

# EVALUATING NATURALLY-OCCURRING PETROLEUM HYDROCARBON RESIDUALS IN SOIL

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## **Abstract**

Human-health risk assessments at sites impacted by releases from leaking underground storage tanks, pipelines or crude production, require an evaluation of the extent and severity of residual petroleum hydrocarbon concentrations that remain after remedial activities have been completed. Recent data collected from several Indiana sites has begun to document the potentially widespread presence of low-level (commonly less than 100 milligrams per kilogram) concentrations of naturally-occurring petroleum hydrocarbons often detected within certain glacial deposits during subsurface investigations at environmental sites. These natural hydrocarbons, the result of site soils derived from the weathering and incorporation of shale bedrock fragments into their matrix during depositional processes, are composed of a number of chemical constituents that may have environmental risk consequences when evaluated without the knowledge of their origin. This presentation provides geologic study, analytical GC/FID chromatographic signature evaluation, downhole geophysical logging, and statistical analyses as a means of characterizing these naturally-occurring constituents in order to differentiate them from historical petroleum releases, and provide a basis for evaluating their risk to human health and the environment.

## **Introduction**

The proper environmental evaluation of residual petroleum hydrocarbons in soils and groundwater at sites impacted from previous human activities remains a significant concern. The results of these investigations, often in the form of human-health risk assessments, may be complicated by the presence of detectable concentrations of naturally-occurring organic chemical constituents that are present in the soil. Since the inability to distinguish between human-impacted soils and nonhuman-impacted soils can affect the manner in which a 'nature and extent' investigation is carried out as well as recommendations for appropriate remedial alternatives for cleaning up these sites, it is important to understand what the source and characteristics of these background organics may be. Recent data collected from a number of central Indiana sites has indicated that low-level (less than 100 mg/Kg) residual petroleum hydrocarbons may be present in glacial soils as a result of processes that occurred during the deposition of these materials. The technical approach used to evaluating these soils has led to a means of distinguishing their presence at project sites in order to characterize their risk to potential receptors and select appropriate remedial strategies.

## Project Characteristics

The project site is the location of a proposed dam and 40-acre flood control reservoir along Pogues Run near the intersection of Interstate 70 and Emerson Avenue on the east side of Indianapolis, Indiana (Figure 1). An initial Phase I Environmental Site Assessment (Phase I ESA) completed as part of the initial round of studies for the project indicated the likelihood of past illegal dumping and disposal of miscellaneous fill dirt and demolition and construction debris. Subsequent Phase II ESA investigations were completed over the site that consisted of the advancement of 51 Geoprobe soil borings and 43 soil borings with soil sampling and testing for volatile organic chemical, RCRA heavy metals, PCBs, and total petroleum hydrocarbons (TPH). The results indicated that elevated TPH concentrations (above 100 mg/Kg) were observed in two fill areas at the site, one an eastern fill area approximately 7 acres in area, and another, a western area of about 3 acres in size (see Figure 1). These

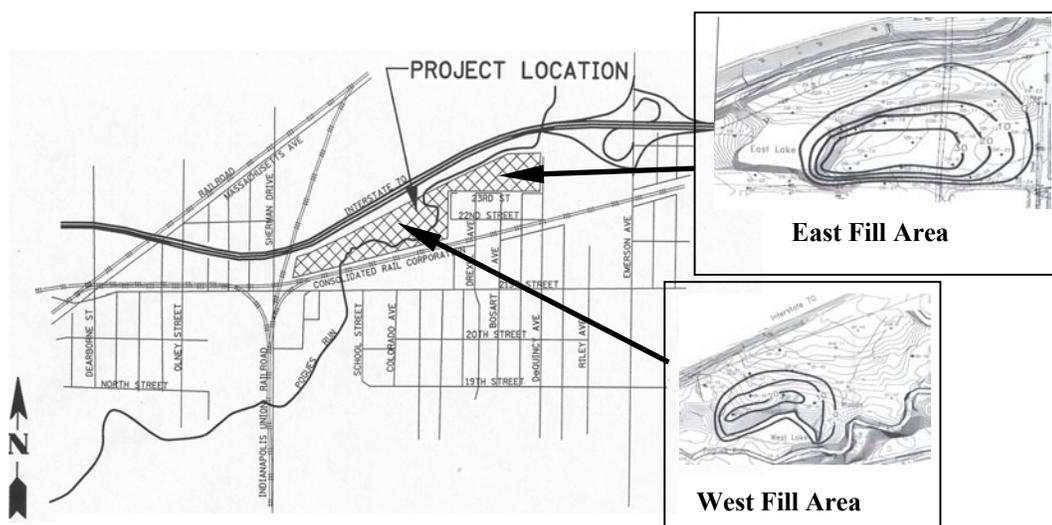


Figure 1. Project Site

TPH levels were noted within the fill and native soils immediately adjacent to or beneath the site fill soils. In addition, elevated TPH levels (greater than 20 to 98 mg/Kg) were also noted throughout the entire site. Since the project called for the construction of a large water reservoir, excavation and off-site disposal of any impacted soils was required. Several questions arose during this phase of the study. Has the entire site been impacted by past human activity? What is the source of the observed impacts? Are all impacts of a human-health risk concern? Will all excavated soils require landfill disposal? To answer these questions, potential sources of the elevated TPH levels were considered, including naturally-occurring ones.

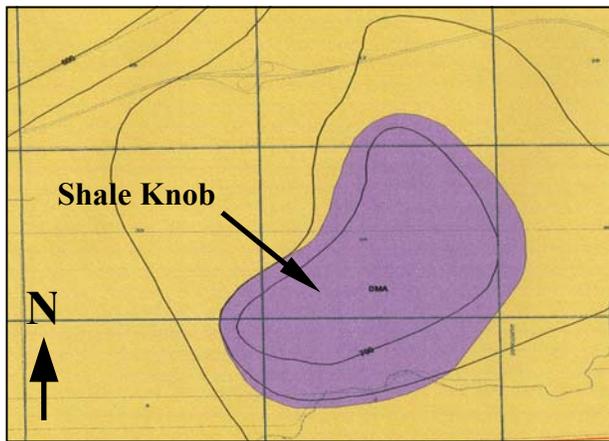
### Source of TPH in Marion County Glacial Soils

Bedrock deposited during four periods of the Paleozoic Era are present directly beneath the unconsolidated glacial drift underlying Marion County. Devonian rocks at the bedrock surface consist of the Geneva Dolomite, the Jeffersonville Limestone, and the New Albany Shale. While dolomite or limestone is expected to directly underlie the soils at the project site, New Albany Shale is also present at the bedrock surface within less than one mile east-southeast of the site (Fleming et al., 1993). The

bedrock surface appears to have been modified by glacial activity, particularly by channelized meltwater. Most of the bedrock uplands have, at one time in the past, undergone direct erosion by glacial ice, and have provided sources of material for the generation of newly-deposited soils and sediments. It should be noted that the New Albany Shale is an evenly laminated gray, brown and black, locally organic-rich shale unit with much lesser amounts of limestone and dolomite approximately 100 to 130 ft in thickness (Harrison, 1963). This unit underlies the bedrock surface beneath Marion County in a band running from the south-central edge of the county to the northwest corner. The New Albany shale is known for its petroleum-containing characteristics, and is the source of most of the oil in Devonian and younger oil reservoirs in the Illinois Basin.

The probable flow paths used by Wisconsin and Illinoian ice streams made their way through Canada and the great lakes to Marion County (Harrison, 1960, fig. 3). These ice streams, part of the Ontario-Erie major lobe of the Wisconsin ice sheet, incorporated rock fragments from each of the many different bedrock formations that lie along the path. It is believed that the ice eroded about the same weight of bedrock per unit area from each of the various bedrock formations that it traversed (Harrison, 1960). In general, softer rock varieties were worn down more readily than the harder ones, and those rocks that were transported greater distances became more pulverized. Thus, the sand and pebble size particles within the tills are made up primarily of the harder pulverized igneous and metamorphic rocks, and the silt and clay fractions are composed more of pulverized shales.

Based on the glacial soil depositional history and glacial ice sheet movement, either Devonian-age New Albany shale from the Marion County area or Antrim shale from northern Indiana (the New Albany equivalent) are believed to be the specific units from which any shale contained within the soil



**Figure 2. New Albany Shale Knob One Mile East of Site (Flemming et al., 1995).**

was derived. In the vicinity of the site, the Indiana Geological Survey (IGS) (Flemming et al., 1993) has identified an elevated bedrock knob of Devonian-age New Albany shale within about 1 mile east-southeast of the project site immediately south of Brookside Creek and east of Emerson Avenue (Figure 2). Because of its proximity to the site, this approximately 1.5 square mile buried New Albany shale hill could have acted as a local source of shale within the glacial till and sand soil matrix as the Illinoian and Wisconsin ice sheets moved across this portion of Marion County. The northern Indiana Antrim shale encountered by the ice sheets along their path to Marion County could also represent a potential source of parent shale material for portions of the site soils.

This contribution would most likely be within the finer-grained silt and clay-size fractions since a more complete pulverization would have occurred as a result of greater transport distances from the north-northeast in the general direction of glacial ice flow.

### **Characteristics of Marion County Glacial Tills**

It has long been recognized that textural, lithologic and geochemical variations observed in glacial soils may provide clues relating to their depositional origins and sequences (Kruger, 1937; Krumbein, 1933). A number of studies have attempted to correlate textural and compositional data with

glacial drift depositional characteristics with varying success (Gravenor, 1951; Shepps, 1953; Forslev, 1957; Harrison, 1957; Horberg and Potter, 1955). Harrison (1959) performed fraction analyses (mineralogy and lithology versus size) on eleven Wisconsin-age glacial till samples collected throughout Marion County to evaluate the potential for using these properties for correlation with different till sheets. The particle size distribution composing each till sample was determined and the composition of each particle size fraction was identified, with the fraction analyses expressed in weight percentages. The typical till, indicated by the average textural and compositional data, is high in carbonates and reflects the high percentages of limestone and dolomite bedrock that were eroded by the ice streams that flowed in Marion County. Plotting of the fraction-analysis data on trilinear diagrams by Harrison indicated the till samples were too similar in texture and composition to adequately distinguish them based on the data. He concluded that the pronounced textural and compositional similarity implied a uniformity in the glacial processes and parent source materials between successive glacial events.

**Table 1.**  
**Shale and Illite Content Variation Within**  
**Eleven Glacial Till Samples (evaluated from Harrison, 1959)**

<i>COARSE SILT TO COARSE GRAVEL PARTICLE SIZE</i>		
<i>Particle Size (mm)</i>	<i>Average Weight Percent of Total</i>	<i>Average Shale Percent by Weight of Total</i>
0.031 to 32	59.25	2.73
<i>FINE SILT TO CLAY SIZE PARTICLE RANGE</i>		
<i>Particle Size (mm)</i>	<i>Average Weight Percent of Total</i>	<i>Average Illite Percent by Weight of Total</i>
<0.00098 – 0.0312	40.76	10.54
<i>Total Shale + Illite</i>	<i>100.01</i>	<i>13.27</i>

A re-analysis of the Harrison (1959) data was completed to determine the average percent of shale within the eleven till samples, with the final results shown in Table 1. The analysis indicates that the percentage of shale within each of the particle size fractions increases from a low of 1.6 percent of the 0.031 to 0.062 mm (coarse silt size) fraction to a maximum of 9.8 percent of the 0.500 to 1.0 mm (medium sand size) fraction, before decreasing again in the coarse sand and gravel size. The average shale percent of the total till sample within the coarse silt to coarse gravel size particle range was about 2.7 percent by weight for the eleven till samples. Although Harrison (1959) could not do an evaluation specifically for shale in the finer silt and clay size fractions, a mineralogic analysis indicated a significant portion (approximately 10.5 percent by weight) of illite in this particle size range. This mineral most likely represents a contribution from a pulverized shale parent rock. Based on this re-analysis, it is apparent that Marion County Wisconsin (and most likely Illinoian) glacial tills contain shale parent materials either in visible sand or gravel particle sizes (approximately 3 percent by weight) or in pulverized, fine-grained silt and clay size fractions (about 11 percent by weight).

Recent visual observations and testing of other Marion County glacial soils (outwash sands and gravels) in the downtown Indianapolis area have indicated the presence of from 3 to 5 percent shale by weight within the granular matrix (MUNDELL, 1997).

### Shale Petroleum Hydrocarbon Characterization

From the preceding literature review and experience with other projects in Marion County, it is highly likely that naturally-occurring shale fragments and pulverized shale parent material exist within the site glacial soils. To determine if the presence of this shale could impact the observed organic geochemical composition of the glacial soils, it is necessary to review what is known of the organic chemical characteristics of the likely shale parent materials. As stated previously, the New Albany shale is known for its petroleum hydrocarbon-containing characteristics throughout Indiana, and its presence within the site glacial soils at the site could result in a naturally-occurring elevation of petroleum hydrocarbons within these materials.

Stevenson and Dickerson (1969) collected about 350 samples of the Upper Devonian-Kinderhookian New Albany Group throughout Illinois and found that organic carbon contents range from less than 1 percent to near 9 percent. Frost (1980) collected 371 samples of the New Albany Group and reported that 319 had organic carbon contents greater than 1 percent; the highest value being 15.6 percent. From 21 samples of New Albany shale tested by Hatch et al. (1990), the median organic carbon content is 3.7 percent, with a range of 0.2 to 9.3 percent.

The identification of the relative amounts of specific petroleum hydrocarbons within a shale sample is obtained with the use of gas chromatography. This analytical technique produces a graph, or chromatogram, of the relative

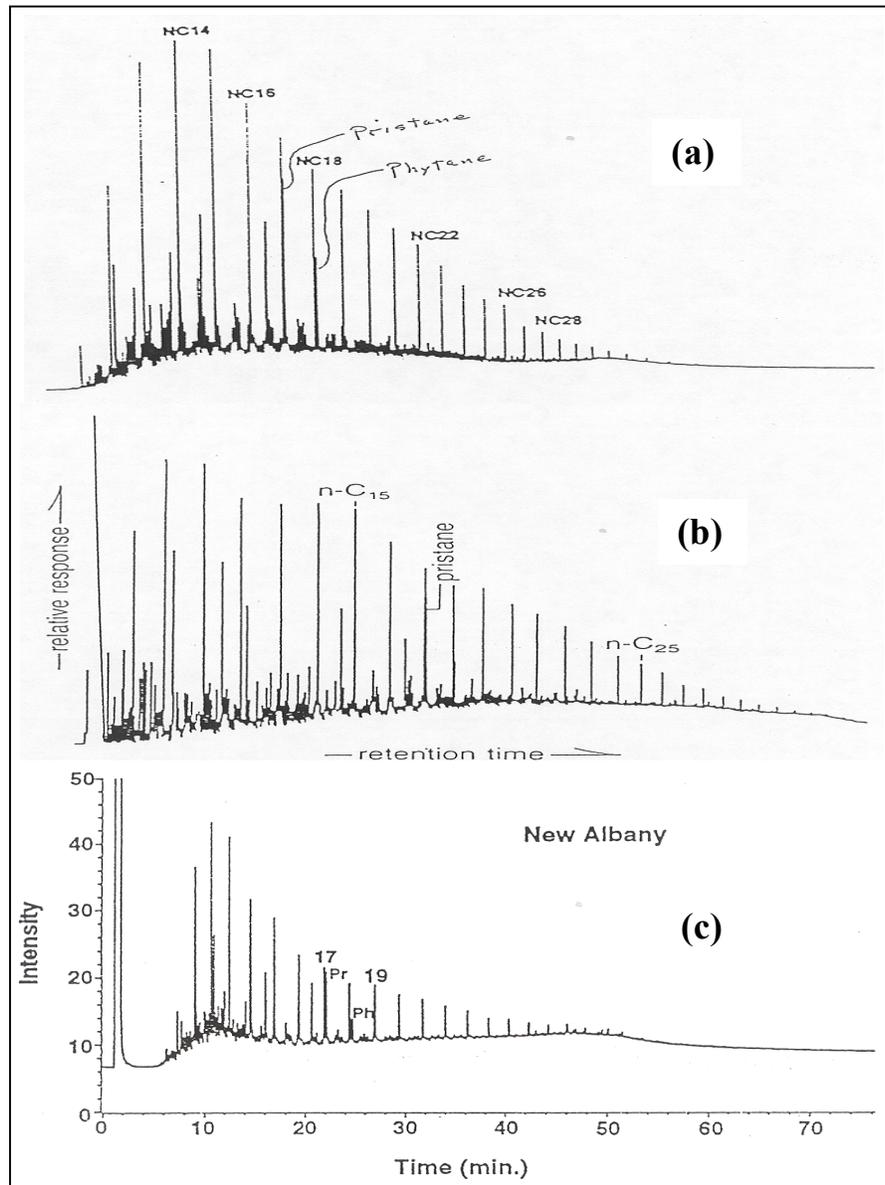


Figure 3. Typical New Albany Shale Chromatograms (a) Bethke et al. (1991), (b) Hatch et al. (1991), and (c) Guthrie and Pratt (1995).

abundance of the various hydrocarbon constituents versus the retention time that these constituents are held during the testing process. This chromatogram provides a particular signature or fingerprint which is unique to the type of petroleum hydrocarbon present, and may be used to determine the likelihood that two particular hydrocarbons are the same or from the same rock formation, or whether they have undergone any natural or human-induced degradation or refinement. Figure 3 illustrates three examples of published chromatograms for extracts taken from New Albany shale (Bethke et al., 1991; Hatch et al., 1991; Guthrie and Pratt, 1995). Although the results are from three samples taken from widely different locations, similarities exist in the general shape and relative distribution of hydrocarbons, and provide evidence that the New Albany shale's chromatogram has unique characteristics which make it readily identifiable.

Typical geochemical characteristics or indices of oils extracted from the matrix of shale bedrock can be developed using various organic chemical constituent ratios (Philp, 1985). These indices provide a means of identifying particular petroleum hydrocarbon sources and correlating bedrock units. One of the most common ratios is that of pristane to phytane. Pristane occurs adjacent to C<sub>17</sub>, and phytane occurs adjacent to C<sub>18</sub> on the gas chromatogram profiles (Killops and Killops, 1993). Pristane and phytane are regular isoprenoids with head to tail linkage (Philp, 1985).

The New Albany shale extract chromatogram has been shown to be characterized by a lack a predominance of the odd-carbon-numbered n-alkanes (i.e., it exhibits smoothly decreasing amounts of n-alkanes) and a relative abundance of isoprenoids. For thirteen New Albany shales, Hatch et al. (1990) determined that the pristane/phytane ratios ranged from 1.6 to 2.1. The relative amounts of C<sub>19</sub> to C<sub>29</sub> tricyclic and C<sub>24</sub> tetracyclic terpanes (m/z = 191) from New Albany shale extract was characterized by relatively abundant C<sub>23</sub> tricyclic terpane and relatively low amounts of C<sub>19</sub> tricyclic and C<sub>24</sub> tetracyclic terpanes.

Guthrie and Pratt (1995) have recently tested a New Albany shale extract. The gas chromatogram for the New Albany Group bitumen showed high abundances of pristane (Pristane/n-heptadecane ratio, Pr/n-C<sub>17</sub> of 0.92) and phytane (Phytane/n-octadecane ratio, Ph/n-C<sub>18</sub> of 0.40) relative to the adjacent n-alkanes. The New Albany shale extract also exhibited a low odd-carbon predominance in mid-chain n-alkanes (average Mid-chain carbon preference index (MC-CPI) of 1.10), and a low relative abundance of mid-chain-molecular-weight n-alkanes (average Mid-chain molecular weight/high-chain molecular weight ratio (MC-MW/HC-MW) of 2.85).

## **Comparison of TPH Testing of Project Site Glacial Soils to Published Testing**

In order to identify if the chromatograms observed from the testing of on-site soils may have resulted from the presence of shale within their matrix, a comparison of published selected chromatogram peaks with the analytical testing results of the on-site undisturbed glacial soils was made. Relative peak heights versus retention times were reviewed from all TPH testing. Table 2 summarized selected peaks which have been shown in the literature to be characteristic of New Albany shales. As indicated by the table, pristane/phytane ratios for the on-site undisturbed soils ranged from 1.5 to 2.2, compared to the published range of 1.6 to 2.1. Pristane to n-C<sub>17</sub> ratios fell within 0.81 to 1.25 and Phytane to n-C<sub>18</sub> between 0.50 to 0.80. Based on a review of the general chromatogram shape and relative peak characteristics, the undisturbed on-site glacial soils strongly correlate with both published shale geochemical characteristics (Figure 3) as well as shales tested from other Indianapolis area projects (MUNDELL, 1997), and therefore the TPH detected in undisturbed, native soils is concluded to be derived from the naturally occurring shale within the glacial soil matrix.

A peer review of the site undisturbed glacial soil chromatograms, selected site soil chromatograms was completed by the Indiana Geological Survey. The IGS determined after its review that the chromatograms from the testing on selected till and sand samples from the site were not consistent with those of refined (human-made) products (e.g., gasoline, diesel fuel, motor oil, kerosene), but were consistent with the signature observed naturally in New Albany Shale.

**Table 2.  
Comparison of Selected Published  
Chromatographic Peak Ratios to On-site Results**

<i>Sample Identification</i>	<i>Pristane/Phytane</i>	<i>Pristane/n-C17</i>	<i>Phytane/n-C18</i>
Hatch et al. (1990)	1.6 - 2.1	-	-
Guthrie and Pratt (1995)	-	0.92	0.40
On-site, undisturbed glacial tills and sands	1.5 - 2.2	0.81 - 1.25	0.50 - 0.80

### TPH Testing of Indiana Shales

In order to better quantify the potential TPH contribution from the presence of shale clasts within on-site soils, several off-site and on-site shale samples were tested. Two samples of the (upper Devonian) Antrim Shale were obtained from the IGS for total petroleum hydrocarbon testing. These IGS samples came from two locations in northern Indiana thought by the IGS to yield representative Antrim Shale that could potentially be a source of shale material for some of the Marion County glacial till and sands. The shale samples were submitted for testing using U.S. EPA SW846 Method 8015M and total organic carbon content analysis.

In addition, one New Albany shale sample from a southern Indiana bedrock outcrop was collected. Shale clasts were also found and removed from three on-site glacial till samples at depths of 8 to 20 ft below the ground surface. The results of the shale TPH testing are summarized in Table 3 together with a previously tested off-site shale sample obtained from a downtown Indianapolis glacial sand (MUNDELL, 1997).

The results shown in Table 3 indicate the detection of TPH in tested offsite shale samples in the range of 540 to 1100 mg/Kg, with the average shale (New Albany and Antrim) containing about 747 mg/Kg TPH. The shale clasts from the project site exhibited TPH levels ranging from 101 to 481 mg/Kg, with an average TPH of 270 mg/Kg. The total on-site soil samples from which the shale fragments were taken exhibited a TPH concentration range of 34 to 78 mg/Kg, with an average TPH of 52 mg/Kg.

Testing of unimpacted, naturally occurring outwash sands and gravels from samples taken in downtown Indianapolis (MUNDELL, 1997) indicated that for samples with approximately 3 to 5 percent shale content, analytical testing indicated a TPH range between less than 20 mg/Kg to about 70 mg/Kg, with the majority of samples exhibiting TPH concentrations in the range of 20 to 40 mg/kg. The chromatograms from these sands and gravels were observed to match those of New Albany shale

fragments that were removed and tested from the sands and gravels, providing clear evidence that the shale was the cause of the elevated TPH.

**Table 3.  
Results of Total Petroleum Hydrocarbons and Total Organic Carbon Testing of Indiana Shale Samples and On-site Shale Clasts**

<i>Sample Identification</i>	<i>TPH 8015M, mg/Kg</i>	<i>Total Organic Carbon, mg/Kg</i>
Antrim Shale North American #1 Sinn, 125.1-125.9 ft (IGS Sample)	540	79,000
Antrim Shale NIPSCO #1 Taelman, 269.7 - 269.9 ft (IGS Sample)	1,100	70,000
New Albany Shale Outcrop (Fluor Daniel GTI Sample)	557	-
Project Site GP25, 13-15 ft, Silty Sand (SM) B37, 8-10 ft, Sand (SP) B32, 18-20 ft, Silty Clay/Clayey Site (ML/CL)	481*, (78)** 101*, (44)** 228*, (34)**	- - -
New Albany Shale (Sand) (MUNDELL, 1997)	790*	-

\*Shale clasts removed from entire soil sample and tested

\*\*Entire soil sample

### Predicting Naturally Occurring TPH

Knowing the percentage by weight of shale content within the glacial tills and sands, it is possible to predict the variation in the naturally occurring TPH concentration within the soils. Based on the previously cited literature and project experience, it is likely that shale content within some Marion County soils may range between about 3 to 13 percent by weight. With TPH testing of shale fragments from project sites and New Albany and Antrim shale samples from other locations in Indiana, an expected TPH range of about 540 to 1100 mg/Kg has been observed. Therefore, potential naturally occurring TPH levels in the undisturbed glacial soils could be expected to be on the order of:

$$\begin{aligned}
 \text{TPH}_{\text{natural}} &= (\text{Shale fraction in Soil}) / \text{TPH}_{\text{shale}} \\
 &= (0.03 - 0.13 \text{ kg shale/Kg soil}) (540 - 1100 \text{ mg TPH/Kg shale}) \\
 &= 16 - 143 \text{ mg/kg}
 \end{aligned}$$

Based on the review of TPH testing of all undisturbed soils at the site, it is apparent that the TPH levels at the Pogues Run project site fall well within this potential range, generally exhibiting TPH from less than 20 mg/Kg to 98 mg/Kg, with an average of about 46 mg/Kg.

### Natural Gamma Response from Glacial Soils

Based on previous geophysical logging of borings in the Midwest, it has been determined that there is a general correlation between certain geophysical responses and soil and bedrock composition. Merritt (1961) measured the natural radioactivity of samples of Devonian shale from localities in northwestern Ohio to southern Michigan around the Erie basin. High natural radioactivity of over 2000 counts per minute per kilogram were observed for shale samples, and over 500 counts per minute per kilogram for lake clay samples. Others (Bates and Strahl, 1957; Swanson, 1969) have reported relatively high natural radioactivity of Devonian shales in the Great Lakes region. Gooding (1973) attributed an observed increase in the natural radioactivity of tills from south to north in eastern Indiana to the increased Devonian shale content (as discrete rock clasts in the coarse sand fraction and as comminuted shale in the finer sand, silt and clay fractions) related to the closer proximity of the tills to the source of the Devonian shale.

Natural gamma-ray logs of boreholes in soil and bedrock record photons of gamma radiation received by a detecting crystal over a period of time. Gamma radiation is emitted during the radioactive decay of uranium, thorium, their decay series, and the unstable isotope of potassium, <sup>40</sup>K, contained in the subsurface soils and rock. In the Midwest, the gamma log is a measure of the general clayeyness or ashaliness in soils and sedimentary rocks, indicating the emission of <sup>40</sup>K contained in the clay mineral illite, a significant component of Paleozoic shales and Pleistocene glacial tills (Bleuer, 1998).

To determine if the variation in the natural clay or shale content in glacial sites at the project site can be correlated with the TPH levels, two soil borings, SB-44 and SB-45, were drilled in the western and eastern portions of the site, respectively, each to a depth of 40 ft.

These borings were advanced using hollow-stem augers and 2 ft length discrete soil samples were taken at 5 ft intervals to the bottom of the boring using a split-spoon sampler. The soil samples were field-screened, classified, placed in sample containers, and submitted for analytical testing for TPH by U.S. EPA SW846 Method 8015M. In general, the borings encountered brown to dark olive-gray fine-grained glacial tills (classified with the Unified Soil Classification System as clayey silt (ML) or silty clay (CL)) to the maximum depths of the borings.

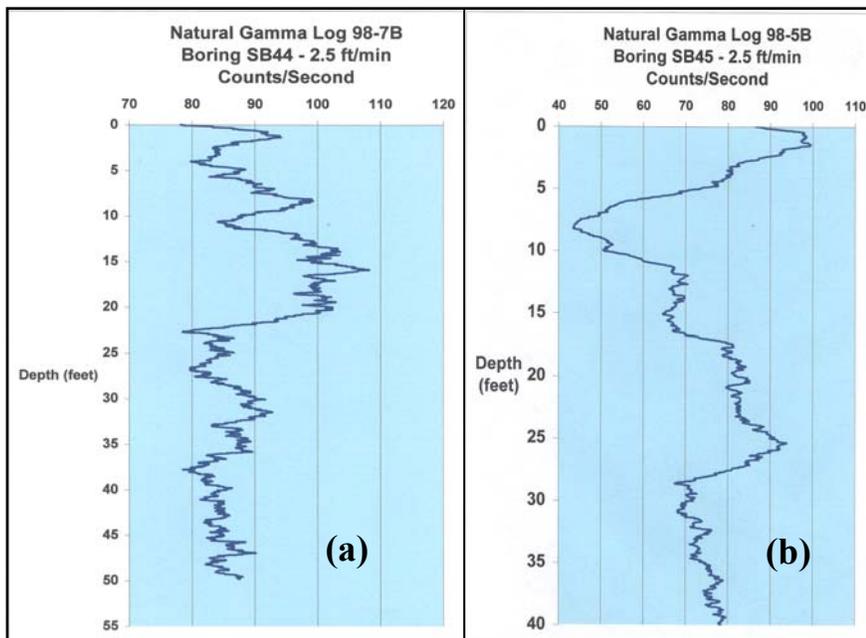


Figure 4. Natural Gamma Response with Depth – (a) Boring SB44B and (b) Boring SB-45B.

Immediately adjacent to each boring, a second offset boring (SB-44B and SB-45B) was drilled for the purpose of natural gamma-ray logging. The borings were advanced to depths of 45 to 49 ft below the ground surface. A 4-inch diameter PVC standpipe was placed in each hole prior to natural gamma logging. The natural gamma-ray logs generated from the borings are shown in Figure 4. Variations in the natural gamma response of the glacial tills can be easily observed with depth.

In boring SB44B (Figure 4a), the upper 11 ft exhibited highly variable response counts between about 80 to 100 counts per second (cps). From about 11 ft to a depth of 22 ft, the response increased and was observed to be more consistent, typically ranging between approximately 95 to 105 cps. Between 20 to 22 ft, the gamma response decreased and randomly varied between about 80 to 90 cps to the maximum depth of the logging (49 ft).

In boring SB-45B (Figures 4b), the natural gamma response reached a maximum of about 100 cps in the upper 2 ft, and gradually decreased to about 42 cps at a depth of approximately 8 ft. From 8 ft to about 11 ft, the response increased to near 68 cps and consistently remained near that level until about 16 ft. Between 16 and 17 ft, the gamma response increased, and exhibited a relatively consistent level just above 80 cps from about 17 to 23 ft. At 23 ft, the response increased steadily until it reached a maximum of about 92 cps near 25 ft before decreasing at a constant rate to a depth of about 28 ft. Below 28 ft to about 40 ft, the response gradually increased from about 70 cps to nearly 80 cps before reaching the bottom of the test boring.

Based on the natural gamma-ray logs, the changes in the gamma observed response may be interpreted as distinguishing features which mark separations between glacial soils of different ages. Based on these variations, and the IGS's interpretation of nearby gamma logs, the upper site soils (22 to 28 ft below the ground surface) appear to belong to a Wisconsin period of deposition. During this period, it appears that there may have been at least two and possibly three separate depositional events (e.g., as represented by distinct till sheets as shown in SB45 from 0 to 10 ft, 10 to 16 ft, and 16 to 28 ft). Below this depth, the gamma response is distinctly lower and more consistent, and appears to represent a pre-Wisconsin (most likely Illinoian) depositional age.

The results of the TPH concentration versus gamma response for the Wisconsin and pre-Wisconsin deposits are shown in Figure 5. As indicated in the figure, a moderate linear correlation

( $r^2 = 0.51$ ) between gamma response and TPH exists, indicating that soil units with higher natural shale or clay contents (as indicated by the higher natural gamma response) generally yield higher natural TPH levels. It should be noted that for the purposes of this study, samples were tested at 5 ft depth intervals, whereas variations in the gamma response were observed to occur over a much smaller scale length. It is expected that the correlation would improve (i.e.,  $r^2$  would increase) as the testing frequency with depth is increased. In addition, other factors

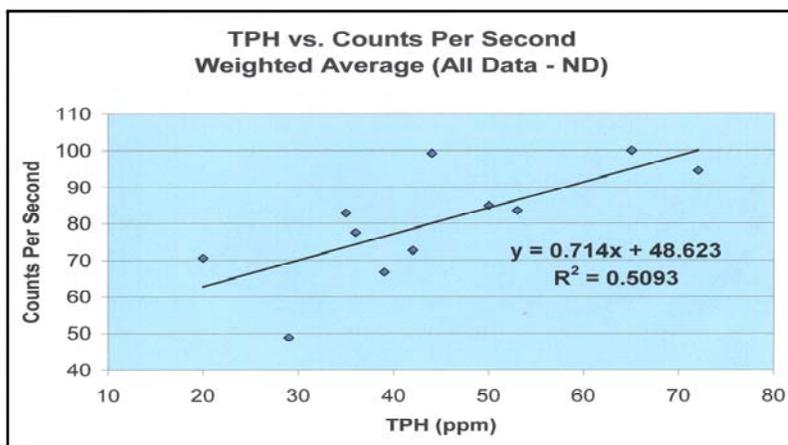


Figure 5. Correlation Between Naturally-occurring TPH and Gamma Counts

may impact the degree of correlation that can be expected (e.g., shale type, variation of uranium content or the unstable isotope of potassium,  $^{40}\text{K}$ , with petroleum hydrocarbon content, etc.). In general, for the intensity of sampling selected for this study, the magnitude of the correlation is sufficient to support the

conclusion that the observed TPH in the undisturbed, native glacial soils is a naturally-occurring phenomenon, resulting from the presence of shale in the soil, and observed to vary with both depth and glacial soil unit, and is not a result of a human-induced petroleum source.

## **Statistical Evaluation of TPH Chromatographic Data**

A statistical analysis of TPH chromatographic data was completed to determine if the New Albany Shale pattern was unique and could be identified using a pattern recognition program. Using discriminant analysis techniques, a classification function was developed from a subgroup of 36 known New Albany shale TPH chromatograms using 10 target petroleum peaks that exhibited a characteristic pattern. This known data set was used to develop a classification function. Using the classification function, a 94 % accuracy rate was achieved for classification of the known subgroup, indicating an exceptionally reliable function had been developed. Subsequently, an additional 74 new (unknown) soil sample TPH observations measured outside of the project site fill areas were run through the discriminant model to verify the sample classification.

A variance assessment and geostatistical evaluation were also performed on the site TPH soil data. The results of the study indicated that the New Albany shale group variance was an order of magnitude less than the Unknown Hydrocarbon group variance (i.e., soil samples within or near the fill areas), indicating the naturally-occurring TPH was less variable and more consistent across the entire site than the TPH impacts caused by human-induced activity. In addition, the New Albany shale TPH concentrations were found to be randomly distributed both in horizontal and vertical spatial directions, and are most likely naturally-occurring and not caused by petroleum hydrocarbon releases from specific source areas.

## **Conclusions**

Based on this study, the following may be concluded:

- 1) Naturally-occurring total petroleum hydrocarbons (TPH) are present in glacial soils in Marion County, Indiana;
- 2) The naturally-occurring TPH is the result of the presence of Devonian-age (New Albany and Antrim) shale rock fragments (clasts) and pulverized shale that were incorporated into the soils during the erosion of shale bedrock during the advancement of glacial ice;
- 3) New Albany shale content within the glacial soils has been estimated to be between 3 to 13 percent by weight;
- 4) Indiana Devonian-age shales (New Albany and Antrim) have been shown to contain naturally-occurring petroleum hydrocarbons at TPH concentrations in the range of 540 to 1,100 mg/Kg, with total organic concentrations of about 7 to 8 percent by weight;
- 5) Analytical testing of undisturbed, glacial soils by a gas chromatograph produced a distinctive chromatographic signature, or *Afingerprint@* of petroleum hydrocarbon constituents closely resembling the relative magnitudes and types also produced by the

- testing of Indiana shales. Comparison of characteristic petroleum peak ratios known within the shales (e.g., pristane/phytane, pristane/n-C<sub>17</sub>, and phytane/n-C<sub>18</sub>) to those detected in the glacial soils indicated a close similarity, and supports a shale origin for the TPH levels detected in the soils;
- 6) Naturally-occurring TPH concentrations in undisturbed soils of up to 143 mg/Kg are predicted in Marion County, based on expected shale content of glacial soils (3 to 13 percent) and the measured shale TPH range (540 to 1,100 mg/Kg). This predicted magnitude compares favorable with actual TPH levels measured in undisturbed soils at project sites in Marion County (less than 20 to 98 mg/Kg, with an average of 46 mg/Kg);
  - 7) On-site downhole natural gamma-ray logging provided an indication of the natural variability of the glacial soils  $A_{shaliness}$  or  $A_{clayeyness}$  dependent on depositional characteristics of the glacial soils;
  - 8) A moderate correlation has been shown to exist between the naturally-occurring levels of TPH found at the project site in undisturbed glacial soils and the gamma response observed during downhole logging at selected site locations. This supports the hypothesis that natural variations in the glacial till sequences produce the variations observed in the TPH concentrations detected in the soils.
  - 9) Statistical techniques using discriminant analysis, variance assessment, and geostatistical methods can be very useful in developing site-specific predictive methods for classifying TPH due to naturally-occurring processes and human-induced activities.

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