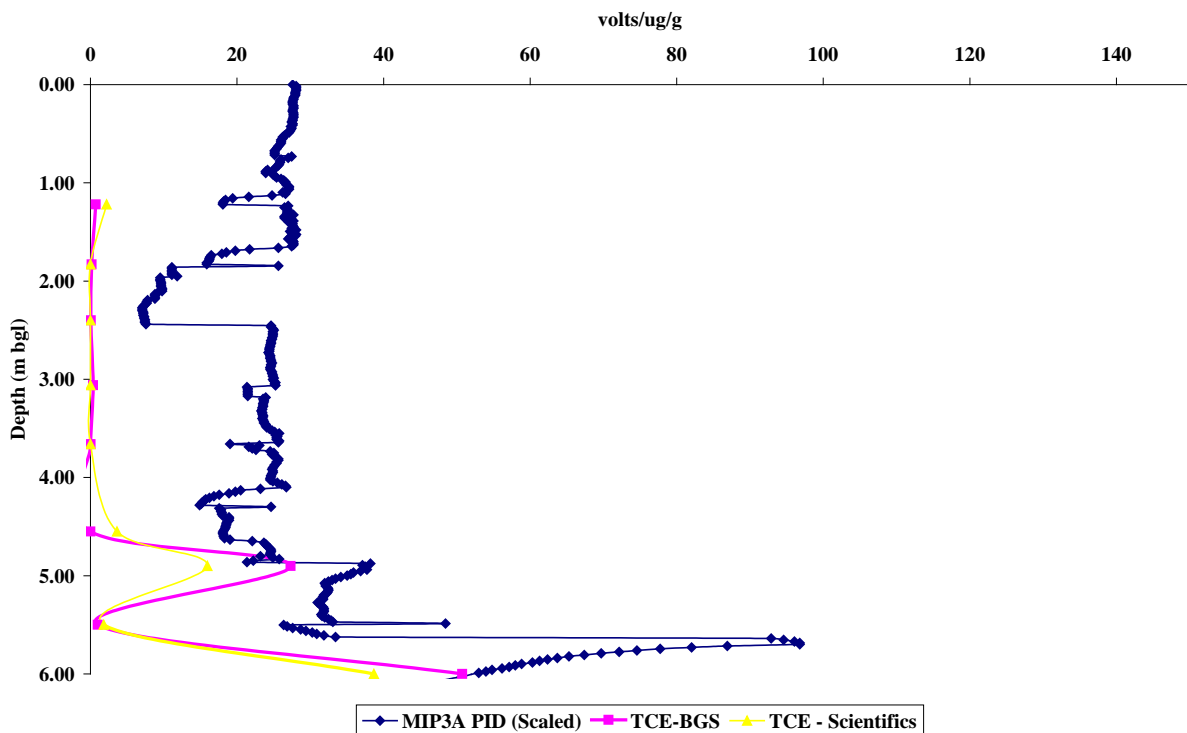


Figure 15 MIP-PID response compared with soil data for TCE in MIP3A

4.5 SOIL DATA COMPARISON WITH GAS PROFILES

On-site soil data has been used for the comparison with the on-site gas data. In the MIP2 borehole the soil cDCE profile matches that of the gas profile very closely although the gas concentrations are lower (486 ppm against 794 ppm). However, the TCE profiles do not compare as well, soil concentrations are significantly lower and the gas peak is seen at a lower depth (Figures 16 and 17). Vinyl chloride was not detected in the gas samples.

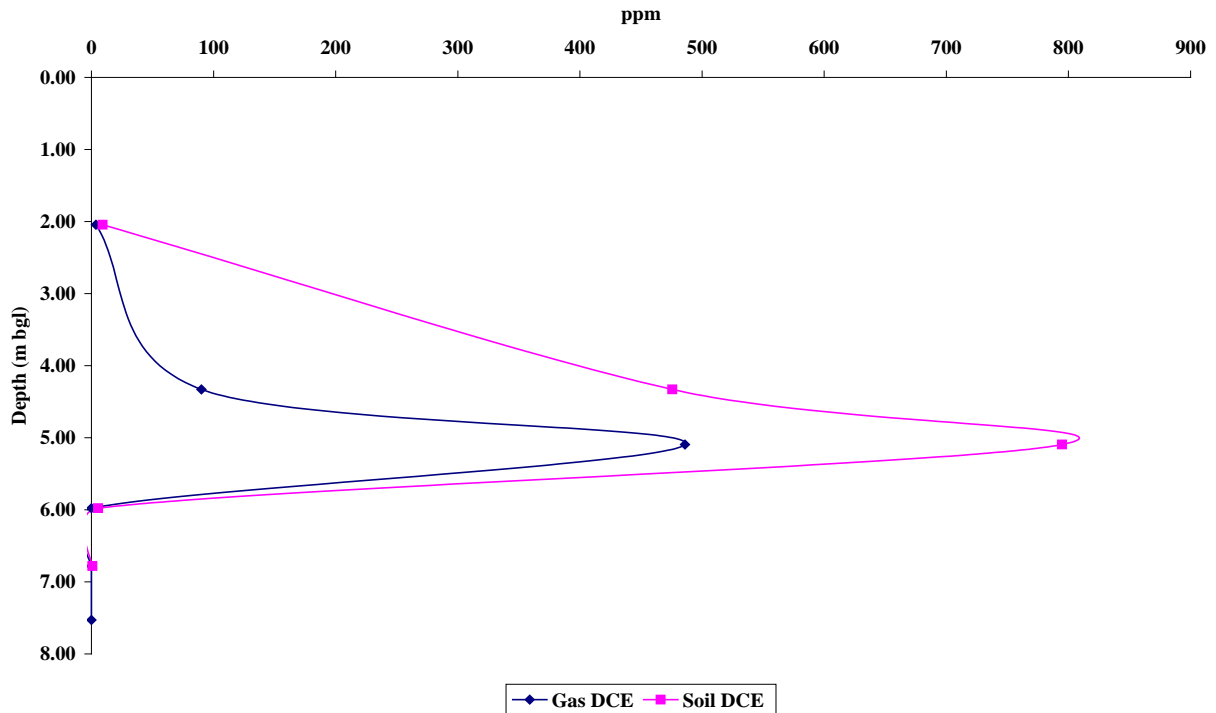


Figure 16 MIP2 Gas and soil cDCE comparison

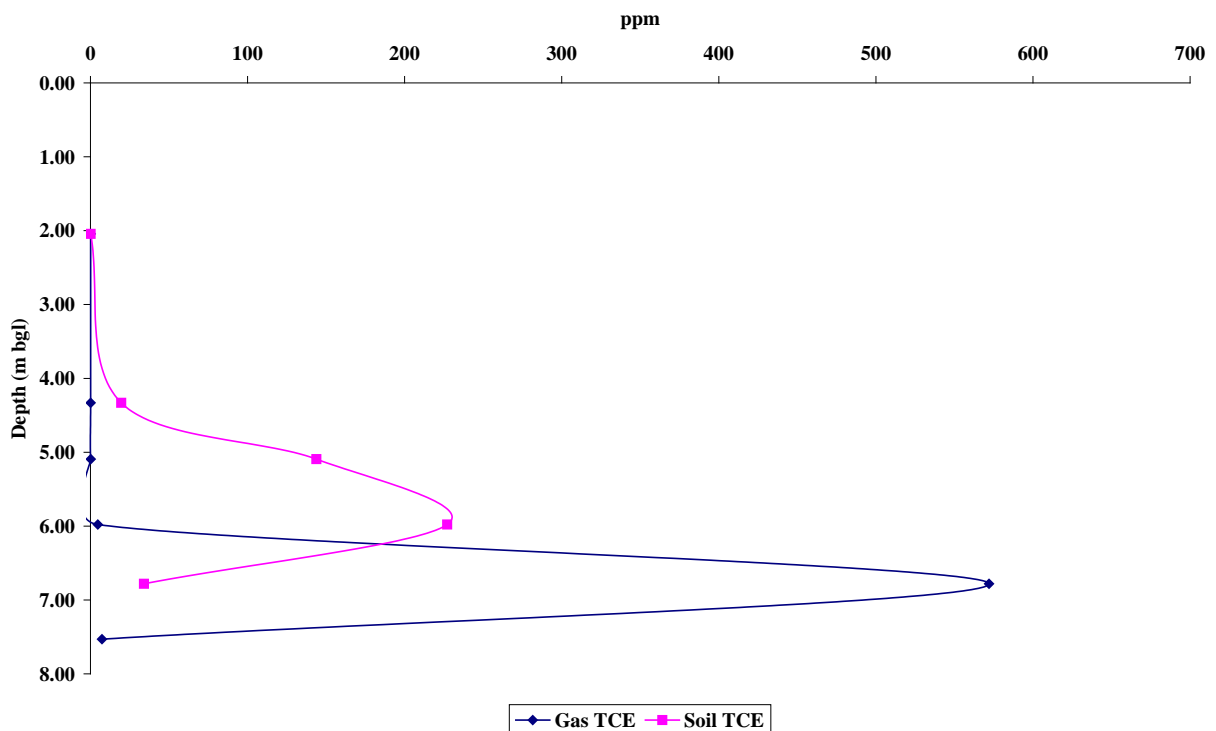


Figure 17 MIP2 Gas and soil TCE comparison

Soil and gas data do not correlate well in borehole MIP3A. cDCE, is on average one order of magnitude lower in the gas sample than the soil samples (Figure 18). TCE profiles have a better match although a peak at 5 m bgl in the soil data was not detected in the gas profile (Figure 19).

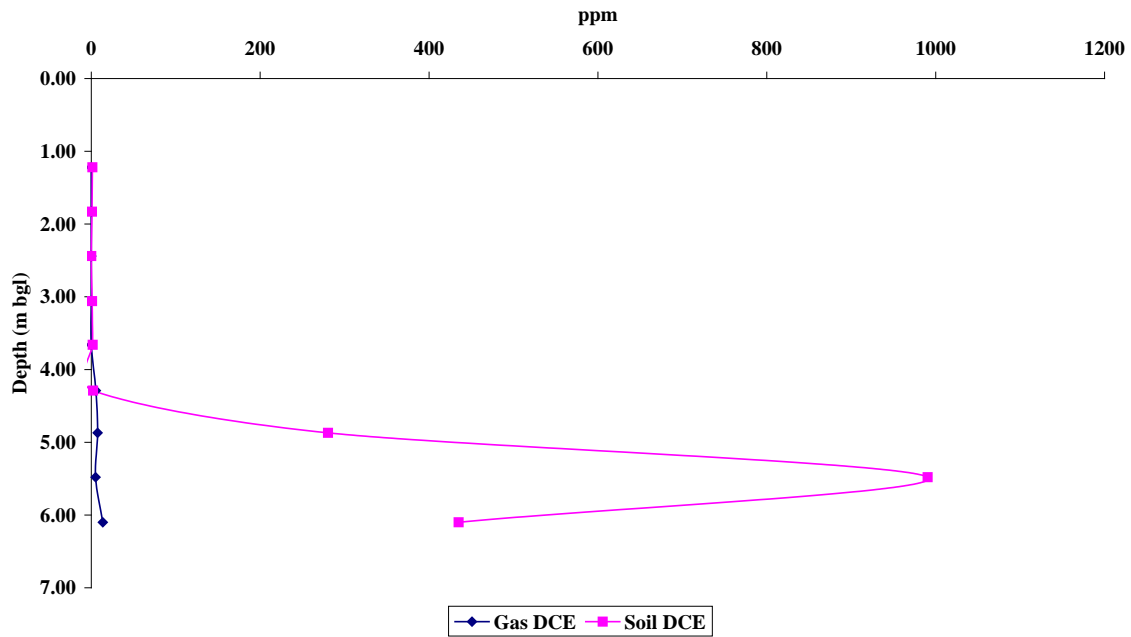


Figure 18 MIP3A Gas and soil cDCE comparison

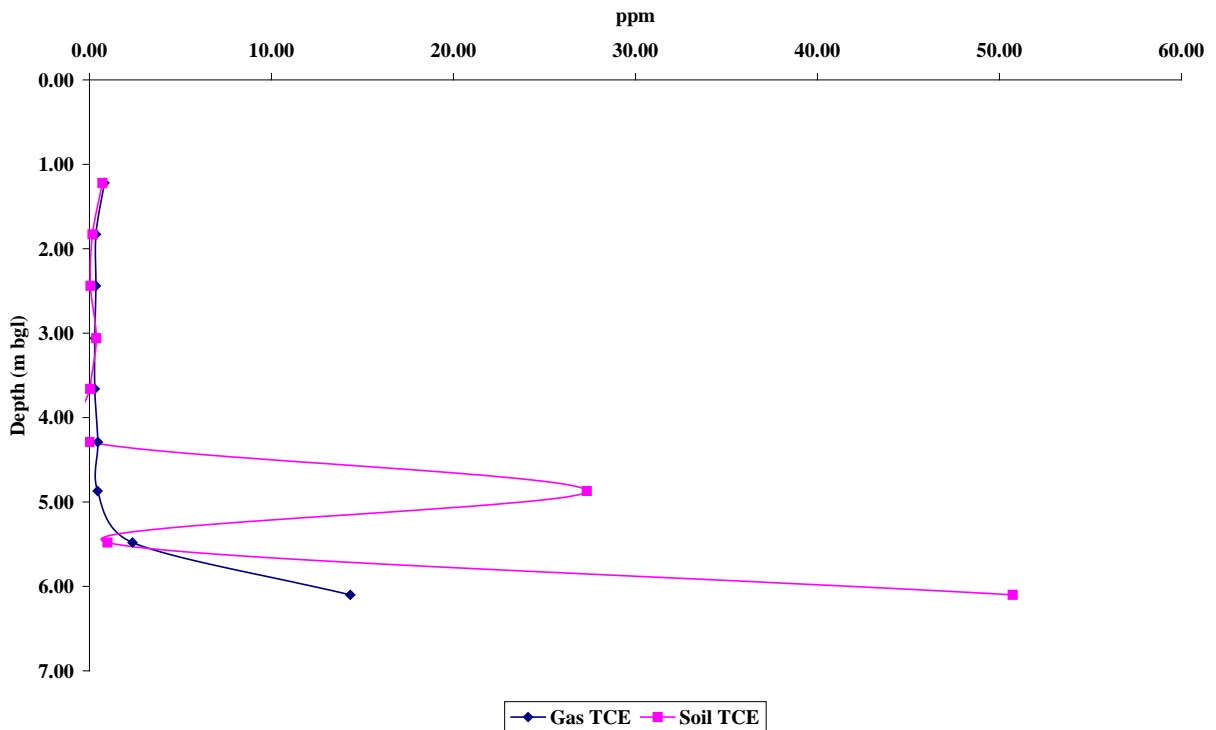


Figure 19 MIP3A Gas and soil TCE comparison

5 Discussion

5.1 MIP – GC-MS INTEGRATION

This study is based on three sampling locations at the research site. Splitting the gas stream between the MIP and the GC-MS while sampling produces problems with the MIP analysis due to possible interruption of the gas stream. This affects the sensitivity of the method and the MIP responses. This needs to be taken into account when interpreting MIP responses and comparing MIP logs.

The concentration recorded by the MIP varied with temperature and time during sampling events due to probe temperature stabilisation and sample extraction for the GC-MS. This difference in exposure time could account for the discrepancy between the semi-quantitative MIP peaks and the MS peaks.

MIP drilling as well as sonic core drilling of the three locations enabled the full use of the MIP data and allowed core sampling horizons to be predetermined for the soil GC-MS analysis. However, the benefit of fast site characterisation is lost as twice as many holes need to be drilled. Further data uncertainty is introduced due to the heterogeneity of the contaminants across the site. This might even be seen between the two boreholes at a location

Sampling and MIP data acquisition in one drive did not necessarily optimise the zones of sampling for the highest concentrations and the disrupted gas flow meant that partial data gaps were present in the MIP log at horizons of sampling due to temperature/time/response changes. Some MIP peaks were reduced as the gas flow was switched to collection in Tedlar® bags although the benefits of contaminant identification by GC-MS outweigh losses on the MIP detectors.

Sampling at regular intervals of 30 to 60 cm is the slowest option but provides the best compromise for both detection systems. Gaps in the MIP detector logs are filled by GC-MS data and vice versa. In the standard MIP operation the probe is held at depth whilst new rod lengths are attached, this time can be utilised to collect gas for GC-MS analysis after the gas flow has been through the MIP detectors. Additionally the operator has the option to collect gas samples at any time. This method also compensates for the lower sensitivity of the MIP detectors, as by relying on a response from the MIP, contaminants present in lower concentrations will be missed by conventional MIP methods.

It is apparent that the PID response is non-linear with regard to contaminant concentration however, this may be a function of membrane temperature, time of sampling and the geology and hydrogeology of the sample location. At higher voltages (>1v) the magnitude of response is indicative of greater contaminant concentrations. By plotting MIP - PID voltage response against log TCE concentrations and fitting an exponential curve it is possible to calculate concentrations for voltage responses without undertaking GC-MS analysis on every MIP push. Measured and calculated results generally compared favourably in all three locations for TCE, and, although the contribution from cDCE can't be differentiated, a site specific calibration is feasible. These data can only be considered semi-quantitative due to the nature of the probe and the uncertainties associated with it, however the qualitative nature of the GC-MS data, for instance, identifying cDCE when the MIP detectors gave no response is of great benefit.

5.2 ON-SITE SOIL ANALYSIS

On-site soil analysis compares well to the off-site data. On-site data was higher than the off-site for all compounds but particularly for vinyl chloride which is the most volatile of the compounds detected. Laboratory studies have shown up to 50% losses of volatiles within 24 hours and this is an example of the benefits of analysing samples in as short a time frame as possible.

Soil data identifies peaks of contaminants in relation to MIP detector peaks and again the magnitude of response is indicative of greater contaminant concentrations. Gas analysis however, failed to identify vinyl chloride in any of the boreholes and was generally one to two orders of magnitude lower than the corresponding soil data at the higher concentrations of all identified compounds.

5.3 PREVIOUS SITE DATA

A detailed comparison with data previously collected at the site is beyond the scope of this project however a number of trends were observed:

- TCE concentrations increase with depth with the highest values at the contact between the River Terrace deposits and the mudstone
- TCE concentrations decrease in the down-gradient boreholes (MIP2A and MIP3A)
- cDCE concentrations were detected in the River Terrace deposits in all the boreholes, with greater concentrations in the down-gradient boreholes.
- Vinyl chloride was not detected in the gas samples but was detected in the corresponding soil analysis with increasing concentrations in the down-gradient boreholes. This is probably lost due to the high volatility of VC coupled with the high temperature of the probe.

6 Conclusions / Recommendations

The HAPSITE portable GC-MS was successfully integrated with the MIP system and provided accurate identification of contaminants present at the site. Quantitative data for both gas and soil samples were available within one hour of sample collection for both sample types, although gas data proved to be semi-quantitative due to the unknown sample size inherent in the MIP system. On-site soil analysis proved to be comparable to off-site analysis and highlighted the potential for loss of volatiles during transport and storage at a fixed base laboratory.

The main issues associated with integrating the HAPSITE portable GC-MS with the MIP are:

- 1 Uncertainties associated with the probes sphere of influence – related to geological; and hydrogeological conditions – e.g. void space, degree of saturation etc
- 2 The effect of holding the probe at a sampling horizon during sample collection – at what point does the increasing temperature draw contaminants from greater distances ?
- 3 Gas flow rates from the MIP are too low to directly couple with the HAPSITE instrument
- 4 Direct coupling with a full GC-MS run would take at least 30 minutes per sample
- 5 Soil data from corresponding depths indicate significantly higher concentrations of VOCs than on-site gas data would suggest.

Direct coupling of the MIP GC and the GC-MS may be possible if the MIP flow rate is maintained at 40 ml/m and split at desired horizons, and although a 50/50 split would reduce sensitivity, a measurable detector response should still be achievable. The reduced 20 ml/m gas sample could be diverted to a holding vessel prior to loading in to the GC-MS. Multiple samples could then be collected without undue delay to investigation progress and a make up gas applied to allow a 100ml/m input to the GC-MS and the results back calculated for the contaminant dilution. Alternatively small sample traps may be employed for short duration flow diversion which would not unduly disrupt the MIP data, again a make up gas would be required to fill the current configuration on the GC-MS and a dilution factor applied. This method has been tried in the USA by Geoprobe and Vironex.

This study has shown that site specific calibration of the MIP response is possible although the effect of complex mixtures of contaminants is unknown.

The uncertainties associated with the MIP and the difficulty determining sample size at the membrane interface mean that data will always be semi-quantitative at best and therefore the reduction in MIP sensitivity and the time taken to analyse the samples outweighs the benefits of full GC-MS analysis on all boreholes.

An alternative would be to quickly screen for volatile compounds by running the HAPSITE in 'Survey' mode where sample is drawn directly into the mass spectrometer, bypassing the GC column. This method would provide tentative identification of compounds by using either target mass spectra (i.e. compounds of interest) or by searching the total mass spectra response against an in-built library (AMDIS). The instrument would provide a real time plot of response versus sampling time, the mass spectrum or a list of detected compounds. Although compound identification is hindered by complex mixtures and the issue of flow rate would still need to be resolved.

Appendix 1 GC-MS Calibration details

Appendix 2 MIP Logs

Appendix 3 On-site GC-MS gas data plots for MIP drives 2, 2A and 3A

Appendix 4 On-site v Off-site soil VOC comparison

Glossary

AMDIS – Automated Mass Spectral Deconvolution and Identification System Software

cDCE – cisDichloroethene

DELCD – Dry Electrolytic Conductivity Detector

FID – Flame Ionisation Detector

GC – Gas Chromatography

GC-MS Gas Chromatography-Mass Spectrometer

HAPSITE – Analytical module acronym that stands for Hazardous Air Pollutants on Sites

MIP – Membrane Interface Probe

MS – Mass Spectrometer

NIST – National Institute of Standards and Tecnology

PID – PhotoIonisation Detector

SABRE – Source Area BioREmediation

SIM – Selective Ion Monitoring

SRS – SABRE Research Site

SVOC Semi-volatile organic compound

TCE – Trichloroethylene

Tedlar® - propriety bags for gas sample collection

VC – Vinyl Chloride

VOC – Volatile Organic Compound

References

LELLIOTT MR, CHENEY CS AND WEALTHALL GP. 2004. SABRE Research Site: Data Review. *British Geological Survey Internal Report*, CR/04/244. 4000pp.

Hapsite GC-MS - Mass spectra and Calibration data

Interferences: The HAPSITE was calibrated using full-scan mass spectra. Some of the VOCs could not be calibrated (poor linearity or software could not recognise the compounds), this was attributed to co-elution interferences combined with shared ions. As a result, single ion monitoring (SIM) was used and selected ions used to avoid interferences (**Table 1**).

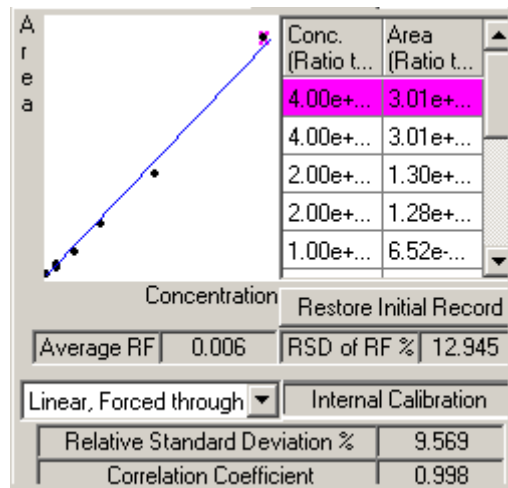
A 2 x 6 point calibration was used at: 0, 20, 50, 100, 200, and 400 µg/L whilst keeping the internal standard concentration at 50µg/L. This calibration gave excellent correlation coefficients (r^2) and linearity. It was considered not advisable to extend the range greater than 400 µg/L because this concentration resulted in memory effects and gave a peak height count of 12-14 M counts at m/z 91 (the mass spectrometer detector has an over-load trip out at 60M counts).

Retention time, ions, and internal standards used.

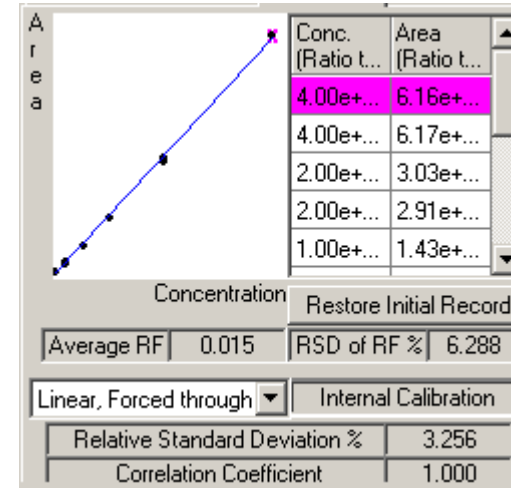
Set	Type	Name	BGS Abbreviation	CAS No.	Mol. Wt.	1° m/z	2° m/z	Anal. m/z	Ret. time (mins.)	Int. Std. Used
1	analyte	chloroethene	VC	75-01-4	62	62		62	1.39	PFB
	analyte	ethyl chloride	EC	75-00-3	64	64	66	64	1.50	PFB
	analyte	1,1-dichloroethene	1,1-DCE	75-35-4	96	61	96	61	1.75	PFB
	analyte	E-1,2-dichloroethene	trans-DCE	156-60-5	96	61	96,98	61	1.96	PFB
	analyte	1,1-dichloroethane	1,1-DCEa	75-34-3	98	63	65,83,98	98	2.00	PFB
	analyte	tert-butylmethylether	MTBE	1634-04-4	88	73	57,41,29,43	73	1.89	PFB
	analyte	Z-1,2-dichloroethene	cis-DCE	156-59-2	96	61	96,98	61	2.29	PFB
	int.std.	pentafluorobenzene	PFB	363-72-4	168	168	99	168	2.35	-
	analyte	1,2-dichloroethane	1,2-DCEa	107-06-2	98	62	64	62	2.53	PFB
	analyte	1,1,1-trichloroethane	1,1,1-TCEa	71-55-6	132	97	99,61	97	2.62	PFB
	analyte	benzene	B	71-43-2	78	78	67,82	78	2.74	tol d8
	int.std.	1,4-difluorobenzene	DFB	540-36-3	114	114	63	63	2.83	-
analyte	trichloroethylene	TCE	79-01-6	131	95	130,132,134	130	3.33	CB d5	
2	analyte	1,1,2-trichloroethane	1,1,2-TCEa	79-00-5	132	97	83,99	97	4.52	CB d5
	int.std.	toluene d8	tol d8	2037-26-5	100	98	100	98	4.60	-
	analyte	toluene	tol	108-88-3	92	91	92	91	4.75	tol d8
	analyte	1,2-dibromoethane	1,2-DBEa	106-93-4	186	107	109	107	5.61	tol d8
	analyte	tetrachloroethylene	Tet.CE	127-18-4	164	166	94,164,131	166	6.32	tol d8
	int.std.	chlorobenzene-d5	CB d5	3114-55-4	118	117	82,52,117	82	7.39	-
	analyte	1,1,1,2-tetrachloroethane	1,1,1,2-TCEa	630-20-6	166	131	133,117,119,95	95	7.51	CB d5
	analyte	ethylbenzene	EB	100-41-4	106	91	106	91	8.13	tol d8
	analyte	p-xylene & m-xylene	m/p-xyl	106-42-3	106	91	106	91	8.37	tol d8
	analyte	o-xylene	o-xyl	95-47-6	106	91	106	91	8.80	tol d8
	analyte	1,1,2,2-tetrachloroethane	1,1,2,2-TCEa	79-34-5	166	83	85,95	83	8.99	CB d5
	int.std.	1-bromo-4-fluorobenzene	BFB	460-00-4	175	174	95,176	176	9.49	-

Calibrations for the haloethene VOCs

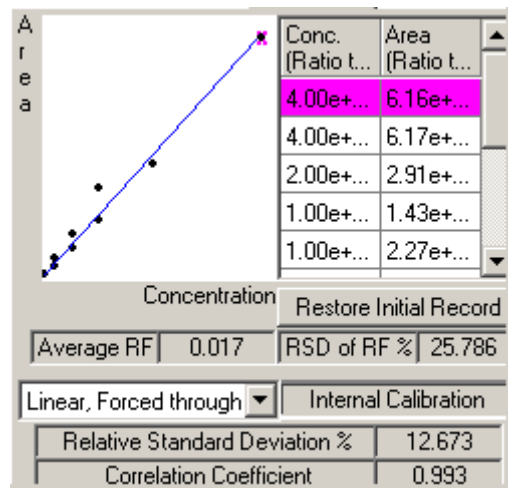
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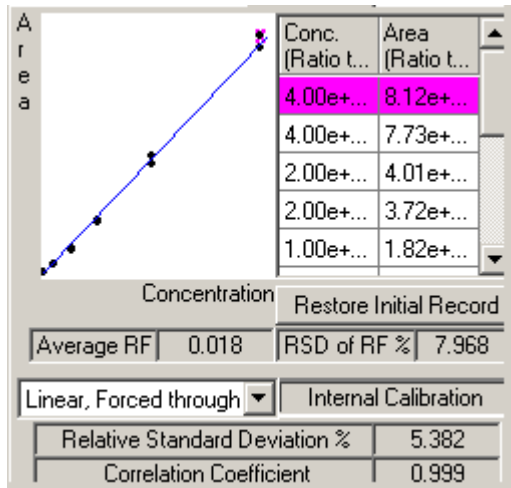
1,1-DCE



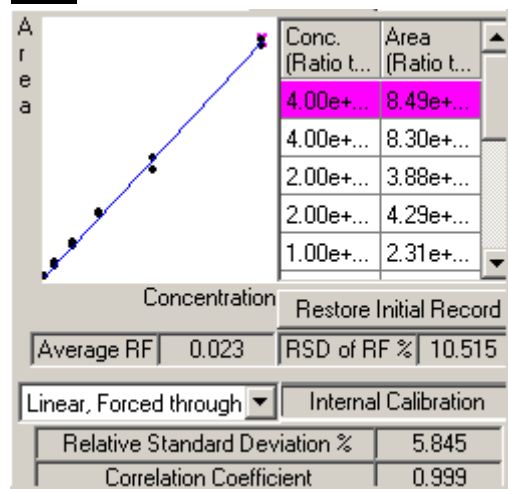
trans-DCE



cis-DCE



TCE

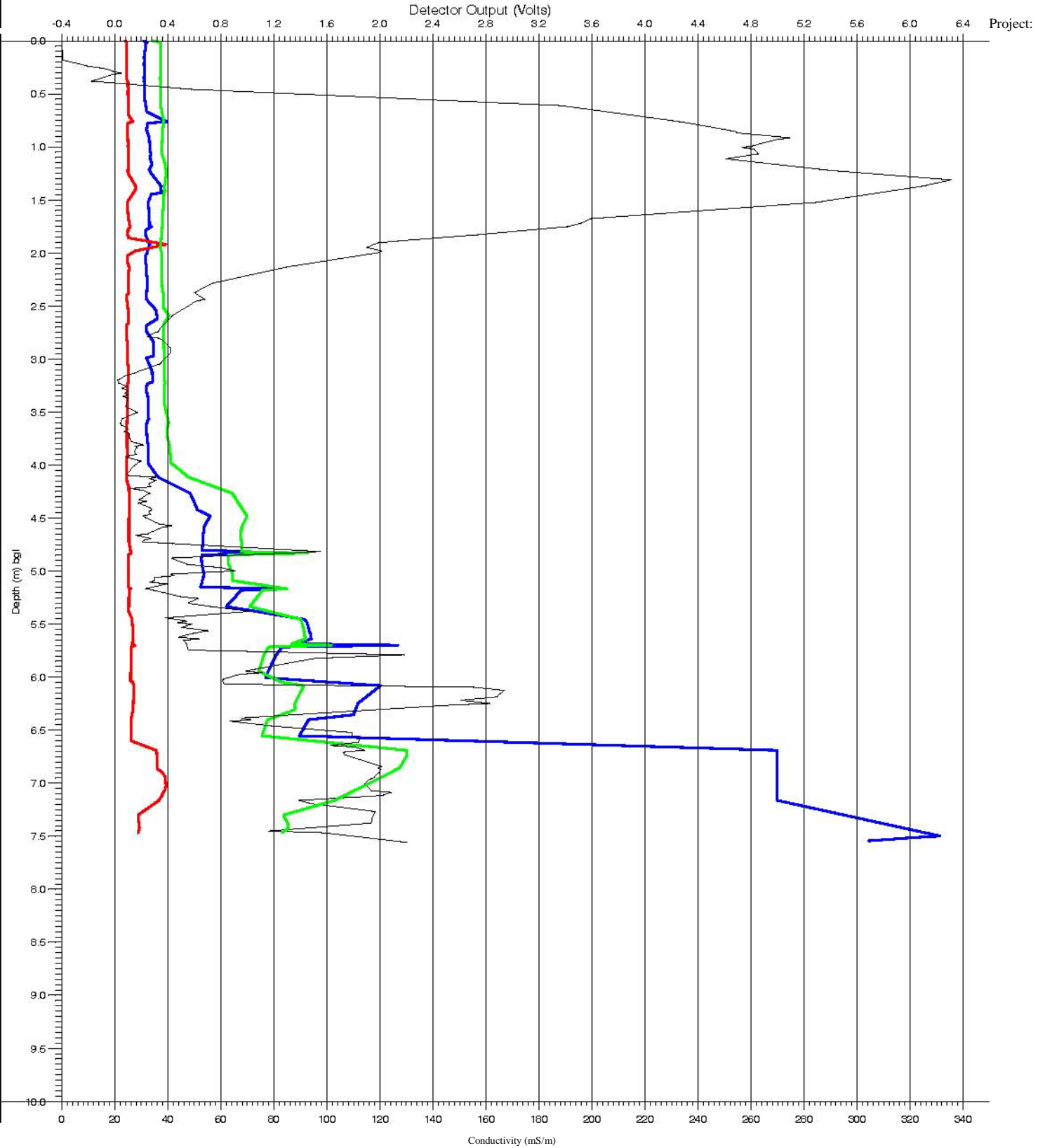




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Project No: 9275700	Date: -	Method: Geoprobe		Checked By:

MIP DATA

Sheet 1 of 1

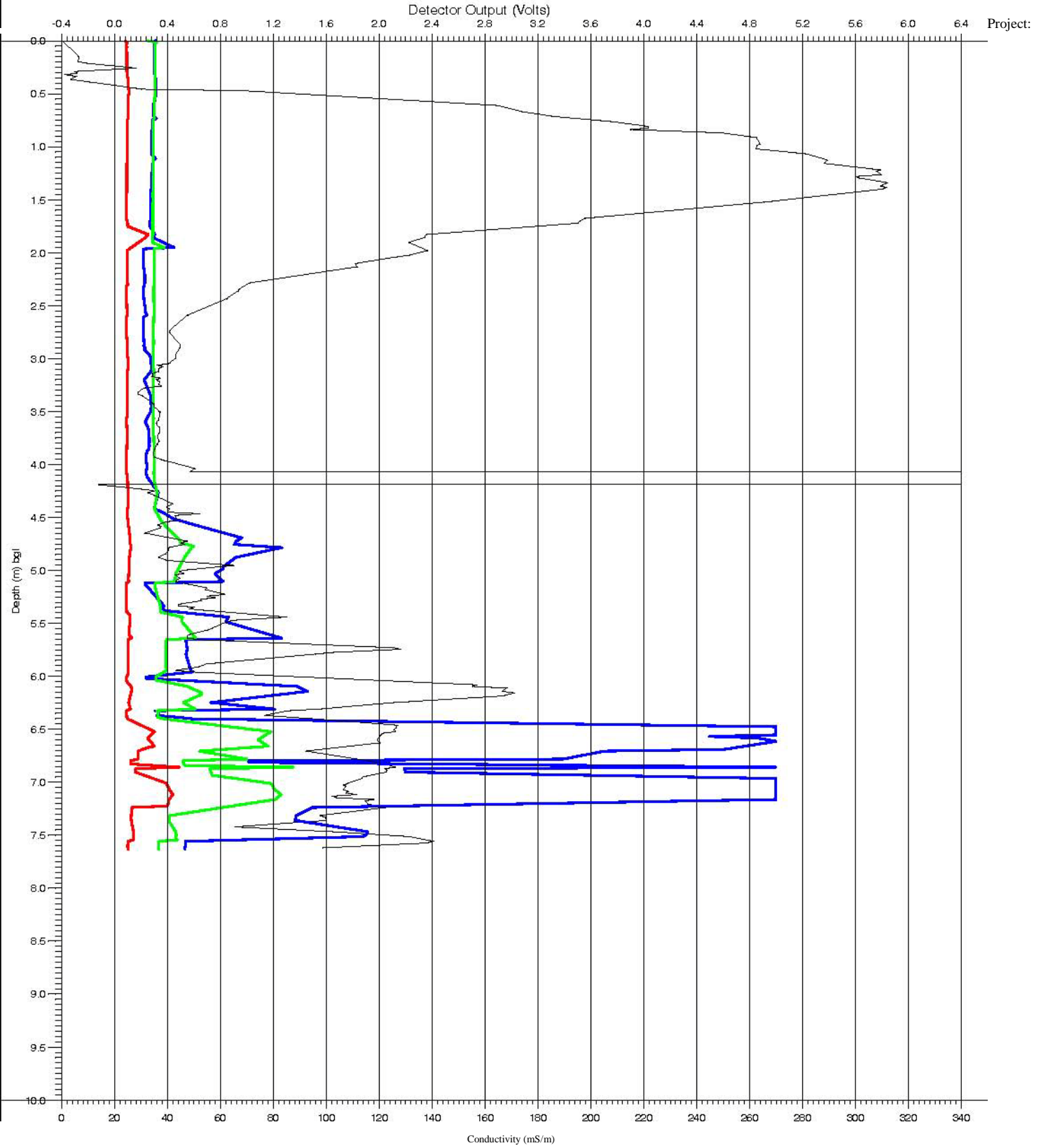




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Project No: 9275700	Date: -	Method: Geoprobe		Checked By:

MIP DATA

Sheet 1 of 1

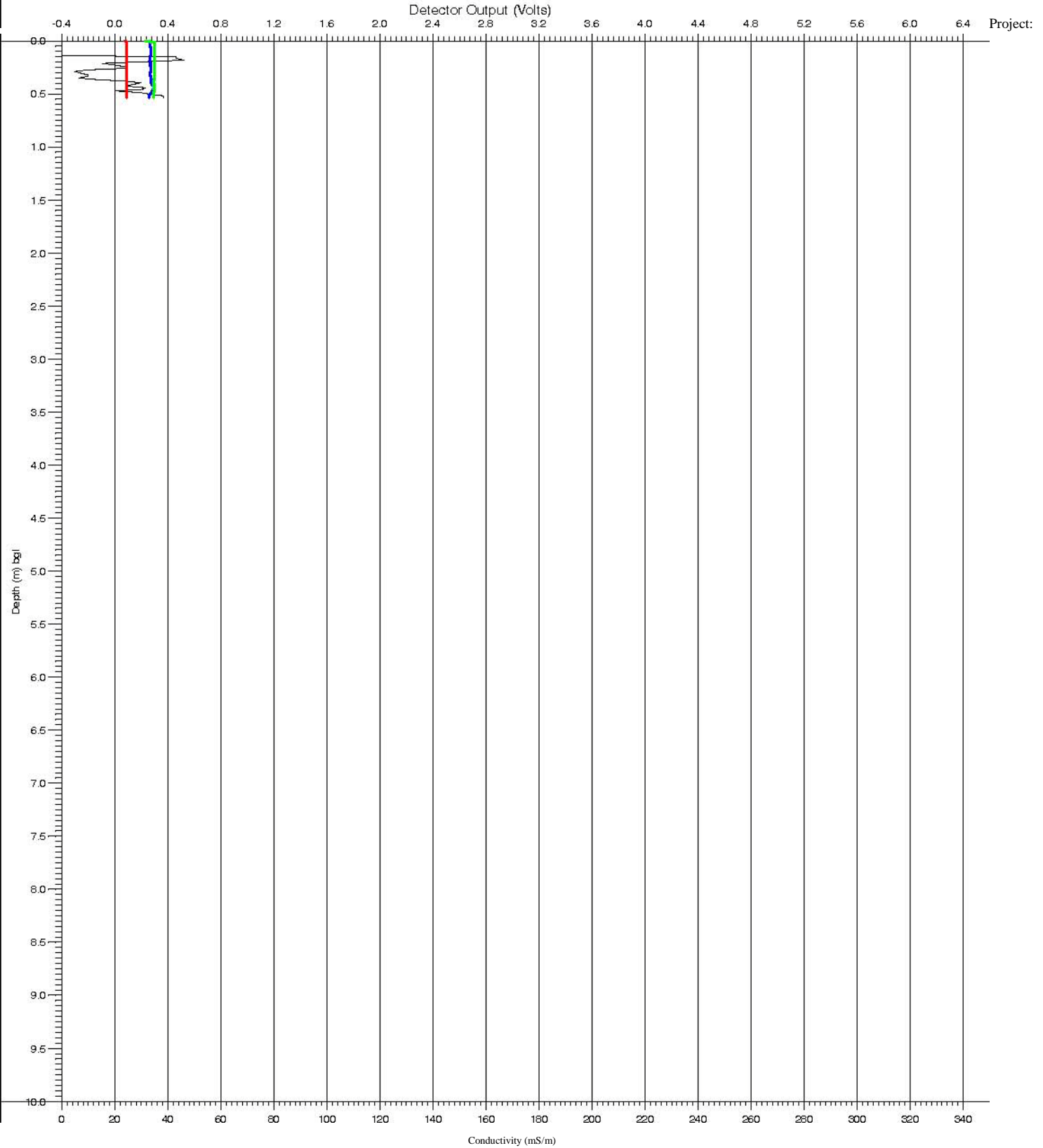




Project: Sabre Research	Location:	Ground Level (m) ASD:	Remarks:	Scale 1:50
Client:		Easting:		Operator:
Project No: 9275700	Date: -	Method: Geoprobe		Checked By:

MIP DATA

Sheet 1 of 1



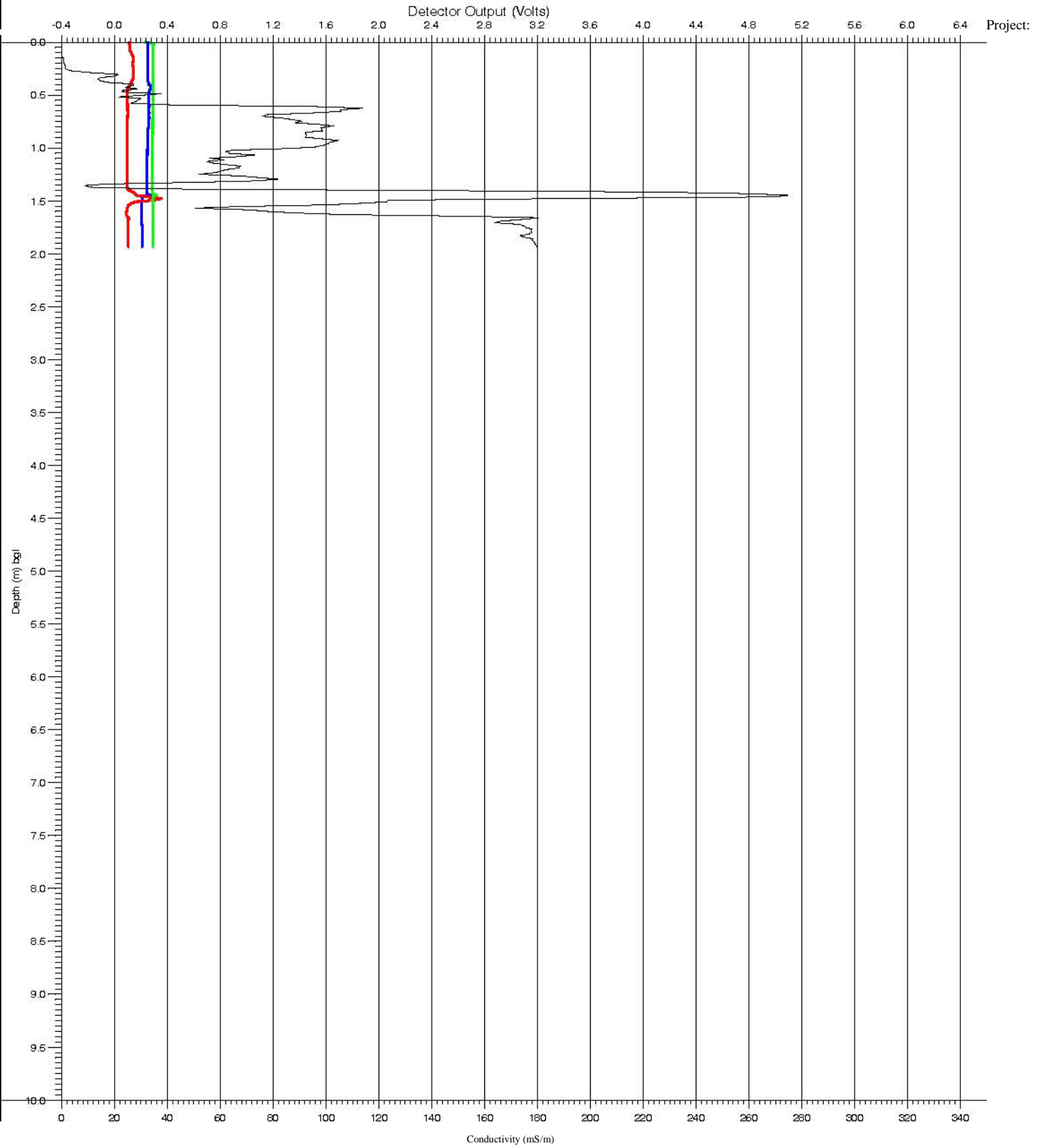
Conductivity (mS/m)



Project: Sabre Research	Location:	Ground Level (m) ASD:	Remarks:	Scale 1:50
Client:		Easting:		Operator:
Project No: 9275700	Date: -	Northing:		Checked By:
Method: Geoprobe				

MIP DATA

Sheet 1 of 1

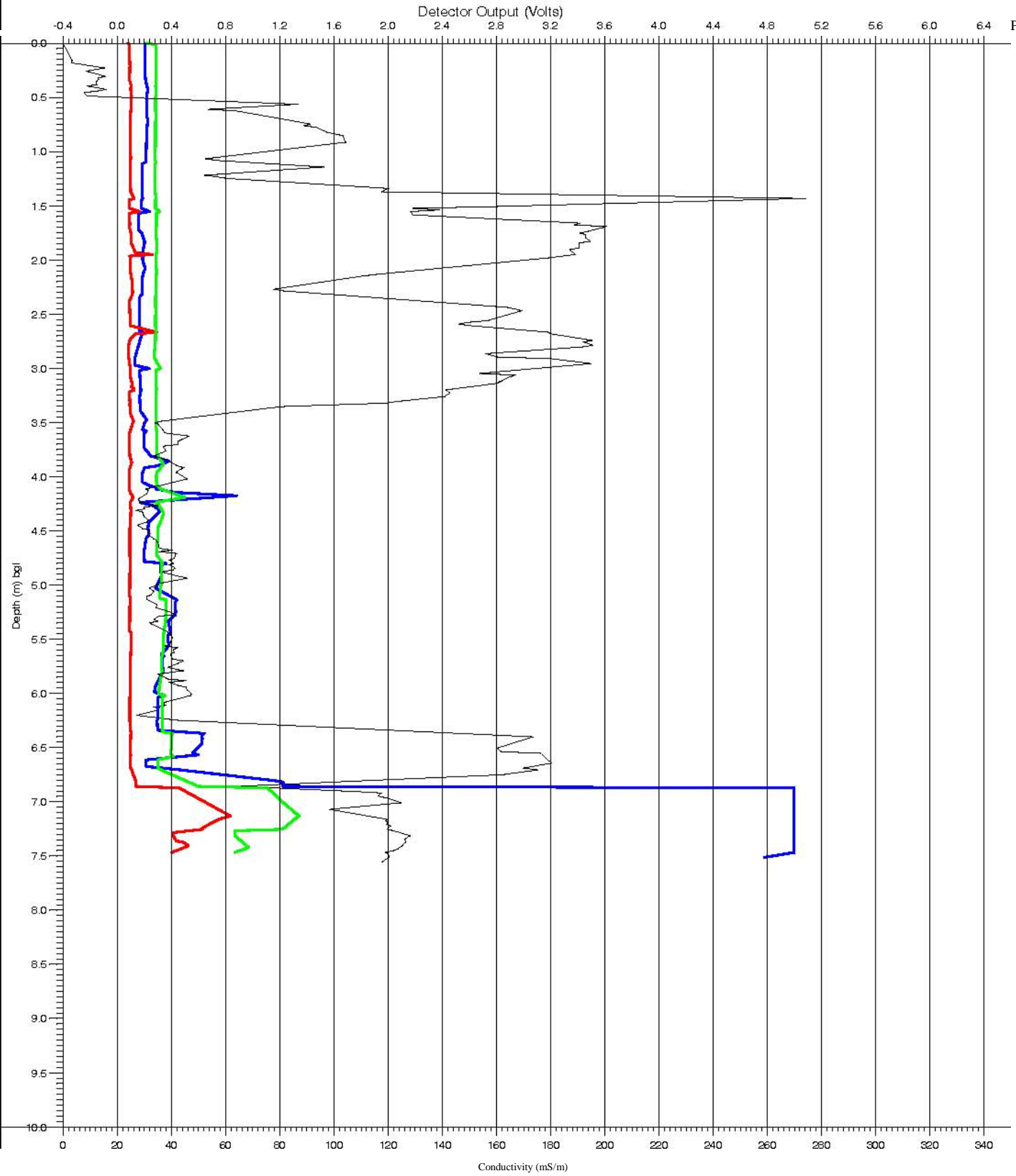




Project: Sabre Research	Location:	Ground Level (m) ASD:	Remarks:	Scale 1:50
Client:		Easting:		Operator:
Project No: 9275700	Date: -	Method: Geoprobe		Checked By:

MIP DATA

Sheet 1 of 1



Project:

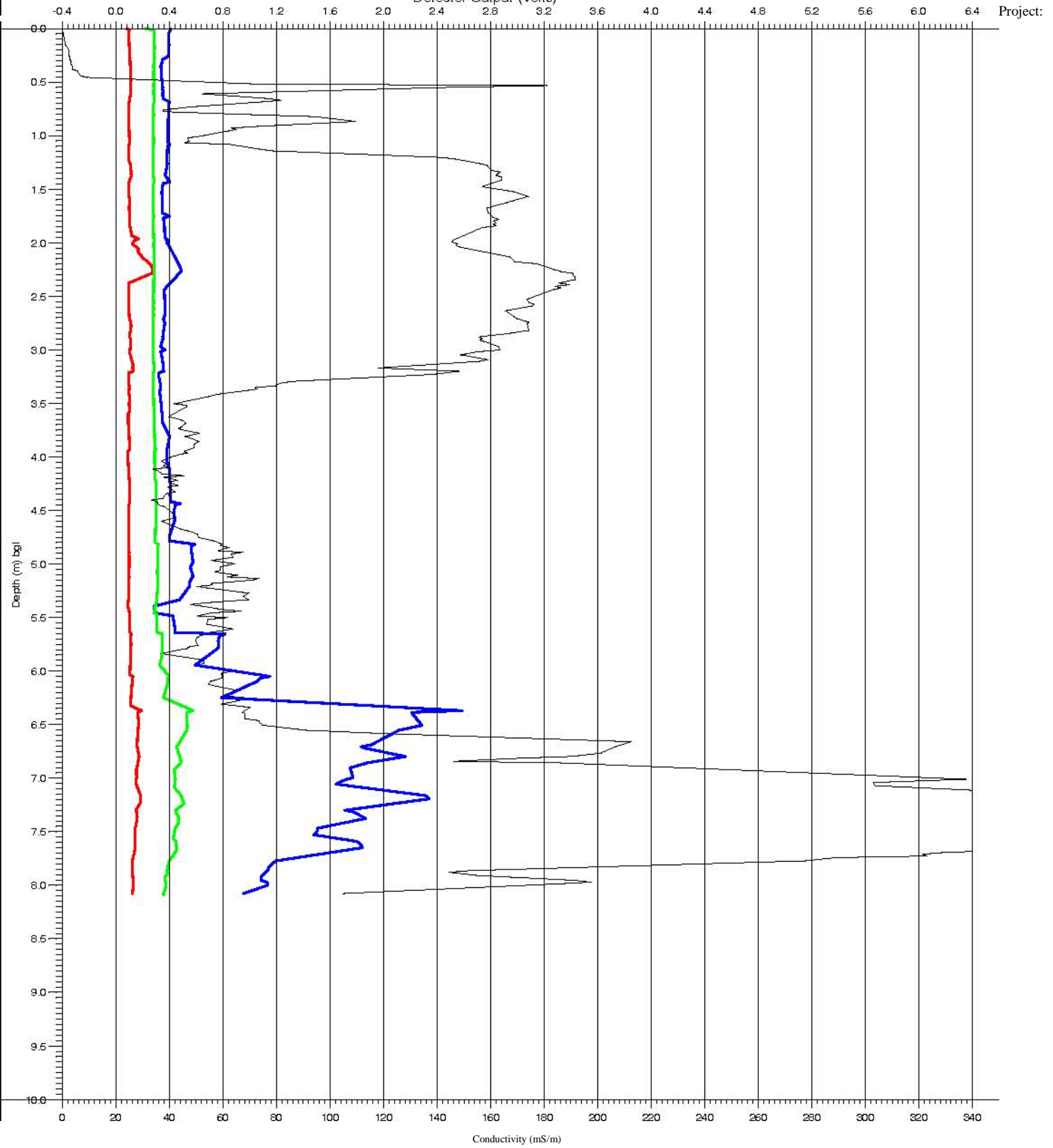


Project: Sabre Research	Location:	Ground Level (m) ASD:	Remarks:	Scale 1:50
Client:		Easting:		Operator:
Project No: 9275700	Date: -	Method: Geoprobe		Checked By:

MIP DATA

Sheet 1 of 1

Detector Output (Volts)



2 Craven Court, Newmarket, Suffolk, CB8 7FA
Tel: +44(0)1638 674767
Fax: +44(0)1638 668191
www.arcadisgmi.com

MIP Test
Number
SAB07

Project: Location: Ground Level (m) ASD: Remarks: Scale Sabre Research

1:50

Client:

Easting:

Operator:

Northing:

Method:

Checked By:

Project No: 9275700

Date: -

Geoprobe

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MIP DATA

Detector Output (Volts)

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5

0 20 40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340



Project:
Sabre Research

Location:

Ground Level (m) ASD:

Remarks:

Scale
1:50

Client:

Easting:

Operator:

Northing:

Checked By:

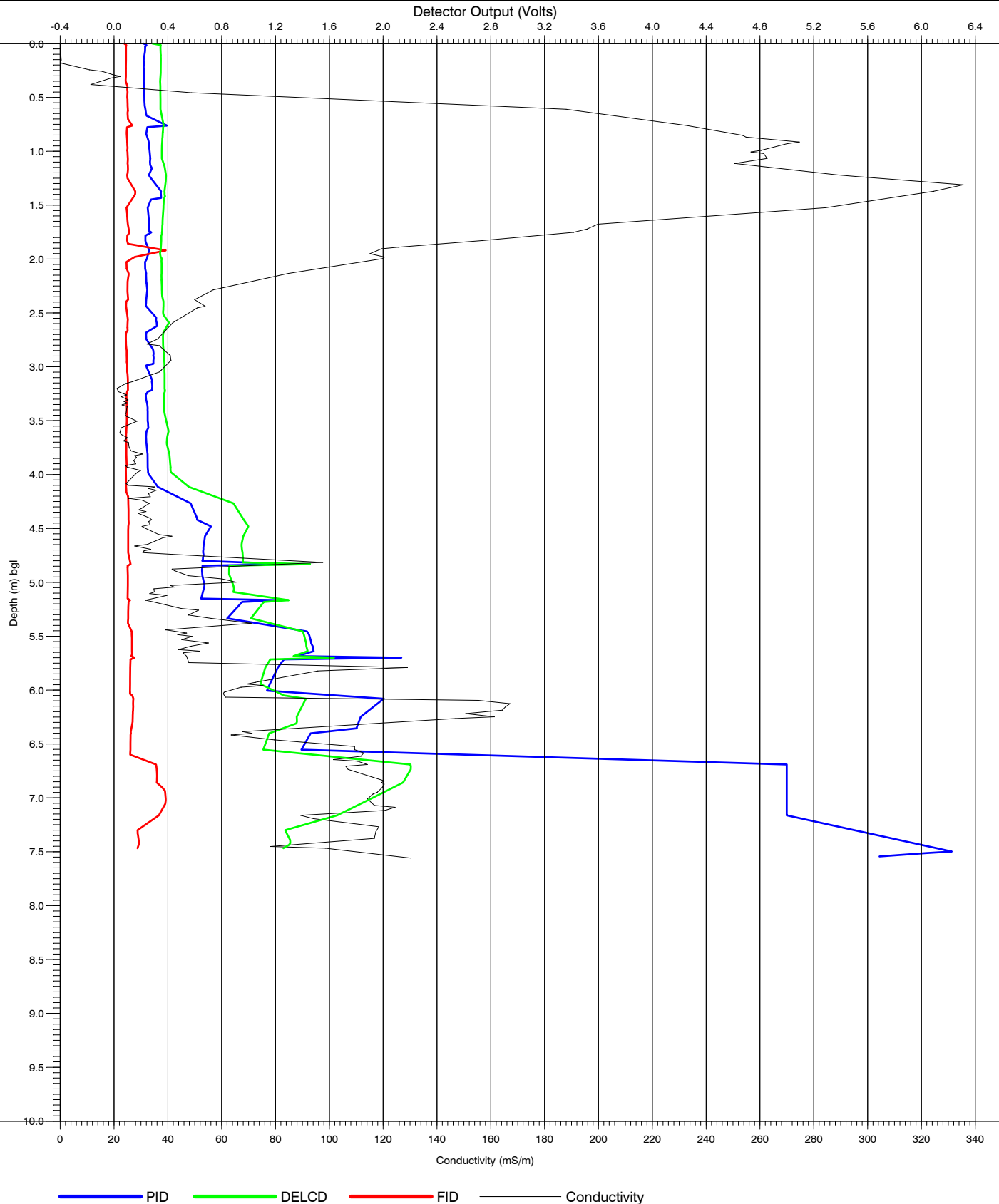
Project No: 9275700

Date: -

Method: Geoprobe

MIP DATA

Sheet 1 of 1





Project:
Sabre Research

Location:

Ground Level (m) ASD:

Remarks:

Scale
1:50

Client:

Easting:

Operator:

Northing:

Checked By:

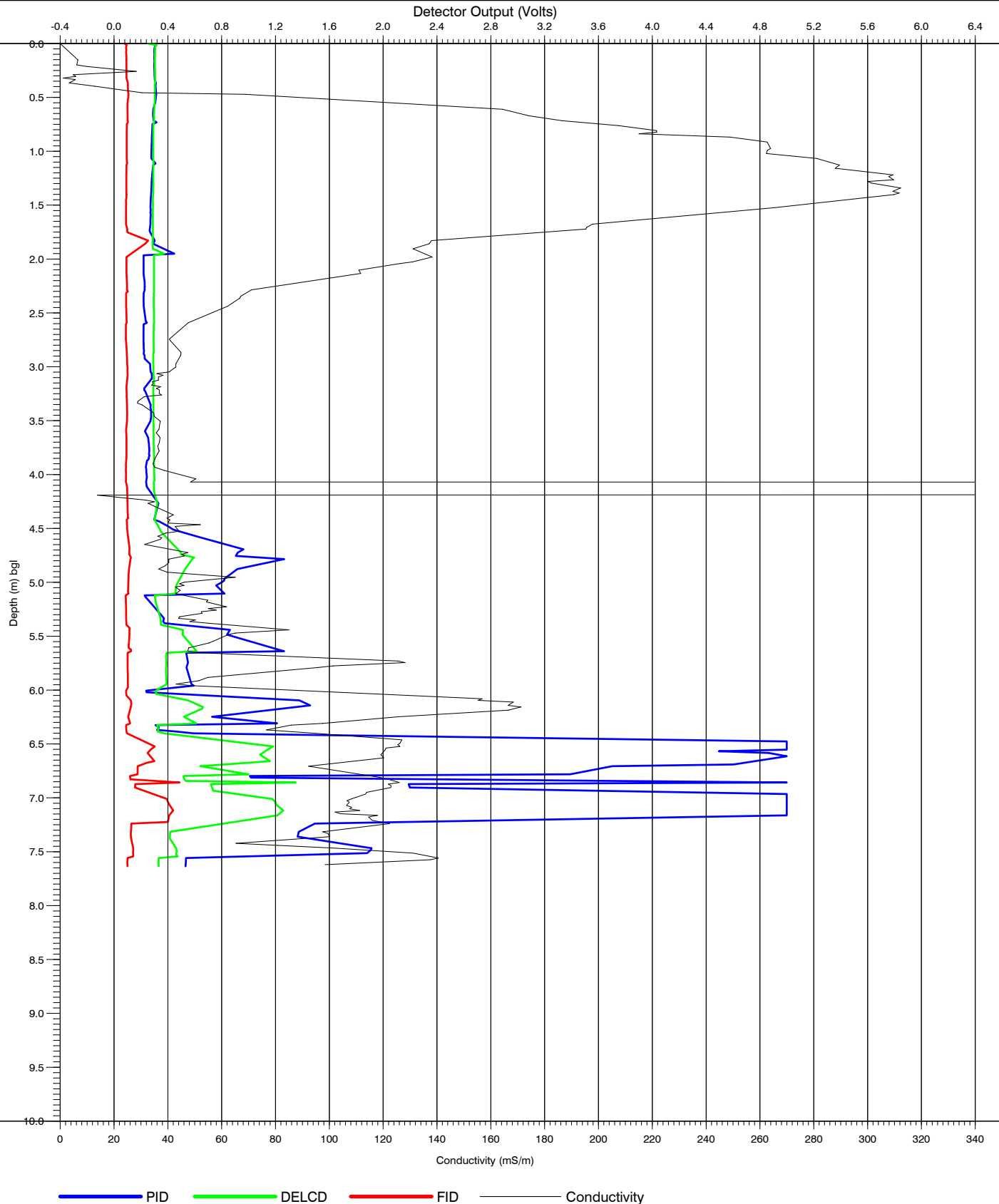
Project No: 9275700

Date: -

Method: Geoprobe

MIP DATA

Sheet 1 of 1





Project:
Sabre Research

Location:

Ground Level (m) ASD:

Remarks:

Scale
1:50

Client:

Easting:

Operator:

Northing:

Checked By:

Project No: 9275700

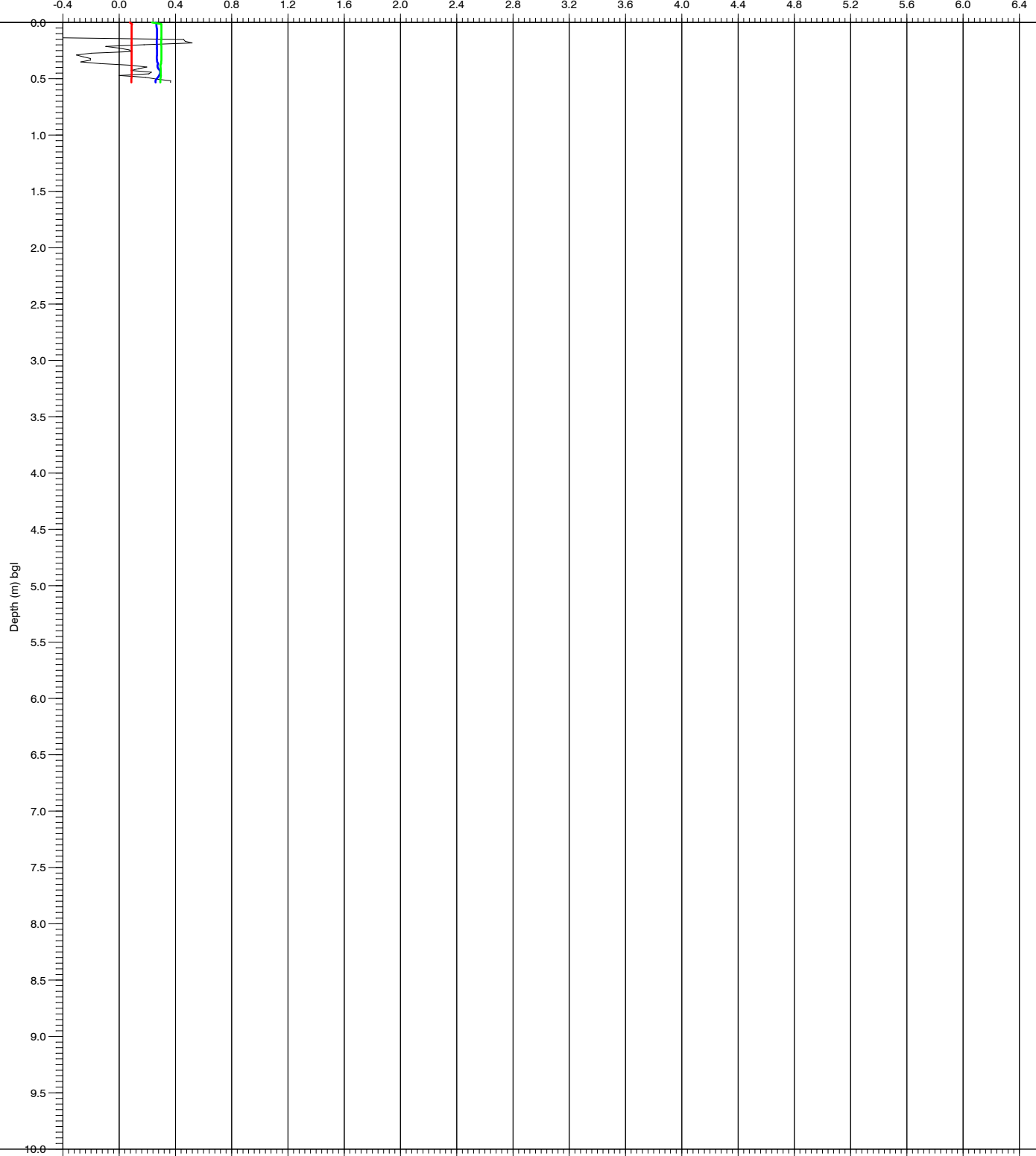
Date: -

Method: Geoprobe

MIP DATA

Sheet 1 of 1

Detector Output (Volts)



— PID — DELCD — FID — Conductivity



Project:
Sabre Research

Location:

Ground Level (m) ASD:

Remarks:

Scale
1:50

Client:

Easting:

Operator:

Northing:

Checked By:

Project No: 9275700

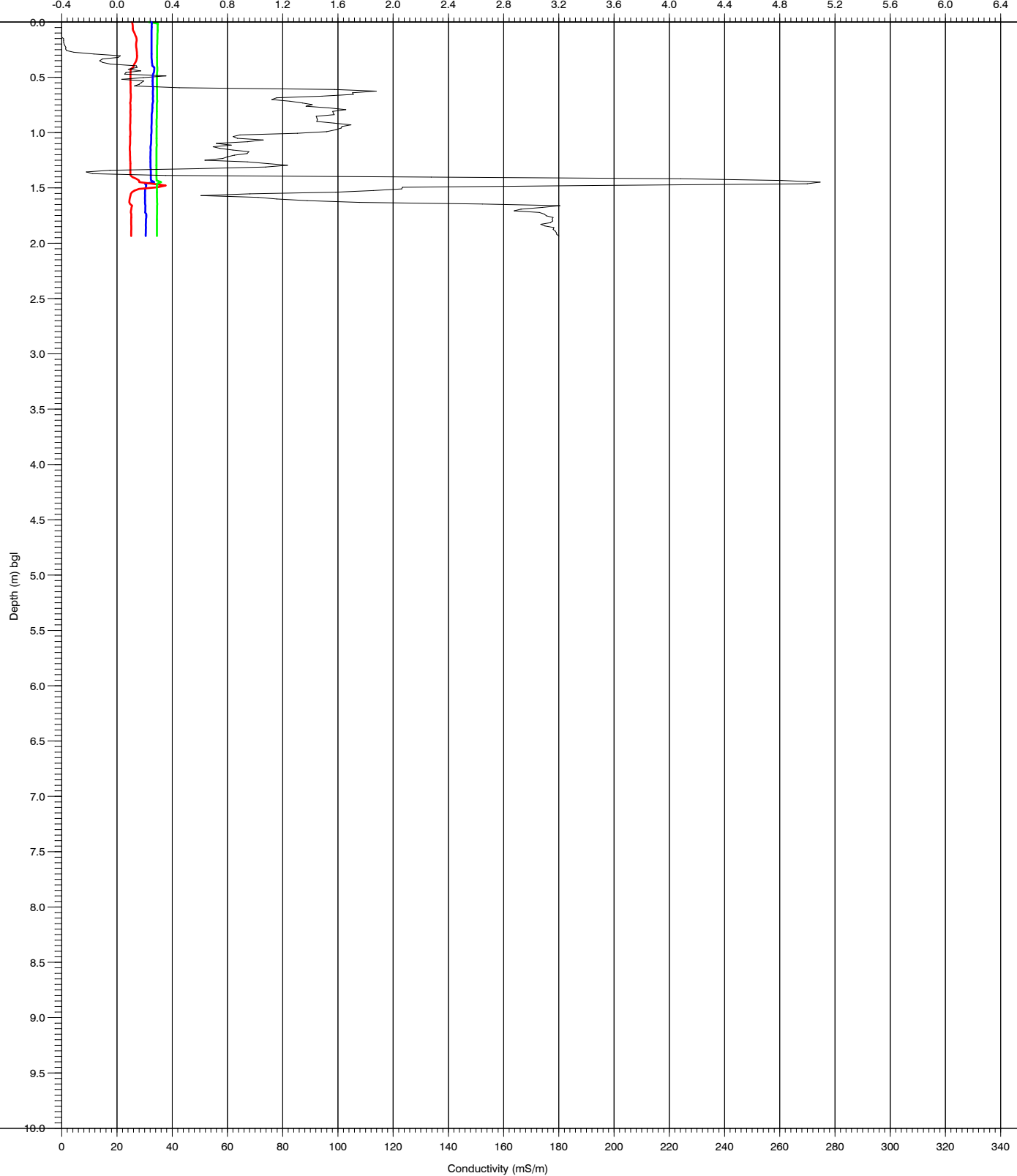
Date: -

Method: Geoprobe

MIP DATA

Sheet 1 of 1

Detector Output (Volts)



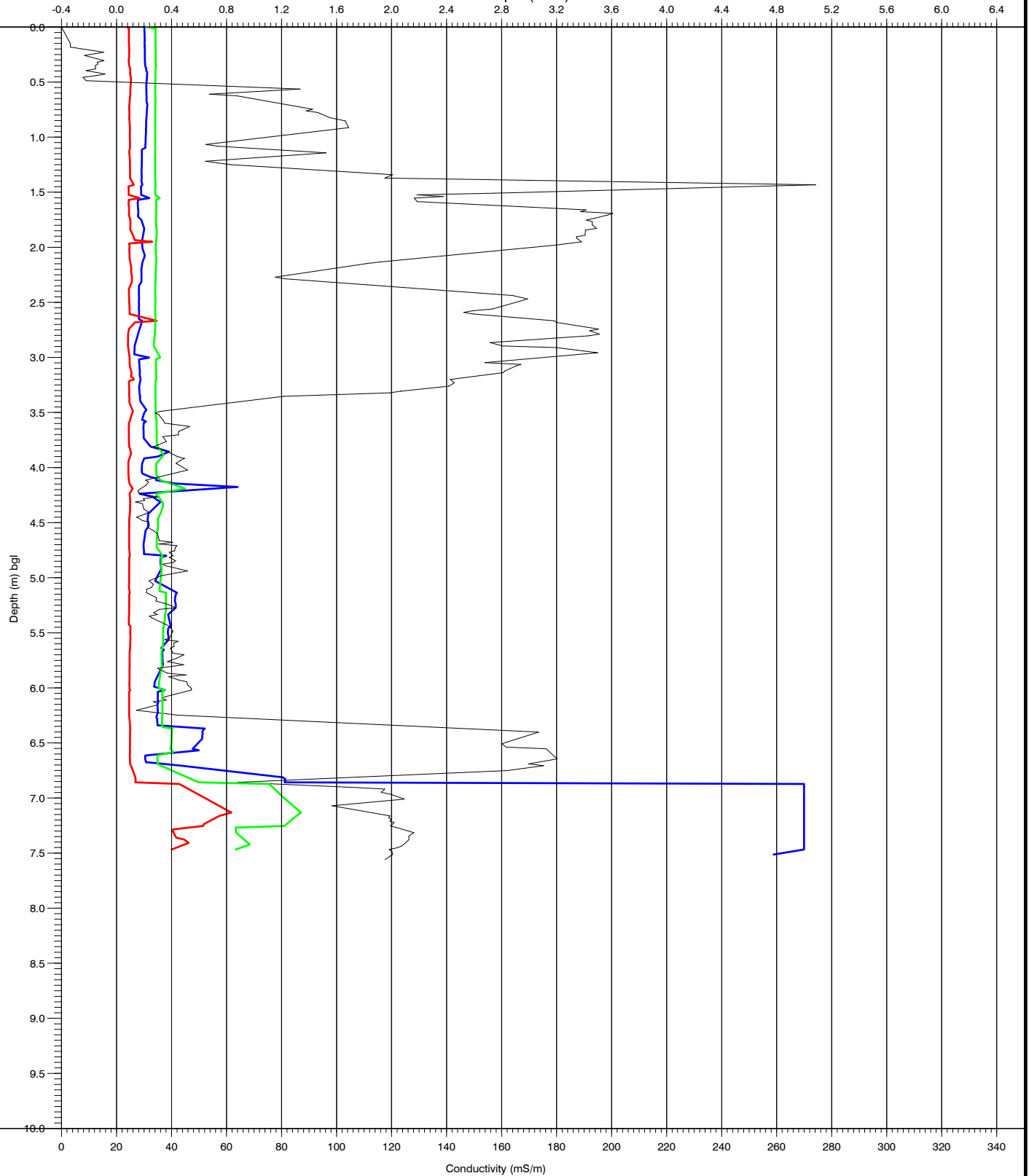
— PID — DELCD — FID — Conductivity



Project: Sabre Research	Location:	Ground Level (m) ASD:	Remarks:	Scale 1:50
Client:		Easting:		Operator:
Project No: 9275700	Date: -	Northing:		Checked By:
Method: Geoprobe			Sheet 1 of 1	

MIP DATA

Detector Output (Volts)



— PID
 — DELCD
 — FID
 — Conductivity



Project:
Sabre Research

Location:

Ground Level (m) ASD:

Remarks:

Scale
1:50

Client:

Easting:

Operator:

Northing:

Checked By:

Project No: 9275700

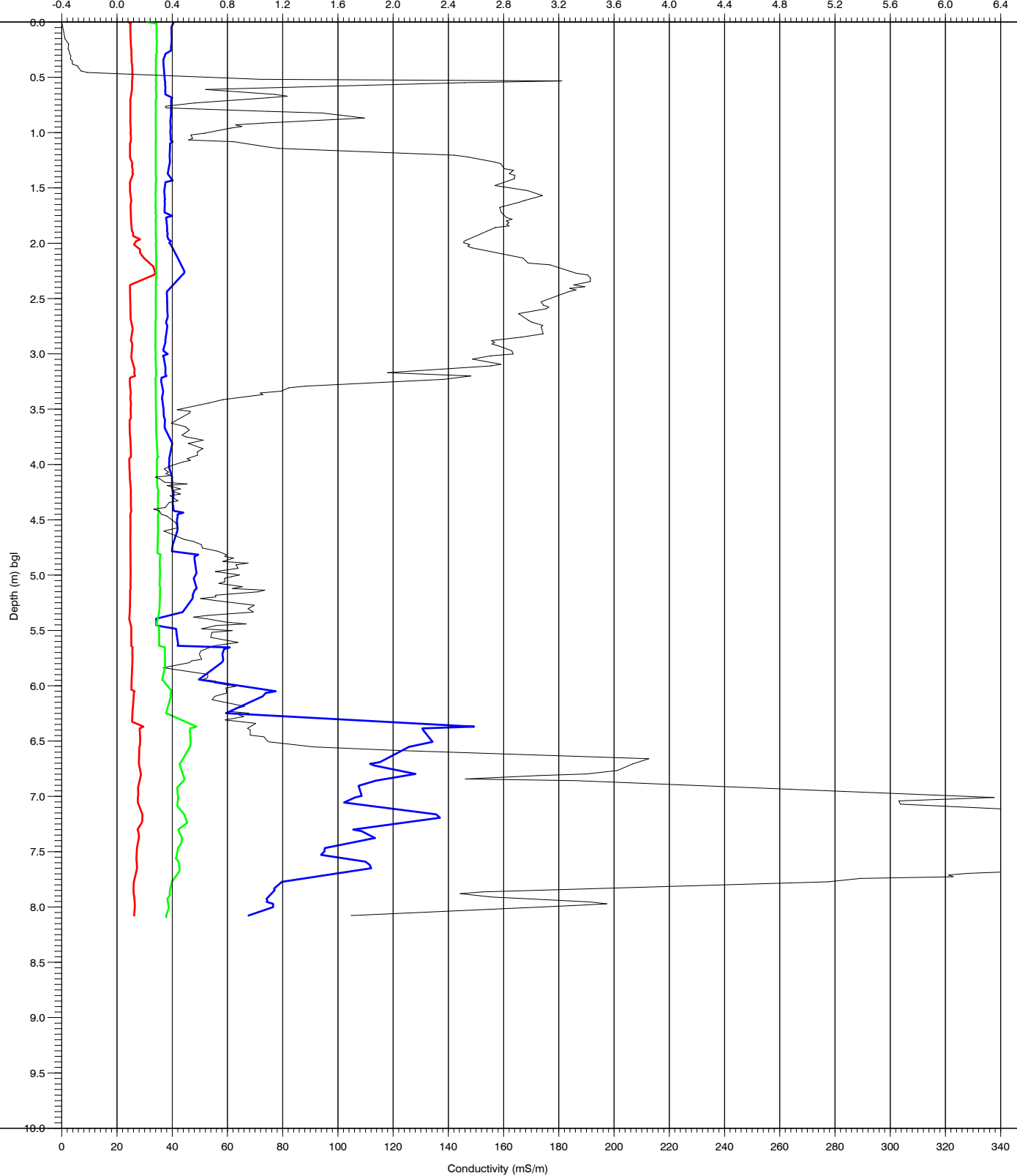
Date: -

Method: Geoprobe

MIP DATA

Sheet 1 of 1

Detector Output (Volts)



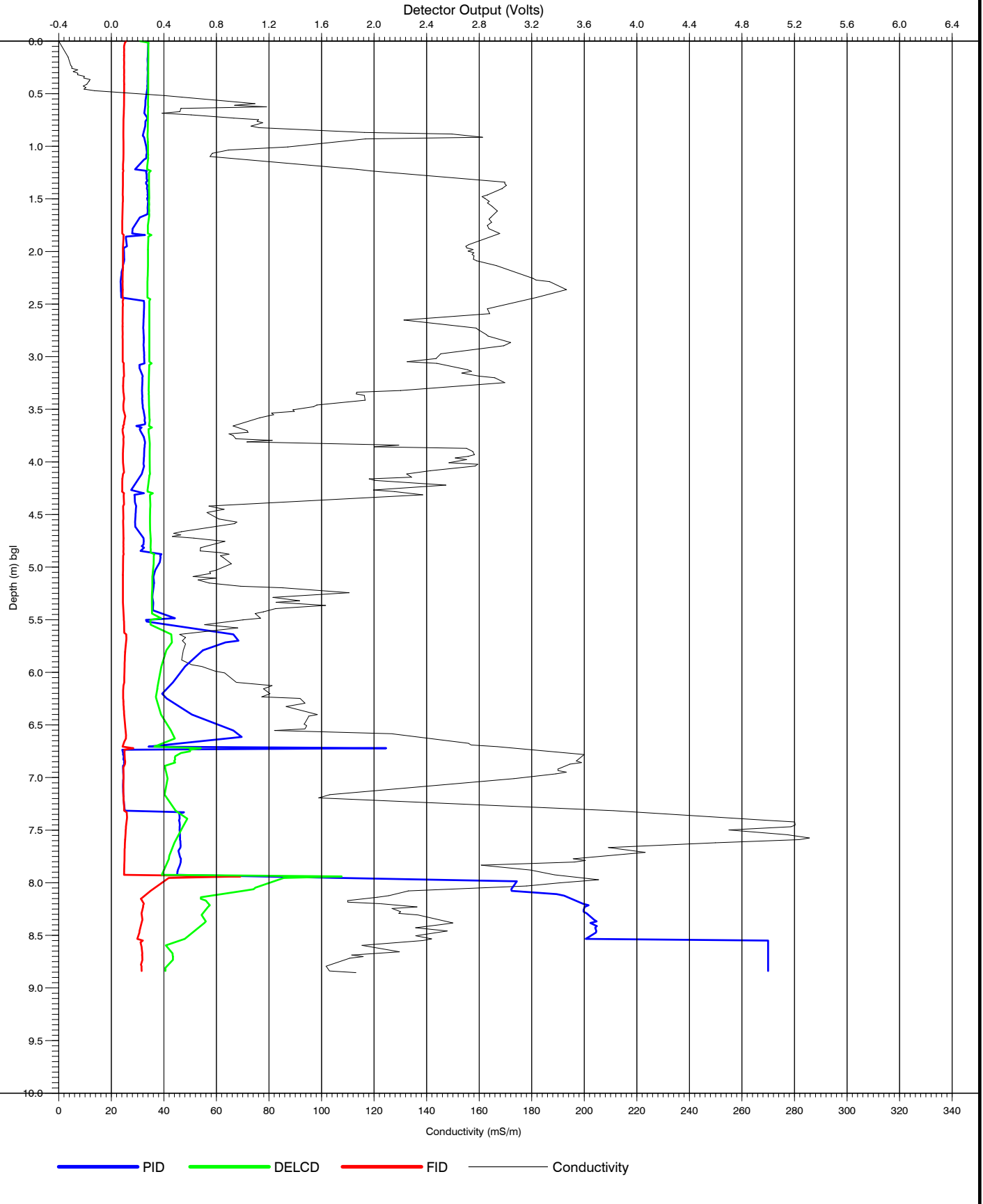
— PID — DELCD — FID — Conductivity



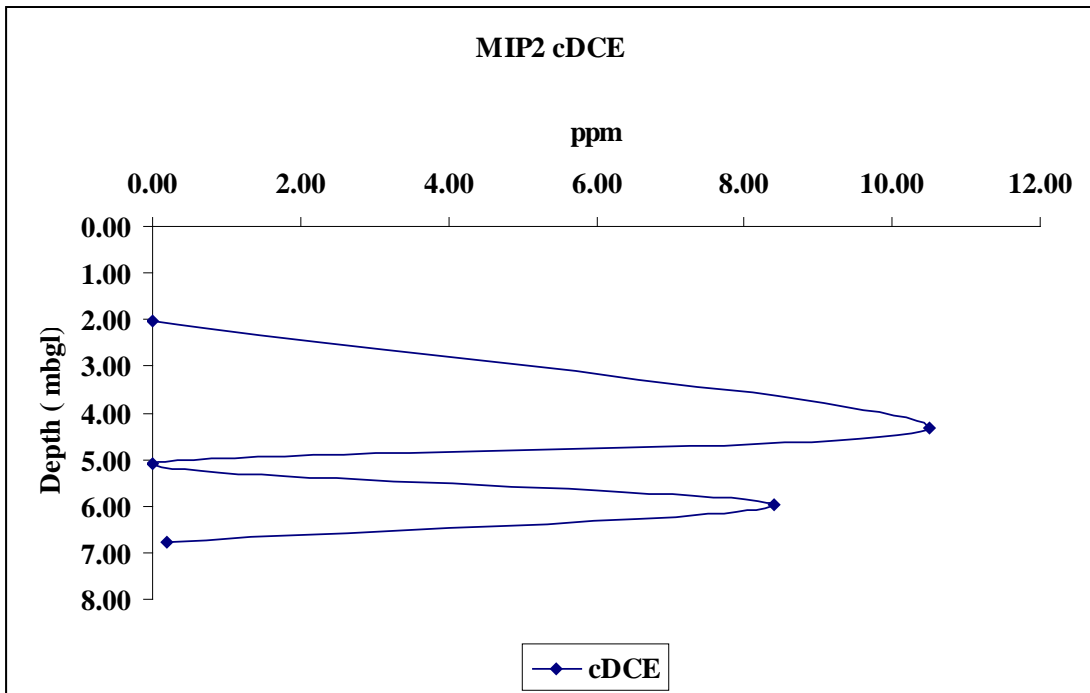
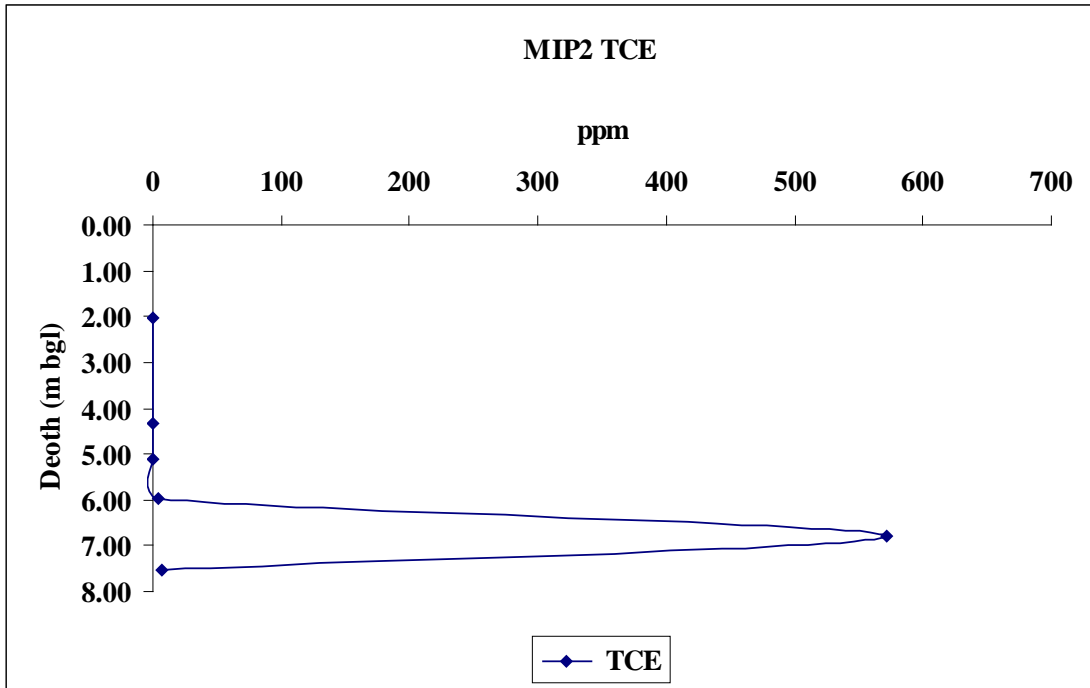
Project: Sabre Research	Location:	Ground Level (m) ASD:	Remarks:	Scale 1:50
Client:		Easting:		Operator:
Project No: 9275700	Date: -	Northing:		Checked By:
Method: Geoprobe				

MIP DATA

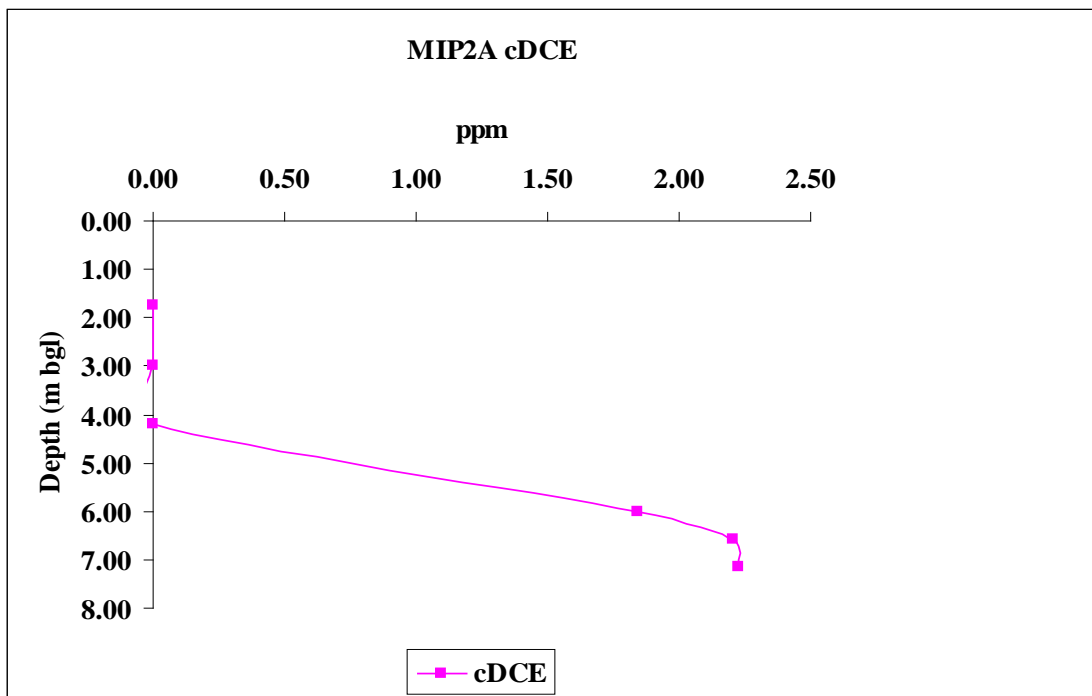
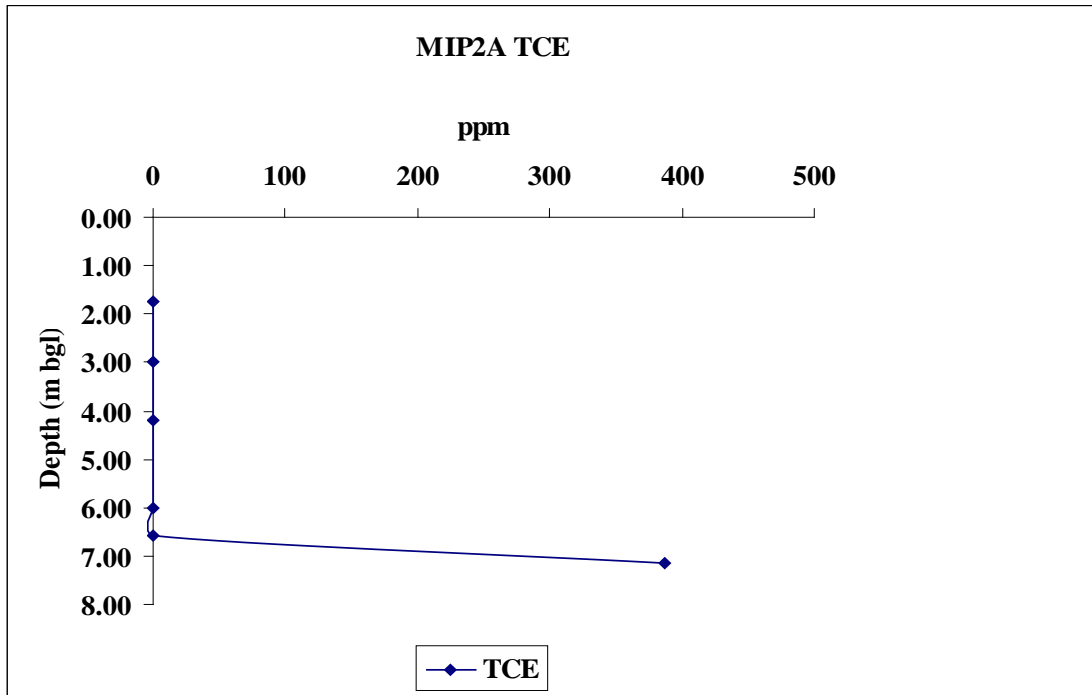
Sheet 1 of 1



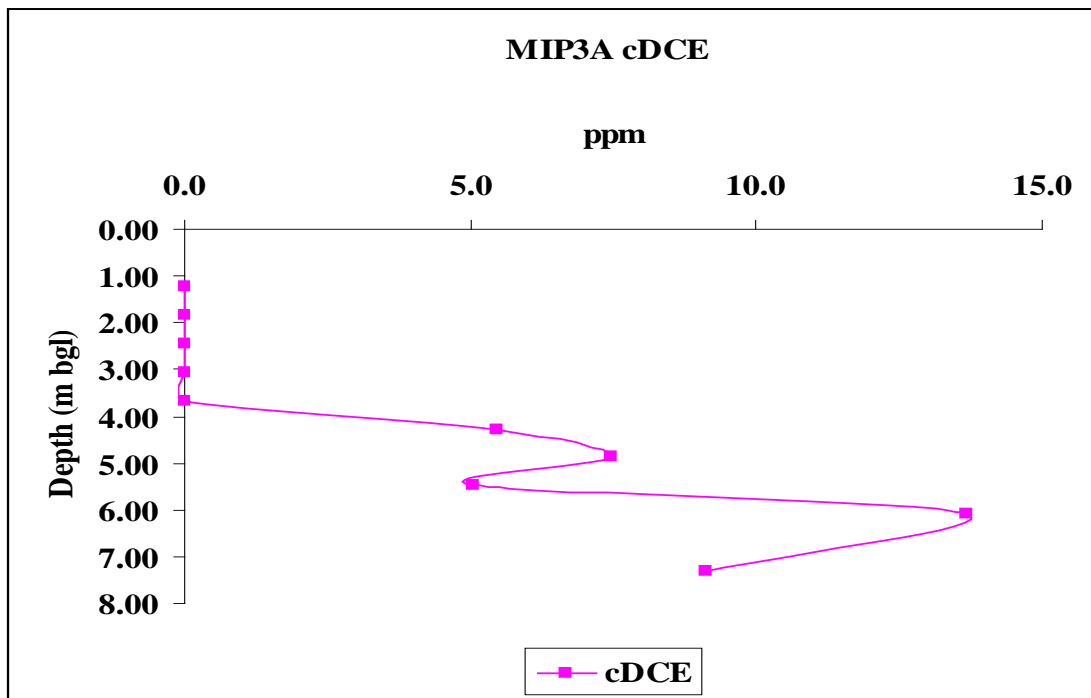
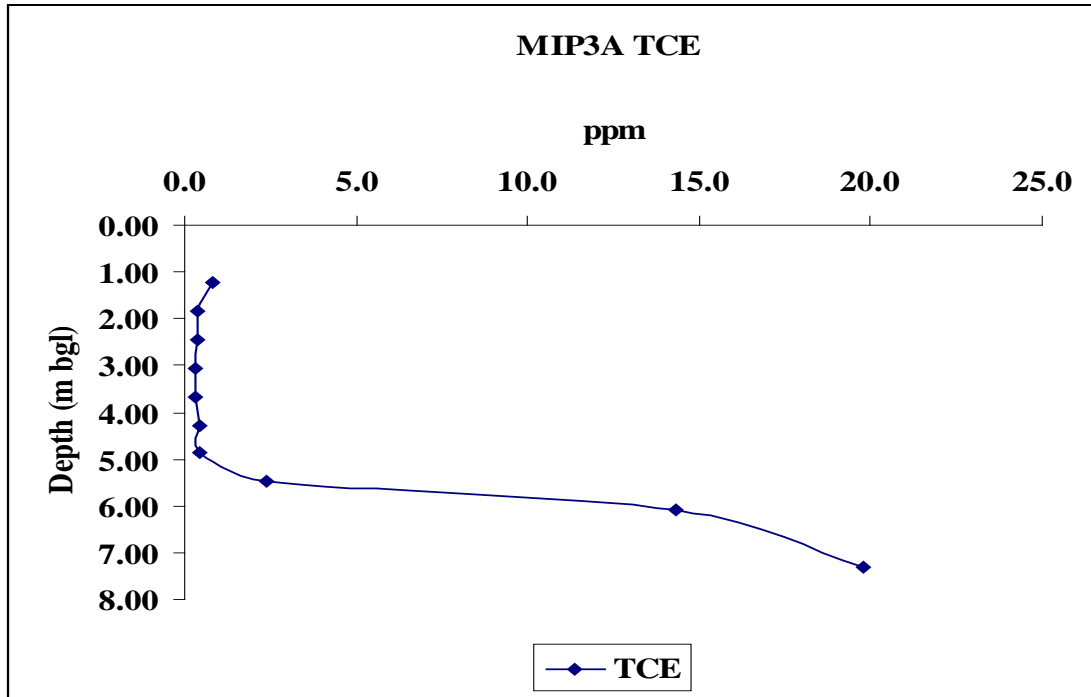
MIP2 GC-MS Gas data



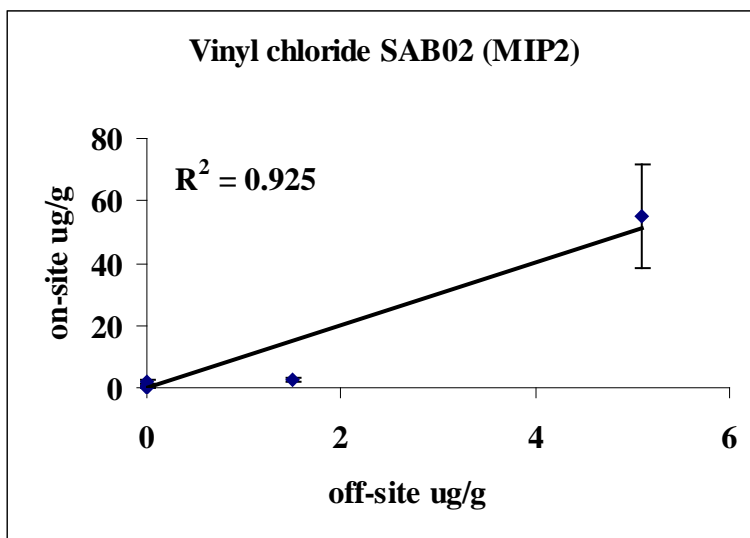
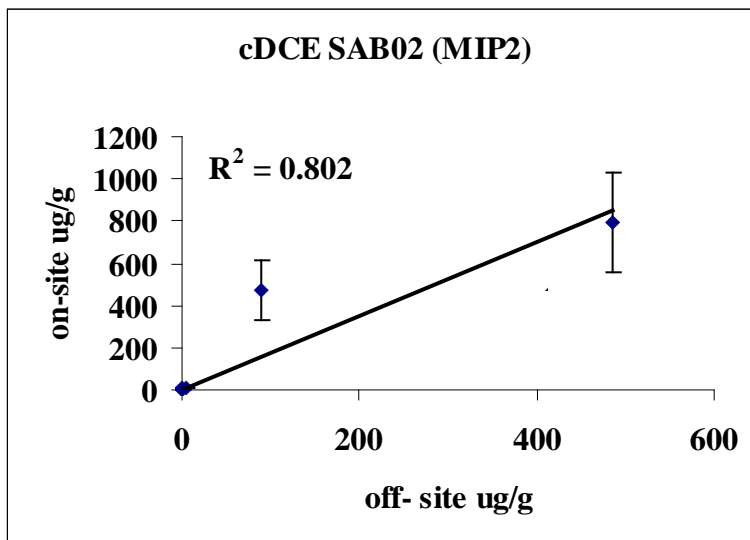
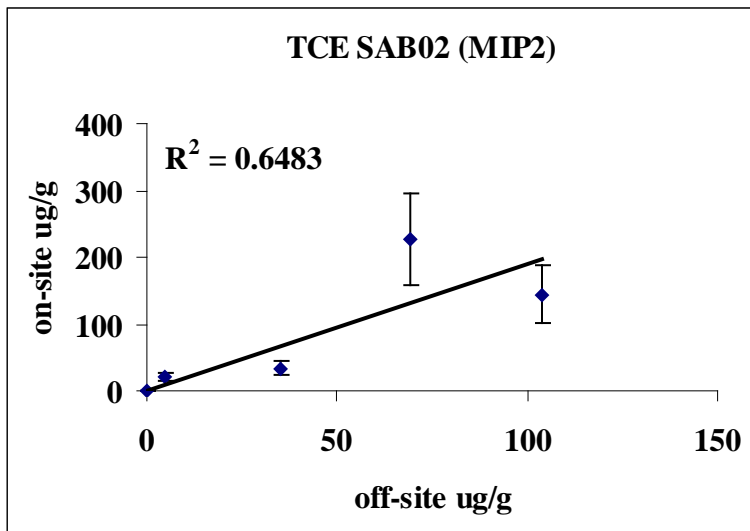
MIP2A GC-MS Gas data



MIP3A GC-MS Gas data



**SAB02 (MIP2) GC-MS On-site v Off-site soil data comparison
(± 30% error bars)**



SAB07 (MIP3A) GC-MS On-site v Off-site soil data comparison
(± 30% error bars)

