Remediation Management Technical Guidance

BP Standard Operating Procedure
Temperature Sampling to Document Hydrocarbon Biodegradation

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Overview of the Temperature Method

This SOP is intended as a tool to use when measuring temperature for evaluation of sub-surface biodegradation of petroleum hydrocarbons and/or changes in rates of biodegradation from *in situ* remediation efforts. BP initiated a technology development program in 2007 that has resulted in the testing and use of temperature at a wide variety of sites including evaluating soil vapor extraction (SVE), air sparge (AS*), in situ* chemical oxidation (ISCO), monitored natural attenuation (MNA), and more recently natural source zone depletion (NSZD).

The basic theory for using temperature as a tool to better understand in situ biodegradation of petroleum hydrocarbon is that heat is released during the breakdown of hydrocarbons (Figure 1). The increase of temperature depends on the rates of reaction and heat transport. The rate of the reaction is largely a function of delivery (including natural diffusion) of oxygen from the surface towards the hydrocarbon source(s) which results in the development of an aerobic/anaerobic (A/A) interface. Temperature can be used to document changes in both the depth of the A/A interface and/or changes in heat released as a result of any type of *in situ* remediation.

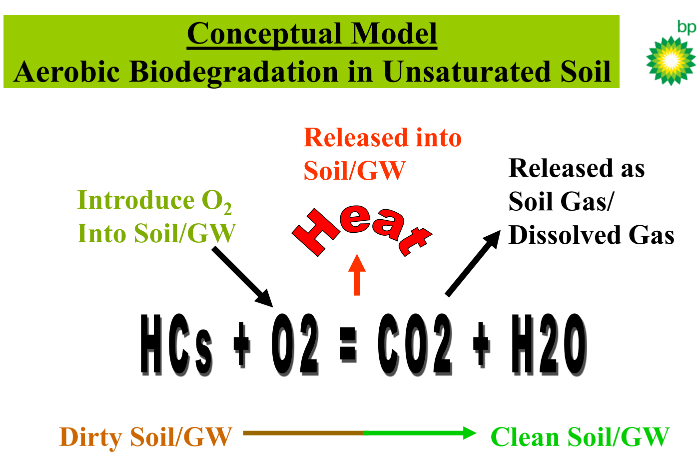


Figure 1: Conceptual model of the aerobic biodegradation of hydrocarbons in the vadose zone showing heat as an important by-product.

A significant amount of energy is needed to change the temperature of soil. The three main components of soil – vapor, water and solid – need different amounts of heat to increase the temperature. The parameter describing the heat needed to raise the temperature is the Heat Capacity of the material. For soil, the volumetric heat capacity (Cv) can be calculated on the basis of soil type and water content. The Cv for air is orders of magnitude lower and can be neglected. Thus, the air within a monitoring well will equilibrate to the temperature of the monitoring well within minutes. This allows for temperature measurements to be made down open monitoring wells.

It has been well established in the agricultural literature that the temperature of soil is a function of air temperature. Heat exchange between soil and the atmosphere continually occurs and is predictable using heat transport models that include the thermal conductivity (k) and heat capacity of soil. For models, the 'thermal diffusivity' factor, or alpha (= k/Cv), is used to combine the heating of soil and thermal flux. A model can be used to project the annual limits in temperature versus depth in the soil. This projection can be compared to measurements to determine whether heat sources (anthropogenic and/or geologic) exist in an area. The mean annual temperature of soil without additional heat sources will be the same as the mean temperature of the atmosphere (Figure 2). By varying alpha and matching the modeled and measured temperature envelopes, the thermal properties of the soil can be better characterized.

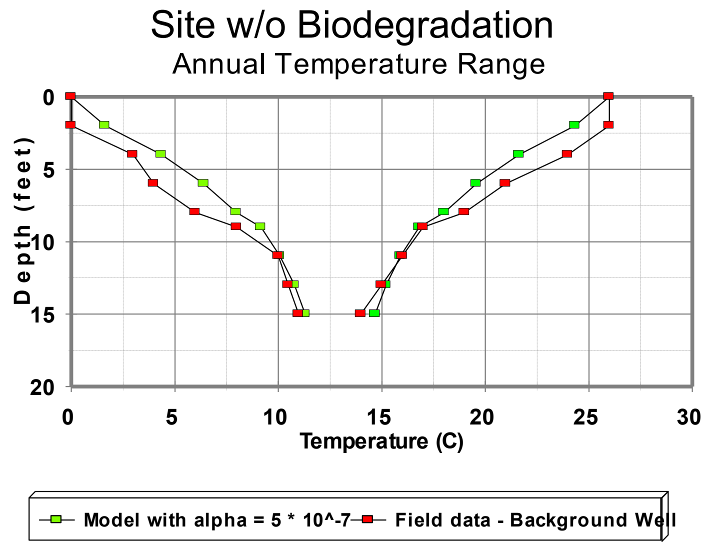


Figure 2: Measured and modeled temperature profile from a site without biodegradation (background).

The general conceptual model for the relationship between aerobic biodegradation and heat released from hydrocarbons is shown in Figure 3, using real data from a monitored natural attenuation site.

'Tailgate' Temperature Measurements

Tailgate temperature measurements are routinely made and recorded during groundwater monitoring events. These measurements are usually made after the groundwater has been brought to the surface. The tailgate measurement may not represent the *in situ* temperature at depth, as changes can occur during transport of water to the surface, and while at the surface before the measurement is made. However, the relative distribution of these measurements has often been a useful indicator of natural attenuation, with the temperature being higher within and downgradient from an area of biodegradation (Figure 4).

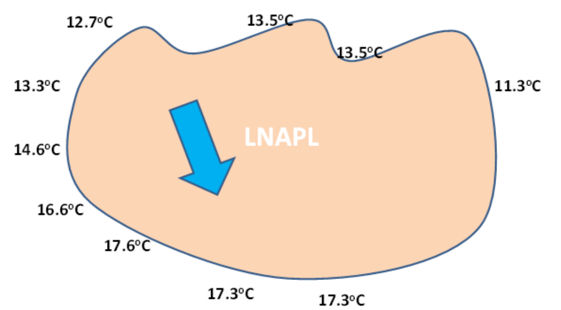
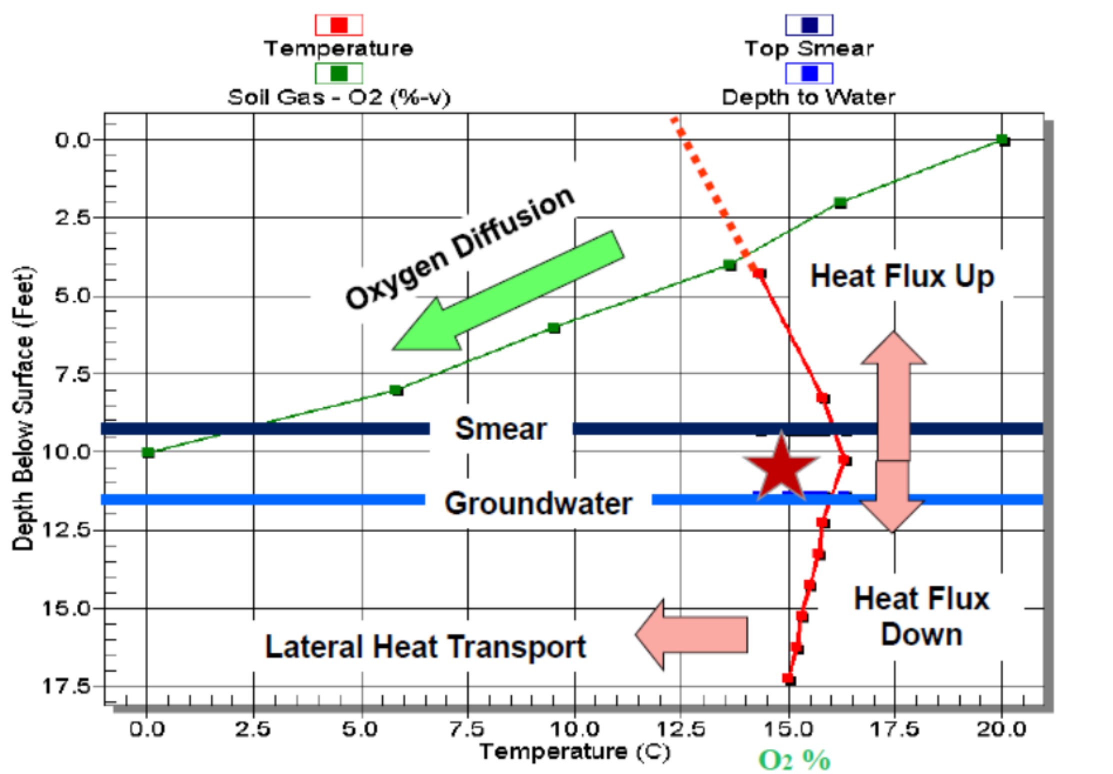


Figure 4: Tailgate groundwater temperature measurements at a site in western U.S.



$$\text{Flux-}O_2 = De * dC / dz \qquad \text{Total Heat} = \text{Flux-}O_2 * \text{Heat of Reaction}$$

Figure 3: Temperature profile at a site with active biodegradation occurring within the smear zone above groundwater.

Conducting *In Situ* Temperature Measurements

In situ Temperature Measurements are made by lowering either a thermistor or sensor down an existing monitoring well. After stabilizing, *in situ* temperatures can be documented at +/- 0.1^{o} C. Sample-specific temperature measurements can be made as part of groundwater monitoring by tying the thermistor cable to the groundwater sampling tube. The best groundwater results will be obtained if the temperature measurement is made at 1 foot below top of groundwater. This method can be used to document MNA and effectiveness of active remediation (Figure 5).

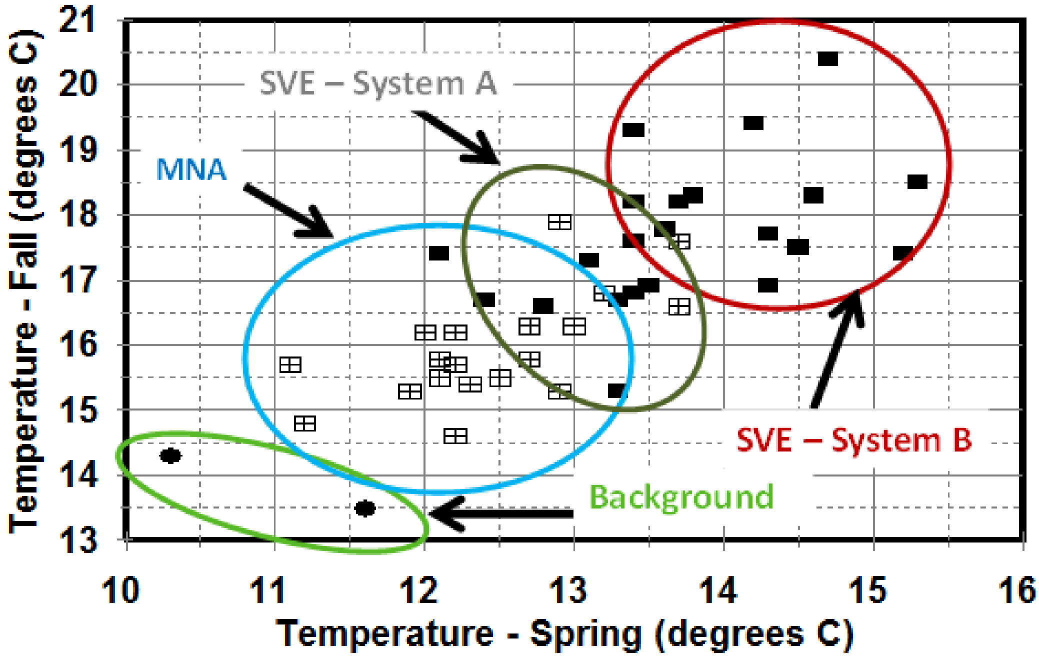


Figure 5: Temperature measurements made at 1 foot below top of groundwater during semi-annual monitoring. Plot used to justify that System A can be changed from SVE to MNA.

The most commonly used *in situ* temperature measurement is a vertical profile or 'snapshot' which are temperature measurements made at multiple depths down an existing monitoring well. Starting at the surface, the probe (Figure 6a) is lowered to different depths, remaining at each depth until the temperature stabilizes with the soil in the vadose zone which can take up to 3 minutes depending on the diameter of the well. Once groundwater is reached the probe should be lowered to a depth of one foot where the stabilization time is reduced to just one minute. Next, the probe should be lowered to three feet below top of water. For a typical well, the full temperature profile will take approximately one hour. It is recommended that profiles for a site be made at the same time of the year, and an upgradient well without contaminated soil or groundwater (background) be measured for comparison.

Figure 6a: Thermistor at the end of a data cable that is marked at one foot intervals and weighted (with a stainless steel bolt in the picture) below the thermistor for long cables (>25 feet).

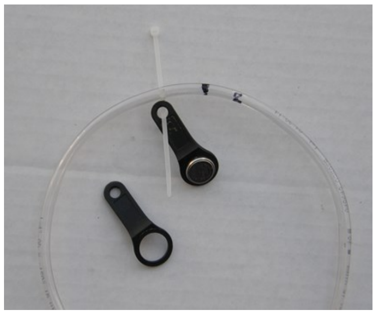


Figure 6b: Sensors (ibuttons) placed in a rubber holder and attached with plastic ties to tygon tubing marked at discrete depths.

Temperature time series data can also be collected using one of a variety of sensors (Figure 6b) that can be left in a monitoring well for a period of time up to 6 months. It is important that the well is sealed sufficiently so that air flow down the well does not occur. The approach discussed further in this SOP has proven to be easy to use, reliable, and low cost.

Project Design

Temperature studies can be one of the most cost-effective methods for documenting, monitoring, and quantifying the rates of *in situ* remediation processes. Temperature measurements can be made in existing wells that are one to four inches in diameter. The procedure below has been used to make temperature measurements to a depth of over 100 feet, and for monitoring temperature changes for a period of up to 6 months. In general, a temperature study should sequentially follow the steps outlined below.

1. Review the existing site conceptual model (SCM) including boring logs, well construction including screened intervals, and tailgate temperature measurements to evaluate the potential for the effectiveness of a temperature study at the site.
2. Measure temperature profiles down existing monitoring wells including upgradient (background wells), wells within the area of known contamination, and wells located downgradient. In the vadose zone, it is recommended to measure temperature starting at a depth of about 2 feet below ground surface, and continue at 2 foot intervals down to the top of groundwater. Once in groundwater, take a measurement at approximately one foot into groundwater then increase the measurement interval to five feet, depending on the depth of the well.
3 Prepare and install sets of temperature sensors down existing monitoring wells. The number of sensors depends on the depth to groundwater. For groundwater down to 20 feet, a 5 foot interval is usually sufficient. It is advisable to have a sensor in the upper one to two feet of groundwater, and one at about 5 below the top of groundwater.
4. Program ibuttons for desired interval of sampling. Longer intervals allow the sensors to be left in the well for longer durations.
5. Retrieve the sensors and download the temperature results for analysis after the desired monitoring duration (e.g. after 3 months).

Step 1: To use temperature to document that natural attenuation is occurring, it is important that the rate of **aerobic** biodegradation is sufficient to create an identifiable increase in the temperature of the soil. Site assessment information should be reviewed for criteria that would limit the influx of O_2 from the atmosphere to the hydrocarbon-impacted soil. It is important to consider:

- Effect of surface cover materials including concrete or asphalt - unless weathered and cracked. Visual observation is usually sufficient.
- Extensive fine-grained soil (silt/clay) layers which can be determined from well logs or grain size measurements.
- Zones of high soil moisture can influence soil temperature and boring logs should be consulted for evidence for their presence.
- Presence of shallow contaminated soil particularly near tanks or lines that might have leaked. Boring logs are useful for identifying these conditions especially the PID readings and any record of soil staining or odor.
- Deep groundwater and any associated smear zone. The magnitude of temperature anomalies becomes less for deeper sources.
- Evidence of methanogenesis at the site. For a deep source, a methane plume in the vadose zone can extend into shallow soil, biodegrade, and create a measurable temperature anomaly in the zone of methane oxidation.

Step 2: Make ‘snapshot’ temperature measurements using a thermistor on a cable. The following procedure has provided reproducible results using wells with a diameter of 1 to 4 inches.

- Calibrate the thermistor daily by placing it into bucket of water along with a thermometer.
- Start with the ‘reference’ monitoring well located upgradient in an area without hydrocarbon contaminated soil. If possible, choose the reference well in an area without surface cover (e.g. asphalt or concrete).
- Field forms should contain the following information:
    - ◊ Well identification – diameter of well
    - ◊ Time, day and year
    - ◊ Weather – cloudy/clear/rain/wind conditions
    - ◊ Surface type – soil, grass, asphalt, concrete, or other
    - ◊ Shade – estimate hours per day well is shaded
- Open the well and measure the depth to groundwater (and LNAPL if appropriate) and to the base of well

- Measure air and surface temperatures using the thermistor
- Procedure for making temperature profile
  - ◊ Make sure that the thermistor is dry
  - ◊ Lower the thermistor down well to a depth of 2 to 4 feet.
  - ◊ Wait 3 minutes then record the temperature (note: at shallow depth, the temperature may still be equilibrating with the soil even after 3 minutes)
  - ◊ Progressively, lower thermistor at 2 foot intervals (for depths to groundwater less than 20 feet) through the vadose zone – wait 3 minutes – record temperature.
  - ◊ Progressively, lower thermistor to approximately one foot below top of groundwater then at 2 foot intervals through groundwater to desired depth – wait 1 minute – record temperature.
  - ◊ Bring thermistor to the surface and air dry.
  - ◊ Review temperature measurements
- There should be a continuous, but not linear, change in temperature through the vadose zone into groundwater; the trend varies with time of year (Figure 7).
- A methane plume in the vadose zone could result in a temperature maximum above the top of groundwater (Figure 8).

Step 3: Prepare and install temperature sensors down existing monitoring wells.

Most contractors prepare and install their own temperature sensors. However, one contractor is available that has developed their own approach using a "Thermal Snake" and will provide services for monitoring temperature down wells (contact RET group for further information).

The procedure that has proven cost effective for routine monitoring at a number of BP sites (Sweeney and Ririe, 2014) involves hanging a series of ibuttons (Johnson, et al., 2005) down the well for 3 month intervals between groundwater monitoring events. For a 3-month deployment, the memory of the sensor allows for measurements to be made on an hourly basis. After the sensors are brought to the surface and the temperature data downloaded, the sensors can be redeployed. The sensor life is about 5 years.

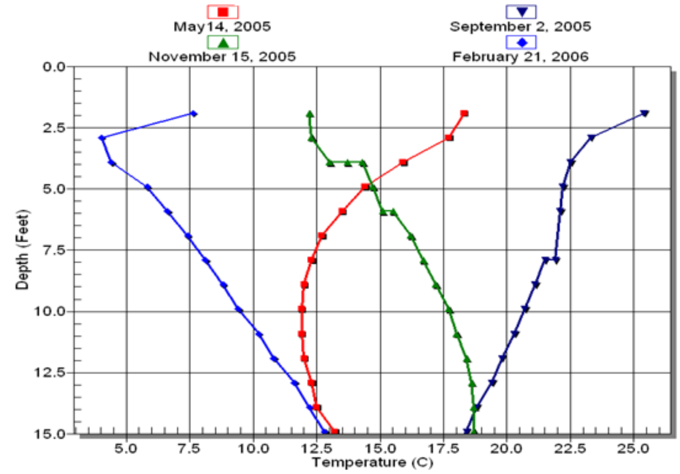


Figure 7: Expected temperature profiles at different times of the year. Trend below 5 feet should be continuous with depth, even into groundwater.

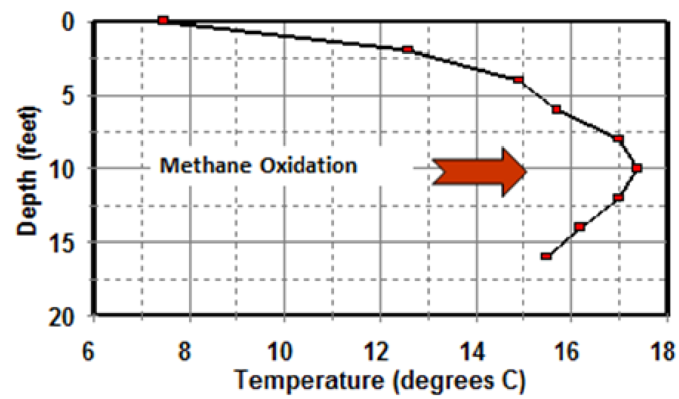


Figure 8: Temperature profile at a location where a methane plume exists in the vadose zone over groundwater which is at 15 feet depth.

Temperature Measurement Materials

In addition to the ibutton sensors themselves, all items listed below can be obtained from the Maxim Integrated company website: http://www.mouser.com/search/refine.aspx?N=4291596096&Keyword=ibuttons:

Materials needed to program temperature sensors are shown in Figure 9:

- Adapter (DS9490R)
- Reader (DS1402D-DR8)
- Free download of driver software (products/digital/1-wire software)
- Free download of 1-wire viewer software

The ibutton sensors are available with different temperature ranges:

Model No.	Temperature Range
DS19212Z	-5 to 26 +/- 0.1°C
DS19212H	15 to 46 +/- 0.1°C
DS19212G	-30 to 70 +/- 0.2°C

Figure 9: Components needed to program the ibutton temperature sensor.

For use in the field, the ibutton is inserted into a key ring mount (DS9093N) as shown in Figure 10a. The ibuttons are programmed while in the key ring, and after waterproofing (Figure 10b) are attached at regular intervals to tygon tubing with plastic ties. Waterproofing of ibuttons is a two-step process – sealing the metal crimp with silicon-based grease, and covering the ibutton with a rubber coating. Alternatively, capsules are available for waterproofing (contact RET for more information on this option).

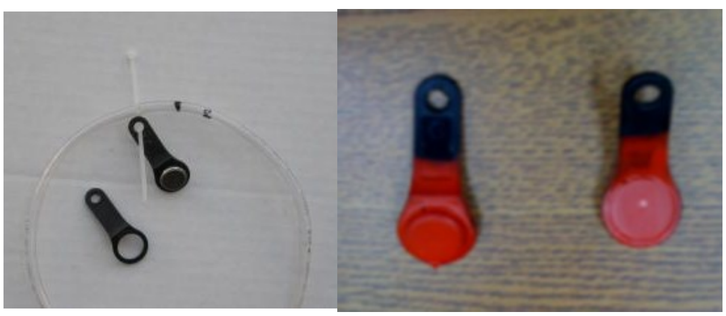


Figure 10: (a on left) shows key ring holder and ibutton as attached to tygon tubing; (b on right) waterproofed ibuttons.

After the ibuttons are programmed and waterproofed, they are attached to tygon tubing at regular intervals from the surface to the lower depth desired. These strings of ibuttons are prepared before going to the field (Figure 11a) so it is important to know the depth to groundwater so that they can be placed directly into the well (Figure 11b).

Figure 11. (a on left) string of ibuttons prepared at 2 foot intervals; (b on right) string of ibuttons lowered into a well.

A stainless steel bolt is inserted into the lower end of the tubing to act as a weight. It is important that the well remains sealed during temperature monitoring. The well cap will need a hook so that the ibutton string can be attached. Figure 12 shows one method for hanging the ibuttons into a monitoring well using tygon tubing attached to a well cap with a plastic tie.

After temperature measurements have been made, the ibutton strings are retrieved from the wells and the individual ibuttons removed, correctly identified, and stripped of their rubber coating.

Figure 12: ibutton string attached to well cap using plastic ties.

Step 4: The ibutton viewer software is used to both program the ibuttons and to download the temperature data from them. If the sensors are to be used for a second monitoring event, the previous data should be downloaded first prior to programming a new sampling scheme ('mission'). The procedure for a typical sampling scheme is as follows:

- Start the software and connect an ibutton to the reader
- **To download data,** go to the Thermochrom tab in the viewer software
  - ◊ Check the status tab – make sure that the current mission is still active
  - ◊ Check the temperature tab – right click on the plot of temperature data to export data in .csv format

- To Set Up a **New Sampling Scheme (Mission),** go to the Thermochrom tab
    - ◊ Check the status tab – make sure the units (C or F) are as desired
    - ◊ Start a new mission
        - Synchronize the clock
        - Enable rollover
        - Set sample rate to 60 minutes
        - Set the delay before start mission time (optional amount of time)
        - Do not enable alarm function
        - Remove the ibutton from the reader

Step 5: Methods to present and interpret temperature measurements.

Useful plots that will illustrate the depth and magnitude of biodegradation usually include a comparison of data collected from a nearby background well. For representative temperature profiles, the measurements need to be made at the same time of the year. As seen in the temperature profile plot in Figure 13, the temperature anomaly at G-35 (background) was used to show that the area of influence from air sparging was significantly larger than determined by other methods.

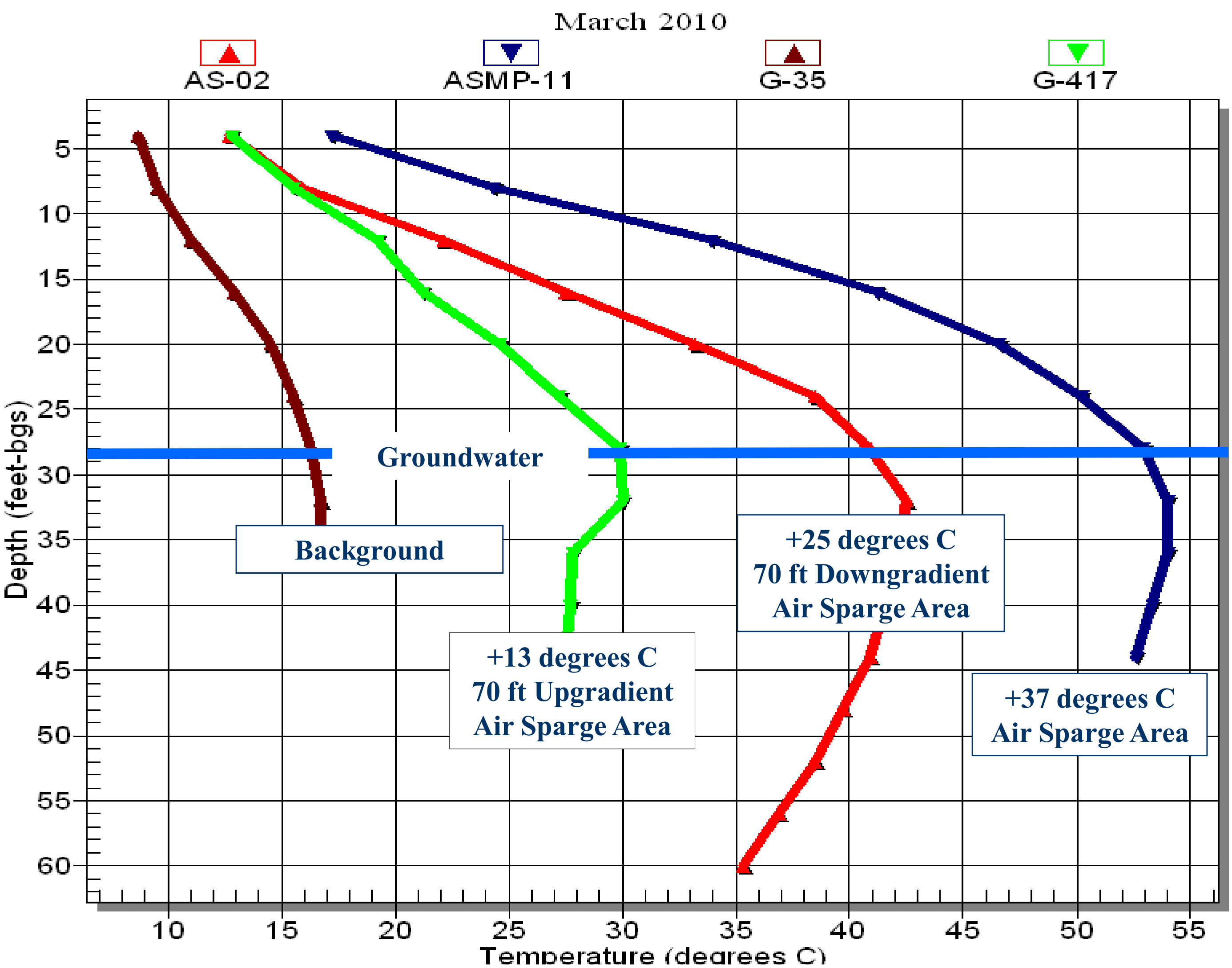


Figure 13: Plot of temperature data for groundwater monitoring wells surrounding an air sparge remediation project. Upgradient temperature profile documented an area of influence much larger than expected.

Temperature sensor measurements from a smear zone can be compared to a background location at a site by using sensor data from equivalent depths (Figure 14). Because the site in this example was warm year round, there was not a significant change in the rate of biodegradation throughout the year. Note that the background changes are consistent with the atmospheric temperature model for the site.

References Cited

Johnson, A.N., B.R. Boer, W.W. Woessner, J.A. Stanford, G.C. Poole, S.A. Thomas, and S.J. O'Daniel. 2005. Evaluation of an Inexpensive Small-Diameter Temperature Logger for Documenting Groundwater – River Interactions. *Ground Water Monitoring and Remediation* 25, no. 4, 68-74.

Sweeney, R.E. and G.T. Ririe 2014. Temperature as a Tool to Assess Aerobic Biodegradation of Hydrocarbons in Contaminated Soil. *Groundwater Monitoring & Remediation* 34, no. 3, 41-50.

Summary of the *in-situ* Temperature Methods

Snap Shot Method

Cost effective and quick

In situ method to avoid surface effects

Produces real time data in field

Requires a background location

Time required is approximately 1 hour per well

Temperature Monitoring with Sensors

Acquires data over time to document changes

Sensors are retrievable and reusable

Variety of time interval options available

Requires well to be sealed at the surface

Can coordinate sensor retrieval and data download with groundwater sampling event

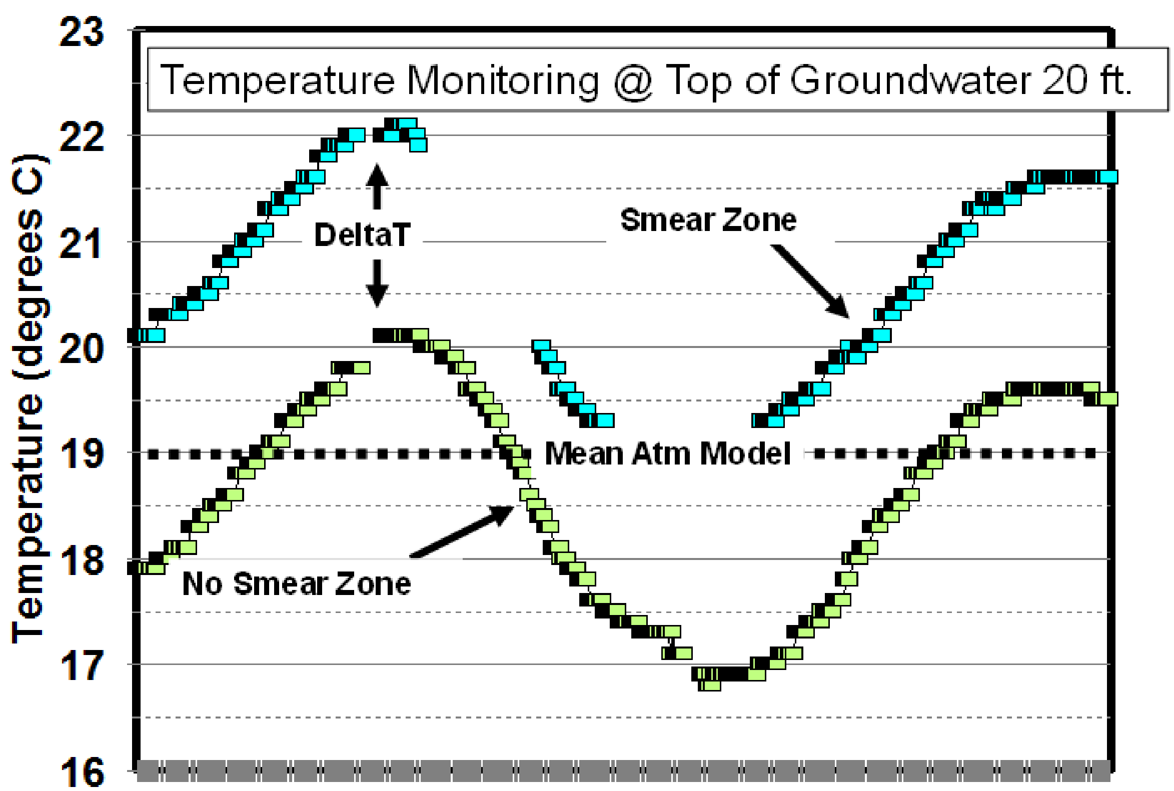


Figure 14: Plot of temperature versus time for 1 year at former service station site. For comparison, the center of the temperature variability modeled from a nearby airport is shown.