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3 January 2012

MEMORANDUM

TO: Mr. Brian Jankauskas, Project Manager **LOCATION:** NYSDEC

FROM: Robert Casey, Project Manager **LOCATION:** EA Engineering, P.C.

SUBJECT: Geophysical Evaluation and Proposed Sampling Locations – Melville Plume Trackdown Site (152229)

As outlined in the work plan template, the field investigation program included proprietary geophysical surveys to identify areas of interest and potential sampling locations for the subsequent field investigation program. The field investigation program was designed to include the collection of approximately 52 aqueous samples and up to 9 soil vapor samples at various locations at the site. The actual location and number of samples were dependent on the results of the geophysical survey. This memorandum provides a brief evaluation of the results of the geophysical surveys and identifies the proposed locations for groundwater profiling and soil vapor sampling at the subject site.

Geophysical Survey Evaluation

Aestus, LLC issued EA a report of the findings for the geophysical survey work performed at the site in September 2011. A copy of the report is included as Appendix A. A summary of the conclusions of that report are as follows:

1. A resistive anomalous zone was identified in the area of monitoring well MW-05 where CVOCs were identified (through groundwater sampling and analysis) above NYSDEC Ambient Water Quality Standards (AWQS) along the downgradient transects (MEL-01 & MEL-03). The location of the strong resistive zone below the water table and groundwater quality results supported Aestus's interpretation that this anomalous zone would be representative of DNAPL impacts. The groundwater contamination at MW-05 has been determined to be originating from the New York Twist Drill (NYTD) site.

2. A less resistive zone was observed in the area of monitoring well MW-06, which indicated that minimal CVOC impacts were present within the subsurface area along the downgradient transect (MEL-01 & MEL-03). This was again confirmed by groundwater quality results from monitoring well MW-06 where CVOC concentrations were reported at concentrations below NYSDEC AWQS.

3. The downgradient geophysical survey transects identified deeper resistive zones, while the upgradient transect did not.

4. Very resistive zones within the aquifer were interpreted as being suspicious based on the findings in the subsurface area at monitoring well MW-05. The detected high resistivity

throughout the vadose zone, which likely represents dry geology. High resistivity near the groundwater table may represent geology or shallow contamination impacts.

5. A large moderate resistivity zone was identified along the upgradient transect (MEL-02) located below the groundwater table. This zone was interpreted as likely representative of native geology with higher moisture content than zones located above the groundwater table along this transect. This data suggested that it is unlikely that contamination exists in this zone, but confirmatory physical data would be needed within this subsurface zone to confirm the interpretation.

Summary of Proposed Sampling Locations

Based on the recommendations provided by Aestus, LLC and a review of historical data from sites located within the area being investigated, EA has summarized the purpose of the proposed sampling locations below and provided the physical locations in figure format (Figure 1).

Groundwater Profiling Points

- Advance groundwater profiling points at six locations (approximate) as identified on Figure 1. The purpose of the groundwater profiling points are as follows:

    - GP-01: Groundwater profiling point will be advanced to depths between 40 – 60 ft bgs for the collection of depth discrete groundwater grab samples. Sample location was selected to investigate high resistivity zone (>5000 ohm-m) along the upgradient geophysical transect to determine if resistivity is due to the nature of the geologic formation or related to groundwater contamination.

    - GP-02: Sample location was selected to further define a resistive zone (<700 ohm-m) identified along the upgradient transect that is representative of possible low level contamination. This same resistive zone was identified along the downgradient transect where low level CVOC concentrations were reported. The groundwater profiling point will be advanced to depths ranging from 100 – 120 ft bgs.

    - GP-03: Groundwater profiling point will be advanced to depths between 80 – 100 ft bgs to confirm conductive zones identified during the geophysical survey activities. Groundwater samples collected from this zone will confirm the Aestus conceptual site model, which identified these zones as areas where subsurface dissolved-phase CVOC groundwater contamination is likely not present.

    - GP-04: Groundwater profiling point will be advanced to depths between 100 – 120 ft bgs to evaluate the potential for dissolved-phase CVOC groundwater impacts at the eastern end of the northern transect and southeast of the facility located at 324 South Service Road.

    - GP-05 and GP-06: Groundwater profiling points which will be advanced to depths between 100 – 120 ft bgs to evaluate the potential for dissolved-phase

CVOC groundwater impacts to the south of the industrial facility located at 70 Maxess Road.

  - GP-07: This sample location was selected to investigate a highly resistive zone adjacent to known groundwater contamination. Based on the geophysical survey results the highly resistive zone could be connected with impacts verified at deeper depth intervals at monitoring well MW-05. The profiling point will be advanced to depths between 60 – 80 ft bgs.

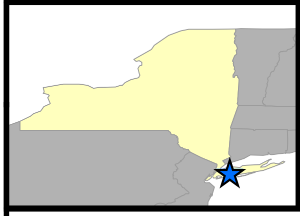
  - GP-08: Groundwater profiling point will be advanced to depths of 100 – 120 ft bgs to confirm the presence of a conductive zone that likely represents groundwater with no impacts.

  - GP-09: This groundwater profiling point will be advanced to depths between 100 – 120 ft bgs to evaluate groundwater quality in an area within the flow gradient from the Henlopen facility.

  - GP-10: : Groundwater profiling point will be advanced to depths between 100 – 120 ft bgs to evaluate the potential for dissolved-phase CVOC groundwater impacts to the southeast of the downgradient transect and south of the industrial facility located at 40 Melville Park Road.

Soil Vapor Points

- Advance and install soil vapor point at nine locations (approximate) as identified on Figure 1. The soil vapor points will be installed to a depth of 10 ft bgs to evaluate soil vapor CVOC concentrations and to identify potential source areas at the target facilities.



- ● Soil Vapor Point
- ● Groundwater Profiling Point
- ⌖ Existing Monitoring Well
- ▬ Groundwater Contour 0.5-ft Interval Above Mean Sea Level (AMSL) - November 2010
- ↖ Interpreted Groundwater Flow Direction

1 inch = 500 '

0 250 500 1,000 Feet

MELVILLE - PLUME TRACKDOWN (152229)
MELVILLE AREA, NEW YORK

FIGURE 1
Proposed Sampling Locations

PROJECT MGR: RSC	DESIGNED BY: JCP	CREATED BY: DCC	CHECKED BY: RSC	SCALE: AS SHOWN	DATE: DECEMBER 2011	PROJECT NO: 14368.45	FILE NO: 1436845/GIS/PROJECTS FIGURE1.MXD

Appendix A

Aestus, LLC Geophysical Report

FINAL REPORT
Aestus GeoTrax Survey™
Site Characterization Work
Plume Trackdown Site
Melville, New York, USA

September 21, 2011

Submitted to:

EA Engineering, P.C.
and its affiliate EA Science, and Technology
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Sole Provider of GeoTrax Survey™ 2-D, 3-D, & 4-D Subsurface Imaging

FINAL REPORT

AESTUS' GEOTRAX SURVEY^{TM}
SITE CHARACTERIZATION WORK
PLUME TRACKDOWN SITE
MELVILLE, NEW YORK, USA

SEPTEMBER 21, 2011

Prepared for:

EA ENGINEERING, P.C. AND ITS AFFILIATE
EA SCIENCE AND TECHNOLOGY

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Appendix C	Reference – Technical Paper (Natural Attenuation of Chlorinated Solvents in Groundwater: Principles and Practices)
Electronic Appendix	3-D Model Files and Viewer Software (w/instructions)

EXECUTIVE SUMMARY

An innovative approach to site characterization was performed by EA Engineering, P.C. and its affiliate EA Science and Technology (EA) at the Plume Trackdown Site located in Melville, New York. Aestus, LLC (Aestus) was retained by EA to scan the subsurface of this site with its high resolution electrical resistivity imaging (GeoTrax Survey™) technology to map subsurface anomalies that may be coincident with environmental impacts (i.e., constituents of primary interest at the Plume Trackdown Site are chlorinated solvents) .

This “scan first and then drill” approach has been very successful in the oil/gas and medical industries and has facilitated a very high data density site characterization effort, relative to simply installing a few more monitoring wells via the conventional “drilling blind” methodology. This report summarizes the work performed by Aestus, data sets generated, data integration efforts, and resulting conclusions and recommendations.

The result of this investigation program is that EA can use Aestus’ GeoTrax Survey™ subsurface images and high data density 3-D model to better understand the vertical and horizontal extent of NAPL and related dissolved-phase constituents. This provides a stronger conceptual site model and will allow EA to focus potential future confirmation drilling efforts, and optimizing the placement of recovery systems (if needed). The geospatially accurate 3-D model provides EA with a high data density framework on which future site data can be integrated.

A total of 3 surveys were performed at the Plume Trackdown Site. Aestus personnel conducted field work on November 15 through November 16, 2010 and collected Surveys MEL-01 and MEL-02 (see survey locations on Figure PV-1). Aestus personnel also conducted field work on July 9, 2011 at NYSDEC's request to perform survey MEL-03 and effectively achieve survey coverage further to the east along the alignment of MEL-01. MEL-03 was originally planned to extend further to the east but had to be truncated due to denied site access by the property tenant.

Aestus employed its “Common Earth Model” approach (see explanation in Section 5.1) to effectively integrate and view all available data (i.e., from our survey work and from previous site investigations) together in 2-D and 3-D, which in our experience is a powerful approach relative to gleaning useful knowledge and meaning from the various data sets. Figures 1 through 3 show the GeoTrax Survey™ 2-D images and Figures 4 through 7 show example 3-D perspective views. The entire 3-D model can be viewed using data files and free viewer software contained on the CD-ROM enclosed with the hardcopy and emailed electronic versions of this report.

Based on review of the “Common Earth Model” results, the following <u>abbreviated</u> set of conclusions are offered at the time of this report and are subject to revision based on any follow up confirmation drilling/sampling data obtained from anomalous subsurface locations detected by Aestus (<u>see Section 6.0 for a full and more detailed set of conclusions along with a discussion of levels of certainty at this stage in the project</u>):

- ✓ There is a very resistive anomalous zone (> 5000 ohm-m) near the bottom of image MEL-01 (Figure 2) which likely represents impact by DNAPL and/or DNAPL-related constituents. Existing monitoring well MW-05 intersects this highly resistive zone in the subsurface, and groundwater sampling shows that several DNAPL-related constituents exceed water quality standards. The location of this strong resistive zone below the water table also supports the conclusion the anomaly is representative of DNAPL-related impacts. Aestus understands from EA/NYSDEC that contamination at this location is believed to be associated with the former New York Twist Drill property located along Melville Park Road (see GeoTrax Survey™ and well locations on Figure PV-1).

✓ The yellow resistive zone on image MEL-01 (Figure 2) likely indicates a zone with very minimal concentrations of dissolved phase DNAPL-related constituents as confirmed by groundwater quality data from existing monitoring well MW-06.

✓ Image MEL-01 has deeper very resistive anomalies while image MEL-02 does not. Because MEL-01 is presumably downgradient from potential source areas, this finding makes sense and could be considered consistent with site history.

✓ Very resistive zones (> 5000 ohm-m) from 0-100 feet BGS are suspicious as this range is the same as the subsurface anomaly discussed on MEL-01 (Figure 2) which has confirmed DNAPL-related impact through sampling. Because these areas are above the water table (Figure 7), these zones may represent dry geology, but could also represent shallow contamination impacts as evidenced by historical groundwater analytical data of wells in the vicinity.

✓ A large moderate resistivity zone (blue-colored) exists along image MEL-02 (Figure 3) and below the modeled water table zone in the 3-D model (Figure 6). The relatively planar geometry of this zone and its position below the water table indicate that this zone is likely representative of native geology that has a higher moisture content that zones above the water table. Assuming this interpretation is correct, then the data suggests that it is unlikely that a significant contaminant source exists immediately upgradient of the survey line MEL-02 location.

Section 7.0 of this report provides Aestus' recommendations for further improving understanding of subsurface issues and focusing remedial efforts at the Plume Trackdown Site. These recommendations include but are not limited to the following topics:

✓ Review of results of this investigation with EA via meeting or web conference.

✓ A limited follow-up confirmation drilling and sampling program would be helpful to further confirm the composition and extent of anomalous zones detected by Aestus.

✓ Discussion regarding sampling methodology and analyte selection for future site monitoring and investigation via drilling.

✓ Updates to Common Earth Model and future Aestus involvement.

Should EA/NYSDEC perform confirmation drilling work to further calibrate the ranges of electrical resistivity detected at the Plume Trackdown Site to chemical/physical/biological properties of the subsurface, Aestus can incorporate these results into our Common Earth Model 2-D figures and 3-D model. Interpretations presented in this Final Report can be updated/revised and submitted as a Revised Final Report if/as appropriate.

1.0 INTRODUCTION

Aestus, LLC (Aestus) performed a high resolution electrical resistivity imaging (GeoTrax Survey™) investigation for EA Engineering, P.C. and its affiliate EA Science and Technology (EA) at the Plume Trackdown Site located in Melville, New York. A total of 3 GeoTrax Surveys™ were performed at the site.

1.1 Project Objectives

The project objectives of this investigation program are to use Aestus' GeoTrax Survey™ technology to assist EA with identifying the extent of DNAPL (chlorinated solvent) and related dissolved-phase constituents, and optimizing the placement of additional monitoring wells and/or recovery systems (if required).

Aestus' scope of work for this project was to use our subsurface imaging technology to scan the earth's subsurface (i.e., to depths of ~180 to 215 feet) at survey locations selected jointly by EA and Aestus during the planning stage to identify subsurface anomalies that may require focused additional investigation via drilling.

1.2 GeoTrax Survey™ Technology Overview

Electrical resistivity measurements have been used since the 1830's to interpret the earth. Electrical resistivity imaging (ERI) works by imparting an electrical current into the ground at a constant rate, and then measuring voltage at one or more other locations along a straight survey line/transect. Based on these data, the apparent resistivity of subsurface materials is calculated using Ohm's Law.

Similar to a single pixel in a digital photo, a single resistivity measurement does not yield significant information. However, modern ERI technology combined with current computer processing speeds, facilitate hundreds or thousands of resistivity measurements in a short timeframe. These measurements are performed along a survey alignment and are subsequently used to produce a two-dimensional (2-D) electrical image (analogous to a CAT-scan in the medical industry) of the subsurface that graphically illustrates the presence or absence of subsurface anomalies. The 2-D continuous images help minimize or eliminate interpolation between 1-D data points such as soil borings or wells, and assists in confirming or redefining the conceptual site model.

Our GeoTrax Survey™ technology is based on conventional ERI techniques. However, we have worked with Oklahoma State University (OSU) to vastly improve this technology and make it useful for the environmental industry. Aestus is the sole worldwide licensee of trade secret intellectual property from OSU that provides proprietary data collection algorithms and software to achieve more comprehensive data collection, higher data quality, and ultimately increased image resolution, relative to standard ERI technology. In addition, we are able to successfully image subsurface anomalies at sites on which competing technologies such as ground penetrating radar and electromagnetic surveys either fail to perform or simply do not have sufficient resolution to achieve the project objective.

The following sections of this report summarize the Aestus' field work, data collection, and data processing activities, and provide our interpretations, conclusions, and recommendations based on the results of our site investigation.

2.0 GEOTRAX SURVEY™ FIELD WORK

A total of 3 surveys were performed at the Plume Trackdown Site. Aestus personnel conducted field work on November 15 through November 16, 2010 and collected Surveys MEL-01 and MEL-02 (see survey locations on Figure PV-1). During this initial mobilization to the site, survey transect MEL-01 was shortened and moved slightly west of the original location requested by NYSDEC.

The reason for the move and shortening of the line length was believed by Aestus' field personnel to be a function of site access issues. However, because written documentation for this adjustment could not be found by either EA or Aestus, Aestus agreed to remobilize to the site at its cost to collect data to the east of survey line MEL-01 to achieve the level of coverage originally envisioned by NYSDEC. This additional work was performed on July 9, 2011 as survey line MEL-03. MEL-03 was originally planned to extend further to the east but had to be truncated due to denial of site access by the property tenant during this field work.

Specifically, when Aestus arrived on site to survey MEL-03, the operating manager of the tenant of the property on the southwest corner of Melville Park Road and Maxess Road would not allow the Aestus crew to access parts of his property where large trucks were driving (southern property drive way). Moving the survey transect to the south of the driveway area was not an option due to dense vegetation and large amounts of suspected poison ivy. Therefore, with concurrence from EA (via email and phone call based approval), MEL-03 was positioned such that Electrode 56 was just east of the southwest corner of the abovementioned property.

2.1 Equipment Layout, Land Surveying, Documentation

Each survey was conducted by installing 56 specialized electrodes into the ground along a straight line and at a specific interval as indicated below. The spacing used on each line was determined on-site to provide the appropriate depth of imaging and/or to conform to lateral space constraints due to buildings, busy streets, property lines, etc. The target depth of interest for investigation at the Plume Trackdown Site was approximately 200 feet BGS and therefore surveys with electrode stake spacing's that would yield the depth of interest were used. The electrode spacing and resulting survey line length and imaging depth at the Plume Trackdown Site are listed in Table 1.

Figure PV-1 shows the location and orientation (i.e., the red ends of the survey lines represent Electrode 1 and the blue ends represent Electrode 56) of the surveys performed at the Plume Trackdown Site and allows for other site features on the base map to be visible to the reader for reference.

The electrodes stakes were connected via geophysical cables and the cables were connected to Aestus' data acquisition field instruments. Electrical resistivity data from the subsurface was then collected as described below in the Data Collection section of this report.

Topography estimations of Aestus survey line locations were performed by Aestus personnel using land survey instrument (i.e., Topcon total station unit with prism). These data were used to assist Aestus in locating our surveys in plan view on the site base map/aerial photo and performing a topographic correction to our survey images as discussed below in the Data Processing section of this report.

To aid EA in locating the GeoTrax Survey™ locations during any follow-up drilling work that may be performed, Aestus marked the end points of each line with either a rebar rod with a yellow cap bearing the inscription 'GEOTRAX SURVEY', a yellow plastic disc with the survey number and endpoint marked, or steel nails with brass survey markers (for end points in asphalt or concrete). A metal detector may be used to locate each GeoTrax Survey™ line should additional confirmation borings be advanced along one or more survey lines in the future. A picture of each type of endpoint marker is shown below:

Rebar Cap End Point Markers

Brass Survey End Point Marker

GeoTrax Survey™ Endpoint Marker

Coordinates for the endpoints (i.e., Electrode Nos. 1 and 56) of each survey line at the site were collected by Aestus personnel using land survey techniques (i.e., total station) and are included in Table 2 for reference. Coordinates are provided in New York State Plane Coordinate System, NAD83.

Aestus also recorded detailed field notes that show a sketch of each survey and surrounding site features (e.g., utility locations, buildings, monitoring wells, etc.) and the distance of these site features from our survey lines. A copy of Aestus' field notes is provided for reference in Appendix A to this report and for assistance with locating survey lines in the field during any follow-up confirmation drilling work that may be conducted.

Finally, as part of Aestus field work documentation, each survey location was photographed along the survey alignment from different vantage points during data collection. Select photographs are' included on Figure 8 of this report. The entire set of photographs taken by Aestus is included as an electronic appendix to this report (see the CD-ROM included on the inside cover of the hardcopy version of this report). These photographs can also be used to field locate GeoTrax Survey™ lines.

2.2 Data Collection

Once each survey line was laid out in the field, Aestus' specialized field instruments gathered a significant amount of data related to the electrical properties of the subsurface.

Aestus used our proprietary techniques to collect significantly more and better quality data than other firms using similar looking equipment.

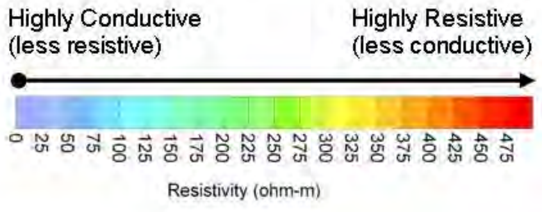
These data were checked for quality and integrity and then partially processed in the field to obtain a high resolution draft subsurface image viewable by EA and Aestus personnel. Full data reduction and processing is performed in Aestus' offices as discussed in the following section.

3.0 DATA PROCESSING

Following field data collection, Aestus used our proprietary data processing techniques to develop a final electrical resistivity image of the subsurface for each survey. This section describes the data processing work that was performed for the Plume Trackdown Site.

The raw data files collected in the field were fully processed, including a thorough review of data quality from the data set so that the resulting survey image is not skewed. A final image for each survey was developed which contains a model of the electrical resistivity of the subsurface in units of ohm-meters. Changes in topography along the survey lines were accounted for during this data processing work.

The final images were developed by contouring and plotting the resistivity data for each survey line using consistent color contouring schemes for Plume Trackdown Site survey data to allow for evaluation of the results of all surveys on a comparative basis. In the case of the generic color contouring scheme example below (i.e., not specific to the Plume Trackdown Site), the electrically conductive areas of the subsurface are illustrated by purple and blue colors and the electrically resistive areas of the subsurface are illustrated by yellow, orange, and red colors.



As part of our overall data quality control process, Aestus compiles resistivity data for an entire site and then normalizes the color contouring scheme (i.e., during our proprietary data post-processing phase) for all of the images across the site. This allows consistency in the color contouring scheme so a reviewer can correlate the results from one survey to the results from another survey performed on the same site during the same timeframe. The survey data is then output in six of our standard color schemes for preliminary internal (Aestus) review. These standard color schemes are evaluated during the data interpretation phase of each project and often times a more appropriate site specific color contouring scheme is developed based on calibration to historical site data (see Section 5.4.2).

The results of Aestus' survey work and our specific interpretations/conclusions based on our work at the Plume Trackdown Site are discussed in the following sections of this report.

4.0 RESULTS (GEOTRAX SURVEY™ 2-D SUBSURFACE IMAGES)

Aestus' geophysical survey work yielded high quality/high resolution two-dimensional (2-D) electrical resistivity images of the subsurface at the Plume Trackdown Site in select locations as shown on Figure PV-1. The final GeoTrax Survey™ images (see Figures 2 and 3) are presented in one custom (site specific) color contouring scheme as discussed below in Section 5.4 (Color Contouring Electrical Resistivity Imaging Data) of this report.

For a select few sites, either the GeoTrax Survey™ 2-D images or data from a site monitoring well network will provide the data required to fulfill the project objectives and develop a solid conceptual site model. However, for most sites, Aestus' experience indicates that data integration of the geophysical images and conventional site investigation data (i.e., from monitoring wells, soil borings, etc.) into a 3-D model is necessary to interpret the collective data sets, develop a useful conceptual site model, and fulfill the project objectives. The following section of this report discusses data integration and data interpretation for the Plume Trackdown Site.

5.0 DATA INTEGRATION AND INTERPRETATION

This section discusses data Aestus' data integration work and subsequent interpretation of our GeoTrax Survey™ data relative to the Plume Trackdown Site issues and existing conceptual site model. These interpretations are based on information available as of the date of this report and applying Aestus' professional judgment based on experience imaging other similar project sites.

The first step in Aestus' interpretation process is to generate a Common Earth Model framework (discussed below) for the Plume Trackdown Site which facilitates calibration of our GeoTrax Survey™ electrical resistivity data/images against surface features (e.g., buildings or tanks) and known subsurface conditions at discrete points (e.g., monitoring wells). Historical site data is incorporated into this Common Earth Model framework in addition to Aestus' electrical resistivity data.

The end goal is to develop the most appropriate color contouring scheme(s) for the electrical resistivity data that best highlights zones of interest in the subsurface (e.g., contaminated versus clean conditions). Because each site that Aestus' images is different electrically due to varying hydrogeology, types and concentrations of contaminants, etc., this is an iterative process that is very site specific and is assisted by use of the Common Earth Model approach.

5.1 Data Integration Using Common Earth Model Framework

From Aestus' perspective, the end goal of any environmental site characterization is to use all available data collected at a site to visualize the earth's subsurface in 3-D and understand where sources of contamination may exist and to where and how contamination may be migrating. This process is most useful if the end result provides a conceptual site model that is more objective (i.e., and therefore less subjective), based on multiple data sets, and relatively easy to understand by different project stakeholders. To this end, Aestus has adapted an approach developed by the Canadian mining industry called the "Common Earth Model" defined as the following by McGuaghey, J. (2006):

> *"An explicit, quantitative model of the earth consistent with all data, testable by drilling, and subject to editing and refinement as the collection of new data proceeds. As a quantitative distillation of everything our data have to tell us about the earth, a common earth model is a requirement for maximizing the value we obtain from our large investment in data collection."*

Our adaptation of this approach for use in the environmental industry is effectively to get all available and geospatially relevant data into one place so that it can be viewed together rather than in separate pieces. For the a typical site this includes assembling data including geophysical data, monitoring well data, soil boring data (including PID data), indoor air quality data, utility line data, UST location data, etc. and posting these data onto our 2-D GeoTrax Survey™ images, and also including as much of this information as practical into our 3-D visualization software. Aestus uses Rockworks™ as our standard approach for 3-D visualization (i.e., used for this project) and sometimes uses Earthvision® for development of a solid 3-D model; if data density warrants this approach and our clients' budgets support this higher level of effort.

As a corollary to the above definition of Common Earth Model, it is important to note that organizations using this approach have learned not to arbitrarily discard one or more particular data sets when these data do not appear to agree to other data sets. This happens frequently in the environmental industry when multiple consulting firms work on a particular site over a period of years or decades and were not directly involved in the collection of each data set.

Seasoned Common Earth Model users have learned empirically to investigate further when two or more data sets do not agree at a specific location at a site, because the probability is high this will result in gaining useful knowledge about the site.

5.2 Historical Site Data Integration onto GeoTrax Survey™ 2-D Images

Aestus reviewed available Plume Trackdown Site data provided by EA, and determined that some monitoring well and soil boring data exists near Aestus' survey locations at the Plume Trackdown Site for use in the Common Earth Model and for correlating the resistivity ranges detected by the GeoTrax Surveys™ to the site geology, groundwater quality, presence of contamination, etc. Specifically, Aestus posted existing nearby monitoring well locations and site characterization data onto the survey images (see Figures 2 and 3).

By superimposing all of these data sets together graphically on each survey image, the reader can better understand the character and makeup of the subsurface. The data posted includes:

- ✓ Location, depth, and screened intervals of existing monitoring wells, if known (data provided by EA)
- ✓ Fluid level measurement data (provided by EA)
- ✓ Groundwater quality data (provided by EA)
- ✓ Plume Trackdown Site features (e.g. buildings, utilities, former UST locations, etc.)

Aestus posted data from borings/monitoring wells located within 15 feet of our survey line locations for the purposes of comparing and contrasting these data sets and calibrating Aestus' electrical images to chemical concentration data. However, when reviewing these data in the Common Earth Model framework, it is important for the reader to understand the following:

1. Conditions in the subsurface can and often do change within a few feet and so the degree of correlation between well data and survey images is expected to decrease as the distance of the well from the survey line increases.
2. Not all of the data sets (e.g., GeoTrax Survey™, boring log data, groundwater analytical data, etc.) viewed on the same page (in Figures of report) were collected at the same point in time.

5.3 Data Integration into 3-D Model

To assist ourselves and EA personnel with visualizing the GeoTrax Survey™ subsurface images as they relate to one another, Aestus used data collected from our 2-D imaging process to generate a 3-D representation of these data in the subsurface of the Plume Trackdown Site. We and our clients typically find that the results of the 3-D visualization work are very helpful in providing a more complete and somewhat simplified understanding of the survey data/images, ultimately yielding a better understanding of the subsurface at a given site. The 3-D visualizations are also very useful in explaining site conceptual models and features to both technical and non-technical stakeholders.

To allow viewing of our survey images to scale in 3-D space, Aestus developed a technique to import and properly position and scale the survey images in 3-D drawing space and relative to the site base map using Rockworks™ 3-D visualization software. Although the perspective 3-D views resulting from these efforts are based on 2-D data sets (i.e., the electrical resistivity data was not collected in 3-D during the survey work), Aestus has a higher confidence in our approach relative to the conventional approach of using only 1-D monitoring well data points and the resulting interpolations between these discrete points.

For Aestus' 3-D visualization work, thousands of field data points (collected in 2-D) were used as input to develop the 3-D perspective views. Screen shots of some 3-D perspective views are shown in Figures 4 through 7, and the entire 3-D model and free viewer are included as an electronic Appendix to this report. Site data imported into Aestus' 3-D model for the Plume Trackdown Site include the following:

- ✓ GeoTrax Survey™ transect locations and identification labels
- ✓ GeoTrax Survey™ images
- ✓ Site monitoring wells (black is casing; yellow is screened interval; location based on survey data provided by EA)
- ✓ Groundwater potentiometric surface (modeled surface based on November 1, 2010 groundwater level data provided by EA)

It should be noted that the monitoring well locations posted in our 3-D model are based on land survey data collected by Aestus. As mentioned above for the data integrated into the 2-D survey images, it is important to understand that not all of these data sets integrated into 3-D are exactly aligned temporally and/or spatially.

A few representative isometric 3-D perspective views of the survey images representing the subsurface of the Plume Trackdown Site are provided as shown in Figures 4 through 7. The GeoTrax Survey™ images shown in these 3-D perspective views are presented in two custom (site specific) color contouring schemes as discussed below in Section 5.4 (Color Contouring Electrical Resistivity Imaging Data) of this report.

Because the 3-D visualization work performed by Aestus was extensive and many different views of these data can be generated using this tool, it is not practical to provide all of these views as part of the hardcopy report. However, Aestus is providing a copy of our 3-D model files for viewing by EA personnel using a free viewer provided by Rockworks™. This data and instructions on downloading and using the free viewer software are contained on the CD-ROM enclosed with the hardcopy of this report.

Aestus is confident that this 3-D visualization work will assist EA with enhanced understanding of the location and extent of anomalous areas at the Plume Trackdown Site, and to better communicate these issues to other project stakeholders.

5.4 Color Contouring Electrical Resistivity Imaging Data

Upon completion of the data processing work discussed in Section 3.0 of this report, the resistivity data set is fixed and is not modified from that point forward. However, Aestus does modify the color contouring scheme(s) used to effectively contour these data (i.e., show various ranges of resistivities detected at the site using different colors) to allow us and our clients to understand what the data means. The color modification process is similar to re-contouring a topographic map (i.e., the elevation points never change, but the contour interval is altered to produce different maps highlighting various features or range of resistivities).

This section provides an overview of the resistivities of common site features and contaminants, and discusses the development of a site specific color contouring scheme for the Plume Trackdown Site.

5.4.1 Resistivities of Common Site Features and Contaminants

The magnitude of subsurface resistivity values will vary from site to site based on a number of factors, and is related to geology composition and to the chemistry of the groundwater and other fluids trapped in the pore spaces within the soil matrix and the presence or absence of buried debris and structures. For a typical site, fine materials such as clay and silt are generally less resistive (i.e., more conductive) while coarse sand and gravel are generally more resistive (i.e., less conductive). Should the soil (clay or sand) be dry, it will appear more resistive when dry and less resistive when wet. Should a distinct groundwater table exist in the area being surveyed, the groundwater interface is often not seen in the survey images because of the "blurring" effects of capillary fringe, and because the resistivity of the ground water is often times similar to the resistivity of the soil matrix.

Additionally, the presence of contaminants within the pore matrix can overshadow (electrically) the signature from native geology and/or the presence of groundwater or degree of saturation. The presence of fractures in bedrock geology often appear as a vertically oriented anomaly and may be either conductive or resistive depending on what type of fluid (e.g., clean groundwater and/or unweathered/weathered contamination) is present within the fracture. Bedrock interfaces are sometimes identifiable depending on the degree of weathering at the transition to bedrock, the degree of saturation, and the presence or absence of contamination.

Should buried tanks or other man-made structures be present coincident with survey line locations, they typically show up in our survey images as either low resistivity/highly conductive (metallic construction) or high resistivity/low conductivity (fiberglass, concrete or other construction). In areas where tanks or sumps have been removed or replaced, these areas may or may not present in our images as an anomaly depending on whether native or non-native fill soils were used as backfill. If contamination is present underneath former tanks and sump areas, it generally presents as described in the following paragraphs.

Subsurface areas impacted with fresh or unweathered light or dense non-aqueous liquids (LNAPLs or DNAPLs, respectively) and related dissolved phase contamination typically present as more resistive anomalous zones relative to areas that contain only non-impacted soils and pore fluids. Based on our experience, areas containing NAPL impacted soils often present as a roughly spherical or lenticular blob shape (obloid) and will typically be identified in our survey images by more resistive values.

Sometimes, the presence of this type of contamination can cause a less resistive (i.e., very conductive) anomaly or zone, particularly with weathered LNAPL-related contamination. Aestus believes the reason that weathered LNAPL-related contamination shows as conductive in our images is naturally occurring bioactivity in the subsurface in contaminated zones that alters the electrical properties of these materials. This phenomenon is well documented in technical literature related to the study of LNAPLs in particular (see example technical paper included as Appendix B) and Aestus' clients have drilled and confirmed the presence of LNAPL within electrically conductive anomalies at many different project sites.

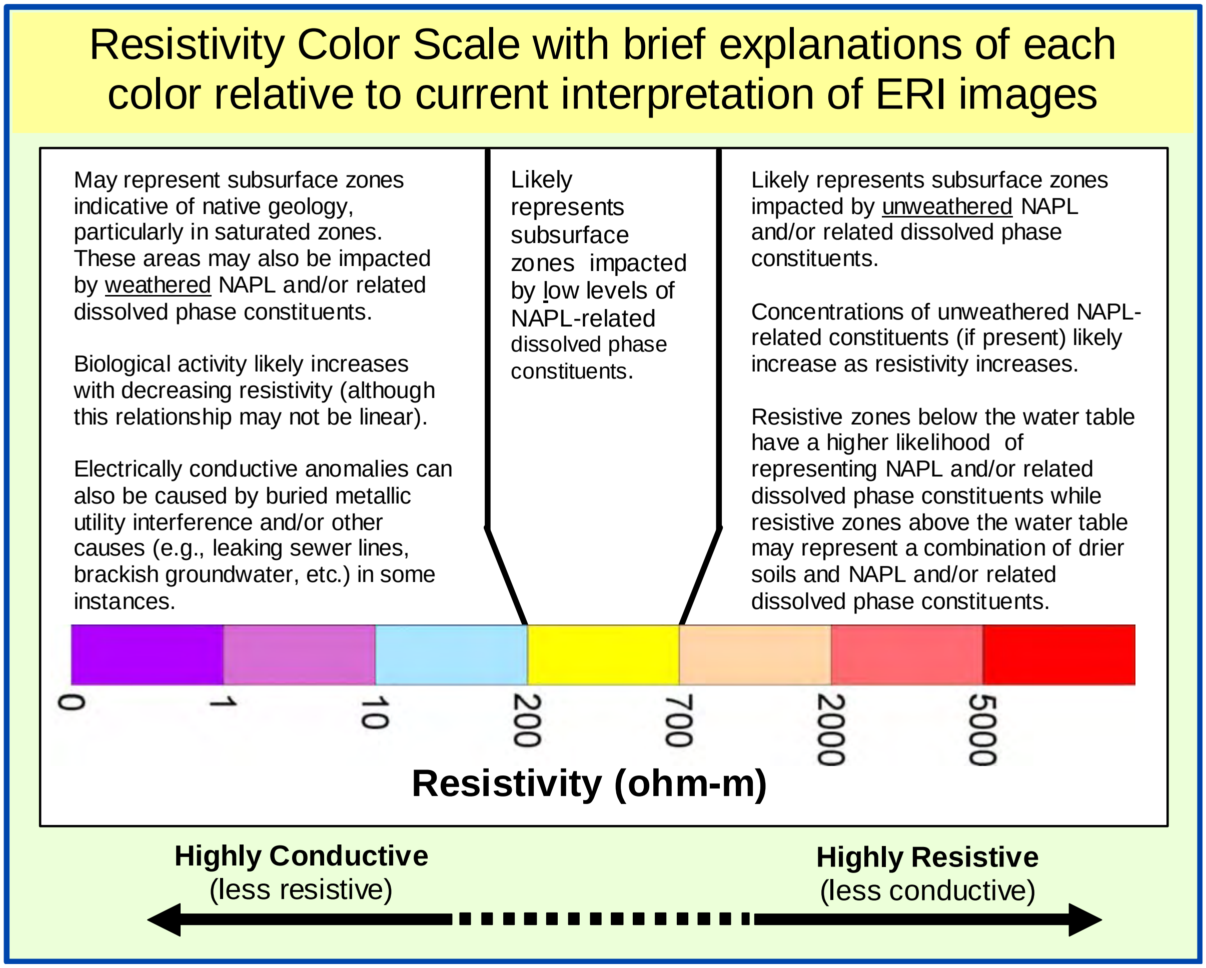
In zones where bio-activity is present, Aestus is actually imaging byproducts of chemical reactions related to bio-activity, versus actual LNAPL-related contamination signatures. Because of this, Aestus is sometimes unable to correlate a specific resistivity (i.e., ohm-meter) range to a certain concentration of contaminant (i.e. free product verses dissolved phase). Conversely, for electrically resistive anomalies that represent the actual electrical properties of the contaminants, Aestus is often able to develop a semi-quantatative relationship between ranges of resistivity and contaminant concentrations.

The mechanism that apparently causes DNAPL-related contamination (e.g., chlorinated solvents) to show as electrically conductive in our survey images is less clear and research conclusions less definitive at the time of this report. However, technical papers exist (see example contained in Appendix C) that discuss byproducts of in-situ chlorinated solvent biodegradation containing chloride amongst other compounds. Aestus theorizes that the presence of chloride and/or other ions in zones of natural attenuation would likely create a very electrically conductive signature detectable by our GeoTrax Survey™ technology in many cases. Our experience to-date indicates that varying degrees of reduction in resistivity can occur depending on levels of ongoing natural and/or enhanced biodegradation.

GeoTrax Surveys™ normally can identify areas impacted by dissolved concentration impacts to the groundwater from a former or existing source of contamination. Sometimes dissolved phase impacts do not present as anomalies because lower levels of dissolved phase contamination cause relatively small changes in electrical properties of the subsurface and have the potential to be masked by changes in resistivity signatures of various soil types that may exist across a typical site. Often times with lower dissolved phase concentrations, Aestus believes that we may be detecting where groundwater is flowing preferentially (and contamination is moving with the groundwater) such that we can locate more contaminated zones in the subsurface. This occurs for example in karstic and/or fractured geologic environments.

5.4.2 Development of Site Specific Color Contouring Schemes

Upon posting of all available nearby monitoring well and soil boring data to our survey images and comparing these data to our survey data visualized in multiple preliminary color contouring schemes, a relatively clear and consistent trend was evident for the Plume Trackdown Site data. Aestus developed the following custom color contouring scheme which correlated as follows with the majority of the Common Earth Model data (shown graphically below and also contained in the Figures section of this report):



Resistivity Color Scale with brief explanations of each color relative to current interpretation of ERI images

May represent subsurface zones indicative of native geology, particularly in saturated zones. These areas may also be impacted by <u>weathered</u> NAPL and/or related dissolved phase constituents.

Biological activity likely increases with decreasing resistivity (although this relationship may not be linear).

Electrically conductive anomalies can also be caused by buried metallic utility interference and/or other causes (e.g., leaking sewer lines, brackish groundwater, etc.) in some instances.

Likely represents subsurface zones impacted by <u>l</u>ow levels of NAPL-related dissolved phase constituents.

Likely represents subsurface zones impacted by <u>unweathered</u> NAPL and/or related dissolved phase constituents.

Concentrations of unweathered NAPL-related constituents (if present) likely increase as resistivity increases.

Resistive zones below the water table have a higher likelihood of representing NAPL and/or related dissolved phase constituents while resistive zones above the water table may represent a combination of drier soils and NAPL and/or related dissolved phase constituents.

As shown in the custom color contouring scheme resistivity scale above (<u>see larger version of this resistivity scale on Figure LS-2</u>), Aestus interpreted zones below 200 ohm-m to be areas of native geology, particularly in saturated zones. It is possible that these zones may be impacted by weathered NAPL-related dissolved phase constituents.

Subsurface zones between 200 and 700 ohm-m are interpreted to be areas that are impacted by low levels of NAPL-related dissolved phase constituents.

Subsurface zones above 700 ohm-m are interpreted to be areas impacted by relatively unweathered NAPL and or NAPL-related dissolved phase constituents. In areas above the water table, zones in this range may indicate geology with lower moisture contents. Below the water table, zones in this range are more likely representative of DNAPL-related impacts. To allow the reader to view these resistive zones more clearly, they are highlighted in red colors (i.e., with the remaining ranges of resistivity shown in gray) in a second color contouring scheme shown in the 3-D model and as shown on Figures 5 and 7.

6.0 CONCLUSIONS

In summary, Aestus believes that our high resolution subsurface imaging technology worked very well at the Plume Trackdown Site to achieve the project objectives at this interim stage in the overall site characterization and remediation project. The GeoTrax Survey™ data set has identified subsurface electrically conductive and resistive anomalous zones that in our experience appear to be consistent with the presence of DNAPL-related impacts. These data will assist EA by focusing follow up investigation) via drilling (if deemed necessary), and ultimately with remedial strategy and optimizing the placement of remedial or containment systems (if needed).

Aestus offers the below conclusions as a result of reviewing the Common Earth Model data set, which includes the 2-D survey images (Figures 2 and 3 with historical drilling investigation data posted) and the 3-D model developed using Rockworks™ 3-D modeling software (example 3-D perspective views of the combined data set generated using the 3-D model are shown in Figures 4 through 7). Because the Plume Trackdown Site and resulting survey images are complex, not all anomalous zones are discussed. As discussed previously, it is important for the reader to recognize that not all of the data sets combined in the Common Earth Model are exactly aligned temporally or geospatially.

As with all environmental assessments, these conclusions are reached with a certain acceptable degree of uncertainty, due to the possibility that relevant subsurface conditions may exist beyond the scope of this geophysical investigation. The below conclusions are subject to revision based on any follow up drilling/sampling data from anomalous locations detected by Aestus.

Conclusions Based on Correlative Data

Aestus offers the following conclusions with a relatively high level of confidence at this interim stage in the project, because some correlative data exists (e.g. soil boring and/or monitoring well data, etc.) to verify them.

- ✓ There is a very resistive anomalous zone (> 5000 ohm-m) near the bottom of image MEL-01 (Figure 2) which likely represents impact by DNAPL and/or DNAPL-related constituents. Existing monitoring well MW-05 intersects this highly resistive zone in the subsurface, and groundwater sampling shows that several DNAPL-related constituents exceed water quality standards. The location of this strong resistive zone below the water table also supports the conclusion the anomaly is representative of DNAPL-related impacts. Aestus understands from EA/NYSDEC that contamination at this location is believed to be associated with the former New York Twist Drill property located along Melville Park Road (see GeoTrax Survey™ and well locations on Figure PV-1).
- ✓ The yellow resistive zone on image MEL-01 (Figure 2) likely indicates a zone with very minimal concentrations of dissolved phase DNAPL-related constituents as confirmed by groundwater quality data from existing monitoring well MW-06.

- ✓ Image MEL-01 has deeper very resistive anomalies while image MEL-02 does not. Because MEL-01 is presumably downgradient from potential source areas, this finding makes sense and could be considered consistent with site history.
- ✓ Comparison of survey images from MEL-01 and MEL-03 (Figures 1 and 3), which were essentially run in the same location but months apart temporally, have very good agreement in the parts of the survey that overlap despite minor variations due to different imaging depths. Comparisons can be made in the 3-D model included as an electronic appendix to this report. These data support repeatability of the survey method.

<u>Conclusions Based on Geophysical Data and Aestus' Experience with DNAPL Sites</u>

Aestus offers the following conclusions with a relatively moderate level of confidence at this interim stage in the project based on our experience with using our GeoTrax Survey™ technology at sites across the world.

- ✓ Very resistive zones (> 5000 ohm-m) from 0-100 feet BGS are suspicious as this range is the same as the subsurface anomaly discussed on MEL-01 (Figure 2) which has confirmed DNAPL-related impact through sampling. Because these areas are above the water table (Figure 7), these zones may represent dry geology, but could also represent shallow contamination impacts as evidenced by historical groundwater analytical data of wells in the vicinity.

<u>Conclusions Based on Common Earth Model Data and with Lower Levels of Certainty</u>

Aestus offers the following conclusions based on our review of all data sets integrated into our Common Earth Model and may include discussions apart from electrical resistivity data but which may affect overall interpretation and conceptual site model. These conclusions are reached with a lower level of certainty and additional data or consideration may be required to ground truth these conclusions.

- ✓ When high concentrations of daughter products like cis 1,2 DCE are present in greater amounts than potential parent products like TCE or PCE, Aestus typically sees extremely conductive anomalies (i.e., generally <10 ohm-meters) associated with the biodegradation of the parent products. Although Aestus did not detect extremely conductive anomalies of significance, groundwater sampling for MW-05 indicate concentrations of cis 1,2 DCE at 129 ppb, TCE values of 5.46 ppb, and PCE values of 56.4 ppb, which would seem to indicate that either cis 1,2 DCE was used as a solvent and is a parent product, or some level of degradation may be occurring in nearby subsurface zones. Aestus understands from NYSDEC that enhanced bio work has been performed at this site, which appears to have influenced/decreased concentrations at/near monitoring well MW-05. Our experience to-date indicates that varying degrees of reduction in resistivity can occur depending on levels of ongoing natural and/or enhanced biodegradation.

- ✓ A large moderate resistivity zone (blue-colored) exists along image MEL-02 (Figure 3) and below the modeled water table zone in the 3-D model (Figure 6). The relatively planar geometry of this zone and its position below the water table indicate that this zone is likely representative of native geology that has a higher moisture content that zones above the water table. Assuming this interpretation is correct, then the data suggests that it is unlikely that a significant contaminant source exists immediately upgradient of the survey line MEL-02 location. Confirmation drilling data is required if EA/NYSDEC desires to confirm this interpretation with a higher level of confidence.

The following section of this report provides recommendations based on the aggregate data set and the above conclusions.

7.0 RECOMMENDATIONS

This section provides Aestus' recommendations moving forward, based on the results and conclusions developed from our work.

7.1 3-D Model Review

To be able to fully understand the GeoTrax Survey™ data collected and visualize it in a robust manner in 3-D, Aestus recommends that the reader use the provided free 3-D model viewer to look at these areas more closely on-screen and from different perspectives as screen captures from the 3D model of the site (i.e. imported into Figures 4 through 7) do not provide as complete of an understanding of the available site data. Additionally, the resolution of these hardcopy figures is lower than reviewing the model on a computer monitor screen.

7.2 Web Conference Review

Because this site and the resulting integrated conventional and geophysical survey data sets are complex, Aestus recommends that EA/NYSDEC and Aestus conduct a web conference to review this report together, field questions, and assist in conveying understanding of conclusions based on this work.

7.3 Follow-up Confirmation Drilling & Sampling Program

As discussed during the proposal phase of this project, Aestus' survey results do not immediately identify the composition of anomalies which may be caused by variations in geology and/or moisture content (or other factors) in addition to the presence of subsurface contamination. Final data interpretation is greatly enhanced by calibrating or benchmarking the GeoTrax Survey™ electrical resistivity images against existing site data and/or follow-up confirmation boring/monitoring well data. This process lends much greater understanding of the subsurface and the survey images.

Therefore, Aestus recommends that EA consider performing a focused confirmation drilling program to confirm the composition of the various geophysical anomalies detected at multiple locations across the Plume Trackdown Site, assuming this additional effort is in alignment with overall project strategy and goals. The power and economy of the GeoTrax Survey™ technology is further increased once the cause of various anomaly types is confirmed via drilling. At that point extrapolated conclusions regarding other anomalous areas of the Plume Trackdown Site can be made with a relatively high level of confidence without having to drill every single anomalous zone detected.

Ideally drilling confirmation borings should be performed as soon as possible so that potential changes in site conditions are minimized. Aestus recommends that these borings be completed as monitoring wells such that the presence of NAPL and/or levels of dissolved phase constituents can be better quantified. Additionally, Aestus' GeoTrax Survey™ technology detects groundwater impacts preferentially over soil impact, making groundwater quality data very helpful.

Aestus has provided suggested confirmation boring locations as shown in plan view on Figure PV-2, on the 2-D survey images in Figures 1 through 3. Specific locations of these proposed confirmation borings are summarized in Table 5.

It is critical that confirmation borings/wells be installed exactly on the alignment of our survey lines whenever possible so that drilling data can be directly correlated to geophysical data from a geospatial perspective. This is particularly important on complex sites such as the Plume Trackdown Site where subsurface conditions likely change even within a few feet in some cases.

To assist in properly locating confirmation drilling locations, Aestus has provided geospatial data relative to our survey line endpoint locations in Tables 3 and 4, and our field notes contained in Appendix A. Select site photos are shown in on Figure 8, and the entire set of site photos (contained on CD-ROM included with hardcopy version of this report) can also be used to field locate confirmation borings.

7.4 Sampling Methodology and Analyte Selection for Confirmation Drilling Program

It is important in Aestus' experience that EA carefully consider sampling methodology and analyte selection during work plan development/modifications for confirmation drilling. Sampling methodology is critical to be able to effectively collect samples/measurements at the target anomaly depths identified by the geophysical work. It is important to log geology/lithology during drilling such that we collectively better understand the effects of geology/hydrogeology on contaminant migration pathways at the Plume Trackdown Site.

Aestus' technology "sees" all subsurface features together and was never designed to be a quantitative analytical tool that can automatically screen for one compound or family of compounds. Therefore, if analytes are selected to only screen for DNAPL-related constituents, then it is important to understand that the cause of anomalies detected may not be identified if for instance they are being caused by the presence of LNAPL, heavy metals, and/or other types of contamination.

Aestus also recommends that EA consider sampling for the following groundwater parameters which help indicate the presence of biodegradation:

1. Dissolved Oxygen
2. Temperature
3. PH
4. Conductivity
5. ReDox Potential
6. Alkalinity
7. Nitrate
8. Manganese
9. Iron II
10. Iron III
11. Sulfate
12. Chloride
13. Methane

These parameters will help in identifying areas which are biologically active and areas that would potentially benefit from a remediation strategy involving enhancing naturally occurring bioactivity. Aestus' survey images can sometimes be used to support natural attenuation arguments, after bio-parameter data is used to further calibrate detected resistivity levels to bioparameter data from groundwater samples.

Additionally, EA may want to consider methanol preservation/extraction for any future soil samples collected at the Plume Trackdown Site. Aestus, in our work with various state regulators, consultants, and laboratories has learned empirically that the methanol extraction methodology yields more accurate results by avoiding "false negatives" particularly in fine-grained soils or consolidated matrix.

Finally, future monitoring wells should be screened based on Aestus' survey images and observations during drilling relative to presence/absence of contamination at depth. It may also be useful for EA to verify vertical gradients using nested monitoring wells.

7.5 Updates to Common Earth Model and Future Aestus Involvement

As discussed in Section 5.1 the first part of the definition of the Common Earth Model is:

> "An explicit, quantitative model of the earth consistent with all data, testable by drilling, and subject to editing and refinement as the collection of new data proceeds.

Therefore, Aestus recommends that EA provide the results of future site investigation tasks to Aestus, so we can update our Common Earth Model components (i.e., 2-D images and 3-D model, and related data color contouring schemes) and refine our interpretations, as appropriate, based on these results to further improve the conceptual site model and overall understanding of site issues in the subsurface. These results can be submitted in a revised final report format if desired by EA/NYSDEC.

TABLES

Table 1
Electrode Spacing, Survey Line Length, and Survey Depth
Plume Trackdown Site
Melville, New York, USA

Survey ID	Electrode Spacing (m)	Survey Line Length (ft)	Image Depth (ft)
MEL-01	5	902	180
MEL-02	6	1082	216
MEL-03	6	1082	216

Table 2
GeoTrax Survey™ End Point Coordinates
Plume Trackdown Site
Melville, NY, USA

Survey ID	Coordinate System[1]	Electrode 1			Electrode 56		
		Easting (ft)	Northing (ft)	Elevation (ft)	Easting (ft)	Northing (ft)	Elevation (ft)
MEL-01	NYSP	1,145,534.88	222,109.46	114.52	1146432.53	222207.43	115.57
MEL-02	NYSP	1,145,746.62	223,148.08	119.76	1146815.07	223327.52	117.92
MEL-03	NYSP	1,145,543.92	222,103.01	114.73	1146618.31	222232.77	116.14

Notes:

1. Coordinate system is New York State Plane, NAD83.

Aestus, LLC

Table 3
Distance Along Survey Line from Electrode No. 1 (5.0 m Spacing)
Plume Trackdown Site
Melville, NY, USA

5.0 meter spacing					
Electrode	**Meters**	**Feet**	**Electrode**	**Meters**	**Feet**
1	0.00	0	**29**	140.00	459
2	5.00	16	**30**	145.00	476
3	10.00	33	**31**	150.00	492
4	15.00	49	**32**	155.00	509
5	20.00	66	**33**	160.00	525
6	25.00	82	**34**	165.00	541
7	30.00	98	**35**	170.00	558
8	35.00	115	**36**	175.00	574
9	40.00	131	**37**	180.00	591
10	45.00	148	**38**	185.00	607
11	50.00	164	**39**	190.00	623
12	55.00	180	**40**	195.00	640
13	60.00	197	**41**	200.00	656
14	65.00	213	**42**	205.00	673
15	70.00	230	**43**	210.00	689
16	75.00	246	**44**	215.00	705
17	80.00	262	**45**	220.00	722
18	85.00	279	**46**	225.00	738
19	90.00	295	**47**	230.00	755
20	95.00	312	**48**	235.00	771
21	100.00	328	**49**	240.00	787
22	105.00	344	**50**	245.00	804
23	110.00	361	**51**	250.00	820
24	115.00	377	**52**	255.00	837
25	120.00	394	**53**	260.00	853
26	125.00	410	**54**	265.00	869
27	130.00	427	**55**	270.00	886
28	135.00	443	**56**	275.00	902

* NOTE: Survey MEL-01 had a 5.0 meter electrode spacing.

Table 4
Distance Along Survey Line from Electrode No. 1 (6.0 m Spacing)
Plume Trackdown Site
Melville, NY, USA

6.0 meter spacing					
Electrode	**Meters**	**Feet**	**Electrode**	**Meters**	**Feet**
1	0.00	0	**29**	168.00	551
2	6.00	20	**30**	174.00	571
3	12.00	39	**31**	180.00	591
4	18.00	59	**32**	186.00	610
5	24.00	79	**33**	192.00	630
6	30.00	98	**34**	198.00	650
7	36.00	118	**35**	204.00	669
8	42.00	138	**36**	210.00	689
9	48.00	157	**37**	216.00	709
10	54.00	177	**38**	222.00	728
11	60.00	197	**39**	228.00	748
12	66.00	217	**40**	234.00	768
13	72.00	236	**41**	240.00	787
14	78.00	256	**42**	246.00	807
15	84.00	276	**43**	252.00	827
16	90.00	295	**44**	258.00	846
17	96.00	315	**45**	264.00	866
18	102.00	335	**46**	270.00	886
19	108.00	354	**47**	276.00	906
20	114.00	374	**48**	282.00	925
21	120.00	394	**49**	288.00	945
22	126.00	413	**50**	294.00	965
23	132.00	433	**51**	300.00	984
24	138.00	453	**52**	306.00	1004
25	144.00	472	**53**	312.00	1024
26	150.00	492	**54**	318.00	1043
27	156.00	512	**55**	324.00	1063
28	162.00	531	**56**	330.00	1083

* NOTE: Surveys MEL-02 and MEL-03 had a 6.0 meter electrode spacing.

Table 5
Confirmation Well Locations Suggested by Aestus, LLC[1]
Plume Trackdown Site
Melville, New York, USA

Confirmation Boring No.	GeoTrax Survey™ ID	Confirmation Boring Distance from Electrode No. 1 (feet)	Confirmation Boring Distance from Electrode No. 56 (feet)	Anomaly Center of Mass (Screen Interval TBD in Field)[1] (feet BGS) (See Figures PV-2; 1 -3)	Logic/Purpose for Drilling Confirmation Boring at this Location (Confirm Presence or Absence of Contamination and/or Geologic Anomaly)	Confirmation Boring Locations NY State Plane, NAD83	
						Northing (ft)	Easting (ft)
CW-1A	**MEL-01**	620.0	282.0	15-70'	This confirmation well investigates a highly resistive anomaly that is connected to a similar anomaly in the subsurface which intersects MW-5, a well with known impact.	222176.83	1146151.41
CW-1B	**MEL-01**	750.0	152.0	65-150'	This confirmation well investigates a conductive area which may represent clean geology, or impacts undergoing some level of natural attenuation.	222190.96	1146279.65
CW-3A	**MEL-03**	490.0	592.0	135-210'	This confirmation well investigates a highly resistive anomaly for the presence of contamination.	222162.15	1146030.41
CW-2A	**MEL-02**	220.0	862.0	0-80'	This confirmation well investigates a highly resistive anomaly for potential presence of contamination and/or drier soils.	223187.51	1145963.14
CW-2B	**MEL-02**	400.0	682.0	50-120'	This confirmation well investigates an anomalous zone near the bottom of the image to determine if the presence of contamination caused the anomaly.	223219.55	1146140.59

Notes:

1. Aestus recommends the above confirmation boring locations selected to confirm composition and presence/absence of contamination in the various types of electrical anomalies encountered at the site. Screen intervals for confirmation wells should be based on field observation and PID readings during drilling.

2. Drilling Methodology: Aestus recommends the following for achieving overall project success:

   a. It is critical that confirmation borings be installed directly along the GeoTrax Survey™ alignment, particularly because some of targeted anomalies are very narrow.
   b. Continuous core sampling and detailed logging of cores noting soil type, moisture content, PID, etc.
   c. Use dual tube direct push techniques if soil conditions don't allow an open borehole to remain if using Macrocore techniques
   d. Completion of boreholes as monitoring wells if possible
   e. Sample Analysis: Aestus recommends the following analytes to be included during sampling at a minimum:

- Collect pH/Conductivity/Temp of groundwater samples if possible
- Full VOC suite for groundwater and soil samples (if collected)
- Major Ions (groundwater); EPA Method 300 or equivalent
- Bioparameters
  - -Dissolved Oxygen
  - -Temperature
  - -pH
  - -Fluid Conductivity
  - -ReDox Potential
  - -Alkalinity
  - -Nitrate
  - -Manganese
  - -Iron II
  - -Iron III
  - -Sulfate
  - -Chloride
  - -Methane
- Methanol extraction methodology for analysis of fine-grained soil samples

FIGURES

GeoTrax Survey ™ Investigation Results
Plume Trackdown Site
Melville, New York, USA

Aestus, LLC
1.888.GEO.TRAX
www.aestusllc.com

7 Red Oak Road
Wilmington, DE 19806

2605 Dotsero Court
Loveland, CO 80538

6005 West 19th Avenue
Stillwater, OK 74074

Scale:	NTS unless specified
Drawn By:	MAS
Approved By:	SWM
Date:	09-21-11
Project No.:	10-104-10

GeoTrax Survey ™ Investigation Results
Plume Trackdown Site
Melville, New York, USA

FINAL REPORT

Prepared for

EA Engineering, P.C. and its Affiliate
EA Science and Technology

DEPARTMENT OF ENVIRONMENTAL CONSERVATION • NEW YORK STATE •

FIGURE

TITLE PAGE

Legend and Symbols

(for reference when reviewing all Figures)

Electrode 1 — Electrode 56 **MEL-01**	GeoTrax Survey ™ Orientation and Designation (scale is approximate)
│	Indicates the location where an electric utility line crosses a GeoTrax Survey™ line
MW-01	Indicates the location, depth, and screened interval of site monitoring wells
CB/MW-1A ⋮	Indicates Aestus' suggested confirmation boring/monitoring well location and depth
05-12-10 ▽	Indicates most recent groundwater level per site monitoring well data
←	Indicates groundwater sample collected from well screen interval.
■ □	Indicates various site features which are labeled accordingly on the figures
Ⓜ	Indicates the location of a manhole
▯	Indicates the location of a light pole or phone pole
	In the 3D Figures, indicates the casing (beige) and screen (blue) of wells located onsite.

Groundwater Sample Results

Well		**MW-06**	**MW-05**
Sample Date		**11/15/10**	**11/15/10**
Parameters (µg/L)	**Standards (µg/L)**		
PCE	5	1.91 J	56.4 J
TCE	5	0.4 J	5.46
cis 1-2 DCE	5	0.35 J	129
trans 1-2-DCE	5	0.51	1.48
Methylene Chloride	5	<0.16 U	5.04 J
MTBE	10	<0.16 U	0.88 J
Toluene	5	0.37 J	0.42 J
Aluminum	100	700	210 J
Iron	300	790	230J

Analytical data from groundwater sample from a well or soil boring located within 15 feet of a GeoTrax Survey™ line.
Standards used are "NYSDEC ambient water quality standard class GA".

- J– Analyte positively identified, concentration value is an estimate
- U- Non-detect
- Yellow highlighted cells indicate values that exceed standards

General Notes:

1. *Locations of site features (e.g., utilities, wells, etc.) are approximate*

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Loveland, CO 80538

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Stillwater, OK 74074

Scale: NTS unless specified
Drawn By: MAS
Approved By: SWM
Date: 09-21-11
Project No.: 10-104-10

GeoTrax Survey ™ Investigation Results
Plume Trackdown Site
Melville, New York, USA

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FIGURE
LS-1

Electrical Resistivity Scale Explanation

(Custom Color Contouring Scheme; for reference when reviewing Figures 1 through 3)

Resistivity Color Scale with brief explanations of each color relative to current interpretation of ERI images

May represent subsurface zones indicative of native geology, particularly in saturated zones. These areas may also be impacted by <u>weathered</u> NAPL and/or related dissolved phase constituents.

Biological activity likely increases with decreasing resistivity (although this relationship may not be linear).

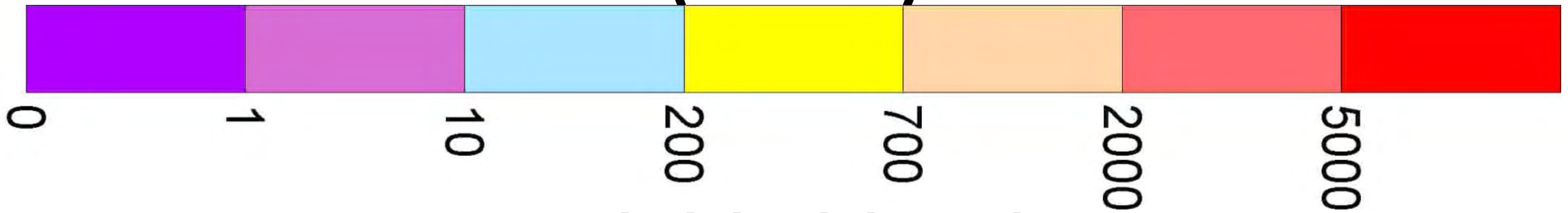
Electrically conductive anomalies can also be caused by buried metallic utility interference and/or other causes (e.g., leaking sewer lines, brackish groundwater, etc.) in some instances.

Likely represents subsurface zones impacted by <u>l</u>ow levels of NAPL-related dissolved phase constituents.

Likely represents subsurface zones impacted by <u>unweathered</u> NAPL and/or related dissolved phase constituents.

Concentrations of unweathered NAPL-related constituents (if present) likely increase as resistivity increases.

Resistive zones below the water table have a higher likelihood of representing NAPL and/or related dissolved phase constituents while resistive zones above the water table may represent a combination of drier soils and NAPL and/or related dissolved phase constituents.



Resistivity (ohm-m)

Highly Conductive
(less resistive)

Highly Resistive
(less conductive)

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FIGURE
LS-2

LEGEND:

Electrode 1 — Electrode 56

GeoTrax Survey ™ Orientation and Designation

🟥 **MEL-01**	**5.0 Meter Electrode Spacing** Survey Line ~ 902 feet Long Image Depth ~ 180 feet
🟩 **MEL-02**	**6.0 Meter Electrode Spacing** Survey Line ~ 1082 feet Long Image Depth ~ 216 feet
MW-03 ⌖	**Site Monitoring Wells**

NOTE:
1. Basemap is not to scale; placement relative to land surveyed locations of GeoTrax Survey™ is approximate.

N

0 250 500
feet

Reference: Aerial courtesy of USGS.

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Plan View Map Showing Site Features
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FIGURE
PV-1

LEGEND:

Electrode 1 — Electrode 56

GeoTrax Survey ™ Orientation and Designation

MEL-01 — **5.0 Meter Electrode Spacing**
Survey Line ~ 902 feet Long
Image Depth ~ 180 feet

MEL-02 — **6.0 Meter Electrode Spacing**
Survey Line ~ 1082 feet Long
Image Depth ~ 216 feet

MW-03 ⌖ **Site Monitoring Wells**

CW-1 ⌖ **Aestus' Suggested Confirmation Wells**

NOTE:

1. Basemap is not to scale; placement relative to land surveyed locations of GeoTrax Survey™ is approximate.

2. **THIS MAP IS FOR REFERENCE ONLY!** **Do not use this map to determine the locations of confirmation borings. Please use Table 8 to locate confirmation borings.**

N

0 250 500
feet

Reference: Aerial courtesy of USGS.

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Proposed Confirmation Boring Locations
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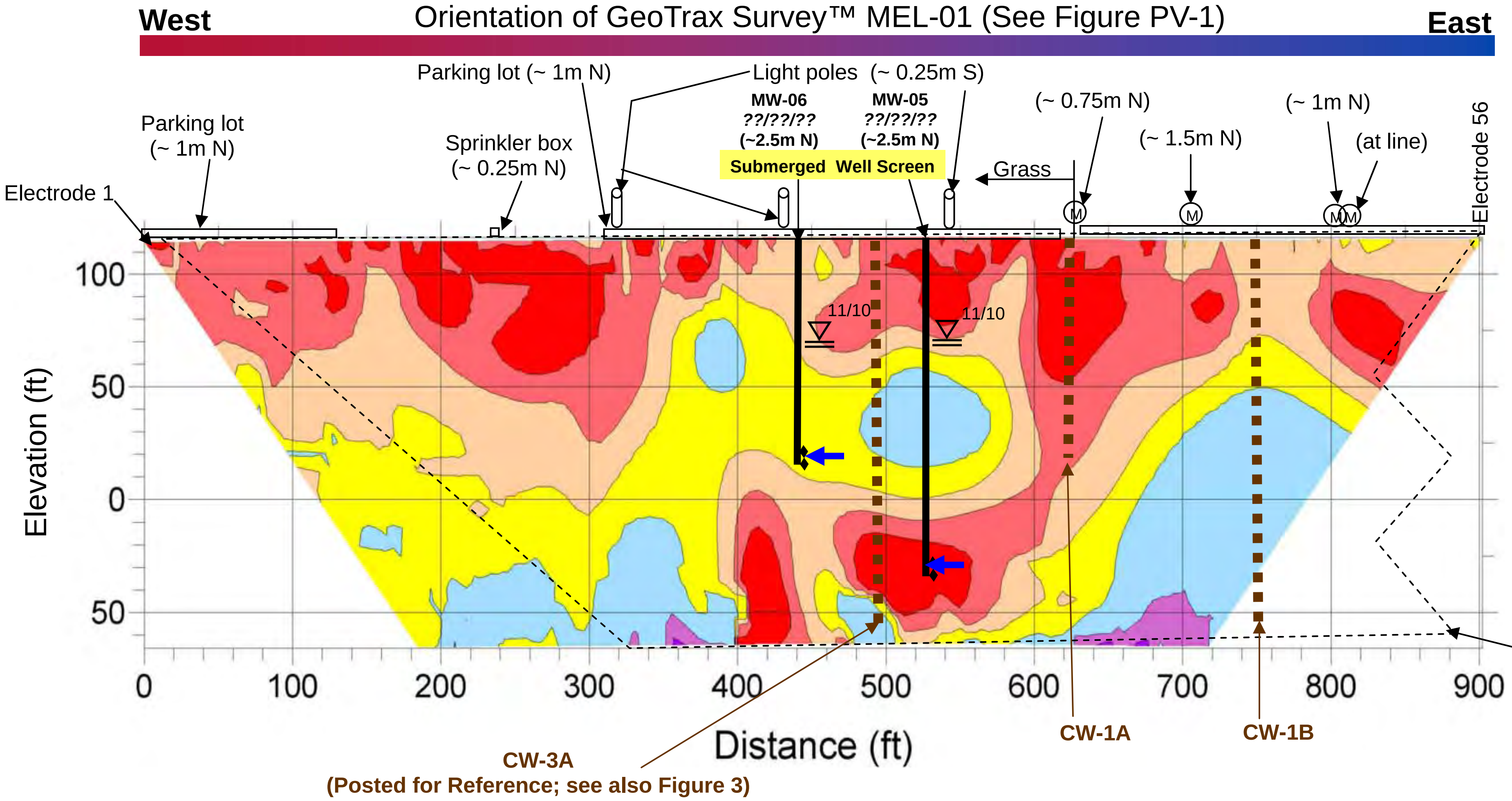
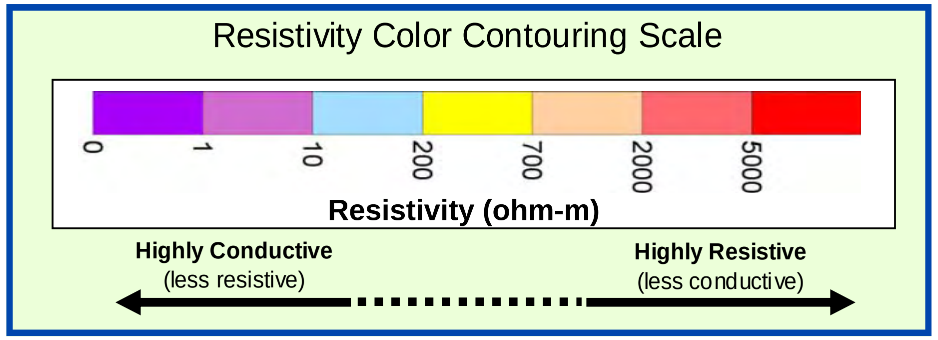
FIGURE
PV-2



Image/Data Interpretation Notes:

1. For this report, Aestus' initial interpretations are provided in conjunction with the resistivity scale bar on the Legends and Symbols page. These interpretations will be revised and/or refined as appropriate based on confirmation boring data.
2. Topographic correction based on topo estimation performed by Aestus field crew using a Topcon total station.



Groundwater Sample Results					
Well		**MW-06**	**MW-06**	**MW-05**	**MW-05**
Sample Date		**11/15/10**	**07/11/11**	**11/15/10**	**07/11/11**
Parameters (µg/L)	**Standards (µg/L)**				
PCE	5	1.91 J	0.84	56.4	42
TCE	5	0.4 J	0.19 J	5.46	8 J
cis 1-2 DCE	5	0.35 J	0.18 J	129	1170
trans 1-2-DCE	5	0.51	ND	1.48	10.5 J
Methylene Chloride	5	<0.16 U	ND	5.04 J	26.5 J
MTBE	10	<0.16 U	ND	0.88 J	ND
Toluene	5	0.37 J	ND	0.42 J	ND
Aluminum	100	700	4200	210 J	180
Iron	300	790	6200	230J	490

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GeoTrax Survey TM Investigation Results
Plume Trackdown Site
Melville, New York, USA

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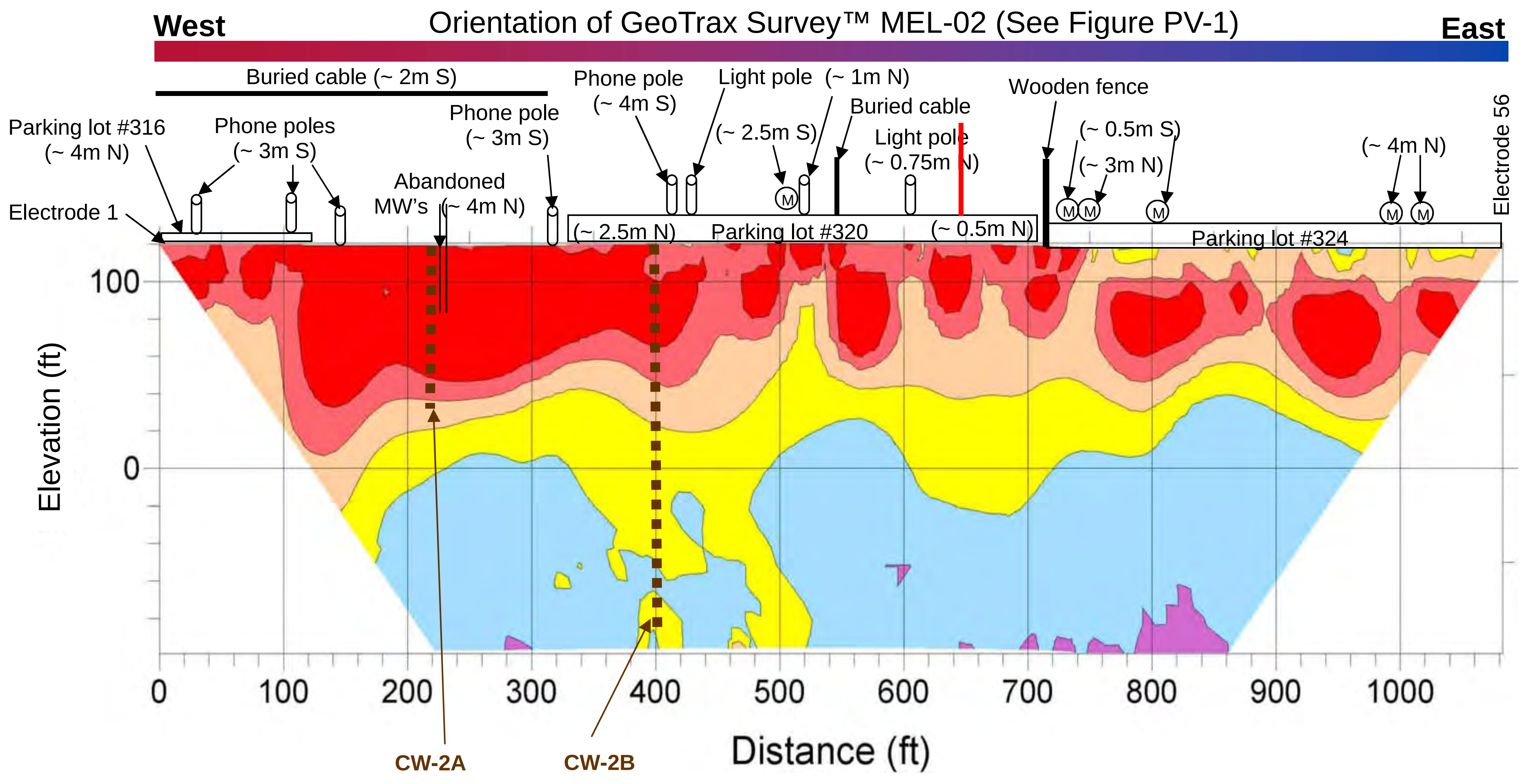
FIGURE
1



Image/Data Interpretation Notes:

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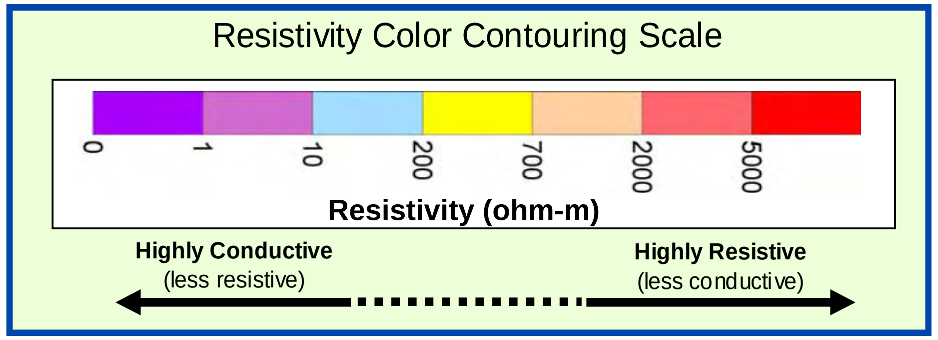
2. Topographic correction based on topo estimation performed by Aestus field crew using a Topcon total station.



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GeoTrax Survey ™ Investigation Results
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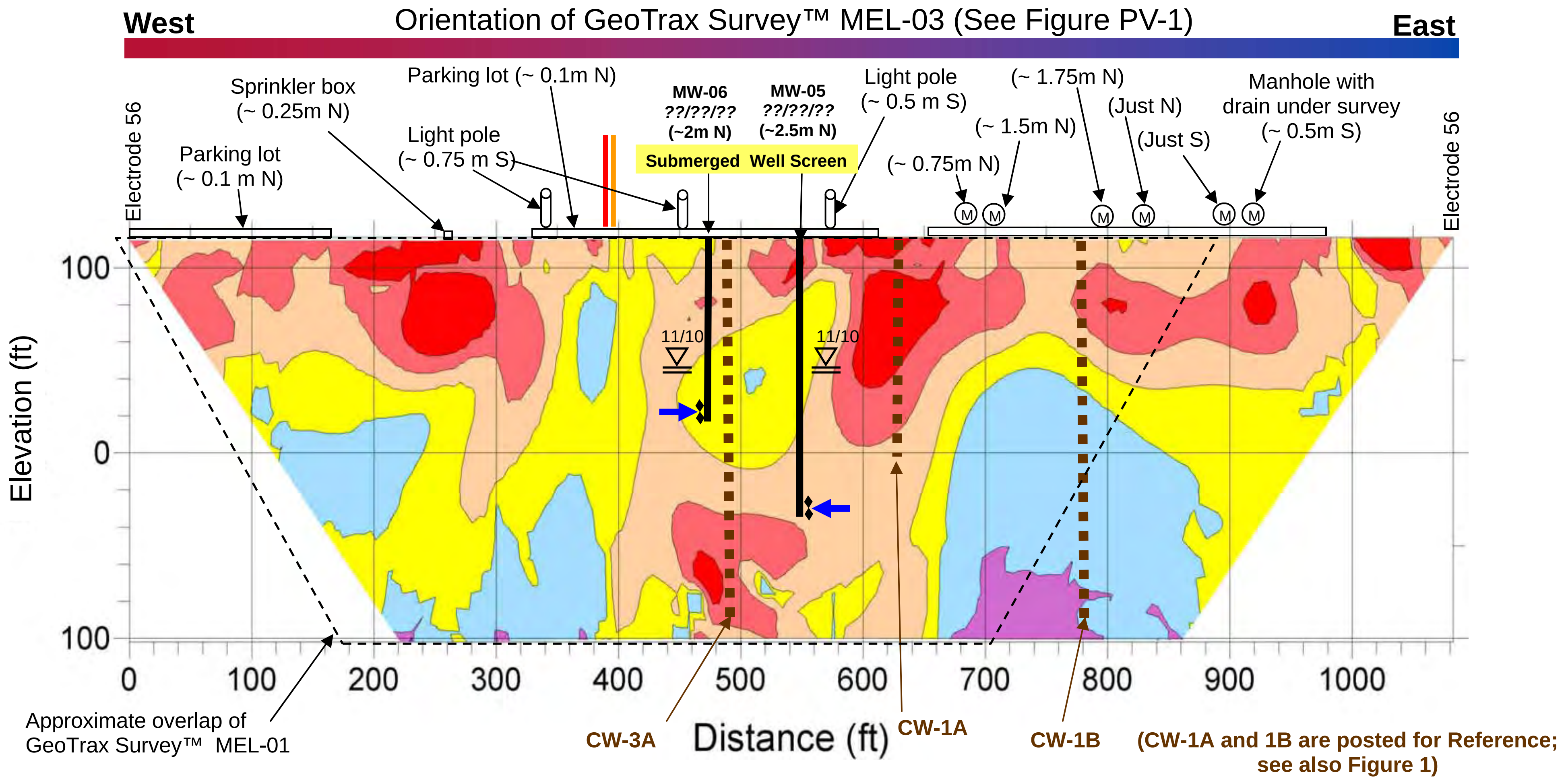
FIGURE

2



Image/Data Interpretation Notes:

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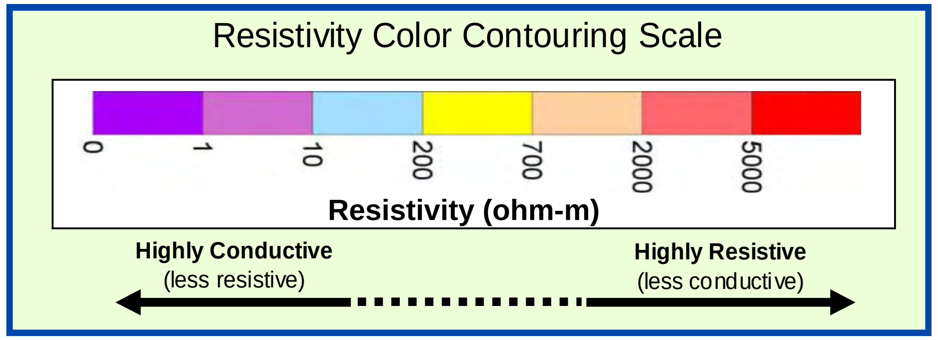

Groundwater Sample Results

Well		MW-06	MW-06	MW-05	MW-05
Sample Date		11/15/10	07/11/11	11/15/10	07/11/11
Parameters (µg/L)	Standards (µg/L)				
PCE	5	1.91 J	0.84	56.4	42
TCE	5	0.4 J	0.19 J	5.46	8 J
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MTBE	10	<0.16 U	ND	0.88 J	ND
Toluene	5	0.37 J	ND	0.42 J	ND
Aluminum	100	700	4200	210 J	180
Iron	300	790	6200	230J	490

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GeoTrax Survey ™ Investigation Results
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Melville, New York, USA

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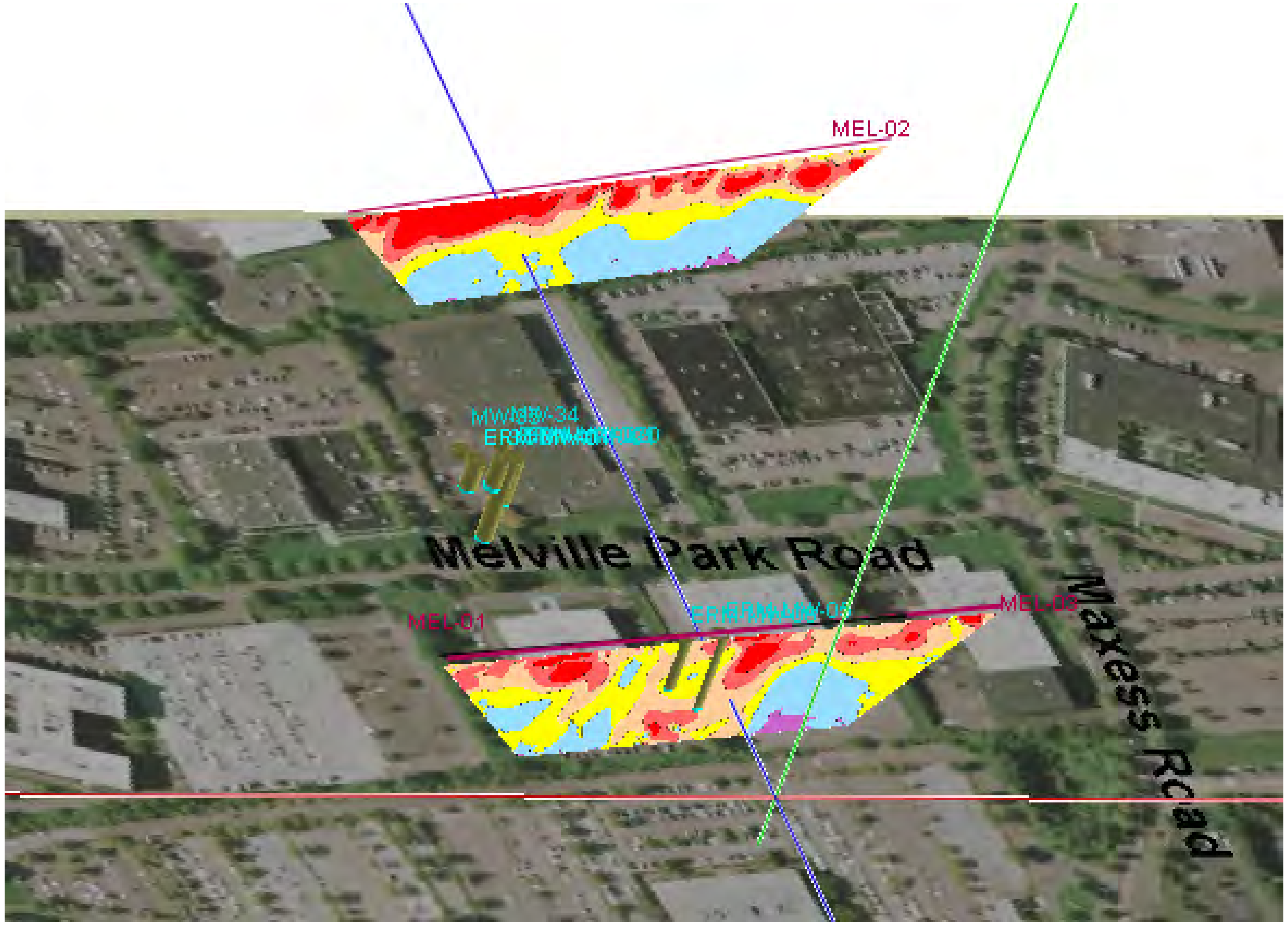
FIGURE
3

3-D Perspective View - GeoTrax Surveys ™

From Above and Looking Northeast at All GeoTrax Survey ™ Images

(Custom Color Contouring Scheme)

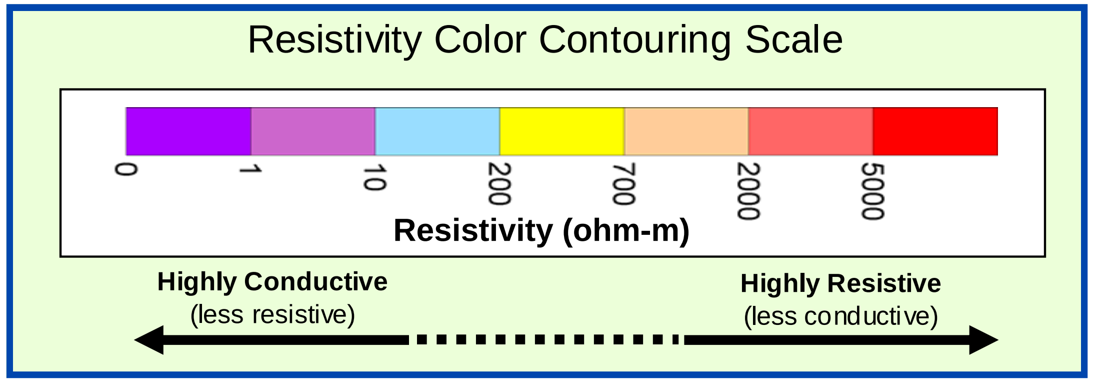


Note on Surveys: Since MEL-01 and MEL-03 are in virtually the same location, only MEL-03 was turned on for the 3-D model screen shots to avoid confusion. All surveys are included with the 3-D model. MEL-03 was chosen because it provides more data coverage length and depth wise. Surveys MEL-02 and MEL-03 are the same length/depth.

N

General Note:

Because this perspective view is rotated at an arbitrary angle away from plan view, the locations of survey images, site features, and text may appear slightly different or inaccurate relative to actual conditions. To ascertain actual locations of data points/features shown in this 3-D perspective view, please refer to electronic 3-D model files included with this report.



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3-D Visualization of GeoTrax Surveys ™
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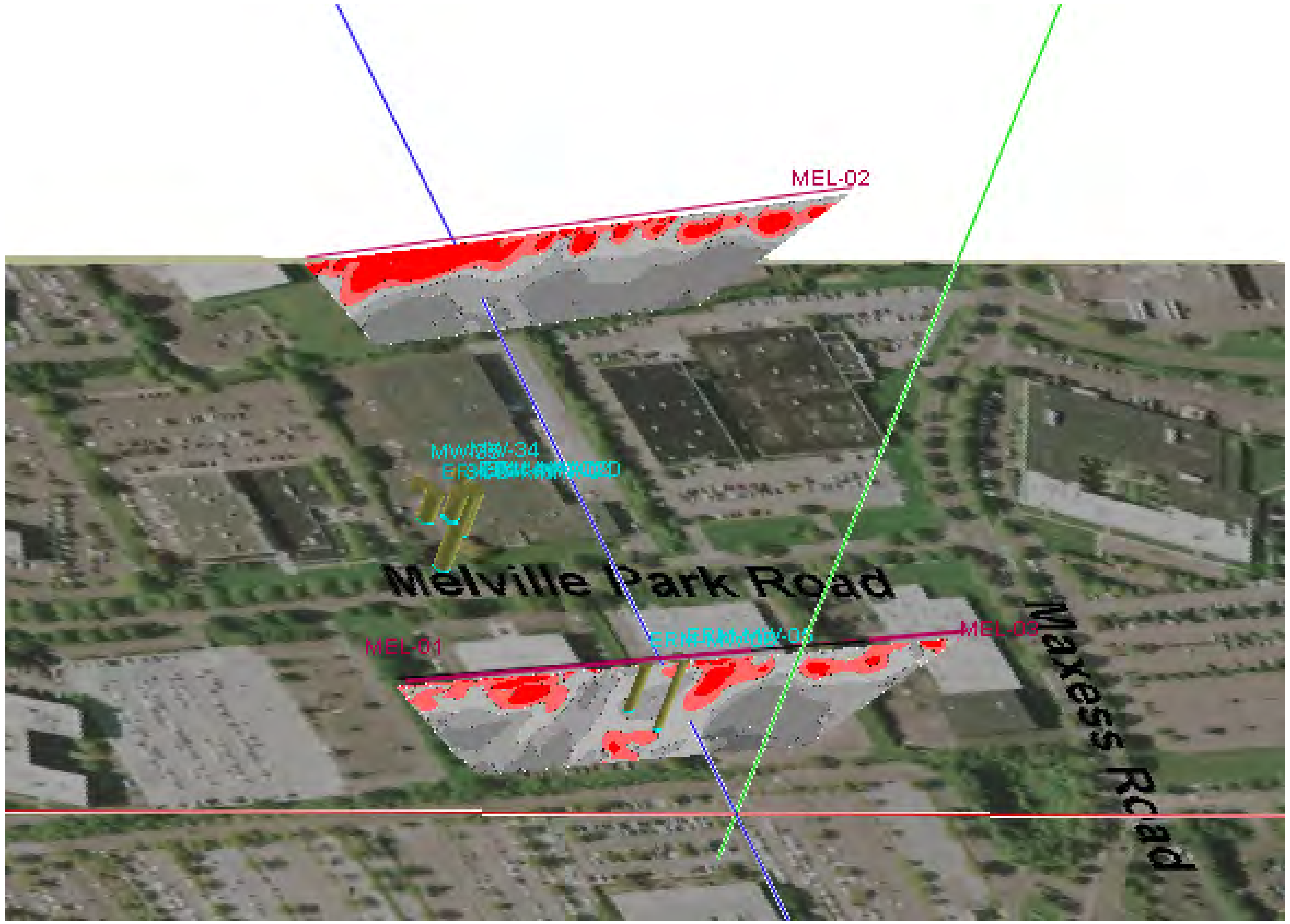
FIGURE

4

3-D Perspective View - GeoTrax Surveys ™

From Above and Looking Northwest at All GeoTrax Survey ™ Images

(Color Contouring Scheme Highlighting Electrically Resistive Anomalies)



Note on Surveys: Since MEL-01 and MEL-03 are in virtually the same location, only MEL-03 was turned on for the 3-D model screen shots to avoid confusion. All surveys are included with the 3-D model. MEL-03 was chosen because it provides more data coverage length and depth wise. Surveys MEL-02 and MEL-03 are the same length/depth.

N ↑

General Note:

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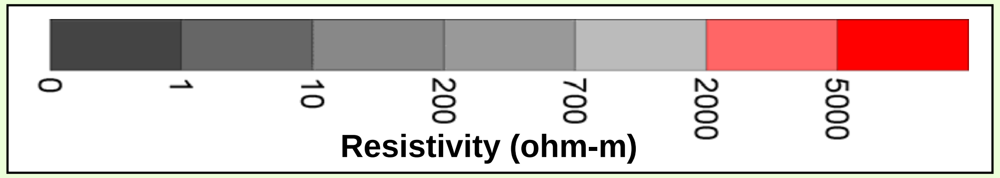
Resistivity Color Contouring Scale



Highly Conductive (less resistive) ← → **Highly Resistive** (less conductive)

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3-D Visualization of GeoTrax Surveys ™
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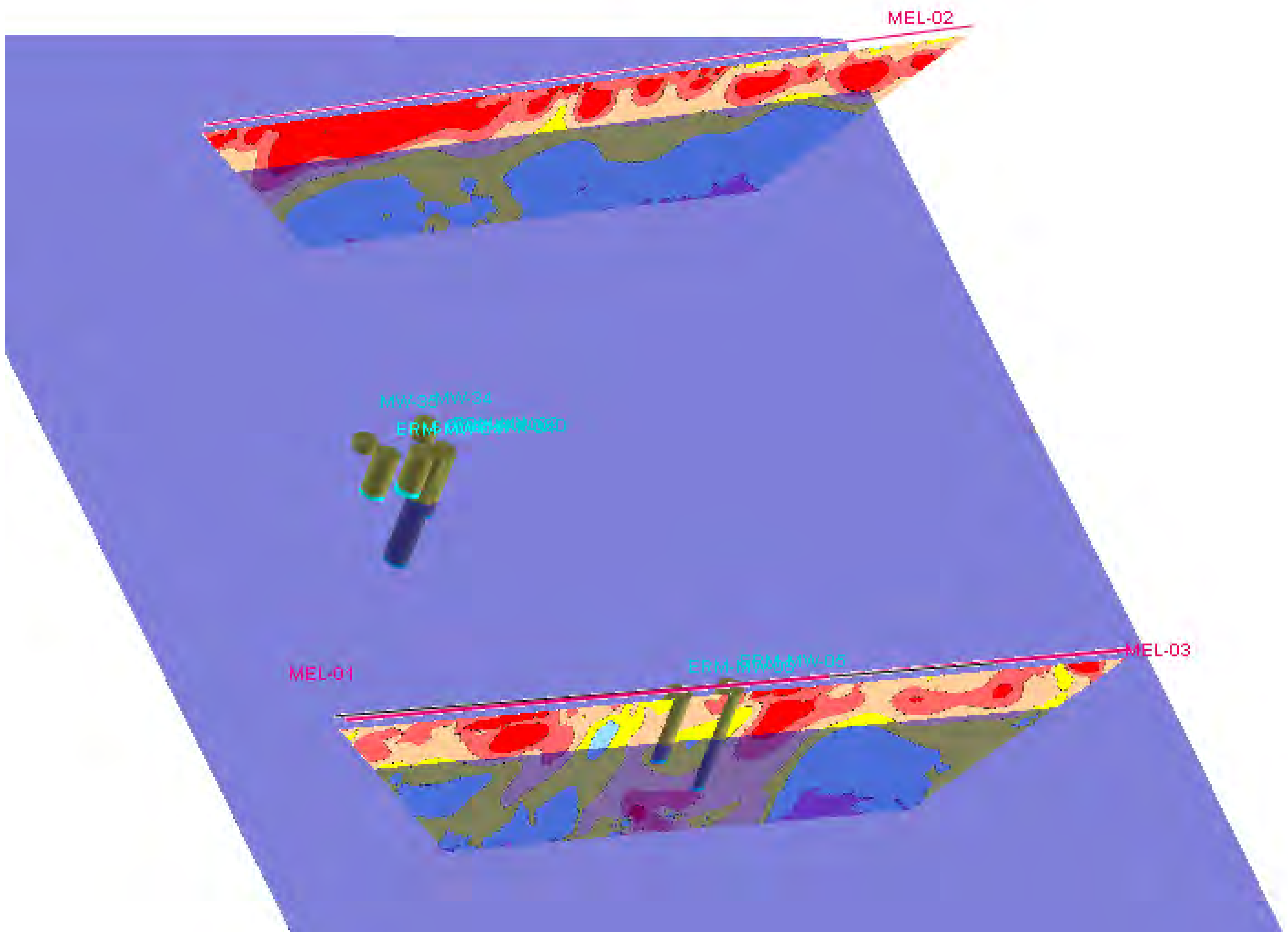
FIGURE

5

3-D Perspective View - GeoTrax Surveys ™

(From Above and Looking Northeast at All GeoTrax Survey ™ Images with Modeled Groundwater Surface) (Blue Plane)

(Custom Color Contouring Scheme)



Note on Surveys: Since MEL-01 and MEL-03 are in virtually the same location, only MEL-03 was turned on for the 3-D model screen shots to avoid confusion. All surveys are included with the 3-D model. MEL-03 was chosen because it provides more data coverage length and depth wise. Surveys MEL-02 and MEL-03 are the same length/depth.

N ↑

General Note:

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Resistivity Color Contouring Scale

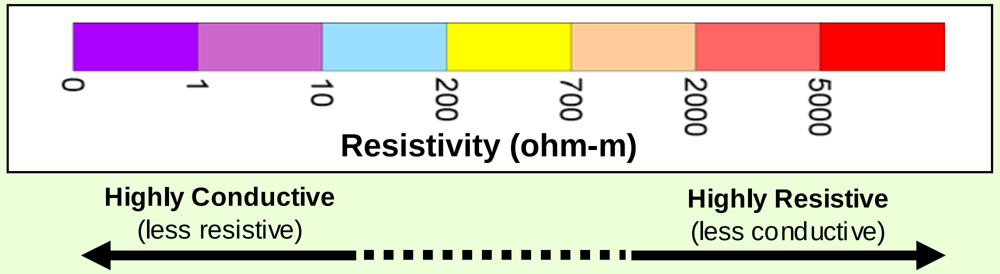

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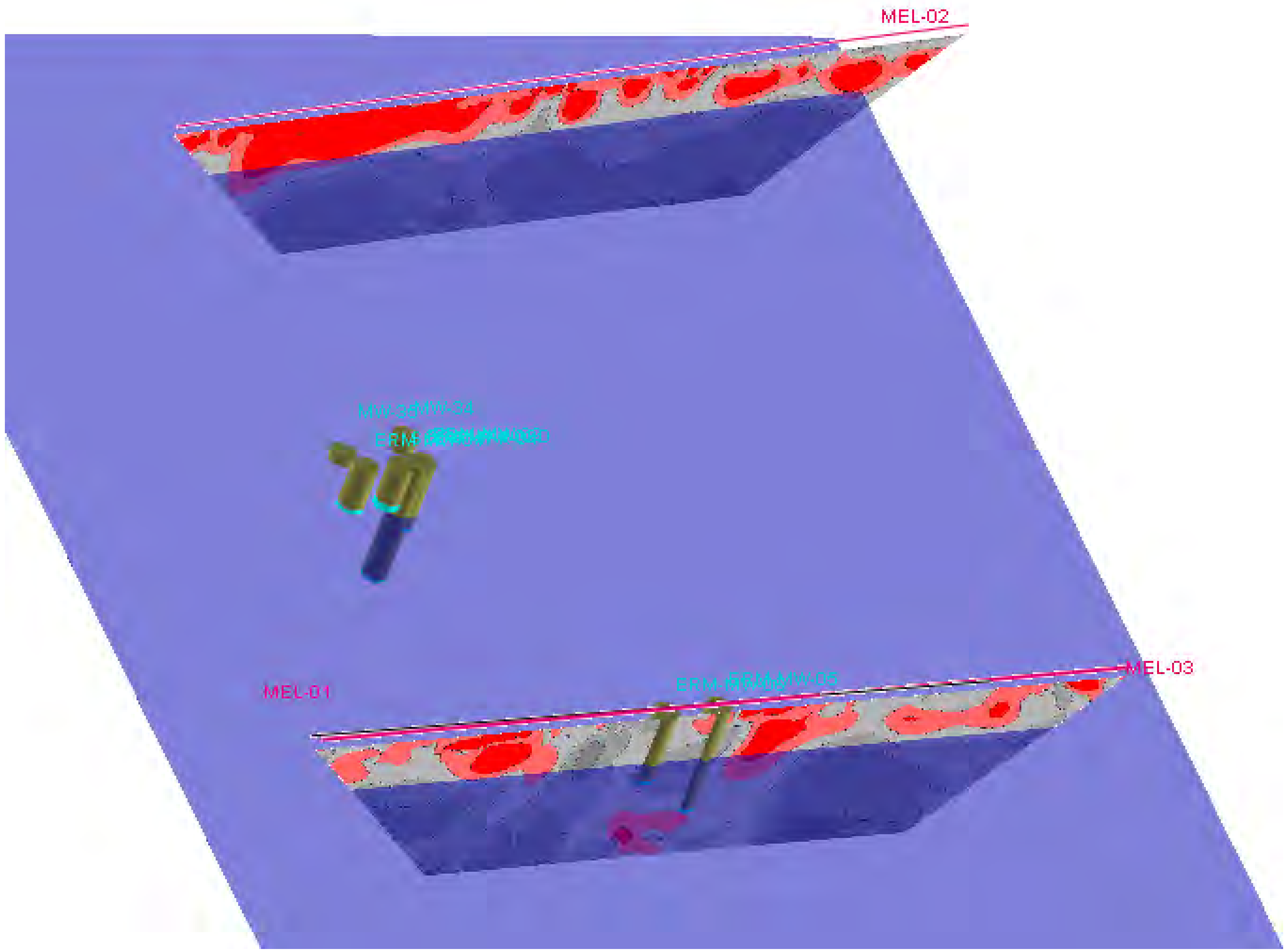
FIGURE
6

3-D Perspective View - GeoTrax Surveys ™

(From Above and Looking Northeast at All GeoTrax Survey ™ Images with Modeled Groundwater Surface) (Blue Plane)

(Color Contouring Scheme Highlighting Electrically Resistive Anomalies)

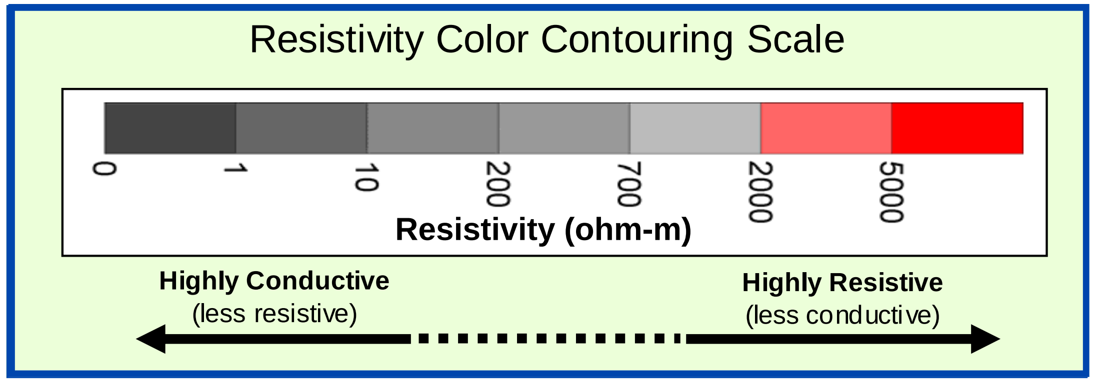


Note on Surveys: Since MEL-01 and MEL-03 are in virtually the same location, only MEL-03 was turned on for the 3-D model screen shots to avoid confusion. All surveys are included with the 3-D model. MEL-03 was chosen because it provides more data coverage length and depth wise. Surveys MEL-02 and MEL-03 are the same length/depth.

N

General Note:

Because this perspective view is rotated at an arbitrary angle away from plan view, the locations of survey images, site features, and text may appear slightly different or inaccurate relative to actual conditions. To ascertain actual locations of data points/features shown in this 3-D perspective view, please refer to electronic 3-D model files included with this report.



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3-D Visualization of GeoTrax Surveys ™
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FIGURE

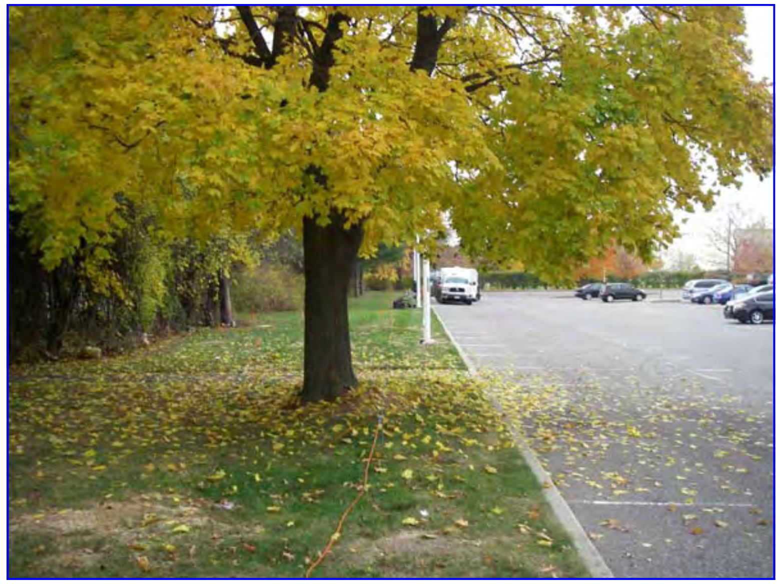
7

Photographs of GeoTrax Survey ™ MEL-01

MEL-01/03 West

MEL-01/03 looking East

Photographs of GeoTrax Survey ™ MEL-02



MEL-02 looking West

MEL-02 looking East

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Scale:	NTS unless specified
Drawn By:	MAS
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Date:	09-21-11
Project No.:	10-104-10

Photos of GeoTrax Survey ™ Locations
Plume Trackdown Site
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FIGURE
8

Appendix A

Aestus' GeoTrax Survey™ Field Notes

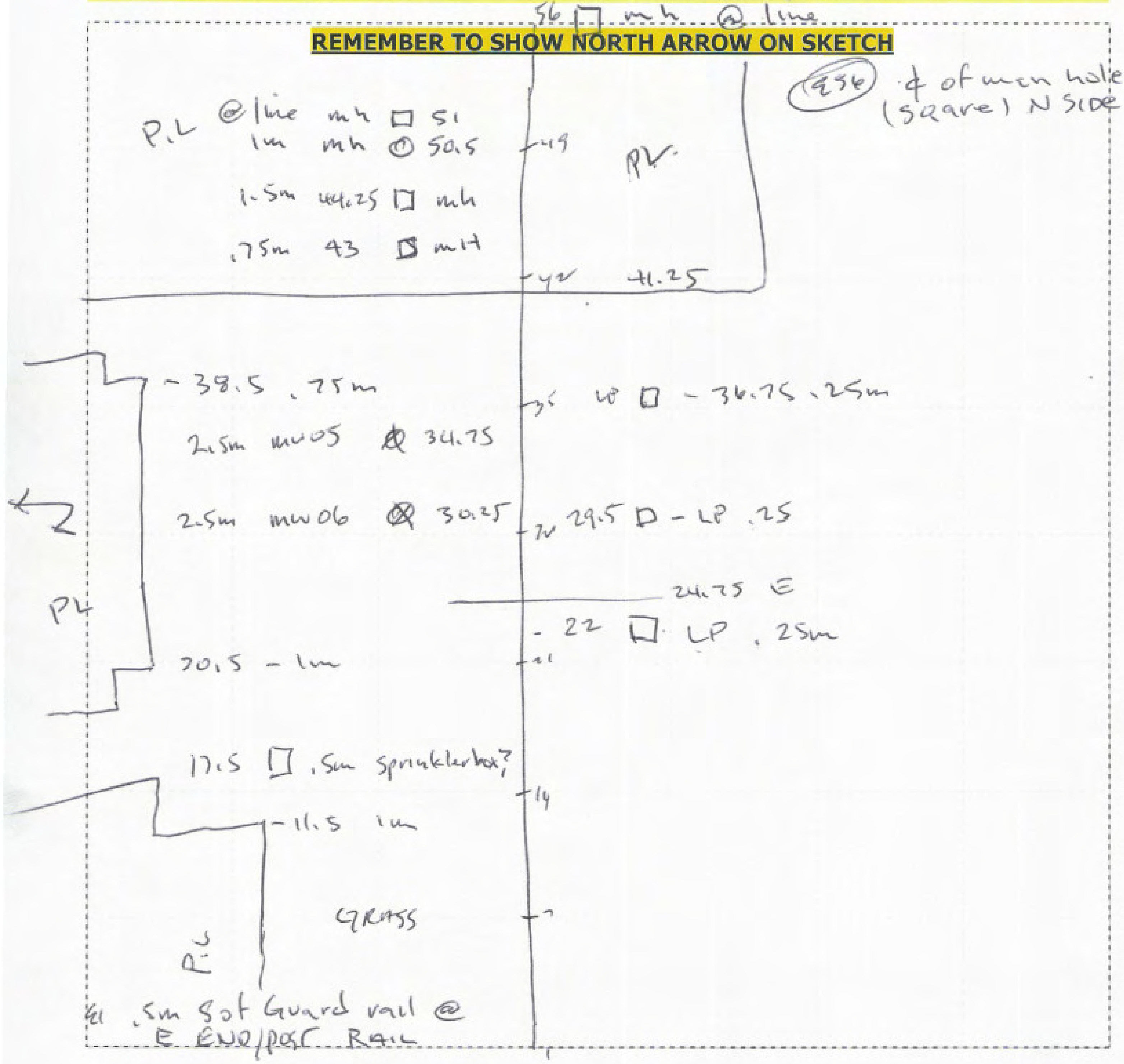
M	E	L	0	1	T

Project Name Melville Plume Trackdown Site Electrode Spacing 5.0 meters

Checklist - Site Features to Sketch/Note:

- ☐ Monitoring Wells (ID and distance away)
- ☐ Underground Utilities (Location and Type)
- ☐ Metallic Light Poles
- ☐ Streets (w/ street names)
- ☐ Potential contamination source areas (tanks, etc.)
- ☐ Buildings (w/ address if known)
- ☐ Other site features within ~15 feet of survey line
- ☐ Legend (if using abbreviations)

REMEMBER TO SHOW NORTH ARROW ON SKETCH



Aestus GeoTrax Survey™ Data Acquisition Field Notes

manhole mh
PARK LOT = P.L
LITE pole = LP

Gully

M	E	L	0	1	E

Project Name Melville Plume Trackdown Site

Electrode Spacing 5.0 meters

GPS Coords. Electrode #1	N: W: Accuracy:	GPS Coords Electrode #56	N: W: Accuracy:

Electrode #	Notes	Electrode #	Notes
1	.5 m S GUARD RAIL (E side of	29 .5	Lite Pole .25m S
2	Gully @ end post of rail	30 .25	MW 06 2.5m N
3		31	
4		32	
5		33	
6		34 .75	MW 05 2.5m N
7		35	
8		36 .75	Lite Pole .25m S
9		37	
10		38 .5	edge P.L. .75m N
11 .5	END P.L. 1m N	39	
12		40	
13		41 .25	P. LOT
14		42	
15		43	MH .25m N
16		44 .25	MH 1.5m N
17 .5	Sprinkler box? .25m N	45	
18		46	
19		47	
20 .5	P.L. 1m N	48	
21		49	
22	Lite Pole .25m S	50 .5	MH 1m N
23		51	MH @ line
24		52	
25		53	
26		54	
27		55	℄ of SQUARE MH ON
28		56	N. SIDE

25m Gully

Aestus GeoTrax Survey™ Data Acquisition Field Notes

GeoTrax_SurveyTM_Field_Forms_EA NYDEC Melville, NY 11-11-10

Aestus

Aestus, LLC

PL = Parklot

MH = man hole

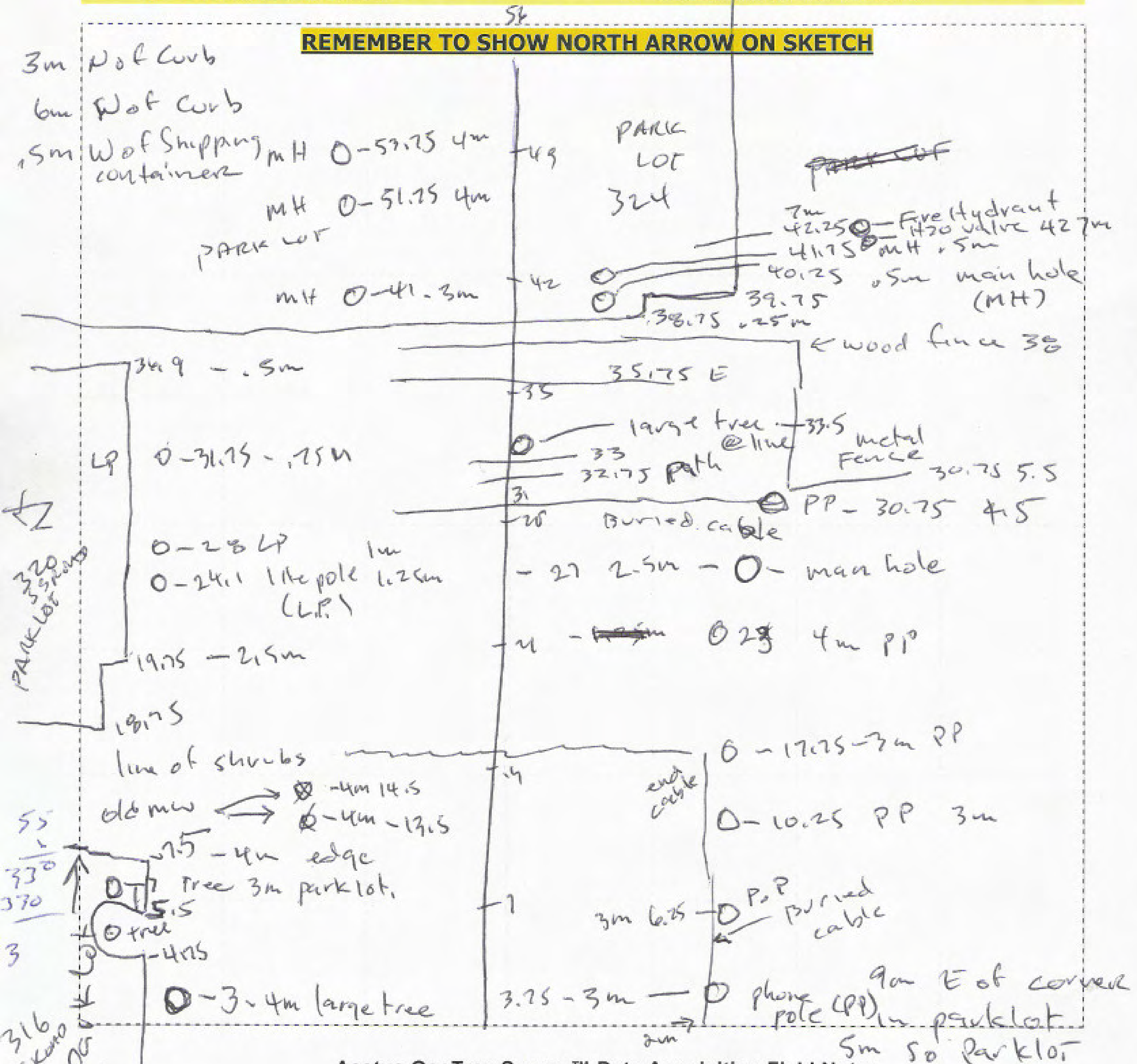
M	E	L	0	2	T

Project Name Melville Plume Trackdown Site Electrode Spacing 6.0 meters

Checklist - Site Features to Sketch/Note:

- ☐ Monitoring Wells (ID and distance away)
- ☐ Underground Utilities (Location and Type)
- ☐ Metallic Light Poles
- ☐ Streets (w/ street names)
- ☐ Potential contamination source areas (tanks, etc.)
- ☐ Buildings (w/ address if known)
- ☐ Other site features within ~15 feet of survey line
- ☐ Legend (if using abbreviations)

REMEMBER TO SHOW NORTH ARROW ON SKETCH



Aestus GeoTrax Survey™ Data Acquisition Field Notes

GeoTrax_SurveyTM_Field_Forms_EA NYDEC Melville, NY 11-11-10

M	E	L	0	2	vm

Project Name Melville Plume Trackdown Site

Electrode Spacing 6.00 meters

GPS Coords. Electrode #1	N: W: Accuracy:	GPS Coords Electrode #56	N: W: Accuracy:

Electrode #	Notes	Electrode #	Notes
1	9m E of Corner PARK LOT, 5m So	29	
2	3 large tree 4m N	30 .75	PP 4.5m 5 (corner of metal fence
3 .75	P.P. 3m S	31	Buried cable 31.75 LP .25m N .5m S
4.75 - 5.5	island into PARK LOT	32 .75 - 33	asphalt Path
5		33 .5	Large tree @ line
6 .25	PP 3m S	34	
7.5	end of P.L (4m N 316 SS ROAD	35 .75	E
8		36	
9		37	
10 .25	PP 3m S	38	Fence (WOOD) 38.25-39.75 jog in
11		39 .75	(Corner PL .25m S P.L .25m S #324 SS ROAD PL
12		40 .25	MH .5m S
13 .5	abandoned mw	41	m.H. 3m N 41.75 MH .5m S
14 .5	" "	42	- H2O m 7m S 42.25 Fire Hydrant 7m S
15		43	
16		44	
17 .75	PP 3m S - line of Shrubs	45	
18 .75	PARK LOT 320 10m N	46	
19 .75	Corner P.L 2.5m N	47	
20		48	
21		49	
22		50	
23	PP 4m S	51 .75	m.H. 4m N
24 .1	LP 1.25m N	52	
25		53 .75	m.H. 4m N
26		54	
27		55	3m N of Curb in P.L
28	LP 1m N	56	6m W of Curb P.L.

PARK LOT = P.L
MH - manhole
PP phone pole
LP - lite pole

Buried cable 2m S
17.75

320 Property

Aestus GeoTrax Survey™ Data Acquisition Field Notes

GeoTrax_SurveyTM_Field_Forms_EA NYDEC Melville, NY 11-11-10

1. .5m W of shipping container

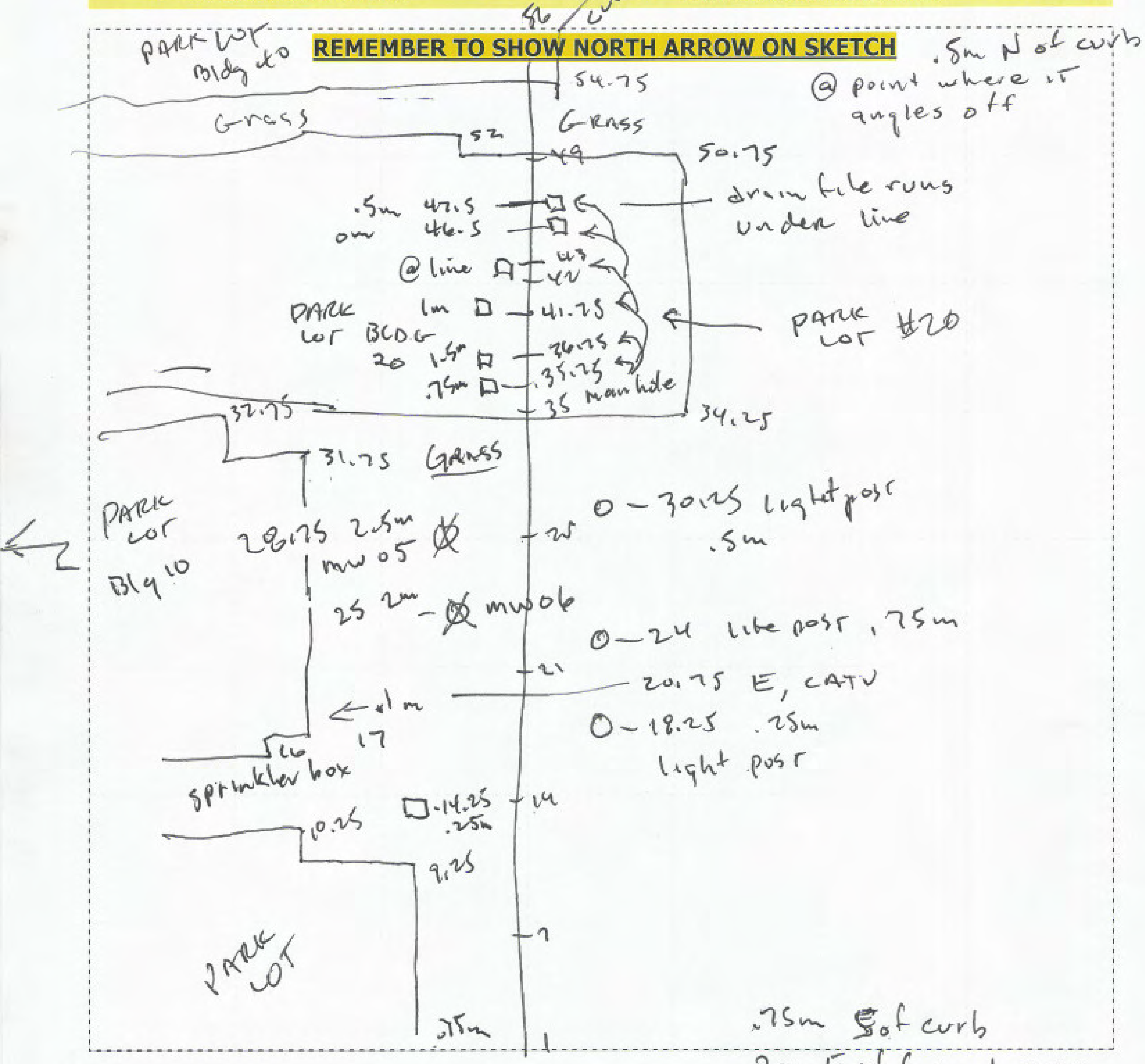
M	E	L	0	3	T

Project Name Melville Plume Trackdown Site   Electrode Spacing 6.0 meters

Checklist - Site Features to Sketch/Note:

- ☐ Monitoring Wells (ID and distance away)
- ☐ Underground Utilities (Location and Type)
- ☐ Metallic Light Poles
- ☐ Streets (w/ street names)
- ☐ Potential contamination source areas (tanks, etc.)
- ☐ Buildings (w/ address if known)
- ☐ Other site features within ~15 feet of survey line
- ☐ Legend (if using abbreviations)

REMEMBER TO SHOW NORTH ARROW ON SKETCH



.75m S of curb
2m E of Guard RAIL
@ culvert in park
lot S. of Bldg 10

Aestus GeoTrax Survey™ Data Acquisition Field Notes

GeoTrax_SurveyTM_Field_Forms_EA NYDEC Melville, NY 11-11-10

M	E	L	0	3	T

Project Name Melville Plume Trackdown Site Electrode Spacing 6.0 meters

GPS Coords. Electrode #1	N: W: Accuracy:	GPS Coords Electrode #56	N: W: Accuracy:

Electrode #	Notes	Electrode #	Notes
1 .75	m S @	29	
2	.75m S of curb & 2m E	30	
3	of guard Rail @ culvert	31 .75	Corner Park lot #10
4	in park lot S of Bldg 10	32 .75	Corner Park lot
5		33	
6		34 .75	edge Park Lot #20
7		35 .75	Man hole .75m N
8		36 .75	" " 1.5m N
9 .25	Corner park lot .1m N	37	
10 .25	" "	38	
11		39	
12		40	
13		41 .25	m hole 1.75m N @ [illegible])
14 .25	Sprinkler box .25m N	42	
15		43	man hole beside line to N
16	Corner Park lot	44	
17	" "	45	
18 .25	lite pole .75m S	46 .5	man hole to S of line (0m)
19		47 .5	manhole .5m S (has drain
20 .75	E, CATV	48	running under line)
21		49	
22		50 .75	edge Park lot #20
23		51	
24	lite pole .75m S	52	
25	MW 06 2m N	53	
26		54 .75	EDGE PARK LOT #40
27		55	
28 .75	MW 05 2.5m N	56	.5m N of curb @ point where curb angle off

#1

Grass

GRASS

PARK LOT #20

GRASS

PARK LOT #40

Appendix B

REFERENCE - TECHNICAL PAPER

The Effects of LNAPL Biodegradation Products on Electrical Conductivity Measurements

Aestus, LLC

The Effects of LNAPL Biodegradation Products on Electrical Conductivity Measurements

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[2]Uiniversity of Missouri-Rolla. Department ot‘ Geology & Geophysics. Rolla, MO. 65409, U.S.A.
[3]Western Michigan University. Department of Biological Sciences, Kalamazoo, Mich. 49008. C.S.A.

ABSTRACT

Field geophysical Studies have identified anomalously high conductivities in and below the free product Tone at many sites with aged contamination by light. non-aqueous phase liquid\ (LNAPL). Laboratory experiments were conducted to test the hypotheses that these anomalously high conductivities can result from products of LNAPL biodegradation. Soil from a hydrocarbon-impacted site with anomalously high conductivities was washed repeatedly IO remove soluble constituents, re-contaminated with diesel fuel (DF), and the port\ tilled with water to simulate a saturated smear Tone. Nutrients were provided at level? observed at the site. which resulted in anaerobic conditions due to DF biodegradation. Within 121) days. the increase in specific conductivity from microbial activity was 2, 100 *µ*S/cm. caused by an increase in total dissolved solids (DS) of over 1,700 *mg/L*. The increase in DS was due to mineral (mostly carbonate) dissolution and to the production of organic acids and biosurfactants. Under aerobic conditions (i.e., without added nutrients) products of DF biodegradation increased the total DS and conductivity by 340 mg/L and 440 *µ*S/cm. respectively. The results show that products of LNAPL biodegradation can drastically increase the conductivity at impacted sites.

Introduction

The collection. preparation. and analysis of ground water samples at contaminated sites constitute a major portion of the total cost for remediation (Granato and Smith, 1999) Geophysical surveys using resistivity and ground penetrating radar (GPR) are convenient, non-invasive tools 10 detect and map subsurface contamination with light, nonaqueous phase liquid\ (LNAPL). Recent reports suggest that LNAPL biodegradation can change biogeochemical properties sufficiently to have a significant impact on resistively and GPR measurements (Sauck, 2000, Werkema *et al.* 2000: Atekwana *et al.* 1998, 1999). If the geophysical responses caused by these Microbially-induced changes in pore water biogeochemistry can be better understood geophysical measurements could possibly be used to monitor contaminants and their breakdown products in the subsurface. This could allow resistivity techniques to be used as a surrogate or ground-water sampling and analysis to achieve lower cleanup costs.

Typical products of LNAPL biodegradation ale acids and biosurfactants. Carbonic and organic acids are produced during LNAPL biodegradation (Cozzarelli *et al.* 1990, 1994 1995; Eaganhouse *et al.* 1993; Hiebert *et al.* 1995: Baedecker *et al.* 1993; McMahon *et al.* 1995). These products increase conductivity directly by increasing the dissolved solids (DS) concentration, and indirectly by promoting mineral dissolution (Hiebert *et al.* 1995; McMahon *et al.* 1995). High DS concentrations in LNAPL-impacted zones have been invoked to explain anomalously low bulk electrical resistivity (Sauck *et al.* 1998; Bermejo *et al.* 1997). However. it has not yet been shown that temporal changes in geoelectrical properties of pore water occur due to LNAPL biodegradation.

Biosurfactants are produced by many genera of soil micro-organisms during growth on NAPL (Alexander. 1994; Miller. 1995: Desai and Banat. 1997). When present at concentration above the critical micelle concentration (CMC). Surfactants product microemulsions of NAPL m water. Biosurfactant are produced by aerobic and anaerobic microorganisms (Desai and Banat. 1997: Cooper *et al.* 1980; Mclnerney *et al.* 1990). Biosurfactants increase DS concentrations. Perhaps more importantly. emulsion of NAPL resulting from biosurfactants could promote a change in conditions from LNAPL-wetted to water-wetted. This can increase the contact area between water and solids. providing more nutrients and promoting further biogeochemical changes. Hence, biosurfactant production he> the potential to impact both resistivity and GPR measurements tremendously. While biosurfactants have been linked with NAPL biodegradation in mixed soil reactors (Cassidy, in press). in situ biosurfactant production and NAPL emulsification have not been demonstrated.

The efficacy of resistivity surveys rests in a high electrical resistivity of LNAPL relative to subsurface materials. This “insulating layer” model has been verified in short-term laboratory and controlled spill experiments (Schneider and Greenhouse. 1992). However, investigations at numer-

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ous sites with aged contamination show that the LNAPL smear zone has a lower resistivity (higher conductivity) than the bulk formation (Atekwana *et al.*, 1998, 1999; Benson and Stubben, 1995; Gajdos and Kral, 1995; Sauck. 1998). It has been hypothesized that anomalously low apparent resistivities are the result of LNAPL biodegradation (Atekwana *et al.* 1999: Sauck, 2000). However, to confirm this hypothesis changes in geoelectrical properties must be co! related with biodegradation products over time. This paper describes laboratory experiments designed to correlate temporal changes in the concentrations of diesel fuel (DF) degradation products with changes in specific electrical conductivity. under aerobic and anaerobic conditions. The production of biosurfactants and the resulting emulsification of DF were also monitored.

Materials and Methods

The soil was obtained from a hydrocarbon-impacted site described by Atekwana *et al.*. (1999) and Werkema *et al.*. (2000). The contaminated soil was washed five times with deionized water to remove soluble constituents. Fresh, no. 2 diesel fuel (DF) was mixed into the soil. The reactor-x consisted of 20-L plastic vessels. Approximately 18 L of soil was packed into each reactor, and deionized water was added to bring the water level up to the surface of the soil. A visible NAPL layer was present after adding water. The reactor setup was designed to simulate conditions in the saturated smear zone. A slotted, fully-penetrating PVC tube allowed composite pore water samples to be drawn and probes to be inserted into the saturated zone.

Duplicate reactors of three types were maintained for 120 days; one with added nutrients, one without added nutrients. and one "killed" (autoclaved) control without nutrients. Nutrients (4 mg/L NO_3-N,$_4$ mg/L NH,-N. and I mg/L PO,-P) were added to the reactors with the deionized fill water. These nutrient concentrations arc similar- to those observed at the site. Addition of nutrients resulted in anaerobic conditions within 10 days. The reactor with added nutrients was labeled "anaerobic." Anaerobic conditions also predominate at the bite. The reactor without added nutrients maintained aerobic conditions and was labeled "aerobic."

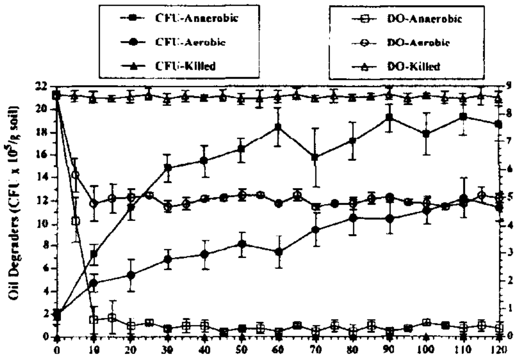

Figure 1. Average concentrations of oil degrading mi croorganisms and DO with time.

Dissolved oxygen (DO), pH. and conductivity were measured in situ. Pore water samples were drawn to quantify volatile organic acids (VOA), aqueous DF concentration. surface tension (ST), biosurfactant concentration, and C^{2-} concentrations. The samples were first passed through a 0.45-μm Whatman filter paper to remove suspended solids and non-emulsified DE Emulsified DF passes through this filter and is measured as aqueous DE Volatile organic acids (VOA) and Ca^{2-} concentrations were quantified with *Standard Methods* 5560-B and 35000 D. respectively (Eaton *et al.* 1995). ST and concentrations of aqueous DF and biosurfactants. were measured according to Cassidy (in press). Biosurfactant concentration was measured using critical micelle dilution, which provides units of "times the critical micelle concentration" (x CMC). Dissolved solids (DS) were measured on filtrate at the end of I20 days. Total. inorganic. and organic DS were measured using Standard Methods 2540-B & C (Eaton *et al.*, 1995). The concentration of DF-degrading microbes was quantified as described by Werkema *et al.* **[2000].**

Results and Discussion

Figure 1 shows the average measurements of oil-degrading microorganisms and DO with time. The killed controls showed no decrease in DO from the saturation concentration of 8.5 mg/L throughout the entire experiment. The killed reactors also had microbial concentrations that were essentially zero throughout the experiment. This shows that autoclaving was successful ill killing the micro organisms. In contrast, the biologically active reactors showed significant increases in microbial concentrations and decreases in DO within the first 5 to 10 days. These results show that there was considerable aerobic microbial activity in the biologically active systems. It can be concluded that this microbial activity was driven by DF biodegradation, since DF was the only major food source available. The greatest increase in CFU and decrease in DO was observed in the anaerobic systems, because adding nutrients promoted more biological activity than was possible in the aerobic systems. The anaerobic reactors showed an increase in the number of oil-degrading microbes from roughly 2 $X10^5$ CFU/g to 1.9 X 10^6 CFU/g after 120 days. This represents an increase of nearly an order of magnitude. DO in the anaerobic reactors decreased to less than 0.5 mg/ L within 10 days, and remained at this concentration thereafter. The aerobic reactors showed an increase in the number of oil degrades from roughly 2 x 10^5 CFU/g to

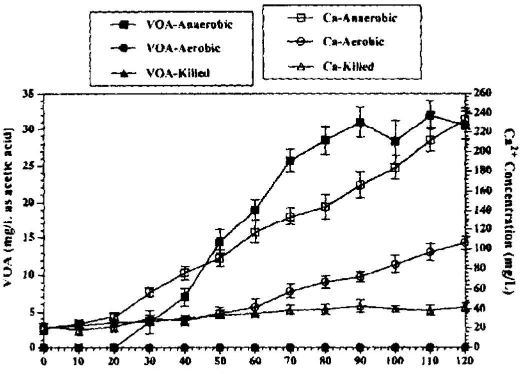

Figure 2. Average concentrations of VOA and Ca^{2+} with time.

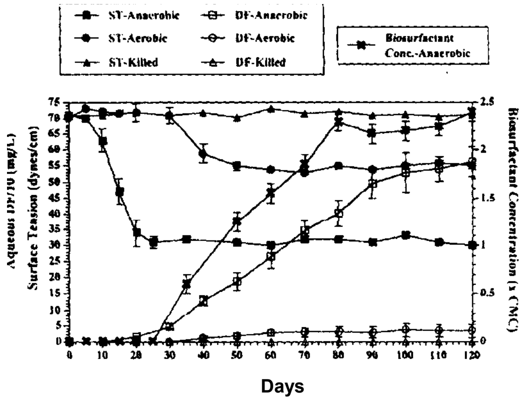

Figure 3. Average values of surface tension, aqueous DF concentration, and biosurfactant concentration with time.

to 1.3 X 106 CFU/g during the experiment. The DO in the reactors without added nutrients reached a steady state concentration of approximately 5 mg/L, which is considered aerobic.

The anaerobic reactors were designed to simulate conditions observed in the subsurface at the hydrocarbon impacted site from whence the soil was obtained (Werkema *et al.*, 2000) and at many such sites. Nutrients were provided at concentrations observed at the site, where the presence of sufficient nutrients and hydrocarbons have resulted in anaerobic conditions (*i.e.*. DO < 0.5 mg/L) caused by microbial activity (Werkema Pl al., 2000). Anaerobic conditions exist in the saturated zone at nearly all LNAPL impacted site& (Alexander, 1994). Nitrate (NO^{3-}), which is present at the site and was added to the anaerobic systems. promotes the growth of denitrifying bacteria that degrade DF by providing a necessary electron acceptor. It is important to remember that aerobic reactions occur in anaerobic systems along with anaerobic reactions. which is what continually consumes oxygen and maintains anaerobic conditions. Therefore, both aerobic and anaerobic reactions took place in the anaerobic systems. The aerobic reactors were maintained as a control to observe the effects of nutrients at the site on biogeochemistry and conductivity. and to simulate a nutrient-starved, aerobic site. Killed reactors provided an abiotic system for comparison with the biologically active reactors.

The average values for measurements of VOA and Ca^{2+} concentrations are plotted in Fig. 2. VOA levels were zero throughout the experiment in the killed and aerobic systems. However, VOA concentrations in the anaerobic systems began to increase on day 20 and stabilized at values between 30-35 mg/L as acetic acid between days 90 and 120. Since VOAs are biodegradable, an accumulation of VOA indicates that rates of production exceed rates of degradation during that time. Concentrations of Ca” started at a background value of approximately 25 mg/L and increased with time in all the reactors. Increases in Ca” concentrations with time were probably to due to dissolution of carbonates, which comprised approximately 2% (by weight) of the soil. The lowest levels of Ca^{2+} at the end of the experiment (40 mg/L) were observed in the killed reactors, which represent\ Ca^{2+} concentrations achieved by carbonate dissolution in the absence of microbial activity. In contrast. the Ca^{2+} concentration in the aerobic and anaerobic systems reached levels of 105 mg/L and 235 mg/ L, respectively.

The results in Fig. 2 show that microbial activity promoted the dissolution of carbonates, most pronounced under anaerobic conditions. The greater dissolution of carbonates achieved in the anaerobic systems is consistent with the accumulation of VOA and the overall enhanced microbial activity in these reactors compared with the aerobic reactors. While VOA was not detected in the aerobic reactors, it may have been present in low levels. CO_2 is another common product of microbial activity (not measured in this study), and its production is proportional to overall microbial activity (aerobic and anaerobic). Considering that more microbial activity was observed in the anaerobic systems than the aerobic ones, and that both aerobic and anaerobic reactions took place in the anaerobic systems, it is likely that more CO_2 was produced in the anaerobic systems than the aerobic ones. CO_2 and organic acid production has been demonstrated at LNAPL-impacted sites (Cozzarelli *et al.* 1990, 1994, 1995; Eaganhouse *et al.*, 1993; Hiebert *et al.* 1995: Baedecker *et al.* 1993; McMahon *et al.* 1995) and is known co enhance the dissolution of carbonate\ and other minerals.

Figure 3 shows the average values of biosurfactant related measurements: ST and concentrations of aqueous DF and biosurfactants. Killed controls showed no significant decrease in surface tension from 72 dynes/cm (the value for distilled water al 25 C) throughout the entire experiment. In contrast. ST measurements in the anaerobic reactors decreased from 72 dynes/cm to approximately 30 dynes/cm after 20 days. and remained al these levels until the end of the experiment. ST in the aerobic systems decreased after day 30 IO values between SO and 55 dynes/ cm, where they remained for the remainder of the experiment. Aqueous DF concentrations were zero for the first 20-X) days in all the reactors, and remained zero throughout the experiment in the killed reactors. The aqueous concentration of DF is roughly 5 mg/L (Testa and Winegardner, 1991). hut DF sorbs readily to soil, which explains the initial absence of DF in the aqueous phase. Aqueous DF concentration\ in the aerobic systems increased after day 30 to final values of nearly 5 mg/L. Aqueous DF concentrations in the anaerobic systems increased dramatically after day 20. reaching values of 550 mg/L (over 100 times the aqueous solubility). Biosurfactant concentrations in the killed and aerobic systems (not shown) were below the CMC throughout the experiment. However, biosurfactant concentrations in the anaerobic reactors increased after day 20 to levels over 2 times the CMC during the last 40 days of the experiments.

The results in Fig. 3 show that biosurfactants were produced in the anaerobic systems to levels over twice the CMC. The drop in ST to 30 dynes/cm observed in the anaerobic reactors coincided with biosurfactant concentrations above the CMC. and is a clear indication of surfactant concentrations above the CMC (Zajic and Seffens, 1984; Desai and Banat. 1907). Common metabolic products (e.g., organic acids) are not able to reduce ST to 30 dynes/cm. even at concentrations above 10% (Zajic and Seffens. 1984). indicating that the low ST reached in the anaerobic systems was not due to the accumulation of such products. Another unmistakable sign of biosurfactant concentration observed in the anaerobic systems was the increase in aqueous; DF concentrations coinciding with increasing biosurfactant concentrations after day 20. Aqueous DF measurements two orders of magnitude greater than the solubility limit is explained by emulsification of DE Emulsified NAPL droplets are le\s than 0.1 +m in diameter (Miller, 1995). and can pass through the 0.4%-μm filter, whereas non-emulsified NAPL cannot. Biosurfactant are biodegradable and sorb readily to soil (Miller, 1995: Desai and Banat. 1997). so the accumulation of biosurfactants in the anaerobic systems indicates that the rate of production exceeded rates of biodegradation and sorption. While biosurfactant concentrations above the CMC were not measured in the aerobic systems. ST values decreased and aqueous DF concentrations increased noticeably. This suggests that biosurfactants may have been in excess of the CMC in some pores. but that the concentrations dropped to below the CMC by dilution during sampling. Increasing aqueous DF concentrations with time in the aerobic systems support this. Numerous aerobic and anaerobic species produce biosurfactants (Zajic and Seffens, 1984: Desai and Banat, 1997). However. this study is the first to demonstrate in situ biosurfactant production accompanying microbial growth on NAPL.

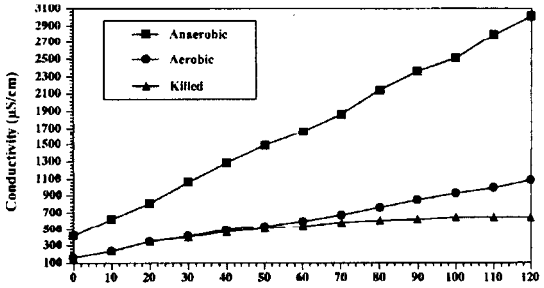

Figure 4. **Average values of specific electrical conductivity with time.**

Figure 4 shows the average values of specific conductivity measurements in pore water r:lmple\ over time. Conductivity increased in all reactors, hut the increase was by far the greatest in anaerobic systems. The initial conductivity of the anaerobic systems began at approximately 420 μS/cm. which was considerably higher than m the killed and aerobic reactors because of the added nutrients. Conductivity then increased in the anaerobic systems to over 3,000 μS/cm after 120 days. The initial conductivity in the killed and aerobic reactors was approximately 150 μS/cm. Conductivity increased to final values of roughly 650 μS/cm and I.100 μS/cm in the killed and aerobic systems. respectively. Since conductivity increases in the killed reactors are strictly from abiotic processes. subtracting these values from those observed in the biologically active systems gives an estimate of the increases in conductivity due to DF biodegradation processes in those systems. After 120 days in the killed reactors, conductivity increased 500 μS/cm (650 μS/cm- 150 μS/cm). Subtracting this value from the conductivity increases observed after 120 days in the aerobic systems (2,600 μS/cm) and anaerobic systems (950 μS/cm). yields an increase in conductivity of the aerobic and anaerobic systems of approximately 2,100 μS/cm and 450 μS/cm, respectively. From this analysis it is clear that specific conductivity increased roughly 4.5 times more in the anaerobic reactors than in the aerobic ones. This IS consistent with enhanced microbial activity, greater VOA production and carbonate dissolution. and enhanced production of biosurfactants in the anaerobic systems relative to the aerobic ones (Figs. 1-3).

Table 1. Measurements of dissolved solids in the pore waters from the three systems at the conclusion of the 120-day experiment.

Measurement	Anaerobic	Aerobic	Killed
Total DS (mg/L)	2130 ± 64 (8)[a]	758 ± 46 (8)	416 ± 28 (8)
Inorganic DS (mg/L)	1518 ± 54 (8)	602 ± 35 (8)	416 ± 28 (8)
Organic DS (mg/L)	612 ± 36 (8)	156 ± 31 (8)	0
Inorganic DS/Organic DS	2.5	3.9	NA
Total DS/Conductivity	0.72	0.69	0.64

[a] mean ± standard deviation (number of measurements). NA = not applicable.

Bulk conductivity was not measured in the reactors. However, specific conductivity is the major variable affecting bulk conductivity measurements, as described by Archie's Law. Using a soil porosity of 0.4 (common for unconsolidated sands) and other commonly used values for Archie's Law the ratio of specific conductivity to bulk conductivity is 10 (Telford *et al.*, 1990). This means that the increase in specific conductivity observed in the anaerobic systems due to DF biodegradation processes was 210 µS/cm (2,100 S/cm/10). This represents a significant increase in bulk conductivity measured in the field. Furthermore, the reactors in this study were only operated for 120 days. These results clearly show that biodegradation of DF can have a significant effect on bulk conductivity measurements at NAPL-impacted sites.

Table 1 lists results from the dissolved solids (DS) measurements of pore waters from the three systems at the end of the 120-day experiment. Total DS concentrations ranged from 416 mg/L in the killed controls to 2,130 mg/L in the anaerobic reactors. The value in the killed control (416 mg/L) was strictly due to abiotic processes, and subtracting this value from the total DS concentration in the anaerobic and aerobic systems gives an indication of the increase in those system due to DF biodegradation processes. This analysis yields an increase in total DS due to DF biodegradation in the anaerobic and aerobic systems of 1,714 mg/L and 342 mg/L, respectively. The organic DS concentration in the killed controls was zero, which is supported by the lack of microbial activity and lack of associated products (Figs. 1–3). The ratios of inorganic DS to organic DS concentrations in the anaerobic and aerobic reactors were 2.5 and 3.9, respectively. The lower ratio for the anaerobic system is explained by the greater concentrations of biosurfactants and emulsified DF (Fig. 3). The ratio of total DS concentrations to conductivity in the reactors on day 120 ranged from 0.64 to 0.72. These ratios are within the range of 0.55–0.75 reported for a survey of natural groundwaters (Hem, 1970).

The results clearly show that products of DF biodegradation in the reactors increased with increasing microbial activity and were greater for the anaerobic systems (with added nutrients) than for the aerobic ones (without added nutrients). DF biodegradation resulted in an increase in inorganic DS due to mineral dissolution and in organic DS due to organic acid and biosurfactant production. The increase in DS resulted in increases in conductivity. The anaerobic reactors simulated subsurface conditions at a LNAPL-impacted site with anomalously high conductivities (Atekwana *et al.*, 1999; Werkema *et al.*, 2000). The results from this study show that products of LNAPL biodegradation can explain those anomalous resistivities.

Conclusions

The results show that LNAPL biodegradation, under aerobic and anaerobic conditions, can substantially change pore water biogeochemistry, producing dramatic increases in electrical conductivity. These results help explain anomalously high conductivities reported in recent geophysical investigations at several LNAPL-contaminated sites. It has been known for some time that LNAPL biodegradation produces CO_2 and can produce organic acids, which enhance mineral dissolution. However, this study is the first to link these biogeochemical processes to enhanced pore water conductivity. This is also the first study demonstrating in situ biosurfactant production and LNAPL emulsification. The results suggest that biosurfactant production can accelerate a change in conditions from NAPL-wetted to water-wetted solids over time. The resulting increase in water/solids contact area could affect resistivity and GPR measurements.

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Appendix C

REFERENCE - TECHNICAL PAPER

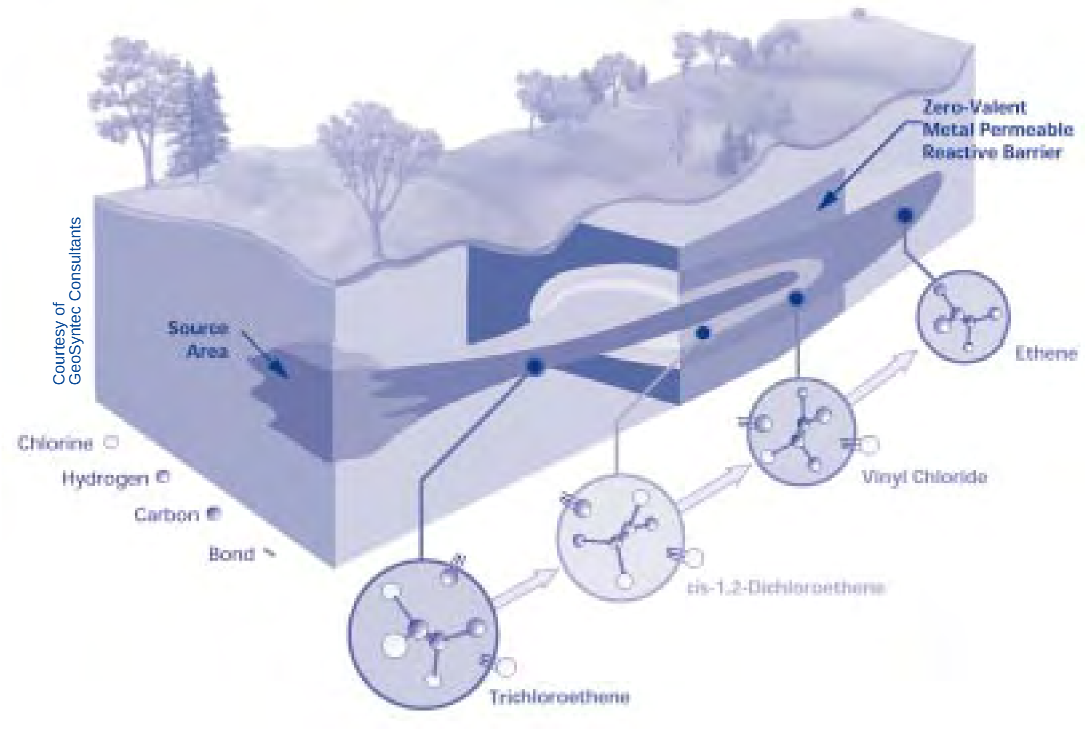
Natural Attenuation of Chlorinated Solvents in Groundwater: Principles and Practices

Note:
Appendices to this technical paper are not included in Appendix C for brevity. They are downloadable at the following web link:

http://www.itrcweb.org/Documents/ISB-3.pdf

Technical/Regulatory Guidelines

Natural Attenuation of Chlorinated Solvents in Groundwater: Principles and Practices



Courtesy of GeoSyntec Consultants

September 1999

Prepared by
Interstate Technology and Regulatory Cooperation Work Group
In Situ Bioremediation Work Team
and
Industrial Members of the Remediation Technologies Development Forum (RTDF)

- GeoSyntec Consultants
- Dow Chemical Company
- DuPont Company
- General Electric Company
- Imperial Chemical Industries
- Monsanto Company
- Novartis
- Zeneca Inc.

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FOREWORD

This Principles and Practices Document was prepared by the Industrial Members of the Bioremediation of Chlorinated Solvents Consortium of the Remediation Technologies Development Forum (RTDF) to disseminate up-to-date scientific information regarding **natural attenuation** (also referred to as **intrinsic remediation**) of **chlorinated solvents**. This information was assembled from research activities of the RTDF and from the experience and knowledge of the following participating companies and organizations of the RTDF Bioconsortium: Beak International, Dow Chemical Company, DuPont Company, General Electric Company, Imperial Chemical Industries, Monsanto Company, Novartis, and Zeneca Inc.

The RTDF is a public and private sector collaboration to develop innovative solutions to complex hazardous waste problems. The mission of the RTDF Bioconsortium is to accelerate the development of cost-effective bioremediation processes for degrading chlorinated solvents and to achieve public and regulatory acceptance that these processes are safe and effective.

The industrial members of the RTDF intend for this document to be as consistent as possible with the Air Force Center for Environmental Excellence and United States Environmental Protection Agency (AFCEE/EPA) Protocol which is currently under development. However, this document is not a “how to” manual; its purpose is to provide a "framework" to evaluate natural attenuation of chlorinated volatile organic compounds (VOC), that is, how to think about natural attenuation based on science. As a scientific document, its intent is not to dispense regulatory information. A separate document that provides the industrial members of the RTDF responses to reviews of previous versions of this document, issues requiring further discussion, and planned future revisions/additions to the document, is also available to the public.

ACKNOWLEDGMENTS

The RTDF appreciates the efforts of the following individuals in preparing this document: Dr. David Major, Evan Cox, and Dr. Leo Lehmicke of Beak International; Dr. David Ellis, Dr. Ron Buchanan, Ed Lutz, and Dr. Mike Lee of DuPont; Dr. Joseph Salvo, Dr. Jay Spivak, and Dr. Mark Harkness of General Electric Company; and Dr. Gary Klecka of Dow Chemical Company.

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NATURAL ATTENUATION OF CHLORINATED SOLVENTS IN GROUNDWATER: PRINCIPLES AND PRACTICES

INTRODUCTION

Q 1: What is natural attenuation?

A 1: Natural attenuation (also known as intrinsic remediation or natural restoration) was defined by the Office of Solid Waste and Emergency Response (OSWER) of the EPA as follows:

> *The term "natural attenuation" refers to naturally-occurring processes in soil and groundwater environments that act without human intervention to reduce the mass, toxicity, mobility, volume or concentration of contaminants in those media. These in-situ processes include biodegradation, dispersion, dilution, adsorption, volatilization and chemical or biological stabilization or destruction of contaminants.*

Simply stated, natural attenuation would be an accepted remedy when physical, chemical, and/or biological processes act to reduce the mass, toxicity, and/or mobility of subsurface contamination in a way that reduces risk to human health and the environment to acceptable levels.

The National Contingency Plan permits the use of natural attenuation as a remedy or a portion of a remedy for Superfund sites. In addition, several states (e.g., New Jersey, South Carolina, Wisconsin) have developed regulations and/or guidance regarding the evaluation and implementation of natural attenuation.

Q 2: Is natural attenuation a "do nothing" approach?

A 2: Natural attenuation is <u>not</u> a "do nothing" approach because it involves:

- Characterizing the fate and transport of the chlorinated solvents to evaluate the nature and extent of the natural attenuation processes;
- Ensuring that these processes reduce the mass, toxicity and/or mobility of subsurface contamination in a way that reduces risk to human health and the environment to acceptable levels;
- Evaluating the factors that will affect the long-term performance of natural attenuation; and

- Monitoring of the natural processes to ensure their continued effectiveness.

Q 3: How often is natural attenuation effective?

A 3: It has been estimated by the EPA (J. Wilson, pers. comm.) that natural attenuation will be effective as the sole remedy at approximately 20% of all chlorinated solvent sites. It has also been estimated that natural attenuation may serve as a portion of the remedy at an additional 50% of all chlorinated solvent sites (Ellis et al., 1996).

Q 4: Why should natural attenuation be evaluated?

A 4: Natural attenuation should be evaluated at chlorinated solvent sites because it is:

- A common sense approach to protect human health and the environment;
- A cost-effective alternative that can be used as a stand-alone technology or in association with other remediation technologies to reduce overall remediation costs;
- Minimally intrusive and usually less disruptive of facility operations and infrastructure compared to most remediation technologies; and
- Important to understand natural geochemical processes before implementing any remedial measure.

The advantages and disadvantages of natural attenuation are listed in Table 1.

Q 5: What is the intent of this Principles and Practices Document?

A 5: The intent of this document is to:

- Distill the practical aspects of the current state of the science into a framework to efficiently and economically assess natural attenuation;
- Develop a document that describes the status and benefit of natural attenuation in layman’s terms and can be continually updated as new information becomes available and as feedback from stakeholders is received;
- Guide readers on how to easily integrate natural attenuation into new and/or ongoing site characterization or groundwater monitoring programs;
- Provide guidance to the public, regulators, site managers, and practitioners on how to evaluate, interpret, and validate the contribution of natural attenuation of chlorinated solvents; and

- Reference appropriate sampling and interpretation protocols and guide readers to other relevant materials.

These goals will allow the RTDF Bioconsortium to keep pace with the rapid advances in the science and knowledge that serves as the basis of this technology and to update the document on the world wide web (http://www.rtdf.org) and in print form. In the near future, the RTDF Bioconsortium will also publish documents on two other technologies: **accelerated anaerobic bioremediation** and **co-metabolic bioventing**

Q 6: Who should read/use this Principles and Practices Document?

A 6: This document has been designed to be a valuable resource tool for the public, regulators, site managers, and practitioners

Q 7: How is the Principles and Practices Document Organized?

A 7: The Document is divided into four topic sections. The first section titled "Introduction" provides information on the intent of the document, who should read/use it, what natural attenuation is and why it should be considered. The second section titled "Background" provides information regarding the technical challenges associated with sites contaminated with chlorinated solvents and the types of chlorinated solvent attenuation processes that are known to occur. The third section titled "Evaluating Natural Attenuation" provides information on how natural attenuation studies are generally conducted and what types of information are typically required to document natural attenuation. The fourth section titled "Methods" presents a step-wise process, accompanied by a flow chart that can be used to evaluate and implement natural attenuation at sites contaminated by chlorinated solvents.

Q 8: Where can key terms and definitions be found?

A 8: Appendix A provides a glossary of key terms that are commonly used in natural attenuation of chlorinated solvents. Words that appear in bold type in this document are defined in the glossary. Appendix E contains a list of acronyms that are used throughout this document.

BACKGROUND

Q 9: Why is this document focusing on chlorinated solvents?

A 9: Chlorinated solvents such as tetrachloroethene (also known as perchloroethene, PCE), trichloroethene (TCE), trichloroethane (TCA), and carbon tetrachloride (CT) are commonly used as degreasing agents at manufacturing, maintenance and service facilities around the world. They are among the most common soil and groundwater contaminants. Some of these chlorinated compounds and some of their degradation intermediates may be toxic or carcinogenic. Chlorinated solvents are a class of chemicals that can be amenable to natural attenuation but such naturally-occurring mechanisms have not been the subject of much research in the past. Consequently, such mechanisms have been over looked by both the regulated community and the regulators.

Q 10: What are the most common misconceptions regarding chlorinated solvents and their natural attenuation?

A 10: Three of the most common misconceptions regarding chlorinated solvents and their natural attenuation are that:

- Chlorinated solvents can be easily found and remediated;
- Only biological processes are important or should be considered; and
- More toxic intermediates are likely to accumulate.

Questions 11 through 14 address the first misconception, question 15 addresses the second misconception, and question 17 addresses the third misconception.

Q 11: What are the technical challenges associated with sites contaminated with chlorinated solvents?

A 11: The physical properties of many chlorinated solvents make them extremely difficult to locate, remove or treat in the subsurface. Chlorinated solvents can exist and migrate in multiple phases depending on how they were released and site conditions. These phases include:

- Vapor phase in unsaturated soils;

- Dissolved phase in groundwater; and

- Liquid phase in the subsurface (e.g., droplets, coatings, or pools) as shown in Figure 1. Chlorinated solvents in this phase are referred to as **nonaqueous phase liquids** (NAPL), which do not mix with water (i.e., they form a separate layer from water). NAPL that are less dense than water float on the water table and are referred to as light

NAPL (LNAPL). NAPL that are denser than water sink below the water table and are referred to as dense NAPL (DNAPL). Most chlorinated solvents are DNAPL.

Q 12: What are the technical challenges associated with DNAPL?

A 12: The properties of DNAPL that make their investigation and remediation difficult and, in some cases, technically impracticable include:

- <u>Complex Distribution:</u> The distribution of DNAPL is strongly controlled by small variations in site geology and cannot be readily simulated or predicted. A released DNAPL will generally sink below the water table, spreading until it reaches confining layers (e.g., clay lenses, **aquitards**, **bedrock**) or becomes bound to the geologic matrix. Once below the water table, DNAPL do not necessarily move in the direction of groundwater flow. As a result, all of the DNAPL mass in the subsurface cannot be accurately located with current investigation technologies or techniques. An accurate determination of location is a prerequisite for effective source removal or treatment. The movement of DNAPL into small fractures and pore spaces in the subsurface prevents the effective removal of much of the DNAPL mass. Missing even a small amount of DNAPL mass means that recontamination of the groundwater can occur. It is estimated that at most DNAPL sites, over 99.9% of the DNAPL would have to be removed in order to approach the restoration levels needed to allow use of the aquifer as a drinking water supply (Pankow and Cherry, 1996).

- <u>Low Solubilities:</u> The low solubility of DNAPL means that it generally takes decades to centuries for DNAPL to dissolve into the groundwater. This significantly limits the utility of groundwater extraction and treatment as a remediation technology for cleanup of DNAPL sites.

- <u>Slow Diffusion:</u> The rate of diffusion from the geological matrix is much slower than the rate of sorption and diffusion onto/into the geological matrix. This means that even if free-phase DNAPL are treated, the slow diffusion out of the geological matrix may cause chlorinated solvents to be present in groundwater for long periods of time.

- <u>Potential to Exacerbate the Problem through Investigation and Attempted Treatment:</u> Improper drilling techniques in the vicinity of a DNAPL source area may result in penetration of an aquitard or confining layer, creating a new pathway for DNAPL to move downward. Similarly, treatment techniques such as de-watering to expose free DNAPL for vapor extraction may promote DNAPL migration by reducing their buoyancy.

Q 13: Can the presence of DNAPL be determined?

A 13: Site investigations designed to find DNAPL are generally impractical and ineffective. The presence of DNAPL should be suspected at sites where chlorinated solvents were typically used and disposed of (in tanks and/or waste ponds) as immiscible phase, unless historical records can account for waste solvent volume (e.g., recycling, off-site treatment/disposal).

Visual observation of DNAPL during the site investigation is not required to infer DNAPL presence. As a general rule, detecting chlorinated solvents in groundwater at concentrations exceeding 1% of their solubility suggests the presence of DNAPL or residuals (Pankow and Cherry, 1996).

Q 14: How does the presence of DNAPL affect site remediation strategy?

A 14: Proven, safe, and cost-effective technologies to remediate DNAPL sources in most groundwater environments are currently not available. Conventional groundwater remediation technologies in place at chlorinated solvent sites (e.g., groundwater extraction and treatment) remove solvents that have dissolved in the groundwater. These technologies employ long-term, active processes that are often costly and quickly reach a point of diminishing returns. As indicated above, small amounts of DNAPL mass can re-contaminate groundwater, generally making remediation of DNAPL sources to current regulatory criteria technically impracticable. Technical impracticability (TI) waivers are an appropriate regulatory mechanism and have been recognized by the EPA as appropriate for DNAPL sources.

Remediation/management strategies for most DNAPL sites should focus on integrating innovative, cost-effective techniques that will operate over the long term to mitigate risk to human health and the environment through containment. Natural attenuation is ideally suited for integration into long-term site management programs to address chlorinated solvents dissolved in groundwater. At some point in the future, more effective source removal or destruction technologies may become available. In the interim, mass removal via natural attenuation processes should be considered.

A thorough understanding of DNAPL is essential in any discussion of chlorinated solvents in groundwater. The reader is referred to Pankow and Cherry (1996) for detailed information on DNAPL behavior and its implications on remediation.

Q 15: What processes contribute to the natural attenuation of chlorinated solvents?

A 15: The processes that contribute to natural attenuation of chlorinated solvents include:

- **Degradation**: The degradation of most chlorinated solvents in groundwater occurs by **oxidation-reduction reactions** that are predominantly carried out by bacteria in the environment. These are referred to as **biodegradation** reactions. Biodegradation is usually the predominant process of natural attenuation at chlorinated solvent sites. Because of the significant and varied contributions of biodegradation to natural attenuation, biodegradation processes are discussed further in Questions 16 through 18. Some chlorinated solvents may also degrade by chemical reactions with metals (e.g., iron and iron-complexes) or water (e.g., hydrolysis reactions). Table 2 provides a list of case studies where degradation by theses processes have been documented to occur.

- **Advection, Dispersion, and Dilution**: Advection is the transport of molecules dissolved in water. During advection, molecules will also spread along and away from the expected groundwater flow path. This process is called dispersion and results from the mixing of groundwater (the solvent) and other molecules (the solute) in individual pores and channels. The combined processes of advection and dispersion result in a reduced concentration of the molecules (dilution) in the groundwater.

- **Diffusion**: Diffusion is a dispersive process that results from the movement of molecules along a concentration gradient. Molecules move from areas of high concentration to low concentration.

- **Sorption/Desorption**: Molecules can adsorb onto and, in some cases, be absorbed by geologic materials. Over time, these molecules will desorb from the geologic materials in response to concentration gradients. Sorption affects the advective rate of molecules dissolved in groundwater

- **Volatilization**: The transfer of a molecule from a liquid phase or an aqueous solution to the vapor phase (phase transfer) is termed volatilization. Chlorinated solvents are volatile organic compounds (VOC) that partition between liquid and gas phases, with the less chlorinated compounds having a tendency towards higher volatility. Volatilization may contribute to natural attenuation through the transfer of VOC from the liquid phase in the subsurface (NAPL, groundwater) to vapors in the vadose zone or to the atmosphere.

- **Stabilization**: Stabilization is a process whereby chemical molecules become chemically bound or transformed by a stabilizing agent (e.g., clay, humic materials), reducing the mobility of the molecule in the groundwater. It is usually a more irreversible reaction than adsorption.

The processes of advection, dispersion, dilution, diffusion, sorption/desorption, volatilization and stabilization are physical processes that are included in the EPA's definition of natural attenuation and are legitimate attenuation processes. They may have only a small impact at sites with high concentrations of chlorinated solvents, but may be sufficient, in and of themselves, at some sites where concentrations are low. A search of the EPA Record of Decision (ROD) database in 1995 using the search words "natural attenuation," "intrinsic bioremediation," and "intrinsic remediation" indicated 35 RODs in which natural attenuation or intrinsic remediation was selected as all or part of the remedy (Hagemann and Gill, 1995). Of these 35 sites, 17 had chlorinated solvents as one or more of the chemicals of concern. Review of these 17 sites indicate that physical attenuation mechanisms were the predominant removal mechanism at many of them; several sites had only parent compound at low concentrations (< 200 micrograms per liter [ug/L]).

Q 16: How do chlorinated solvents biodegrade?

A 16: Chlorinated solvents biodegrade by several processes, including:

- **Direct oxidation**, whereby the chlorinated compound is directly used as a **growth substrate** (**electron donor**/food source) and broken down to inorganic molecules such as carbon dioxide, water, and chloride;

- **Reductive dehalogenation**; whereby the chlorinated compound is converted to another chemical by replacing chlorine atoms with hydrogen atoms; and

- **Co-metabolism**, whereby the chlorinated compound is converted to another chemical while microorganisms use other carbon compounds for their growth substrate (food source).

Table 3 lists common chlorinated solvents and their current known degradation pathways. Figure 2 presents common degradation pathways for common chlorinated solvents.

In contrast to the biodegradation of **petroleum hydrocarbons**, evidence suggests that only a few chlorinated solvents can be used as growth substrates. Specific chlorinated solvents that can be directly oxidized are vinyl chloride (VC); dichloroethene (DCE); dichloromethane (DCM); chloromethane (CM); 1,2-dichloroethane (1,2-DCA); and chloroethane (see Table 3 and Figure 2). In **aerobic** environments (in the presence of oxygen which serves as the **electron acceptor**), chlorinated solvents are co-metabolized (i.e., used as a secondary food source) by non-specific microbial **oxygenase enzymes** that are produced by microorganisms to metabolize other growth substrates (e.g., methane, propane, toluene, ammonia, ethene, ethane). In **anaerobic** environments (in the absence of oxygen), chlorinated solvents act as **electron acceptors** in a process called **reductive dechlorination**, where hydrogen atoms replace chlorine atoms on the chlorinated solvent molecule. Other carbon substrates (e.g., alcohols, ketones, hydrocarbons, and/or natural organic compounds) serve as **electron donors** in these reactions. Figure 3 shows a "cut-away" of a TCE plume naturally attenuating, with reductive dechlorination being the predominant process.

It should be noted that all of the biological processes described above have been discovered since 1980. Biodegradation of chlorinated solvents is a new science and the state of the science is changing constantly; at least two new processes were documented for the first time in 1996.

Q 17: What are the products of chlorinated solvent biodegradation?

A 17: The aerobic mineralization of chlorinated solvents ultimately yields carbon dioxide, water, and chloride. Aerobic co-metabolic biodegradation of chlorinated solvents generally proceeds via an unstable epoxide intermediate that spontaneously decomposes to environmentally acceptable water-soluble products, carbon dioxide, and chloride (Roberts, et. al 1989). The aerobic oxidation of chlorinated solvents can ultimately yield carbon dioxide, water, and chloride or other organic by-products such as acetate. The anaerobic biodegradation of chlorinated solvents via sequential dechlorination of the parent chlorinated compound proceeds to non-chlorinated products such as ethene, ethane and methane. For example, the anaerobic dechlorination of PCE proceeds via TCE; 1,2-DCE (the cis-isomer is the predominant isomer formed); and VC to ethene and ethane. Each successive step in the dechlorination process is theoretically slower than the proceeding step and, therefore, at some sites, biodegradation may not proceed to completion. As a result, intermediate compounds (e.g., DCE) may accumulate. For a long time, it was commonly believed that VC would accumulate. However, it is now known that VC can be biodegraded under almost all of the potential conditions found in the subsurface because it can undergo direct biodegradation under both aerobic and anaerobic conditions. Complete dechlorination products such as ethene or chloride are not deemed to be a problem. For example, the maximum contaminant level (MCL) for chloride is 1,000 mg/l. TCE biodegradation in the 100 mg/l range would result in the slow release of approximately 80 mg/l of chloride over a long period of time.

Q 18: Are all of the appropriate bacteria present at every site?

A 18: In general, all "types" of bacteria (e.g., aerobic, anaerobic) are present at all sites. However, all bacteria involved in all of the potential biodegradation pathways for chlorinated solvents are not necessarily present at every site. For example, it is believed that all of the bacteria needed for the reductive dechlorination of PCE or TCE to DCE are present at approximately 90% of all sites, and all of the bacteria needed for the reductive dechlorination of PCE or TCE to ethene are present at approximately 75% of all sites.

EVALUATING NATURAL ATTENUATION

Q 19: When should natural attenuation be evaluated?

A 19: Natural attenuation should be evaluated to some degree at every site, preferably early in the site investigation process. It is important to understand the natural attenuation processes before implementing any remedial measure. A thorough understanding of natural attenuation processes is necessary if natural attenuation is to be implemented as the remedy, a portion of the remedy, or when an alternative remedy such as enhanced bioremediation is being considered. Natural attenuation should be evaluated thoroughly when:

- Natural attenuation processes are observed or strongly expected to be occurring; and
- There are no human or ecological receptors that are likely to be impacted or potential receptors in the vicinity of the plume are, or can be protected.

In addition, natural attenuation should be considered as the remedy or portion thereof when:

- It is protective of human health and the environment;
- A continuing source that cannot cost effectively be removed or contained will require a long-term remedial effort;
- Alternative remediation technologies are not cost-effective or are technically impracticable; and
- Alternative remedial technologies pose significant added risk by transferring contaminants to other environmental media, spreading contamination or disrupting adjacent ecosystems.

Q 20: When should natural attenuation <u>not</u> be considered in the remedy?

A 20: Natural attenuation should <u>not</u> be considered as the remedy or a portion of the remedy when natural attenuation will not be protective of human health and the environment or alternative remediation technologies can more reliably and cost-effectively treat the contaminants to minimize risk. Comparative costs for different technologies are presented in Table 4.

In some instances, specific regulatory guidelines or the desires of regulatory agencies at a specific site may prevent the use of natural attenuation even though it may be sufficiently protective of human health and the environment.

Q 21: What evidence is required to evaluate and implement natural attenuation?

A 21: Natural attenuation is generally evaluated using a "lines of evidence" approach. This approach forms the basis for all current protocols and guidance documents. The suggested lines of evidence are:

1. Documented reduction of contaminant mass at the site;
2. Presence and distribution of **geochemical** and **biochemical** indicators of natural attenuation; and
3. Direct microbiological evidence.

Q 22: How are the three lines of evidence documented?

A 22: Typically, the first line of evidence (i.e., loss of contaminants) is documented by reviewing historical trends in contaminant concentration and distribution in conjunction with site geology and hydrogeology to show that a reduction in the total mass of contaminants is occurring at the site. This mass loss may be in the source area and/or along the groundwater flowpath. Because most chlorinated solvents do not biodegrade on their own like petroleum hydrocarbons, biodegradation rates are more site-specific (e.g., dependent on redox conditions, electron donor concentration). Therefore, it is more important to estimate a biodegradation rate at chlorinated solvent sites from field data (Buscheck and Alcantar 1995; Weaver et.al 1996).

The second line of evidence is documented by examining changes in the concentrations and distributions of geochemical and biochemical indicator parameters that have been shown to be related to specific natural attenuation processes.

The third line of evidence (i.e., microbiological evidence) is documented through laboratory microcosm studies and is used to: 1) confirm specific chlorinated solvent biodegradation processes that cannot be conclusively demonstrated with field data alone (e.g. anaerobic VC oxidation) and/or 2) estimate site-specific biodegradation rates that cannot be conclusively demonstrated with field data alone. The need to collect the third line of evidence is evaluated on a case-by-case basis and is generally only required when field data supporting the first two lines of evidence are insufficient to adequately support natural attenuation.

Q 23: What data are required to support the three lines of evidence?

A 23: The types of data that are required to support the three lines of evidence depend on the type of site and the nature and extent of attenuation processes that are occurring. Table 5 summarizes several common patterns of chlorinate solvents in groundwater including their distribution and relates these patterns to suggested data collection tiers to support natural attenuation. The conceptual model for a given site can be compared to these common patterns to determine what data collection tier is appropriate to evaluate and support the lines of evidence approach. The specific data that should be collected for each data collection tier are listed in Table 6. Information on the ideal use of each parameter in evaluating natural attenuation and the status of its measurement (e.g., commercially available or research) is also provided in Table 6.

The list of parameters for each tier has been developed based on the experience of the authors. Collection of all parameters may not be required for all sites. The reader may benefit from customizing the data collection tiers to suit specific site conditions.

METHODS

This section provides the reader with a step-wise framework that can be used to review data for a given chlorinated solvent site, evaluate whether the natural attenuation of chlorinated VOC is occurring, identify and collect additional data that support the three lines of evidence of natural attenuation, and integrate natural attenuation into a long-term site remediation/management strategy. It is anticipated that these activities can be conducted concurrent with other investigation and remediation planning activities. Figure 4 summarizes this information in a flowchart format.

Step 1. Review Available Site Data

The first step in evaluating natural attenuation is to review available site data. For Superfund sites, data is typically available from Remedial Investigation (RI), Risk Assessment, and Feasibility Study (FS) documents. For Resource Conservation and Recovery Act (RCRA) facilities, data will typically be available from RCRA Facility Investigation (RFI) and Corrective Measures Study (CMS) documents, and/or RCRA Alternate Concentration Limit Demonstration reports. Monitoring reports for existing remediation systems may also be available for review. It is important to identify potential receptor exposure points (e.g., drinking water wells, surface or groundwater discharge points) at this time if not yet identified.

Site characterization is necessary for sites with insufficient data. Appendix B references site investigation protocols. Evaluating natural attenuation should be incorporated into the site investigation at uncharacterized sites since the costs of collecting the additional data to evaluate natural attenuation are outweighed by the cost savings that may be realized if natural attenuation is integrated into the long-term site remediation strategy. Step 4 discusses the level of natural attenuation data that should be collected at uncharacterized sites.

Step 2. Review/Develop the Site Conceptual Model

Review the available data to determine whether a **site conceptual model** has been developed. The site conceptual model is a representation of the site-specific groundwater flow and solute transport system. This model is typically used to:

- Present and explain chemical distributions in the site groundwater in relation to groundwater flow and transport processes; and

- Facilitate the identification of risk assessment elements used in exposure analysis, including sources, release mechanisms, transport pathways, exposure points, and potential receptors.

RI documents typically present a site conceptual model that is based on available geological, hydrogeological and chemical data. These models generally do not adequately integrate chemical fate due to degradation (biological and abiotic) processes, and these processes are very site-specific for chlorinated solvents. However, as they exist, site conceptual models are useful to identify:

- Reduction of chemical mass in relation to groundwater flow and transport;

- Locations at the site (relative to sources, receptors or site boundaries) where additional data is required to document reduction of chemical mass and presence of geochemical indicators of natural attenuation processes; and

- Specific types of data that should be collected at the locations selected.

A site conceptual model is necessary if it is not presented in the available site documents. Appendix B references protocols for conceptual model development.

Step 3. Screen the Data for Evidence of Natural Attenuation and Develop Hypothesis to Explain the Attenuation Processes.

The available site data and site conceptual model should be screened both to assess whether natural attenuation is occurring and to develop a hypothesis regarding the processes that are promoting the attenuation. Screening for natural attenuation can be conducted by reviewing the information and answering the following questions:

1. Do the existing data provide evidence for reduction of chemical mass (line of evidence #1)?

    - Have concentrations of known or suspected parent chlorinated solvents decreased over time?

- Do observed chlorinated solvent distributions differ (decrease along the flow path) from distributions predicted from expected transport in groundwater?

2. Do the existing data provide evidence for the presence of geochemical or biochemical indicators of natural attenuation (line of evidence #2)?

    - Are known degradation products (e.g., cis-1,2-DCE, VC, or ethene at a TCE site, see Table 5) present in the groundwater? Have ratios of dechlorination daughter products to parent solvents increased over time and is cis-1,2-DCE the predominant DCE isomer?

    - Do available data indicate production or consumption of carbon sources or production of inorganic constituents consistent with known biodegradation reactions (e.g., increased alkalinity, chloride and/or dissolved iron concentrations in source area wells)?

Yes answers to any/all of these questions typically indicates that biodegradation processes are occurring and should be further evaluated following Steps 4 through 9. Figures 5 and 6 provide examples (accompanied by explanations) of several common patterns of chlorinated solvent biodegradation in anaerobic and sequential anaerobic/aerobic systems, respectively. Sites where screening does not indicate the occurrence of these **biological** processes may still be candidates for natural attenuation, depending on the results of exposure pathways analysis, and should be further evaluated by advancing to Step 8.

Step 4. Identify Additional Data Requirements

Identification and selection of additional data to test the natural attenuation hypothesis and support the lines of evidence approach is a site-specific process. However, the process can generally be conducted as follows:

1. Compare the conceptual model for the given site to the common patterns of chlorinated solvent presence and distribution presented in Table 5. Select the pattern that best approximates conditions at the given site and identify the suggested data collection tier. Using Table 6, identify the specific data parameters that correspond to the selected data collection tier. As an example, the conceptual model for a site having 1,2-DCE and VC in the groundwater near a TCE storage or disposal area should be similar to Pattern 3 and would warrant collection of Tier 2 data.

2. Select locations for additional data collection based on the site conceptual model. Locations should be selected to represent upgradient (background), lateral, source and several downgradient conditions, including at least one well beyond the terminus (toe) of the VOC plume. For sites having significant vertical flow components, locations should be selected to represent the vertical profile as well. The adequacy of existing well coverage to test/support the natural attenuation hypothesis should be evaluated.

Additional monitoring locations may need to be installed to adequately test/support the natural attenuation hypothesis. For example, the capacity of the natural system to degrade chlorinated hydrocarbons that are directly oxidized is almost totally dependent on the amount of electron acceptors in background groundwater just as it is with petroleum hydrocarbons; therefore, the need for a true "background" well is important. However, the installation of new wells in what might be considered the "source area" at a DNAPL site is highly discouraged (see Chapter 13 of Pankow and Cherry , 1996).

3. Critically evaluate the need for microcosm studies. Microcosm studies provide direct microbiological evidence and are used to: 1) confirm specific chlorinated solvent biodegradation processes and/or 2) estimate site-specific biodegradation rates that can not be conclusively demonstrated with field data alone. Because microcosm studies are both expensive and time consuming, they should only be performed when the information cannot be obtained from field data. Microcosm studies are designed using aquifer sediment and groundwater samples collected from the site and should provide direct evidence for natural attenuation of chlorinated solvents under simulated redox conditions that occur at the site. If these studies are required, they can also be used to characterize: i) soil adsorption potential; ii) mass balance; iii) the role of available electron donors/co-metabolites in supporting natural attenuation processes; and iv) factors that may affect/inhibit natural attenuation over time, including the ability to enhance the natural processes.

For uncharacterized sites, a minimum of Tier 1 data should be collected during site characterization to evaluate the potential for natural attenuation. An evaluation of site use history should indicate whether Tier 2 or Tier 3 data should also be collected. For example, if site records indicate that waste solvents (e.g., TCE) were used and disposed of along with sewage, petroleum hydrocarbons, or other solvents (e.g., acetone, methanol, methylene chloride), then it is likely that some degree of intrinsic biodegradation has occurred; therefore, collection of Tier 2 or 3 data during site characterization may be warranted.

Step 5. Collect Additional Data

Data should be collected following appropriate protocols to ensure the quality and integrity of the data. Appendix B is a resource guide that references accepted protocols for well installation and development, well purging and sampling, field parameter measurement, chemical and microbial analyses, and QA/QC procedures.

Step 6. Refine the Site Conceptual Model

The site conceptual model should be refined by incorporating new data and reinterpreting site conditions as indicated below. Appendix B references protocols for tasks listed below (e.g., calculation, modeling).

1. Reconstruct:

    - Potentiometric surface (water table) maps with updated data and data from any new monitoring points to assess lateral components of groundwater flow.

    - Hydrogeologic cross-sections parallel and perpendicular to the groundwater flow path with updated data and data from new monitoring points to assess vertical (upward/downward) components of groundwater flow.

    - Isopleth contour maps and vertical cross sections (if warranted) of key groundwater chemistry parameters. Maps existing for the initial site conceptual model (e.g., VOC, possibly anions) should be updated to include new data. Maps should be prepared for new data parameters [e.g., degradation products, redox parameters, electron donors/co-metabolites, electron acceptors, conservative tracers (chloride)].

    - Plots of concentration versus time or concentration versus distance for key groundwater chemistry parameters for wells located on the groundwater flowpath(s).

2. Estimate:

    - Mass balance for parent and daughter products, including both metabolic intermediates (e.g., DCE, VC) and final products (e.g., ethene, ethane, methane, inorganic chloride).

    - Flux of parent and daughter products and, if possible, electron donors, electron acceptors, and co-metabolites.

    - Sorption and retardation of chemicals (from literature or laboratory tests).

    - Biodegradation kinetics such as half-life or degradation rate constants. Biodegradation kinetics can be estimated by evaluating field data (changes in concentration over distance) or laboratory microcosm studies.

    - Estimate the long-term capacity of the aquifer to sustain natural attenuation (e.g., half-life/degradation rate of electron donors/acceptors/co-metabolites promoting degradation).

3. Conduct:

- Fate and transport modeling if the site hydrogeology is complex enough to warrant the effort to better understand the flow regime. Groundwater fate and transport models are currently available to simulate groundwater flow and solute transport (see Appendix B). Models incorporating biodegradation kinetics for natural attenuation of chlorinated solvents are currently under development.

- Compare concentration profiles generated for various time intervals in model simulations conducted with and without incorporating biodegradation kinetics.

- Perform a sensitivity analysis for key geological, hydrogeological, and attenuation factors. Assess the need to refine the available data.

Step 7. Interpret the Data and Test/Refine Conceptual Model

Review the refined site conceptual model and determine whether the data fit this conceptual model.

If the data support the natural attenuation hypothesis developed in Step 3 (i.e., distributions of parent and daughter products are consistent with redox and distribution of electron donors/acceptors, metabolic products and site hydrogeology), then exposure pathways analysis should be conducted (Step 8).

If data do not support the hypothesis developed in Step 3 (i.e., the redox and/or distributions of electron donors/acceptors or metabolic products do not support the distribution of parent and daughter products), then the hypothesis should be refined and re-tested. In most cases, the available data is sufficient to test new or refined hypotheses. However, some additional data collection (a return to Step 4) may be required to test new/refined hypotheses at complex sites.

Step 8. Conduct an Exposure Pathway Analysis

The refined conceptual model should be examined in association with identified human and ecological risks and the following questions should be answered:

- Are the rates of natural attenuation processes sufficient to reduce risk (now and in the future) to human and ecological receptors to acceptable levels?

If yes, then the site is a strong candidate for a natural attenuation alternative and implementation of natural attenuation should be considered as discussed in Step 9. If no:

- Can other engineering controls or technologies control or further reduce this risk such that natural attenuation is sufficient?

If yes, then these options should be further evaluated/implemented. Integration of natural attenuation into the overall remediation strategy should then be considered where it may be cost-effective. If implementation of engineering controls is technically impracticable (e.g., at some DNAPL sites), then natural attenuation may be the primary mechanism of risk reduction and therefore natural attenuation should be incorporated into the long-term site management strategy.

Step 9. If Accepted, Integrate Natural Attenuation into the Long-Term Site Management Strategy

The long-term prognosis of natural attenuation should be assessed by answering the following question:

- Will factors promoting natural attenuation be sustained over the long term (e.g., is the amount of available electron donor/acceptor/co-metabolite sufficient to maintain intrinsic degradation or will additional electron donor need to be added at a later date, and when)?

If yes, then develop a strategy for long-term management that incorporates monitoring and process validation to ensure that regulatory requirements are met (e.g., no adverse impact). If no, evaluate whether it will be possible to enhance the naturally occurring processes in the future (at such time this is required) or whether other remediation technologies can be implemented currently or at a later date to support natural attenuation. A backup remedial technology should be selected at a conceptual level along with natural attenuation even when natural attenuation is selected as the sole remedy.

Findings and the proposed strategy should be presented to regulatory agencies (and the public where appropriate) and final acceptance should be pursued. Upon acceptance, a natural attenuation strategy should be implemented. This final step occurs here exactly as in the AFCEE protocol. In the future, when natural attenuation is as accepted a technology as others currently in use, this step will belong here. In the interim, it is highly recommended that any proponent of natural attenuation actively seek the involvement of regulatory agencies and other stakeholders as early as possible in the process. Involvement should ideally occur after Step 2 or 3, when the proponent has convinced themselves that natural attenuation is worth investigating, but prior to collection of additional data. Acceptance by regulatory agencies at this point will ensure that money is not wasted on additional investigation and that all required data is collected efficiently.

Table 7 contains the elements of a long-term monitoring plan and Figure 7 shows the locations of monitoring wells.

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