Enbridge Line 6B MP 608
Marshall, MI Pipeline Release

White Paper: Evaluation of Metals in Soil and Groundwater

Prepared for Enbridge Energy, Limited Partnership

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LIST OF ACRONYMS

DWC	Generic Default Residential Drinking Water Criteria
DWPC	Generic Default Residential Drinking Water Protection Criteria
Enbridge	Enbridge Energy, Limited Partnership
ES	Enforcement Standard
HQ	Hazard Quotient
IDEM	Indiana Department of Environmental Management
IEPA	Illinois Environmental Protection Agency
IRIS	Integrated Risk Information System
Line 6B	The pipeline owned by Enbridge Energy, Limited Partnership that runs just south of Marshall, Michigan
MCL	Maximum Contaminant Level
MDEQ	Michigan Department of Environmental Quality
MDH	Minnesota Department of Health
Metals White Paper	*White Paper: Evaluation of Metals in Soil and Groundwater*
mg/kg	milligrams per kilograms
mg/l	milligrams per liter
MP	Mile Post
MPCA	Minnesota Pollution Control Agency
NOAEL	No Observed Adverse Effects Level
NREPA	Natural Resources Environmental Protection Act
NTU	Nephelometric Turbidity Units
OEHHA	Office of Environmental Health Hazard Assessment
OEPA	Ohio Environmental Protection Agency
PAL	Preventative Action Limit
Part 201	Part 201 of Michigan's Act 451 of 1994, as amended
%	Percent
PNAs	Polynuclear Aromatic Hydrocarbons
PRG	Preliminary Remediation Goal
RCL	Residual Contaminant Level
RfD	Reference Dose
RODS	Record of Decisions System
RSL	regional screening level
SPLP	Synthetic precipitation leaching procedure
SU	Standard Units
U.S. EPA	United States Environmental Protection Agency
UV	ultraviolet
VOCs	Volatile Organic Compounds
WDNR	Wisconsin Department of Natural Resources

1.0 Introduction

On July 26, 2010, Enbridge Energy, Limited Partnership (Enbridge) discovered a release of crude oil from the pipeline owned by Enbridge that runs just south of Marshall, Michigan (Line 6B) in the vicinity of its pump station. The crude oil was released below grade level via a break in Line 6B, emerged onto the ground surface, flowed over land following the natural topography into Talmadge Creek, and proceeded to flow downstream into the Kalamazoo River. Water levels were high in the Kalamazoo River and the released Line 6B Crude Oil potentially impacted soil and groundwater in the inundated area.

Following the release, Enbridge performed response activities under the direction of the United States Environmental Protection Agency (U.S. EPA) and the Michigan Department of Environmental Quality (MDEQ) to remove oil from the system and respond to the release. In addition to remedial activities, Enbridge has conducted numerous investigations involving substantial sampling efforts to define the extent of impacts due to the crude oil release.

This White Paper: Evaluation of Metals in Soil and Groundwater (Metals White Paper) specifically addresses four target metals; beryllium, molybdenum, nickel, and vanadium and their occurrence in soil and groundwater. The data used as a basis for this Metals White Paper are provided in *Table 1* through and including *Table 19*. *Figure 1* provides soil and groundwater sample locations where these data were collected. The MDEQ has requested that Enbridge provide all backup data used in this evaluation of metals. Summary tables listing every sample used as part of this evaluation and a figure depicting every soil boring, monitoring well, and temporary well location is included (the term monitoring well refers to wells installed for the purpose of collecting samples over time at a fixed location and the term temporary well refers to wells installed for the purpose of collecting a single representative sample to determine the necessity for further groundwater investigation at any given location). In addition, the attachments to this Metals White Paper provide all available soil boring logs and corresponding soil core photographs taken under white and ultraviolet (UV) light, as well as all analytical data reports. These data include all unsaturated soil data within the inundation zone collected up through the middle of April 2014 and all groundwater data collected through the second quarter groundwater monitoring event in April 2014. Note that the tables with the monitoring well data (*Table 18* and *Table 26*) include monitoring wells located outside of the inundation zone.

A suite of chemicals of concern has been identified and sampled in soil and groundwater, which includes organic contaminants and metals. Unlike most organic contaminants, metals have natural as well as contaminant-related sources. Therefore, it is important to identify the source of metals detected in soil and groundwater samples. If metals are present as a result of the Line 6B crude oil release, this would be indicated by proximity to the area impacted by the release location as well as association with other Line 6B indicators. If, on the other hand, metals are not related to the Line 6B crude oil release, their concentrations and patterns of distribution should be related to natural sources.

This evaluation describes the occurrence of metals in soil and groundwater at overbank locations along Talmadge Creek and the Kalamazoo River that are within the area impacted by the floodwaters on the date of the release (modeled inundation area). General information about the presence and behavior of metals in the environment is discussed as well as how this behavior applies to the occurrence of metals in soil and groundwater.

1.1 Objective

The objective of this evaluation is to determine if metals detected in soil and groundwater within the modeled inundation area originated from the Line 6B crude oil release or are a result of expected naturally occurring sources unrelated to the Line 6B crude oil release. Several lines of evidence have been explored during this evaluation, including, but not limited to:

- The frequency and magnitude of metal concentrations in soil and groundwater greater than applicable MDEQ criteria in samples from the inundation zone compared to background samples;
- Concentrations in and near the source area (where the release occurred);
- Presence or absence of other observations, chemicals or visual (or UV) indicators associated with the Line 6B crude oil;
- Data quality and replication in subsequent samples;
- For soil data, the presence of metals in associated groundwater samples; and,
- Other lines of evidence.

This comprehensive evaluation will be used to develop a strategy to achieve No Further Action pursuant to Part 201 of Natural Resources Environmental Protection Act (NREPA).

2.0 Soil, Leachability, and Groundwater

2.1 Natural Occurrence of Metals in Rock and Soil

Metals are natural components of Earth's crust and soil. For example, iron is considered the 4th most abundant element in Earth's crust, after oxygen, silica, and aluminum, and vanadium is considered the 19th most abundant element in Earth's crust (Smith and Huyck, 1999). *Table 20* lists crustal rankings of metals detected in soil and groundwater within areas along Talmadge Creek and the Kalamazoo River that are within the modeled inundation area.

Through weathering processes, crustal minerals are transformed into soil, which incorporates these naturally-occurring metals. Primary minerals, such as feldspar, biotite, and amphibole are physically and chemically weathered out of bedrock. This results in smaller mineral fragments and formation of secondary minerals, such as clays, oxides, hydroxides, or oxyhydroxides, which contain metals. The metal-bearing minerals typically contain aluminum or iron, among other metals, and are incorporated into the soils by the weathering processes, thereby becoming naturally-occurring components of soil. For example, iron originally present in the mineral biotite in a rock formation may become a component of iron oxyhydroxide minerals in soil, often as thin coatings on soil particles, particularly clay.

Table 20 provides data for metal rankings in eastern United States soil (east of the 96th meridian) and average soil concentrations. The soil data are from samples collected at a depth of approximately 20 centimeters. The selected sample locations had surficial materials that were very little altered from their natural condition (Shacklette and Boerngen, 1984).

As indicated in *Table 20*, aluminum and iron are two of the most abundant elements in Earth's soil, along with oxygen, silicon, and carbon. Trace metals, such as vanadium, are associated with these abundant elements. Vanadium is known to be associated with iron and with titanium (Fischer, 1959), which occur in accessory minerals in the Mississippian Marshall Sandstone. This sandstone is the bedrock underlying soils in part of the study area and outcropping in the Ceresco area. According to descriptions (Heinrich, 2001), the Marshall Sandstone consists of quartz particles set in a cement of clay, detrital muscovite and siderite; limonite (hydrated iron oxyhydroxide) is also listed as a component. Other iron-containing minerals (i.e., magnetite, pyrite, biotite, and hornblende) and/or titanium-containing minerals (i.e., leucoxene, ilmenite, brookite, and rutile) were among the observed accessory minerals. The main impurities in the sandstone include high iron content in secondary limonite, heavy accessory minerals, and green

clay minerals (Heinrich, 2001). Therefore, vanadium is an expected component of Marshall Sandstone and soils that develop from it.

Although no specific studies were found of vanadium content of the Marshall Sandstone, clay minerals in sandstone are known to contain vanadium, which can substitute in the clay mineral lattice for aluminum (Meunier, 1994). In fact, vanadium has been commercially extracted from sandstones (Garrels and Larsen, 1959). Therefore, the Marshall Sandstone may be a source of bedrock and soil vanadium in this area.

Clay and iron oxyhydroxide minerals provide a substrate for metals adsorption. For example, arsenic, beryllium, chromium, copper, lead, molybdenum, and vanadium are considered scarcely mobile to immobile under oxidizing conditions, pH greater than 5 standard units (SU) to circumneutral, and in the presence of abundant iron substrates (Smith and Huyck, 1999). Nickel and zinc are adsorbed by goethite, an iron oxyhydroxide, under near neutral, oxidizing conditions (Bruemmer, et al., 1988). Metals that form cations, such as barium, beryllium, copper, lead, nickel, and zinc, also readily adsorb onto clay minerals (Abollino, et al., 2003; ATSDR, 2002; Bagghi, 2004; Goldberg, 2002). Molybdenum also adsorbs to clay minerals (Goldberg, et al., 1996) and vanadium has been shown to adsorb to aluminum oxide (Wehrli and Stumm, 1989). Trace metals occur naturally as part of soil and can also be found in groundwater under two conditions: as particulates that may be incorporated into unfiltered samples, and are evident as turbidity; and in dissolved form if geochemical conditions (such as pH or oxidation-reduction) promote dissolution. The occurrence of metals in groundwater is discussed in *Section 3.1*.

Soil also contains organic matter from vegetation. Metals, such as iron, are components of this organic material (Kuhnlein and Turner, 1991). Therefore, iron, as well as other metals, is naturally present in environments, such as wetlands, where organic material is incorporated into soil. Molybdenum and vanadium are essential trace elements for plants and are part of metalloenzymes that execute key transformations in carbon, nitrogen, sulfur, and halide biogeochemical cycles (Wang, 2007). For example, molybdenum is needed by wetland vegetation for nitrogen fixation as part of the nitrogenase enzyme. When molybdenum is not available, a vanadium-based nitrogenase may fulfill this requirement (Howarth and Marino, 1988). According to a Michigan State University Ag Facts Extension Bulletin, normal plant tissue contains between 0.8 and 5.0 parts per million molybdenum (Robertson, et al., 1981). Therefore, the association of higher molybdenum concentrations with organic soils such as peat and muck is expected (see *Section 2.2.2* and *Figure 2*).

2.2 Occurrence of Metals Associated with Line 6B Crude Oil

In addition to natural occurrence, metals may be added to soil due to contamination. For example, numerous sites of metals pollution have been identified in the Kalamazoo River watershed upstream of the Line 6B crude oil release (Wesley, 2005). Four target metals, beryllium, molybdenum, nickel, and vanadium, have been included in the majority of Line 6B crude oil sample analyses since December 2010. These target metals are based on analysis of crude oil samples collected by the MDEQ from the pipeline in October 2010 and presented in the *Report of Finding for Overbank Soil Background Metals Evaluation* submitted to the MDEQ, dated January 17, 2013 (Enbridge, 2013a). Of these, soil concentrations of molybdenum and vanadium have more frequently exceeded the Part 201 of Michigan's Act 451 of 1994, as amended (Part 201) Generic Default Residential Drinking Water Protection Criteria (DWPC) than beryllium, which is rarely detected, and nickel. Frequencies of detections are presented in the next section.

2.2.1 Comparison of Soil Concentrations to Criteria

The analytical data for soil were compared to Michigan's Part 201 DWPC from Rule 299.20. The DWPC for these metals are the lowest of the criteria for residential soil and so are protective of other exposure pathways in addition to protection of drinking water.

Unsaturated soil samples collected from September 2010 through and including April 2014 were compared to the Part 201 Generic Default Residential Cleanup Criteria. The lowest screening criteria for beryllium, molybdenum, nickel, and vanadium is the DWPC. When a metal result exceeds its respective default generic criterion in a soil sample, Part 201 allows use of the synthetic precipitation leaching procedure (SPLP) to determine if the potential for leaching exits. The SPLP results for the soil are compared to Part 201 Generic Default Residential Drinking Water Criteria (DWC). The SPLP test consists of extraction using a 60/40 sulfuric acid/nitric acid (by weight) solution that has a pH of 4.2 SU and end-over-end rotation at 30 revolutions per minute for 18 hours. Clearly, actual soil is unlikely to experience these conditions. For example, the lowest groundwater pH measured in monitoring wells was 5.88 SU, and the average was 7.14 SU (531 measurements available). Therefore, SPLP is a highly conservative method for evaluating potential impacts to groundwater.

The current practice for this project, as agreed to by the MDEQ, is to collect a groundwater sample at a minimum of every 0.25 mile for the Kalamazoo River or more frequently from a temporary well located at or near soil sample locations where SPLP concentrations of volatile organic compounds (VOCs) or polynuclear aromatic hydrocarbons (PNAs) exceeded the DWC.

In this Metals White Paper, these temporary wells are referred to as "associated wells." In some cases, a monitoring well was close to a soil sample with a metals exceedance; therefore, the monitoring well was used as the associated well.

Table 1, Table 2, and *Table 3* provide metal detections for unsaturated soils within the Source Area (indicated by "SA" in the location and sample identifiers); *Table 4* through and including *Table 8* provide metal detections for unsaturated soils within the Talmadge Creek inundation zone (i.e., an area determined to have been covered by flood water and potentially impacted by Line 6B crude oil); and *Table 9* through and including *Table 14* provide metal detections for unsaturated soils within the Kalamazoo River inundation zone at the time of the Line 6B crude oil release. Also provided in *Table 3*, *Table 6*, *Table 7*, *Table 11*, *Table 12*, and *Table 13* are SPLP and groundwater results for associated samples. *Table 21* summarizes the number of samples analyzed for each of the four metals, percent (%) of samples with metals not detected and detected, and % of samples with exceedances of the DWPC. *Table 22* summarizes the number of samples tested with SPLP and associated groundwater samples, resulting detections, and exceedances of the DWC.

As indicated by data in these tables, there were no DWPC exceedances for nickel and vanadium in unsaturated Source Area soil, for nickel in unsaturated Talmadge Creek soil, and no DWPC exceedances for beryllium in unsaturated soil in the Source Area and the inundation zone of Talmadge Creek and the Kalamazoo River.

Beryllium

Source Area: Beryllium was detected in 1 of 123 unsaturated Source Area soil samples analyzed for the metal and was not detected in the remaining 122 samples. There were no exceedances of the DWPC of 100 milligrams per kilogram (mg/kg) for beryllium.

Talmadge Creek: Beryllium was detected in 105, or 9%, of 1,153 unsaturated Talmadge Creek soil samples and was not detected in the remaining 1,048 samples. There were no exceedances of the DWPC of 100 mg/kg for beryllium.

Kalamazoo River: Beryllium was detected in 759, or 19%, of 4,064 unsaturated Kalamazoo River soil samples and was not detected in the remaining 3,305 samples. There were no exceedances of the DWPC of 100 mg/kg for beryllium.

Molybdenum

Source Area: Soil exceedances of the DWPC of 1.5 mg/kg ranged from 1.7 mg/kg to 53 mg/kg. Exceedances occurred in 65 samples of a total of 128 unsaturated soil samples (51 non-detect and 12 below the DWPC). Therefore, molybdenum was detected in 61% of samples; 51% of concentrations exceeded the DWPC. Molybdenum was detected in most SPLP tests, but there was only one associated groundwater detection in a temporary well (*Table 3*). This groundwater detection was 0.0062 milligrams per liter (mg/l), which is an order of magnitude less than the DWC of 0.073 mg/l. Of the 27 SPLP analyses, there were 25 detections. One SPLP sample, with a concentration of 0.080 mg/l, exceeded the DWC of 0.073 mg/l. This exceedance occurred in soil with a molybdenum concentration of 13 mg/kg.

Talmadge Creek: Soil exceedances of the DWPC of 1.5 mg/kg ranged from 1.6 mg/kg to 53 mg/kg; however, a concentration of 59 mg/kg occurred in a background Talmadge Creek soil sample collected upstream, outside of the Line 6B crude oil release area. Exceedances occurred in 680 samples of a total of 1,158 unsaturated soil samples (208 non-detect and 270 below the DWPC). Therefore, molybdenum was detected in 82% of samples and 59% of concentrations exceeded the DWPC. Of the 141 SPLP analyses, there were 62 detections of molybdenum (44%). Eight of these exceeded the DWC of 0.073 mg/l (ranging from 0.074 mg/l to 0.32 mg/l). These exceedances occurred in soil with molybdenum concentrations ranging from 2.3 mg/kg to 34 mg/kg. However, molybdenum was not detected in any of the temporary wells associated with the locations where the SPLP concentrations exceeded the DWC (*Table 6*).

Kalamazoo River: Although molybdenum soil detections were as high as 34 mg/kg and there were 563 samples with exceedances, there were no groundwater detections out of the 53 associated samples. This is true even where SPLP results were detected. Of the 368 SPLP analyses, there were 23 detections, and 9 exceedances of the DWC of 0.073 mg/l. The 563 soil exceedances occurred out of a total of 4,081 unsaturated soil samples (2,534 non-detect and 984 below the DWPC). Therefore, molybdenum was detected in 38% of samples; 14% of concentrations exceeded the DWPC.

Although molybdenum concentrations in unsaturated soil samples exceed the DWPC of 1.5 mg/kg in 1,310 unsaturated samples or 24% of unsaturated soil samples, results of SPLP testing demonstrate that leaching of molybdenum above the DWC rarely occurs (9 exceedances in 538 samples, or 1.7% of samples). Further, molybdenum was only detected in 1 of the 272

associated groundwater samples (0.37%) and both detections were below the DWC. Therefore, even though 24% of unsaturated soil concentrations exceed the DWPC, these higher concentrations are protective of groundwater because leaching, per SPLP, is rare and molybdenum does not impact associated groundwater. Also, the next most stringent criterion, the Part 201 Groundwater Surface Water Interface Protection Criteria of 64 mg/kg, was not exceeded in unsaturated soil samples.

Nickel

Source Area: Nickel was detected in all 108 unsaturated Source Area soil samples analyzed for the metal. However, there were no exceedances of the DWPC of 100 mg/kg for nickel in those samples.

Talmadge Creek: Nickel was detected in all 1,191 unsaturated Talmadge Creek soil samples analyzed for the metal. However, there were no exceedances of the DWPC of 100 mg/kg for nickel in those samples.

Kalamazoo River: Two exceedances of the DWPC of 100 mg/kg for nickel occurred:

- 1,300 mg/kg nickel with no SPLP result; nickel was detected in groundwater (0.044 mg/l) well below the DWC of 0.10 mg/l, and
- 870 mg/kg nickel but the SPLP result (0.0087 mg/l) is well below the lowest comparative standard, which is the DWC of 0.10 mg/l; groundwater results were not collected at this location.

The 2 soil exceedances occurred out of a total of 3,855 unsaturated soil samples (2 non-detect and 3,851 below the DWPC) collected in the Kalamazoo River area. Therefore, nickel was detected in virtually 100% of samples for the 3 areas (total of 5,159 samples) but only 0.04% of concentrations exceeded the DWPC.

Vanadium

Source Area: Vanadium was detected in 126 of the 128 unsaturated Source Area soil samples analyzed for the metal and was not detected in 2 samples. However, there were no exceedances of the DWPC of 72 mg/kg for vanadium in those samples.

Talmadge Creek: There was one exceedance (110 mg/kg) of the DWPC of 72 mg/kg for vanadium. This location has an SPLP result of 1.5 mg/l, which exceeded the DWC of 0.0045 mg/l. There was no associated groundwater sample for this location. The 1 soil exceedance occurred out of a total of 1,194 unsaturated soil samples; vanadium was detected below the DWPC in 1,192 samples and not detected in 1 sample. Therefore, vanadium was detected in virtually 100% of samples; 0.08% of concentrations exceeded the DWPC.

Kalamazoo River: A total of 62 samples exceeded the DWPC of 72 mg/kg for vanadium, with concentrations ranging from 74 mg/kg to 360 mg/kg. A total of 33 of these samples have SPLP results. All but one SPLP result exceeded the lowest comparative standard, which is the DWC of 0.0045 mg/l. Five comparative groundwater samples were collected. Three exceeded the DWC of 0.0045 mg/l and the other two were non-detect (<0.004 mg/l). The 62 soil exceedances occurred out of a total of 4,081 unsaturated soil samples (3 non-detects and 4,016 below the DWPC). Therefore, vanadium was detected in virtually 100% of samples; 1.5% of concentrations exceeded the DWPC.

Unlike molybdenum and nickel, vanadium SPLP leachate results more frequently (33 of 34) exceeded its DWC of 0.0045 mg/l due to its low groundwater criterion (see discussion in *Section 4.0*). This greater frequency is not surprising considering the order of magnitude lower criterion (compared to 0.073 mg/l for molybdenum and 0.02 mg/l for nickel).

2.2.2 Geographical Distribution of Metals in Soil

An approach to evaluating the contribution of Line 6B crude oil to soil metals is to focus on the areas most likely to be impacted by the Line 6B crude oil release. Two areas have been identified: Sub-units A-1 through A-4, which is also referred to as the Source Area, and Reach 5/Mile Post (MP) 1.75 - MP 2.50, where a number of impacts associated with the release of crude oil from Line 6B were identified and addressed in the *Remedial Investigation Report for Reach 5* submitted to MDEQ, dated September 23, 2013 (Enbridge, 2013b). If the Line 6B crude oil release has impacted soil by contributing metals, then logically the greatest concentrations would be expected to occur in remaining unexcavated, impacted soil within the Source Area and the inundation zone in Reach 5 along the Kalamazoo River (i.e., worst case areas).

Figure 2 and *Figure 3* are graphs illustrating the unsaturated soil concentrations of molybdenum and vanadium, respectively, which exceeded the DWPC. Background soil concentrations collected upstream of the Line 6B crude oil release site on Talmadge Creek or on the Kalamazoo

River upstream of the confluence with Talmadge Creek are also shown on *Figure 2* as filled square symbols. Background soil data collected as part of the *Report of Findings for Overbank Soils Background Metals Evaluation* submitted to the MDEQ, dated January 17, 2013 (Enbridge, 2013a) are also shown. That report presented calculated background concentrations for different soil types. In *Table 23*, soil types with similar calculated values are grouped for each metal. Therefore, each set of soil data is also separated by soil type to reflect large differences in calculated background soil concentration. The horizontal axis of each graph represents distance from the Source Area.

Figure 2 indicates that the highest molybdenum concentration in soil occurred in a background soil sample collected upstream of the Source Area. Molybdenum was detected in soil samples as far as 36 miles downstream of the Source Area at concentrations between 1.6 mg/kg (the lowest concentration shown in soil samples, as the DWPC is 1.5 mg/kg), and about 10 mg/kg. Only a few samples have concentrations that exceed the highest overbank background molybdenum concentration (19 mg/kg in muck soil), and none exceeded the concentration in the background sample collected at Talmadge Creek (59 mg/kg in muck soil). Molybdenum concentrations for the nine samples plotted on *Figure 2* with concentrations greater than 19 mg/kg are provided in *Table 24*.

The two gray-shaded Talmadge Creek samples in *Table 24* are background samples that were collected on the left bank of Talmadge Creek and upstream of the source in areas unknot impacted by the spill; one of these samples had the highest molybdenum concentration detected in unsaturated soil. In addition, there were no lines of evidence that Line 6B crude oil was present at the nine Talmadge Creek background locations. The lines of evidence included no visible oil, no UV fluorescence, and no detections of VOCs or PNAs.

The seven soil samples listed in *Table 24* represent 0.1% of the 5,372 unsaturated soil samples analyzed for molybdenum. Since the background population is expected to include 95% of the background range presented in the *Report of Findings for Overbank Soil Background Metals Evaluation* submitted to the MDEQ, dated January 17, 2013 (Enbridge, 2013a), about 5% of concentrations outside that range is expected. Also, molybdenum is associated with organic soils (note soil types are listed *Table 24* and soil type symbols used on *Figure 2*). This natural association with organic material is discussed in *Section 2.1*. Therefore, there is no evidence that the molybdenum in these or other samples is related to the Line 6B crude oil release.

Figure 3 indicates that only one unsaturated soil sample within three miles of the Source Area had a vanadium concentration exceeding the DWPC of 72 mg/kg. There are no VOCs or PNAs detected associated with the sample, even though this is the nearest sample to the Source Area that has an exceedance of the DWPC. Therefore, there is no evidence that the vanadium in this sample is related to the Line 6B crude oil release.

Most of the higher vanadium concentrations shown on *Figure 3* are clustered around the Ceresco area (MP 4.25 - MP 6.00). Bedrock type soil samples in that area are shown as red triangles on *Figure 3* and range up to 170 mg/kg. Based on accessory minerals and clay found in the Marshall Sandstone, which forms the bedrock in the Ceresco area, these vanadium concentrations are not surprising (see discussion in *Section 2.1*). Only three soil samples in the Ceresco area have concentrations of vanadium greater than 170 mg/kg. Although these samples are not described as bedrock, their logs indicate that gravel was a component of the soil. It is possible that the gravel consisted of weathered bedrock, thereby accounting for elevated vanadium.

If vanadium in soil resulted from the Line 6B crude oil release then vanadium exceedances in soil would be expected to predominate in the Source Area rather than in areas removed and downstream of the Source Area. However, there were no exceedances of the DWPC of 72 mg/kg in the unsaturated Source Area soils. Further, detections of vanadium in groundwater samples associated with unsaturated soil exceedances were obtained from temporary wells where particulates would be more typical in samples than in samples collected from permanently installed and maintained monitoring wells (see discussion in *Section 3.1*). Therefore, turbid groundwater samples collected from temporary wells are not representative of the dissolved phase of metals in groundwater and over represent the concentration of metals dissolved in groundwater. These factors, along with the small percent of exceedances, make the Line 6B crude oil release an unlikely source of vanadium.

2.2.3 Vanadium Leachability from Line 6B Crude Oil

The Line 6B crude oil consists of diluted bitumen, a heavy crude oil from Canada's Athabasca oil sands with volatile hydrocarbon diluents to allow the bitumen to move in the pipeline. Following the Line 6B crude oil release, the volatile hydrocarbon diluents evaporated, leaving the heavier bitumen. The bitumen contains asphaltene, which can make up over 20% of the total mass (University of Alberta, 2011). Asphaltene consists mostly of PNAs. In comparison to whole petroleum or bitumen, the asphaltenes have a higher content of sulfur, nitrogen, nickel, vanadium,

and oxygen. Heavy metals in asphaltenes, such as vanadium and nickel, occur in porphyrin structures (Dechaine, 2010).

Vanadium porphyrins have a significant detrimental impact on crude oil processing units so considerable research has been done on their removal. Special processing of Alberta tar sands fly ash, including burning off carbon and salt roasting, is required to remove vanadium (Gomez-Bueno, et al., 1981). In fact, vanadium has been found to be so stable in the case of petroleum product spills that it can be used as an internal marker of crude oil for the estimation of biodegradation and/or weathering (Sasaki, et al., 1998). Further, vanadium was found not to be removed from burning crude oil at ~1,000 °C. This was found to be the case in an open container, on the surface of water, and on the surface of a fixed size sandy soil (Guidroz and Sneddon, 2002). Other studies have shown that partitioning of vanadium and nickel from the oil phase to the aqueous phase is extremely low and contamination of drinking water by metals released from crude oils through partitioning is small. Additionally, the metals in the aqueous phase are primarily in a complex form, which further reduces toxicity concerns (Cantu, et al., 2000).

2.3 Conclusions about the Occurrence of Metals in Soil

Four metals have been analyzed in over 5,100 unsaturated soil samples because of their possible association with the Line 6B crude oil release. The Michigan Background Soil Survey (MDEQ, 2005) provides “typical range” of background soil data and defines it as “central 95% of data, or two standard deviations”. Therefore, about 2.5% of data are expected to exceed the upper range, 2.5 % are expected to be less than the lower range.

- Beryllium: Detected in 16% of the soil samples but no detected exceedances of the DWPC of 100 mg/kg occurred.
- Molybdenum: Exceeded the DWPC of 1.5 mg/kg in 24% of unsaturated soil samples. However, leaching (per SPLP testing) above the DWC of 0.073 mg/l occurred in only 9 samples or 1.7% of tested samples and molybdenum was detected in only 2 of the 272 (0.7%) associated groundwater samples. Also, only seven soil samples, or 0.1% of samples, had molybdenum concentrations greater than the highest concentration from the *Report of Findings for Overbank Soils Background Metals Evaluation* submitted to the MDEQ, dated January 17, 2013 (Enbridge, 2013a). Since the background population is expected to include 95% of the background range presented in the *Report of Findings for Overbank Soil Background Metals Evaluation* submitted to the MDEQ, dated

January 17, 2013 (Enbridge, 2013a), about 5% of concentrations outside that range is expected. The seven soil samples (0.1% of background samples) represent a fraction of the concentrations that could be expected outside the background range. These seven samples occurred in organic soil types, which would naturally have elevated molybdenum. The highest molybdenum concentration in an unsaturated soil sample occurred in a Talmadge Creek sample taken upstream of the Line 6B crude oil release area.

- Nickel: Detected in virtually 100% of samples but only exceeded the DWPC (100 mg/kg) in two samples. These samples were collected 15 and 25 miles downstream of the Source Area and are unlikely to be associated with the Line 6B crude oil release.
- Vanadium: Detected in virtually 100% of samples but only exceeded the DWPC of 72 mg/kg in 1.2% of samples. None of these exceedances occurred in Source Area samples. The single exceedance within 3 miles of the Source Area at MP 0.75 had no evidence of Line 6B crude oil, including detections of PNAs or VOCs. Most exceedances are near and appear to be associated with Marshall Sandstone outcrops in the Ceresco area.

Very small percentages of soil samples had exceedances of the DWPC. Geographical distribution and comparison to background concentrations indicate the exceedances are not associated with the Line 6B crude oil release, but are naturally occurring and associated with organic soil (molybdenum) or native rock (vanadium). Therefore, results of extensive soil sampling indicate that there is no connection between metals found in unsaturated soil and the Line 6B crude oil release.

3.0 Groundwater

As discussed in *Section 2.1*, trace metals can occur naturally in groundwater under two conditions: as particulates that can be incorporated into unfiltered samples and in dissolved form if geochemical conditions promote dissolution. Particulates typically are not transported by groundwater because they are filtered out by the aquifer media. Although particulates can be collected as part of any groundwater sample, they are characteristically associated with temporary, undeveloped, or recently completed wells or wells completed in silt or clay. Such samples may still be useful even though they over represent the concentration of metals actually dissolved in groundwater. However, for the purposes of this evaluation, groundwater results from monitoring wells were the primary focus of evaluating groundwater concentrations because they typically produce higher quality data and tend to have a higher degree of consistency between sampling events. Temporary well data are used as a secondary source for supporting information.

Metals data for groundwater collected from temporary wells with exceedances of molybdenum, nickel, or vanadium are provided in *Table 15*, *Table 16*, and *Table 17* for the Source Area, Talmadge Creek, and Kalamazoo River, respectively.

3.1 Occurrence of Metals in Monitoring Well Groundwater

Table 18 provides groundwater data from monitoring wells collected between October 2010 through and including April 2014, and *Table 25* summarizes these data. This includes 635 groundwater samples, consisting of 602 unfiltered samples, and 33 filtered samples. *Figure 4* illustrates the locations of molybdenum, nickel, and vanadium concentrations with distance from the Source Area. Metals exceedances are summarized in *Table 26*. The frequencies of detected concentrations and of concentrations above the DWC were quite low. The following detections and exceedances occurred in samples:

- Beryllium: No detections in 562 groundwater samples.
- Molybdenum: 11 detections in 562 groundwater samples (2%) ranging from 0.005 mg/l to 0.28 mg/l and no detections in the remaining 553 groundwater samples. Of the detections, 4 samples (0.7%) exceeded the DWC of 0.073 mg/l.
- Nickel: 26 detections in 599 groundwater samples (4.3%) ranging from 0.0074 mg/l to 0.17 mg/l, and no detections in the remaining 573 groundwater samples. Of the detections, two samples (0.3%) exceeded the DWC of 0.100 mg/l and the Part 201 Groundwater Surface

Water Interface Criterion (0.11 mg/l) when sampled in December 2013. These exceedances occurred when the wells were initially sampled in December 2013. When resampled in January, February, and April 2014, nickel was not detected (< 0.020 mg/l). The initial exceedances may have been related to elevated turbidity (*Table 26*).

- Vanadium: 29 detections in 635 groundwater samples (4.6%) ranging from 0.0049 mg/l to 0.11 mg/l, and no detections in the remaining 606 groundwater samples. Of the detections, 26 samples (4.1%) exceeded the DWC of 0.0045 mg/l.

3.1.1 Molybdenum Occurrence in Groundwater

Only 2% of the Source Area and Kalamazoo River groundwater samples had detected molybdenum and there were only four exceedances of the DWC (0.8% of these groundwater samples). Exceedances occurred in groundwater at the following Source Area wells:

- MWSA0025R540: Five groundwater samples have been collected from this well with molybdenum concentrations ranging from <0.050 mg/l (in two samples) to 0.28 mg/l. The highest concentration occurred in the sample with the highest turbidity (29.7 Nephelometric Turbidity Units (NTU)), which most likely accounts for the elevated molybdenum concentration. This well was installed in 2013 within the excavated part of the Source Area in soil composed of silt and peat, which may be responsible for the turbidity. Filtered ("D" dissolved) and unfiltered ("T" total) samples collected in January 2014 from the same location had lower turbidity (12 NTU) and molybdenum concentrations were 0.051 mg/l and <0.050 mg/l, respectively (*Table 18* and *Table 26*).
- MWSA0025R541: Three groundwater samples have been collected from this well with molybdenum concentrations ranging from <0.050 mg/l to 0.25 mg/l. Molybdenum concentrations do not appear to be related to turbidity at this location.
- MWSA0025R553: Three groundwater samples have been collected from this well with molybdenum concentrations of <0.050 mg/l (two samples) and 0.08 mg/l. Turbidity in the sample with the molybdenum exceedance was 27.3 NTU. Although turbidity was higher in a sample with non-detected molybdenum, the exceedance may be related to turbidity. Turbidity is not expected to have uniform composition among samples, being dependent on numerous factors such as the specific origin of the particulates composing the turbidity. Since metals are not uniformly distributed in soil, not all particulates will contain trace metals.

As shown in *Table 26* and described above, molybdenum concentrations are variable within individual wells and often related to turbidity.

3.1.2 Nickel Occurrence in Groundwater

Only 4% of the groundwater samples had detected nickel and there were only two exceedances of the DWC (0.7% of groundwater samples). The two exceedances occurred at locations MWSA0025R537 (0.16 mg/l) and MWSA0025R543 (0.17 mg/l) in samples collected in December 2013. These wells are located in the Source Area. Turbidity values were elevated in these samples (18.9 NTU and 41.3 NTU), which most likely accounts for the elevated nickel concentrations compared to other samples. The samples with the exceedance were from wells installed in 2013 within the excavated part of the Source Area, which may be responsible for the turbidity. Filtered and unfiltered samples collected in January 2014 from the same locations had lower turbidity values (8 NTU and 16 NTU, respectively) and nickel was not detected, nor was nickel detected in samples collected in February 2014 or April 2014 (*Table 18* and *Table 26*).

3.1.3 Vanadium Occurrence in Groundwater

Only 4.6% of the groundwater samples had detected vanadium and 4.1% of the samples had exceedances of the DWC (0.0045 mg/l). One detection, an exceedance (3.3% of 30 samples), occurred in a groundwater sample from a Talmadge Creek background well located about 1,000 feet upgradient of the Source Area. Most vanadium exceedances occurred in the Ceresco area (*Figure 4*), where vanadium in soil appears to be associated with bedrock outcrop of the Marshall Sandstone (*Section 2.1* and *Section 2.2.2*).

As shown by data in *Table 26*, for 18 wells, a single vanadium exceedance occurred in a groundwater sample and has not been replicated in other samples taken from the well. These unconfirmed vanadium exceedances are often associated with elevated turbidity. One exceedance occurred at a new well (MWSA0025R560) that has had only one sampling event and so the result is unconfirmed. As discussed previously, monitoring wells in the Source Area are generally installed in soil consisting of peat and silt. While the monitoring wells were properly developed, it was often determined that additional purge time was required during low-flow sampling to reduce the turbidity. Only two Kalamazoo River wells have had more than one groundwater sample with vanadium exceedances:

- MWKR0570R03: Vanadium concentrations range from <0.0040 mg/l (two samples) to 0.034 mg/l; the highest of these occurred in an unfiltered (T) sample with 10 mg/l iron

collected in October 2010. Field parameters were not collected for the October 2010 event, but for other events, pH was 6.6 SU to 6.8 SU and oxidizing conditions (oxidation reduction potential greater than 100 millivolts) occurred. These measurements indicate that conditions are favorable for iron adsorption and precipitation. Therefore, iron should not be dissolved in this sample, and it is likely that the vanadium and iron are associated with particulates.

- MWKR0580L03: Vanadium concentrations range from <0.0040 mg/l (one sample) to 0.047 mg/l. Iron was analyzed and detected in three samples (ranging from 4.7 mg/l to 15 mg/l) and titanium was analyzed and detected in one sample (0.054 mg/l). Since field parameters indicate that iron should not be dissolved in this sample, it is likely that vanadium and iron associated with particulates for these three samples. Vanadium is certainly associated with particulates in the fourth sample, as turbidity was 105 NTU.

As discussed in *Section 2.1*, vanadium is known to be associated with iron and titanium in minerals. Both wells with multiple vanadium exceedances are from the Ceresco area where the Marshall Sandstone outcrops and vanadium in soil appears to be associated with bedrock (*Section 2.2.2*).

3.2 Co-occurrence of Metals and Line 6B Crude Oil Indicators in Groundwater

Evaluation of groundwater data from monitoring wells indicates that metal detections or exceedances occur in only a small percent of samples and almost always associated with particulates (*Section 3.1*). *Table 19* provides data for 219 groundwater samples from temporary wells and monitoring wells where a metal exceedance occurred. Indicators of the Line 6B crude oil release are also provided to determine if metals exceedances could be associated with the release. One of these indicators, PNAs, may be pyrogenic or petrogenic. The differentiation is provided because only petrogenic PNAs may be associated with the Line 6B crude oil release. Pyrogenic PNAs result from combustion and can be from numerous sources as diverse as former manufactured gas plants to forest fires (Page et al., 1999). As shown by *Table 19* data:

- PNAs are not detected in any groundwater sample that has a metals exceedance, indicating that the metals are not associated with the Line 6B crude oil release.
- VOCs were only detected in eight groundwater samples with a metal exceedance.
    - Five of these were temporary well samples and only one had a soil interval with detected VOCs. PNAs were not detected in soil. The four associated turbidity

measurements were elevated (31 NTU to 1,000 NTU), which likely accounts for the metals detections.

  - Three of the groundwater samples were from monitoring wells and their exceedances were discussed in *Section 3.1.1* and *Section 3.1.2*. There were no PNA or VOC detections in soil samples collected from the well borings, visual or general observations that might indicate the presence of oil except "trace" UV fluorescence. Therefore, it is most likely that particulates are the source of metals in groundwater from these wells.

- PNAs were detected in seven soil samples associated with temporary wells that had a metal exceedance in groundwater; however, these detected PNAs are generally associated with former manufactured gas plant operations, so not necessarily indicators of the Line 6B crude oil release.
- VOCs were detected in soil samples associated with nine wells that had a metal exceedance in groundwater.
  - Eight of these were groundwater samples from temporary well samples. There were no PNA detections in the groundwater or soil samples. VOCs were detected in one of the groundwater samples but the vanadium exceedance is more likely associated with elevated turbidity of 43.4 NTU in the groundwater sample.
  - One of the groundwater samples was from a monitoring well. There were no detections of PNAs or VOCs in the groundwater sample and no PNAs in the soil sample from the boring. The metal exceedances in groundwater at these wells were not confirmed in two other sampling events.

In conclusion, 16 out of 219 groundwater samples (7.3%) from temporary or monitoring wells with a metal exceedance also have associated VOCs in the groundwater sample or soil collected from the borehole. However, evidence from turbidity measurements, plus the lack of petrogenic PNAs, indicates that metals in groundwater are associated with particulates rather than with Line 6B crude oil.

3.3 Conclusions about the Occurrence of Metals in Groundwater

Beryllium, molybdenum, nickel, and vanadium have been analyzed, depending on parameter, between 564 and 637 groundwater samples from monitoring wells to evaluate their possible association with the Line 6B crude oil release.

- Beryllium: No detections in groundwater.

- Molybdenum: Four exceedances occurred (0.7% of groundwater samples). No PNAs were detected in these groundwater samples and only one sample had a VOC detection. This exceedance most likely is associated with turbidity in the newly installed well located within the Source Area excavation. There is no evidence of association of the exceedances with the Line 6B crude oil release.
- Nickel: Two exceedances occurred (0.3% of groundwater samples). No PNAs were detected in these groundwater samples. One sample had a VOC detection. The nickel exceedances have not been replicated during other sampling events. The exceedances appear to have resulted from turbidity in the newly installed wells located within the Source Area excavation. There is no evidence of association of either exceedance with the Line6B crude oil release.
- Vanadium: 25 exceedances occurred (4.1%) in Source Area or Kalamazoo River groundwater samples plus 1 exceedance in a background Talmadge Creek groundwater sample. No PNAs or VOCs were detected in these groundwater samples. This confirms that the most likely source of vanadium in these samples is from turbidity. Vanadium detections occurred mainly in groundwater in the Ceresco area or further downstream (see *Figure 4)*. This may be associated with the Marshall Sandstone, which outcrops or occurs near ground surface in the Ceresco area (see *Section 2.1*). There is no evidence of association of any exceedance with the Line 6B crude oil release.

4.0 Screening Levels

Screening levels, promulgated remediation objectives (i.e., cleanup levels), and case histories are presented to provide context for screening the potential risks from the occurrence of beryllium, molybdenum, nickel, and vanadium in soil and groundwater. The review of screening level and remediation objective development compares the approach, toxicological information sources, and some general assumptions to demonstrate how a cleanup level may vary depending on subtle differences. Case histories are examined and the remediation goals contained within decision documents are summarized below.

4.1 Screening Levels and Remediation Objectives

Table 27 presents a compilation of residential groundwater and soil-to-groundwater criteria from Michigan, other states within U.S. EPA Region 5, and other U.S. EPA regions. This section compares Michigan's criteria to various criteria developed by neighboring states and the U.S. EPA. Sources of referenced toxicological data are also presented on *Table 27*. A general summary of how each jurisdiction approaches criteria development is presented, followed by a discussion of the ranges of screening levels for beryllium, molybdenum, nickel, and vanadium. None of these metals are presently considered to be human carcinogens.

4.1.1 Criteria Development

Information from the U.S. EPA Regions 3, 6, and 9 (U.S. EPA, 2013), Illinois Environmental Protection Agency (IEPA) (IEPA, 2014a), Indiana Department of Environmental Management (IDEM) (IDEM, 2014), MDEQ (MDEQ, 2013), Minnesota Pollution Control Agency (MPCA) (MPCA, 2008), Ohio Environmental Protection Agency (OEPA) (OEPA, 2008 and OEPA, 2014), and Wisconsin Department of Natural Resources (WDNR) (WDNR, 2012 and WDNR 2014) is summarized below:

- U.S. EPA Regions 3, 6, and 9: According to the U.S. EPA Regional Screening Levels User's Guide (November 2013), generic regional screening levels (RSLs) used by U.S. EPA Regions 3, 6, and 9, "… are based on default exposure parameters and factors that represent Reasonable Maximum Exposure (RME) conditions for long-term/chronic exposures and are based on the methods outlined in EPA's Risk Assessment Guidance for Superfund, Part B Manual (1991) and Soil Screening Guidance documents (1996 and 2002)". The RSLs cited in *Table 27* address a child receptor pathway for tapwater and both child and adult receptors for the soil to groundwater pathway. *Table 27* also presents

screening levels for non-carcinogenic effects hazard quotients (HQ) equal to 1.0. An HQ is a ratio of predicted exposure to acceptable exposure.

- IEPA: The IEPA's Tiered Approach to Corrective Action Tier 1 default non-carcinogenic screening levels are developed similarly to the U.S. EPA RSLs (IEPA, 2014a and IEPA, 2014b). The reference dose (RfD) values used for the derivation of HQs are provided by the U.S. EPA, then a sub-threshold level is set at the no observed adverse effects level (NOAEL), which is then divided by one or more uncertainty factors (usually multiples of 10) to account for sensitive sub-populations and extrapolation from animal studies to humans. The soil to groundwater remediation objectives presented on *Table 27* are for a soil pH range of 6.65 SU to 6.89 SU The screening levels vary with soil pH.
- IDEM: Default residential closure levels for groundwater in the IDEM's Risk Integrated System of Closure are maximum contaminant levels (MCLs), if the MCLs have been established; if not, the default closure level is the lowest of either the risk-based criterion for the ground water pathway or the solubility limit (IDEM, 2014). Soil criteria are based upon the U.S. EPA soil screening equations and default assumptions (U.S. EPA 1996). The RSLs for the soil to groundwater pathway assume a pH of 6.83 SU except for beryllium and nickel (default assumption for beryllium and nickel not indicated). The soil to groundwater pathway screening levels are not applicable outside a soil pH range of 6.0 SU to 8.0 SU.
- MDEQ: The toxicological parameters, exposure assumptions, and equations for Michigan are provided in Administrative Rules promulgated pursuant to Part 201 of Public Act 451, Rules 299.1 through 299.5. Vanadium is an exception, and the criteria for vanadium are based on toxicological parameters, exposure assumptions, and equations that differ from those in those administrative rules. The groundwater criteria are based on MCLs, if available. Beryllium has a MCL. Molybdenum, nickel, and vanadium do not have MCLs.
- MPCA: The MPCA's groundwater quality must meet both the MCLs and secondary drinking water standards issued by the U.S. EPA (MPCA, 2008). Default standards for soil address incidental soil ingestion, dermal contact with soil, and inhalation of outdoor vapors and particulates from soil (MPCA, 1999). Minnesota has no standards for the soil to groundwater exposure pathway.
- OEPA: The OEPA's generic unrestricted potable use groundwater standards are based on MCLs, other regulatory established criteria, or are risk-derived levels. Ohio uses Monte Carlo simulation for probabilistic development of risk-based cleanup standards. The forward risk assessment approach uses input parameters recommended by U.S. EPA

(i.e., Integrated Risk Information System (IRIS)), or are derived from other sources by the OEPA (OEPA, 2008). Ohio does not have criteria for the soil to groundwater exposure pathway.

- WDNR: The WDNR sets groundwater enforcement standards (ES) based on MCLs, when available (beryllium), or a NOAEL divided by an uncertainty factor for non-carcinogens. The preventive action limit (PAL) is set to 10% of the ES for substances that have carcinogenic, mutagenic, or teratogenic properties or interactive effects. Of the site metals, beryllium has a PAL set to 10% of the ES. The PAL is set to 20% the ES for all other substances. The residual contaminant levels (RCLs) promulgated in Wisconsin are derived from the U.S. EPA RSLs and adjusted according to the groundwater ES and a dilution factor of 2.

4.1.2 Screening Level Ranges

The ranges of screening levels and cleanup levels are summarized for beryllium, molybdenum, nickel, and vanadium. These are all based on residential exposures.

- Beryllium: Beryllium is the only one of the four metals that has a federal MCL, which is 0.004 mg/l. The beryllium MCL has been adopted as RSLs by U.S. EPA Regions 3, 6, and 9; as the groundwater remediation objective for class 1 groundwater (drinking water source) in Illinois; as the default residential closure level in Indiana; as the groundwater cleanup criterion in Michigan; as the drinking water standard in Minnesota; as the unrestricted potable use standard in Ohio, and as the ES in Wisconsin.

  Soil to groundwater criteria vary among the jurisdictions examined. Levels ranged from the U.S. EPA RSL of 1.3 mg/kg to 63 mg/kg in Illinois and Indiana. The soil to groundwater criterion in Michigan is 51 mg/kg, which is within the range of other jurisdictions. The U.S. EPA soil guidance and IRIS toxicological information are typically used to derive these benchmarks (U.S. EPA, 2002).

- Molybdenum: The U.S. EPA does not have an MCL for molybdenum. The WDNR's ES is 0.040 mg/l and the lowest U.S. EPA RSL is the tap water non-carcinogenic screening level (ingestion), which is 0.078 mg/l for an HQ = 1. The IDEM also has a screening level of 0.078 mg/l. The MDEQ cleanup level is 0.073 mg/l. The IDEM, IEPA, MPCA, and OEPA do not have groundwater standards for molybdenum. The Minnesota Department of Health (MDH) has set a (non-promulgated) health based screening value of 0.030 mg/l.

Differences in exposure assumptions, such as child weight, quantity ingested, exposure duration and inclusion or exclusion of other pathways (direct contact and inhalation), or the application of safety factors may explain the differences for molybdenum screening levels.

Soil to groundwater criteria range from 1.5 mg/kg (MDEQ) to 32 mg/kg (IDEM). The WDNR's RCL is 1.6 mg/kg. The IEPA, MPCA, and OEPA do not have a criterion for the soil to groundwater pathway.

- Nickel: The U.S. EPA does not have an MCL for nickel. The lowest U.S. EPA RSL is the tapwater screening level of 0.030 mg/l. The IEPA, MDEQ, and WDNR have objectives of 0.1 mg/l, the OEPA standard is 0.32 mg/l, and the IDEM standard is 0.3 mg/l. The Minnesota Department of Health's "Health Risk Limit" for nickel is 0.100 mg/l.

  Risk-based soil screening levels for protection of the groundwater pathway vary widely, ranging from 20 mg/kg (U.S. EPA RSLs) to 520 mg/kg (MPCA). The MDEQ cleanup criterion is 100 mg/kg. The states vary in their use of different sources of toxicological information and uncertainty factors incorporated, potentially explaining the order of magnitude difference between the concentrations.

- Vanadium: The U.S. EPA does not have a MCL for vanadium. The screening levels for vanadium in groundwater range from 0.0045 mg/l (MDEQ) to 0.12 mg/l (OEPA); notably, the MDEQ criterion is one order of magnitude lower than the other criteria reviewed. The U.S. EPA RSL is 0.063 mg/l (non-carcinogenic SL with an HQ=1). The WDNR's ES is 0.030 mg/l and the IEPA has a remediation objective of 0.049 mg/l. The MPCA and IDEM do not have screening levels for vanadium; however, the MDH has set a health risk limit of 0.05 mg/l. The sources of toxicological information referenced vary by jurisdiction. The U.S. EPA RSLs rely on Agency for Toxic Substances and Disease Registry and IRIS sources whereas the states tend to rely upon information presented in the U.S. EPA's 1997 Health Effects Assessment Summary Tables. The MDEQ's groundwater criterion is based upon developmental effects and the RfD from IRIS. California's Office of Environmental Health Hazard Assessment (OEHHA) has proposed a groundwater action level of 0.015 mg/l, citing a paucity of and unclear toxicological information for vanadium (OEHHA, 2000). The OEHHA's value uses an uncertainty factor of 1,000 to account for a lowest observed adverse effects level from a developmental and reproductive rat study

and its extrapolation to a NOAEL, a safety factor for sensitive receptors, and a safety factor for animal to human application.

Risk-based soil screening levels for the groundwater pathway vary widely, ranging from 63 mg/kg (U.S. EPA RSLs) to 1,300 mg/kg (IDEM). The MDEQ soil cleanup criterion is 72 mg/kg, whereas WDNR's and MPCA's risk-based screening levels are 200 mg/kg and 210 mg/kg, respectively.

4.2 Case Histories

A search was conducted on the U.S. EPA Superfund Record of Decisions System (RODS) for decision documents using the keyword search function for each of the four metals. The RODS can be accessed at http://cumulis.epa.gov/superrods/. The search for each metal included a default search for all states and all fiscal years (through 2012) and the search term "groundwater". The search returned 4 sites for beryllium, 146 sites for molybdenum, and 1 site for vanadium. A limited subset of sites is presented in the interest of providing a brief summary. Sites included in this discussion were selected with priority placed to groundwater only operable units, sites that have Preliminary Remediation Goals (PRGs) for more than one of the four metals, and sites with remediation goals for vanadium. *Table 28* presents the limited compilation of groundwater remediation goals, the type of decision document reviewed, risk receptor driving cleanup, and the status of the project. The timeframe over which the decision documents span is approximately 20 years.

A comparison of the PRGs or cleanup levels at these sites to current screening levels summarized in *Section 4.1* yields the following:

- Beryllium cleanup levels from the case histories from varying geographies are typically consistent with the MDEQ current criteria. These reflect the application of the federal MCL for beryllium as an Applicable or Relevant and Appropriate Requirement.
- Only one case study is presented for molybdenum as it was infrequently a risk driver for drinking water in the case histories reviewed. The case history provided has a higher cleanup level than the screening levels presented above and the case history is decades old.
- Nickel cleanup levels are historically consistent with the former federal MCL of 0.1 mg/l, which is the criterion for the IEPA, MDEQ, MPCA, and WDNR. This is lower than the U.S. EPA RSL and the screening levels for the IDEM and OEPA.

- Vanadium cleanup levels are consistent with the higher vanadium screening levels presented by the U.S. EPA RSLs, IEPA, IDEM, and OEPA or are at higher concentrations.

4.3 Summary

A review of screening levels, promulgated remediation objectives, and case histories augments understanding of and the communication of potential risks and also what constitutes acceptable levels of risk. The following are the outcomes of the review:

- Criteria for beryllium in groundwater are consistent across geographies, unified by the federal MCL. This means that regulators from federal and several state jurisdictions have consensus as to what concentration constitutes acceptable risk posed by beryllium in drinking water.
- Criteria for molybdenum in groundwater vary by a factor of two but are within an order of magnitude. Thus, there is a degree of consensus as to potential risks posed by ingestion of groundwater and what concentrations are acceptable risks. However, reviews of case histories suggest molybdenum is not often a primary risk driver.
- Criteria for nickel in groundwater vary by a factor of three but are within an order of magnitude. A review of case studies indicates that groundwater cleanup levels of 0.1 mg/l are typical, suggesting consensus around the risk profile at that concentration.
- Criteria for vanadium in groundwater vary by three orders of magnitude. There is not a consensus as to potential risks posed by ingesting vanadium in groundwater due to uncertainty in the toxicology such as effects on sensitive receptors and extrapolation from limited animal studies. Cleanup levels in recent decision documents are in line with the higher screening levels.

5.0 Conclusions

An extensive investigation has been ongoing since 2010 to determine whether the Line 6B crude oil release was responsible for detectable concentrations of beryllium, molybdenum, nickel, and vanadium in soil and groundwater in areas impacted by the crude oil release. More than 5,100 unsaturated soil samples, 880 temporary well groundwater samples, and 560 groundwater samples from monitoring wells were analyzed for the 4 metals. More than 500 soil samples were analyzed by SPLP for metals leachability. Samples were taken from locations along the Kalamazoo River and Talmadge Creek upstream of the Line 6B crude oil site to more than 35 miles downstream of the point of release.

The objective of this evaluation was to determine if metals detected in soil and groundwater within the modeled inundation area originated from the Line 6B crude oil release or are a result of expected naturally occurring sources unrelated to the Line 6B crude oil release. Conclusions for each metal are presented below, followed by general conclusions of this evaluation.

<u>Beryllium</u>

- Beryllium was detected in 16% of the soil samples, but all concentrations in soil were less than the lowest Part 201 cleanup criterion, which is the DWPC.
- Beryllium was not detected in any groundwater sample.
- Criteria for beryllium in groundwater are consistent across geographies, unified by the federal MCL. This means that regulators from federal and several state jurisdictions have consensus as to what concentration constitutes acceptable risk posed by beryllium in drinking water.

<u>Molybdenum</u>

- Concentrations of molybdenum exceeded the DWPC in 24% of unsaturated soil samples. The SPLP results for soil exceeded the DWC in only 9 samples or 1.7% of tested samples and molybdenum was detected in only 1 of the 272 associated groundwater samples.
- Only seven soil samples, or 0.1% of samples, had molybdenum concentrations greater than the highest concentration from the *Report of Findings for Overbank Soils Background Metals Evaluation* submitted to the MDEQ, dated January 17, 2013 (Enbridge, 2013a). These seven samples occurred in organic soil types, which naturally have elevated molybdenum.

- The highest molybdenum concentration in soil occurred in a sample collected upstream of the Source Area.
- Molybdenum in soil does not leach to groundwater based on results of groundwater samples taken near soil exceedances.
- Concentrations of molybdenum in groundwater exceeded drinking water criterion in four (0.48%) of the groundwater samples.
- No PNAs were detected in these four groundwater samples and only one sample had a VOC detection. This exceedance is most likely associated with turbidity in the newly installed well located within the Source Area excavation.
- Criteria for molybdenum in groundwater vary by a factor of two. Thus, there is a degree of consensus as to potential risks posed by ingestion of molybdenum.

Nickel

- Nickel was detected in almost 100% of soil samples; however, only exceeded the DWPC in two (0.02%) samples. These samples were collected 15 and 25 miles downstream of the Source Area so are unlikely to be associated with the Line 6B crude oil release.
- Only two exceedances of the DWC for nickel occurred in monitoring well groundwater samples (0.4% of samples). The exceedances were likely due to turbidity and have not been replicated.
- No PNAs were detected in these two groundwater samples. One sample had a VOC detection. There is only minimal evidence of association of either exceedance with the Line 6B crude oil release.
- Criteria for nickel in groundwater vary by a factor of three but are within an order of magnitude, suggesting general consensus about risks associated with ingestion of nickel.

Vanadium

- Vanadium was detected in almost 100% of soil samples; however, only exceeded the DWPC in 1.2% of samples. None of these exceedances occurred in Source Area samples. The single exceedance within three miles of the Source Area at MP 0.75 had no detections of PNAs or VOCs, indicating it was likely not related to the Line 6B crude oil release.
- Most soil vanadium exceedances occurred near Marshall Sandstone outcrops in the Ceresco area.

- Vanadium concentrations exceeded DWC in 25 (4.1%) groundwater samples from the Source Area or Kalamazoo River plus 1 exceedance in a background Talmadge Creek groundwater sample.
- No PNAs or VOCs were detected in these groundwater samples. This confirms that the most likely source of vanadium in these samples is from turbidity.
- Vanadium groundwater detections are mainly associated with the Ceresco area or further downstream or were associated with turbidity and not with Line 6B crude oil indicators. Vanadium detections in groundwater in the Ceresco area or further downstream may be associated Marshall Sandstone which outcrops or occurs near ground surface in the Ceresco area.
- There is no evidence of association of any vanadium concentrations in groundwater exceeding DWC with the Line 6B crude oil release.
- Criteria for vanadium in groundwater vary by three orders of magnitude between jurisdictions. There is no consensus as to potential risks posed by ingesting vanadium in groundwater due to uncertainty in the toxicology. The MDEQ criterion for vanadium in residential drinking water is approximately an order of magnitude lower than other jurisdictions in the region.

General Conclusions

Beryllium, molybdenum, nickel, and vanadium occur naturally in soil and minerals. These metals may occur in groundwater under two conditions: as particulates (as evidenced by turbidity in the sample) that may be incorporated into unfiltered samples and in dissolved form, if geochemical conditions promote dissolution. Molybdenum and vanadium are essential trace elements for plants and may have elevated concentrations in organic soils, which are common to areas along Talmadge Creek and the Kalamazoo River.

Multiple lines of evidence and the overwhelming preponderance of data indicate that the metals present in soil and groundwater within the modeled inundation area are due to natural factors and are not associated with the Line 6B crude oil release. Lines of evidence include frequency of detections (or lack of), geographical distribution, comparison to background concentrations, presence of natural sources, lack of replication, and lack of co-occurrence with Line 6B crude oil indicators. The results of extensive sampling indicate that there is no connection between infrequent occurrences of beryllium, molybdenum, nickel, and vanadium (as what would be

expected in a statistical evaluation of natural occurring elements) in unsaturated soil and groundwater at concentrations exceeding criteria with the Line 6B crude oil release.

This comprehensive evaluation will be used to develop a strategy to achieve No Further Action pursuant to Part 201 of NREPA.

6.0 References

Abollino, et al., 2003. Abollino, O., Aceto, M., Malandrino, M., Sarzanini, C., Mentasti, E. *Adsorption of heavy metals on Na-montmorillonite. Effect of pH and organic substances.* Water Research, v. 37, n. 7, p. 1619-1627. 2003.

ATSDR, 2002. Agency for Toxic Substances and Disease Registry. *Toxicological Profile for Beryllium.* U.S. Department of Health and Human Services. Public Health Service. 290 pp. http://www.atsdr.cdc.gov/ToxProfiles/tp4.pdf

Bagghi, 2004. Bagghi, A. *Design of Landfills and Integrated Solid Waste Management*. Third Edition. John Wiley & Sons, Inc. Hoboken, New Jersey, 699 pp. 2004.

Bruemmer, et al., 1988. Bruemmer, G.W., Gerth, J., and Tiller, K.G. *Reaction kinetics of the adsorption and desorption of nickel, zinc and cadmium by goethite. I. Adsorption and diffusion of metals.* Journal of Soil Science, vol. 39, p. 37-52. 1988.

Cantu, et al., 2000. Cantu R., Stencel, J.R., Czernuszewicz, R.S., Jaffe, P.R., Lash, T.D. *Surfactant-enhanced partitioning of nickel and vanadyl deoxophylloerythroetioporphyrins from crude oil into water and their analysis using surface-enhanced resonance raman spectroscopy.* Environmental Science & Technology, vol. 34, p. 192-198. 2000.

Dechaine, 2010. Dechaine, G.P. *Solubility and Diffusion of Vanadium Compounds and Asphaltene Aggregates*. PhD Dissertation. University of Alberta. 2010.

Enbridge, 2013a. Enbridge Energy, Limited Partnership Line 6B MP 608 Pipeline Release Marshall, Michigan*; Report of Findings for Overbank Soil Background Metals Evaluation.* January 17, 2013.

Enbridge, 2013b. Enbridge Energy, Limited Partnership Line 6B MP 608 Pipeline Release Marshall, Michigan; *Remedial Investigation Report for Reach 5*. September 23, 2013

Fischer, 1959. Fischer, R.P. *Vanadium and uranium in Rocks and Ore* Deposits. Part 20 in Garrels, R.M. and Larsen, E.S. (eds.) Colorado Plateau Uranium Ores. U.S. Geological Survey Professional Paper 320. United States Government Printing Office, Washington, D.C. p. 219-230. 1959.

Garrels and Larsen, 1959. Garrels, R.M. and Larsen, E.S. (eds.). *Colorado Plateau Uranium Ores*. U.S. Geological Survey Professional Paper 320. United States Government Printing Office, Washington, D.C. 236 pp. 1959.

Goldberg, 2002. Goldberg, S. *Competitive Adsorption of arsenate and arsenite on oxides and clay minerals.* Soil Science Society of America Journal, v. 66, p. 413-421. 2002.

Goldberg, et al., 1996. Goldberg, S., Forster, H.S., and Godfrey, C.L. *Molybdenum adsorption on oxides, clay minerals, and soils.* Soil Science Society of America Journal, vol. 60, no. 2, p. 425-432. 1996.

Gomez-Beuno, et al., 1981. Gomez-Bueno, C.O., Spink, D.R., and Rempel, G.L. *Extraction of Vanadium from Athabasca Tar Sands Fly Ash.* Metallurgical Transactions B, Vol. 12, No. 2, p. 341-352. 1981.

Guidroz and Sneddon, 2002. Guidroz J.M. and Sneddon J. *Fate of vanadium determined by nitrous oxide – acetylene flame atomic absorption spectrometry in unburned and burned Venezuelian crude oil.* Microchemical Journal, vol. 73, p. 363-366. 2002.

Heinrich, 2001. Heinrich, William. *Economic Geology of the Sand and Sandstone Resources of Michigan*. Geological Survey Division Report of Investigation 21. 2001.

Howarth and Marino, 1988. Howarth, R.W. and Marino, R. *Nitrogen fixation in freshwater, estuarine, and marine ecosystems. 2. Biogeochemical controls.* Limnology and Oceanography, v. 33, no. 4 (part 2), p. 688-701. 1988.

IDEM, 2014. Indiana Department of Environmental Management, 2014. "Remediation Closure Guide with 2014 Screening Levels Tables", accessed at: http://www.in.gov/idem/4153.htm

IEPA, 2014a. Illinois Environmental Protection Agency, 2014. "Part 742, Tiered Approach to Corrective Actions", accessed at: http://www.ilga.gov.

IEPA, 2014b. Illinois Environmental Protection Agency Tiered Approach to Corrective Action Objectives (TACO) Fact Sheet 2: Risk. http://www.epa.state.il.us/land/taco/fact-sheet.html, accessed 5/5/2014.

Kuhnlein and Turner, 1991. Kuhnlein, H.V. and Turner, N.J. *Traditional Plant Foods of Canadian Indigenous Peoples, Nutrition, Botany and Use.* Food and Nutrition in History and Anthropology, Volume 8. Gordon and Breach Publishers, Amsterdam. 1991.

Meunier, 1994. Meunier, J.D. *The composition and origin of vanadium-rich clay minerals in Colorado Plateau Jurassic Sandstones.* Clays and Clay Minerals, v. 42, no. 4, p. 391-401. 1994.

MDEQ, 2005. Michigan Department of Environmental Quality. "Michigan Background Soil Survey." 2005.

MDEQ, 2013. Michigan Department of Environmental Quality. "Part 201 Generic Cleanup Criteria and Screening Levels/Part 213 Risk-based Screening Levels." December 30, 2013.

MPCA, 1999. Minnesota Pollution Control Agency. "Selenium, Molybdenum, Vanadium and Antimony in Minnesota's Ground Water", accessed at: http://www.pca.state.mn.us/index.php/view-document.html?gid=6315

MPCA, 2008. Minnesota Pollution Control Agency. "Chapter 7050, Water Quality Standards for the Protection of Waters of the State." 2008.

OEPA, 2008. Ohio Environmental Protection Agency, The Voluntary Action Program Division of Emergency and Remedial Response. "Support Document for the Development of Generic Numerical Standards and Risk Assessment Procedures." August 2008.

OEPA, 2014. Ohio Environmental Protection Agency. "Ohio Administrative Code 3745-300-08 Generic numerical standards." 2014

OEHHA, 2000. California's Office of Health Hazard Assessment, 2000. Memorandum: Proposed Action Level for Vanadium, August 24, 2000.

Page et al., 1999. Page, D.S., Boehm, P.D., Douglas, G.S., Bence, A.E., Burns, W.A., and Mankiewicz, P.J. *Pyrogenic Polycyclic Aromatic Hydrocarbons in Sediment Record Past Human Activity: A Case Study in Prince William Sound, Alaska*. Marine Pollution Bulletin, volume 38, number 4, p. 247-260. 1999.

Robertson, et al., 1981. Robertson, L.S., Warncke, D.D., and Knezek, B.D. *Molybdenum: An Essential Plant Micronutrient.* Michigan State University Ag Facts Extension Bulletin E-1518. 1981.

Sasaki, et al., 1998. Sasaki, T., Maki, H., Ishihara, M., and Harayama, S. *Vanadium as an Internal Marker to Evaluate Microbial Degradation of Crude Oil.* Environmental Science and Technology, volume 32, number 22, p 3618-1621. 1998.

Shacklette and Boerngren, 1984. Shacklette, H.T. and Boerngen, J.G. *Element Concentrations in Soils and Other Surficial Materials of the Conterminous United States*. U.S. Geological Survey Professional Paper 1270. Washington, D.C. 1984.

Smith and Huyck, 1999. Smith, K.S., and Huyck, H.L.O. An overview of the abundance, relative mobility, bioavailability, and human toxicity of metals, Chapter 2, in Plumlee, G.S., and Logsdon, M.J., eds., The environmental geochemistry of mineral deposits, Part A: Processes, techniques, and health issues, Reviews in Economic Geology, Vol. 6A: Littleton, Colorado, Society of Economic Geologists, Inc., p. 29-70. 1999.

University of Alberta, 2011. University of Alberta. *What are asphaltenes in petroleum, oil sands, and heavy oil?* Accessed December 19, 2013 at: http://www.ualberta.ca/~gray/Links%20&%20Docs/Asphaltenes%20web%20page.pdf. 2011

U. S. EPA, 1996. United States Environmental Protection Agency, "Soil Screening Guidance: User's Guide", Office of Solid Waste and Emergency Response Publication 9355.4-23. July 1996.

U. S. EPA, 2002. United States Environmental Protection Agency, "Supplemental Guidance for Developing Soil Screening Levels For Superfund Sites", Office of Solid Waste and Emergency Response Publication 9355.4-24. December 2002.

U.S. EPA, 2013. United States Environmental Protection Agency Region 3, 6 and 9 Regional Screening Levels, accessed at: http://www.epa.gov/reg3hwmd/risk/human/rb-concentration_table

Wang, 2007. Wang, D. *Biogeochemistry of Redox-sensitive Elements in Natural Waters: Chemical Speciation of Molybdenum and Vanadium*. PhD Dissertation. Stony Brook University, 167 pp. 2007.

Wesley, 2005. Wesley, J.K. *Kalamazoo River Assessment.* State of Michigan Department of Natural Resources, Fisheries Division. Special Report 35. September 2005.

Wherli and Stumm, 1989. Wehrli, B. and Stumm, W. *Vanadyl in natural waters: Adsorption and hydrolysis promote oxidation.* Geochemica et Cosmochimica Acta, vol. 53, p. 69-77. 1989.

WDNR, 2014. Wisconsin Department of Natural Resources. "Soil Residual Contaminant Level Determinations Using The U.S. EPA Regional Screening Level Web Calculator". PUB-RR-890.

WDNR, 2012. Wisconsin Department of Natural Resources. "Administrative Code NR 140, Groundwater Quality Standards." 2012.

Figures

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Approved:	JC	5/28/2014
Project #:	60313732	

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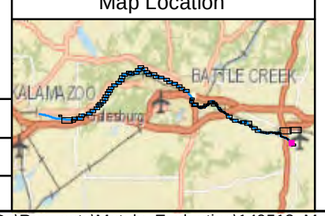

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Metals Evaluation Sample

- Soil
- Temporary Well
- Soil and Temporary Well
- Monitoring Well
- Soil and Monitoring Well

Quarter Mile Grid Segment

N

0 20 40 80

Scale in Feet

FIGURE 1
UNSATURATED SOIL AND GROUNDWATER SAMPLE LOCATIONS WITH METALS ANALYTICAL DATA
METALS EVALUATION
SHEET 1 OF 159

ENBRIDGE LINE 6B MP 608
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ENBRIDGE ENERGY, LIMITED PARTNERSHIP

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Aerial Photography Date: April 2011 over August 2010

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Map Location

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Metals Evaluation Sample

- Soil
- Temporary Well
- Soil and Temporary Well
- Monitoring Well
- Soil and Monitoring Well

Quarter Mile Grid Segment

N

0 20 40 80

Scale in Feet

FIGURE 1
UNSATURATED SOIL AND GROUNDWATER SAMPLE LOCATIONS WITH METALS ANALYTICAL DATA
METALS EVALUATION
SHEET 2 OF 159

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Map Location

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Metals Evaluation Sample

- Soil
- Temporary Well
- Soil and Temporary Well
- Monitoring Well
- Soil and Monitoring Well

Quarter Mile Grid Segment

N

0 5 10 20

Scale in Feet

FIGURE 1
UNSATURATED SOIL AND GROUNDWATER SAMPLE LOCATIONS WITH METALS ANALYTICAL DATA
METALS EVALUATION
SHEET 3 OF 159

ENBRIDGE LINE 6B MP 608
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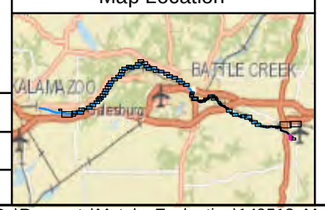

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Metals Evaluation Sample

- Soil
- Temporary Well
- Soil and Temporary Well
- Monitoring Well
- Soil and Monitoring Well

Quarter Mile Grid Segment

N

0 5 10 20

Scale in Feet

FIGURE 1
UNSATURATED SOIL AND GROUNDWATER SAMPLE LOCATIONS WITH METALS ANALYTICAL DATA
METALS EVALUATION
SHEET 4 OF 159

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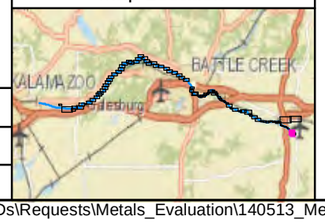

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Metals Evaluation Sample

- Soil
- Temporary Well
- Soil and Temporary Well
- Monitoring Well
- Soil and Monitoring Well

Quarter Mile Grid Segment

N

0 25 50 100

Scale in Feet

FIGURE 1
UNSATURATED SOIL AND GROUNDWATER SAMPLE LOCATIONS WITH METALS ANALYTICAL DATA
METALS EVALUATION
SHEET 5 OF 159

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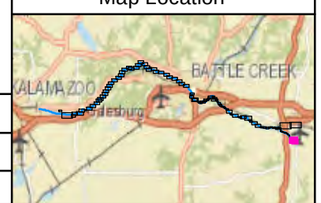

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Metals Evaluation Sample

- Soil
- Temporary Well
- Soil and Temporary Well
- Monitoring Well
- Soil and Monitoring Well

Quarter Mile Grid Segment

N

0 75 150 300

Scale in Feet

FIGURE 1
UNSATURATED SOIL AND GROUNDWATER SAMPLE LOCATIONS WITH METALS ANALYTICAL DATA
METALS EVALUATION
SHEET 6 OF 159

ENBRIDGE LINE 6B MP 608
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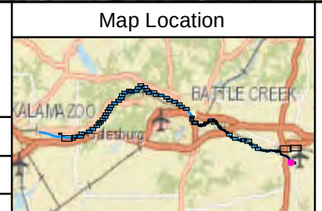

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Metals Evaluation Sample

- Soil
- Temporary Well
- Soil and Temporary Well
- Monitoring Well
- Soil and Monitoring Well

Quarter Mile Grid Segment

N

0 12.5 25 50

Scale in Feet

FIGURE 1
UNSATURATED SOIL AND GROUNDWATER SAMPLE LOCATIONS WITH METALS ANALYTICAL DATA
METALS EVALUATION
SHEET 7 OF 159

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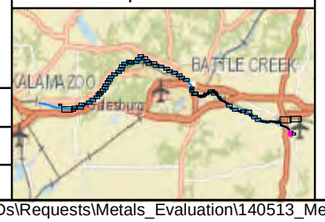

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Metals Evaluation Sample

- Soil
- Temporary Well
- Soil and Temporary Well
- Monitoring Well
- Soil and Monitoring Well

Quarter Mile Grid Segment

N

0 12.5 25 50

Scale in Feet

FIGURE 1
UNSATURATED SOIL AND GROUNDWATER SAMPLE LOCATIONS WITH METALS ANALYTICAL DATA
METALS EVALUATION
SHEET 8 OF 159

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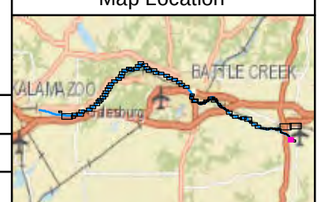

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Metals Evaluation Sample

- Soil
- Temporary Well
- Soil and Temporary Well
- Monitoring Well
- Soil and Monitoring Well

Quarter Mile Grid Segment

N

0 10 20 40

Scale in Feet

FIGURE 1
UNSATURATED SOIL AND GROUNDWATER SAMPLE LOCATIONS WITH METALS ANALYTICAL DATA
METALS EVALUATION
SHEET 9 OF 159

ENBRIDGE LINE 6B MP 608
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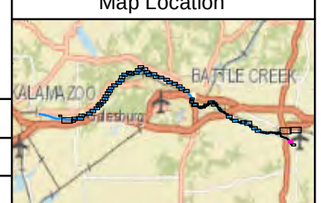

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Metals Evaluation Sample

- Soil
- Temporary Well
- Soil and Temporary Well
- Monitoring Well
- Soil and Monitoring Well

Quarter Mile Grid Segment

N

0 10 20 40

Scale in Feet

FIGURE 1
UNSATURATED SOIL AND GROUNDWATER SAMPLE LOCATIONS WITH METALS ANALYTICAL DATA
METALS EVALUATION
SHEET 10 OF 159

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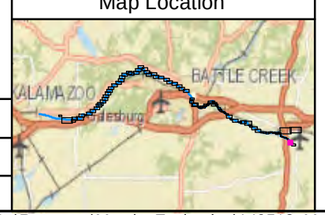

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Metals Evaluation Sample

- Soil
- Temporary Well
- Soil and Temporary Well
- Monitoring Well
- Soil and Monitoring Well

Quarter Mile Grid Segment

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0 10 20 40

Scale in Feet

FIGURE 1
UNSATURATED SOIL AND GROUNDWATER SAMPLE LOCATIONS WITH METALS ANALYTICAL DATA
METALS EVALUATION
SHEET 11 OF 159

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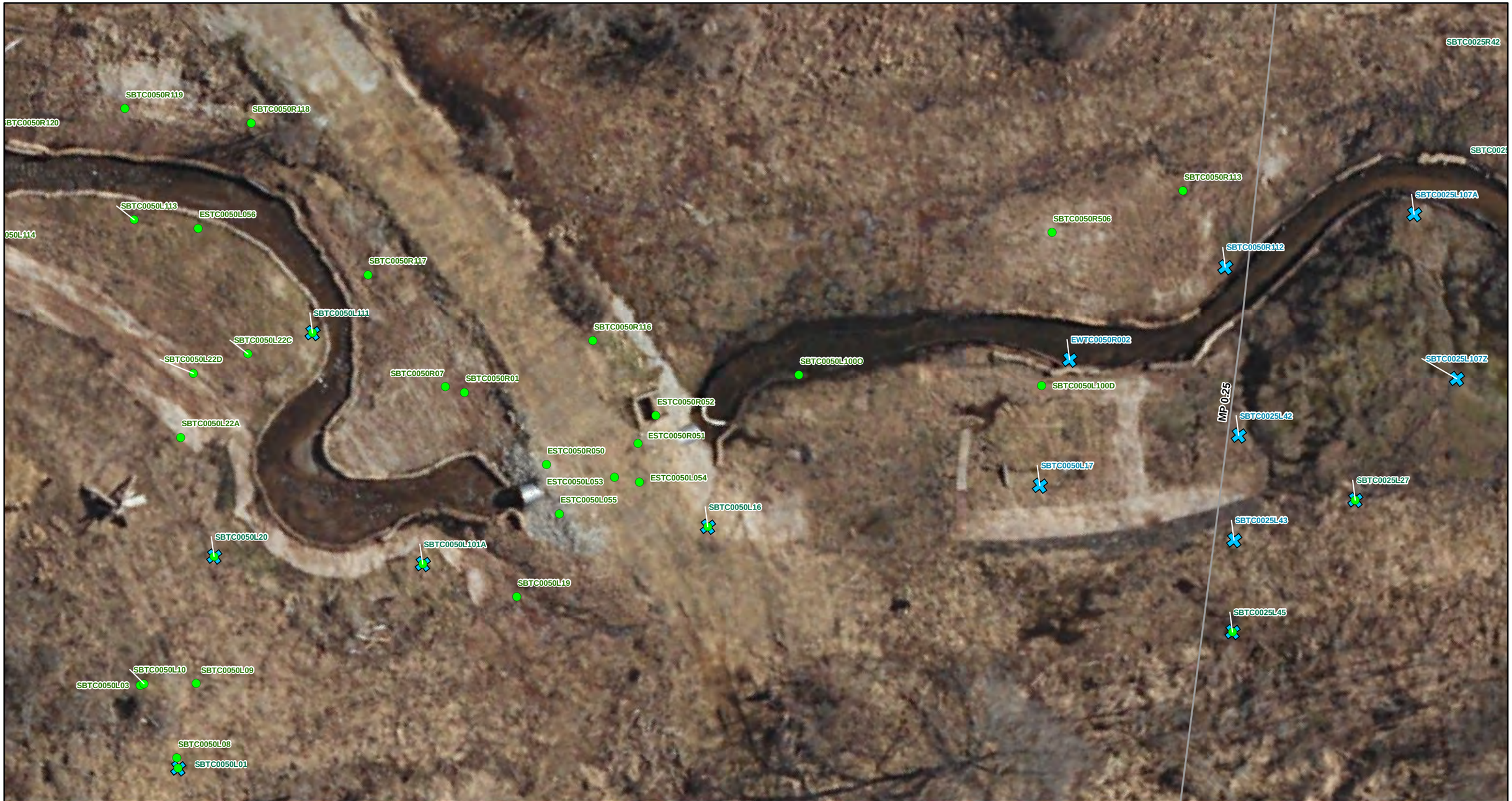

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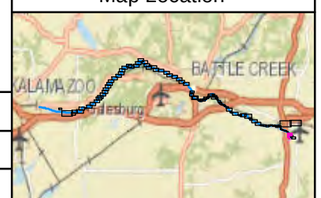

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Metals Evaluation Sample

- Soil
- Temporary Well
- Soil and Temporary Well
- Monitoring Well
- Soil and Monitoring Well

Quarter Mile Grid Segment

N

0 10 20 40

Scale in Feet

FIGURE 1
UNSATURATED SOIL AND GROUNDWATER SAMPLE LOCATIONS WITH METALS ANALYTICAL DATA
METALS EVALUATION
SHEET 12 OF 159

ENBRIDGE LINE 6B MP 608
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Aerial Photography Date: April 2011 over August 2010

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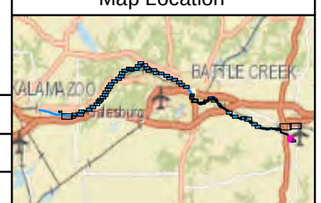
Project #:	60313732	

Map Location



Legend

Metals Evaluation Sample

- Soil
- Temporary Well
- Soil and Temporary Well
- Monitoring Well
- Soil and Monitoring Well

Quarter Mile Grid Segment

N

0 10 20 40

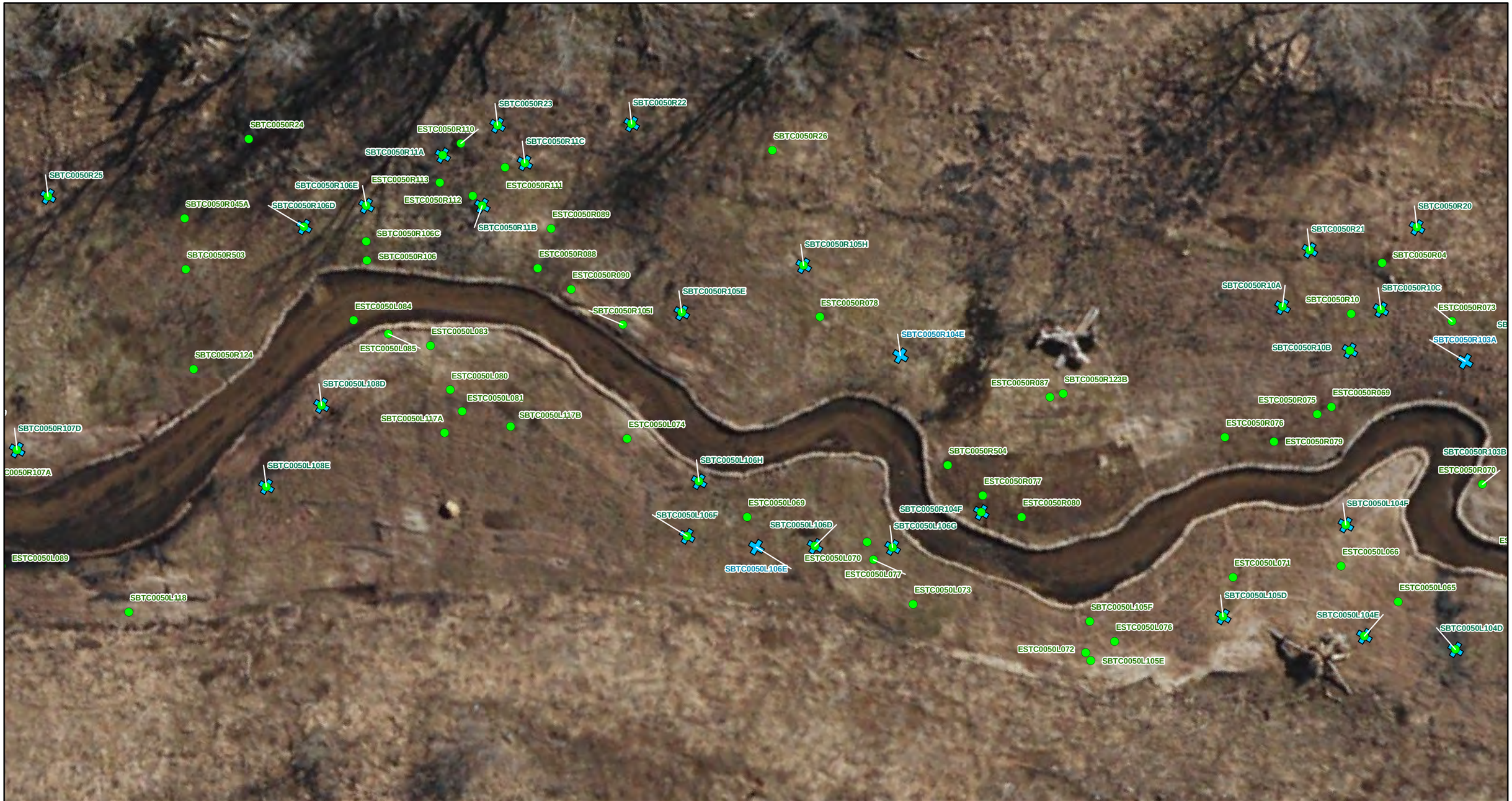
Scale in Feet

FIGURE 1
UNSATURATED SOIL AND GROUNDWATER SAMPLE LOCATIONS WITH METALS ANALYTICAL DATA
METALS EVALUATION
SHEET 13 OF 159

ENBRIDGE LINE 6B MP 608
MARSHALL, MI PIPELINE RELEASE
ENBRIDGE ENERGY, LIMITED PARTNERSHIP

Z:\Work\GIS\Kalamazoo_River_RI\MXDs\Requests\Metals_Evaluation\140513_Metals_Evaluation_Unsaturated_Samples_SA_TC_KR.mxd

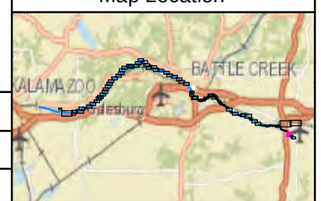
Aerial Photography Date: April 2011 over August 2010



ENBRIDGE

Drawn:	NS	5/28/2014
Approved:	JC	5/28/2014
Project #:	60313732	

Map Location



Legend

Metals Evaluation Sample

- Soil
- Temporary Well
- Soil and Temporary Well
- Monitoring Well
- Soil and Monitoring Well

Quarter Mile Grid Segment

N

0 10 20 40

Scale in Feet

FIGURE 1
UNSATURATED SOIL AND GROUNDWATER SAMPLE LOCATIONS WITH METALS ANALYTICAL DATA
METALS EVALUATION
SHEET 14 OF 159

ENBRIDGE LINE 6B MP 608
MARSHALL, MI PIPELINE RELEASE
ENBRIDGE ENERGY, LIMITED PARTNERSHIP

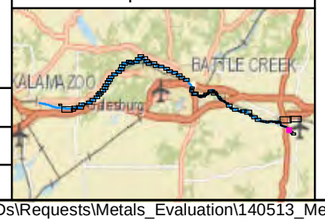
Z:\Work\GIS\Kalamazoo_River_RI\MXDs\Requests\Metals_Evaluation\140513_Metals_Evaluation_Unsaturated_Samples_SA_TC_KR.mxd

Aerial Photography Date: April 2011 over August 2010

ENBRIDGE

Drawn:	NS	5/28/2014
Approved:	JC	5/28/2014
Project #:	60313732	

Map Location



Legend

Metals Evaluation Sample

- Soil
- Temporary Well
- Soil and Temporary Well
- Monitoring Well
- Soil and Monitoring Well

Quarter Mile Grid Segment

N

0 10 20 40

Scale in Feet

FIGURE 1
UNSATURATED SOIL AND GROUNDWATER SAMPLE LOCATIONS WITH METALS ANALYTICAL DATA
METALS EVALUATION
SHEET 15 OF 159

ENBRIDGE LINE 6B MP 608
MARSHALL, MI PIPELINE RELEASE
ENBRIDGE ENERGY, LIMITED PARTNERSHIP

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Aerial Photography Date: April 2011 over August 2010

ENBRIDGE

Drawn:	NS	5/28/2014
Approved:	JC	5/28/2014
Project #:	60313732	

Map Location

Legend

Metals Evaluation Sample

- Soil
- Temporary Well
- Soil and Temporary Well
- Monitoring Well
- Soil and Monitoring Well

Quarter Mile Grid Segment

N

0 10 20 40

Scale in Feet

FIGURE 1
UNSATURATED SOIL AND GROUNDWATER SAMPLE LOCATIONS WITH METALS ANALYTICAL DATA
METALS EVALUATION
SHEET 16 OF 159

ENBRIDGE LINE 6B MP 608
MARSHALL, MI PIPELINE RELEASE
ENBRIDGE ENERGY, LIMITED PARTNERSHIP

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Aerial Photography Date: April 2011 over August 2010

ENBRIDGE

Drawn:	NS	5/28/2014
Approved:	JC	5/28/2014
Project #:	60313732	

Map Location

Legend

Metals Evaluation Sample

- Soil
- Temporary Well
- Soil and Temporary Well
- Monitoring Well
- Soil and Monitoring Well

Quarter Mile Grid Segment

N

0 10 20 40

Scale in Feet

FIGURE 1
UNSATURATED SOIL AND GROUNDWATER SAMPLE LOCATIONS WITH METALS ANALYTICAL DATA
METALS EVALUATION
SHEET 17 OF 159

ENBRIDGE LINE 6B MP 608
MARSHALL, MI PIPELINE RELEASE
ENBRIDGE ENERGY, LIMITED PARTNERSHIP

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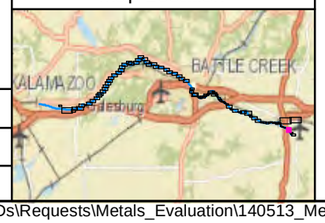
Aerial Photography Date: April 2011 over August 2010

ENBRIDGE

Drawn:	NS	5/28/2014
Approved:	JC	5/28/2014
Project #:	60313732	

Map Location



Legend

Metals Evaluation Sample

- Soil
- Temporary Well
- Soil and Temporary Well
- Monitoring Well
- Soil and Monitoring Well

Quarter Mile Grid Segment

N

0 10 20 40

Scale in Feet

FIGURE 1
UNSATURATED SOIL AND GROUNDWATER SAMPLE LOCATIONS WITH METALS ANALYTICAL DATA
METALS EVALUATION
SHEET 18 OF 159

ENBRIDGE LINE 6B MP 608
MARSHALL, MI PIPELINE RELEASE
ENBRIDGE ENERGY, LIMITED PARTNERSHIP

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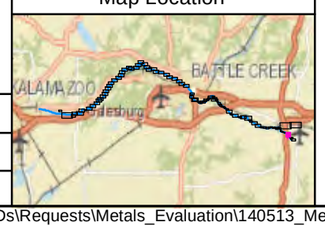
Aerial Photography Date: April 2011 over August 2010

ENBRIDGE

Drawn:	NS	5/28/2014
Approved:	JC	5/28/2014
Project #:	60313732	

Map Location



Legend

Metals Evaluation Sample

- Soil
- Temporary Well
- Soil and Temporary Well
- Monitoring Well
- Soil and Monitoring Well

Quarter Mile Grid Segment

N

0 10 20 40

Scale in Feet

FIGURE 1
UNSATURATED SOIL AND GROUNDWATER SAMPLE LOCATIONS WITH METALS ANALYTICAL DATA
METALS EVALUATION
SHEET 19 OF 159

ENBRIDGE LINE 6B MP 608
MARSHALL, MI PIPELINE RELEASE
ENBRIDGE ENERGY, LIMITED PARTNERSHIP

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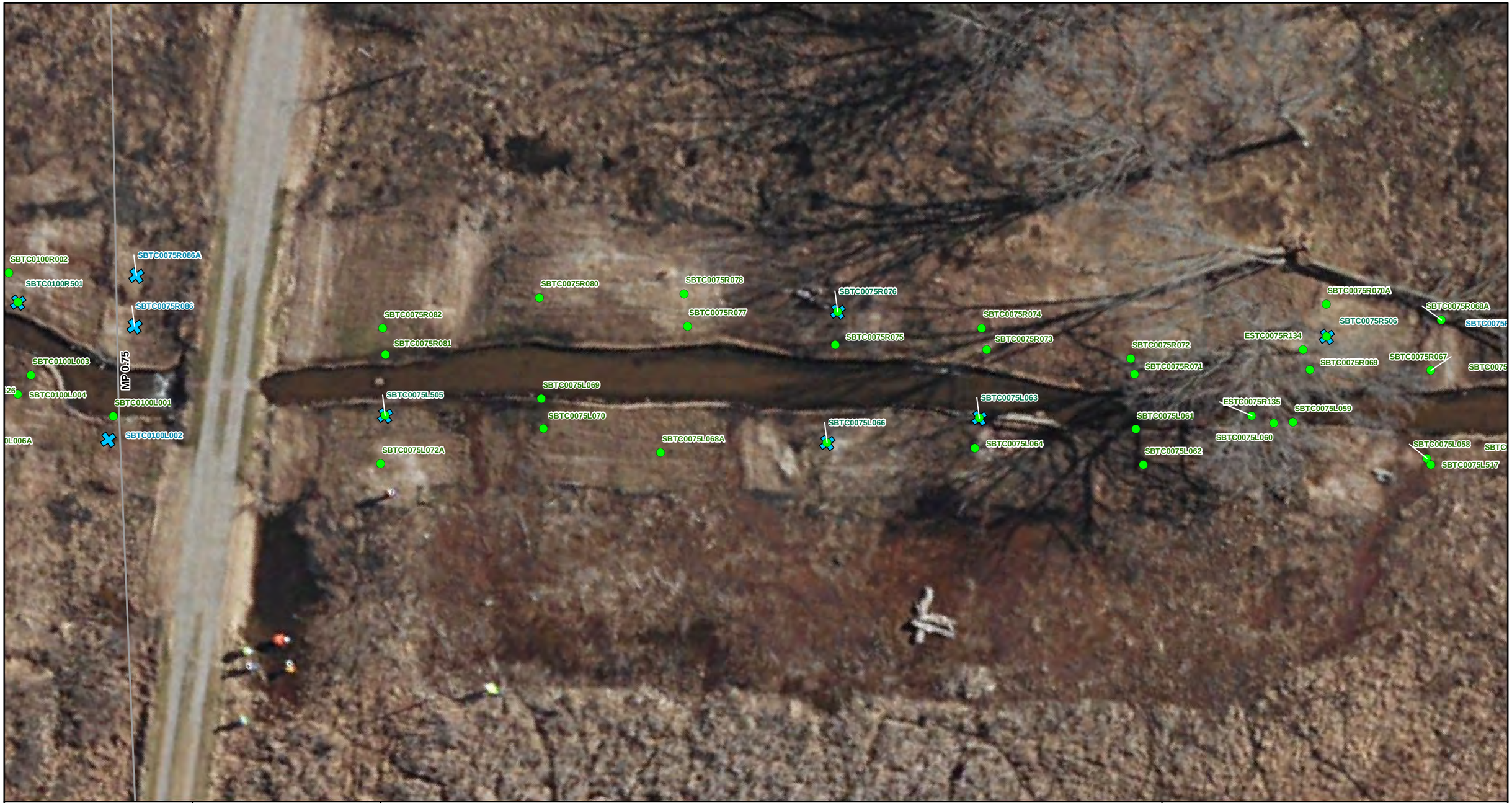
Aerial Photography Date: April 2011 over August 2010



ENBRIDGE

Drawn:	NS	5/28/2014
Approved:	JC	5/28/2014
Project #:	60313732	

Map Location

Legend

Metals Evaluation Sample

- Soil
- Temporary Well
- Soil and Temporary Well
- Monitoring Well
- Soil and Monitoring Well

Quarter Mile Grid Segment

N

0 10 20 40

Scale in Feet

FIGURE 1
UNSATURATED SOIL AND GROUNDWATER SAMPLE LOCATIONS WITH METALS ANALYTICAL DATA
METALS EVALUATION
SHEET 20 OF 159

ENBRIDGE LINE 6B MP 608
MARSHALL, MI PIPELINE RELEASE
ENBRIDGE ENERGY, LIMITED PARTNERSHIP

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Aerial Photography Date: April 2011 over August 2010

ENBRIDGE

Drawn:	NS	5/28/2014
Approved:	JC	5/28/2014
Project #:	60313732	

Map Location

Legend

Metals Evaluation Sample

- Soil
- Temporary Well
- Soil and Temporary Well
- Monitoring Well
- Soil and Monitoring Well

Quarter Mile Grid Segment

N

0 10 20 40

Scale in Feet

FIGURE 1
UNSATURATED SOIL AND GROUNDWATER SAMPLE LOCATIONS WITH METALS ANALYTICAL DATA
METALS EVALUATION
SHEET 21 OF 159

ENBRIDGE LINE 6B MP 608
MARSHALL, MI PIPELINE RELEASE
ENBRIDGE ENERGY, LIMITED PARTNERSHIP

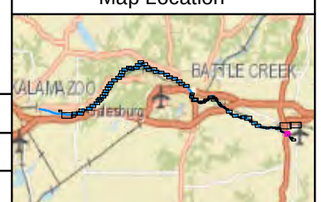
Z:\Work\GIS\Kalamazoo_River_RI\MXDs\Requests\Metals_Evaluation\140513_Metals_Evaluation_Unsaturated_Samples_SA_TC_KR.mxd

Aerial Photography Date: April 2011 over August 2010

ENBRIDGE

Drawn:	NS	5/28/2014
Approved:	JC	5/28/2014
Project #:	60313732	

Map Location



Legend

Metals Evaluation Sample

- Soil
- Temporary Well
- Soil and Temporary Well
- Monitoring Well
- Soil and Monitoring Well

Quarter Mile Grid Segment

N

0 10 20 40

Scale in Feet

FIGURE 1
UNSATURATED SOIL AND GROUNDWATER SAMPLE LOCATIONS WITH METALS ANALYTICAL DATA
METALS EVALUATION
SHEET 22 OF 159

ENBRIDGE LINE 6B MP 608
MARSHALL, MI PIPELINE RELEASE
ENBRIDGE ENERGY, LIMITED PARTNERSHIP

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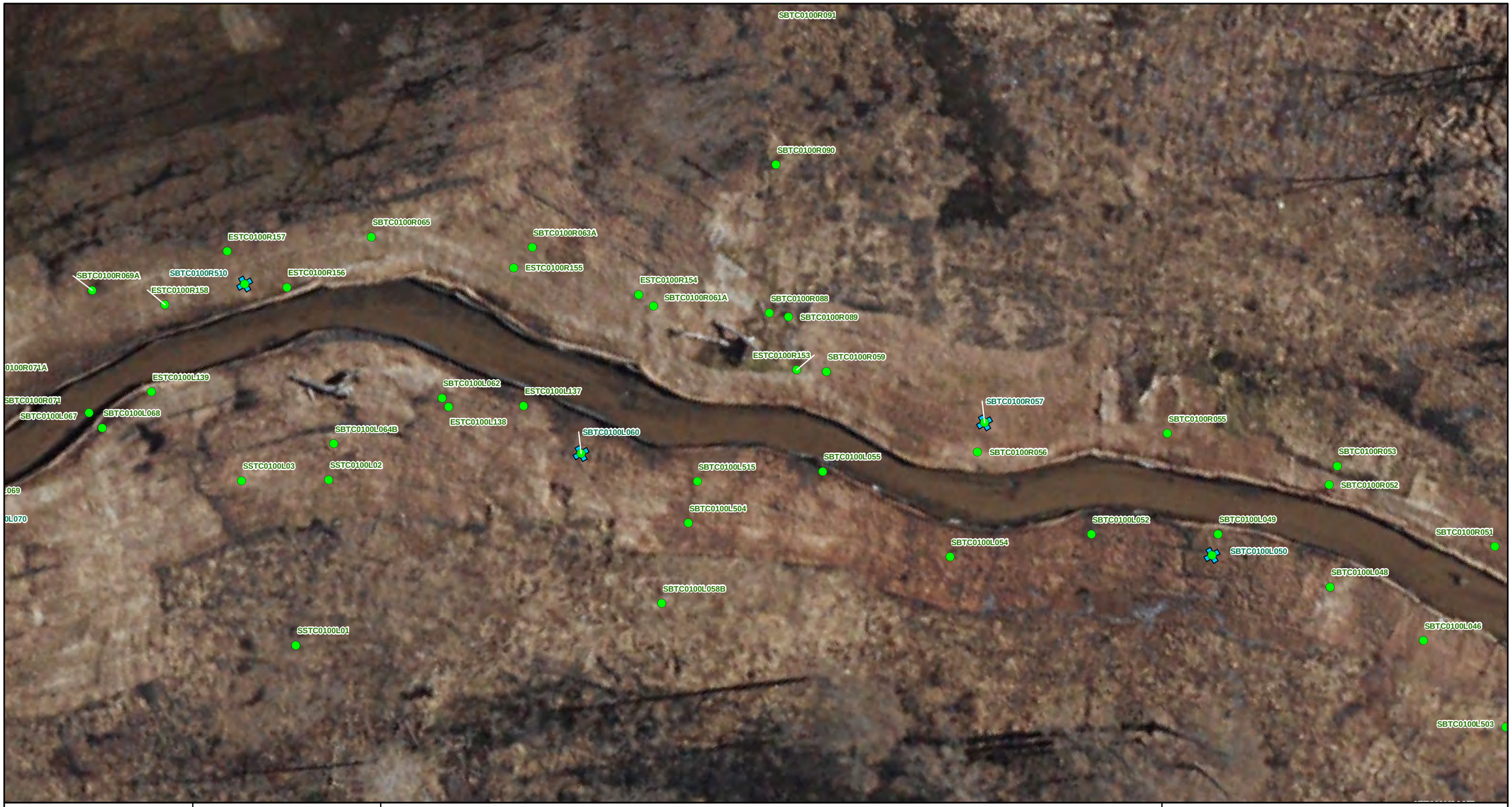
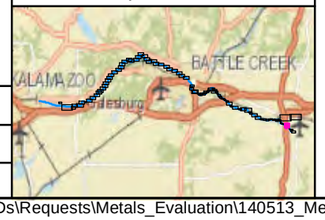
Aerial Photography Date: April 2011 over August 2010



ENBRIDGE

Drawn:	NS	5/28/2014
Approved:	JC	5/28/2014
Project #:	60313732	

Map Location



Legend

Metals Evaluation Sample

- Soil
- Temporary Well
- Soil and Temporary Well
- Monitoring Well
- Soil and Monitoring Well

Quarter Mile Grid Segment

N

0 10 20 40

Scale in Feet

FIGURE 1
UNSATURATED SOIL AND GROUNDWATER SAMPLE LOCATIONS WITH METALS ANALYTICAL DATA
METALS EVALUATION
SHEET 23 OF 159

ENBRIDGE LINE 6B MP 608
MARSHALL, MI PIPELINE RELEASE
ENBRIDGE ENERGY, LIMITED PARTNERSHIP

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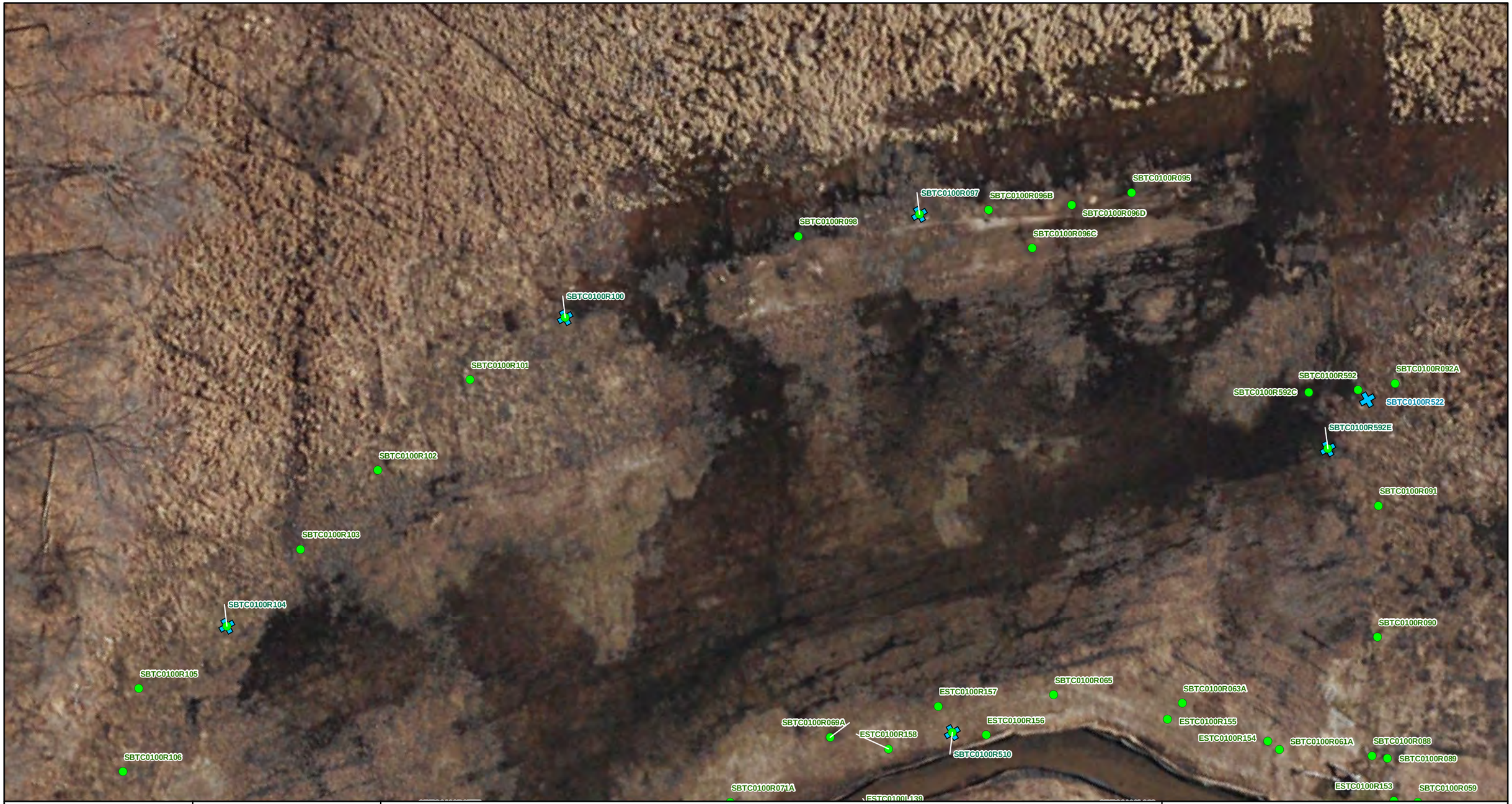
Aerial Photography Date: April 2011 over August 2010



ENBRIDGE

Drawn:	NS	5/28/2014
Approved:	JC	5/28/2014
Project #:	60313732	

Map Location

Legend

Metals Evaluation Sample

- Soil
- Temporary Well
- Soil and Temporary Well
- Monitoring Well
- Soil and Monitoring Well

Quarter Mile Grid Segment

N

0 12.5 25 50

Scale in Feet

FIGURE 1
UNSATURATED SOIL AND GROUNDWATER SAMPLE LOCATIONS WITH METALS ANALYTICAL DATA
METALS EVALUATION
SHEET 24 OF 159

ENBRIDGE LINE 6B MP 608
MARSHALL, MI PIPELINE RELEASE
ENBRIDGE ENERGY, LIMITED PARTNERSHIP

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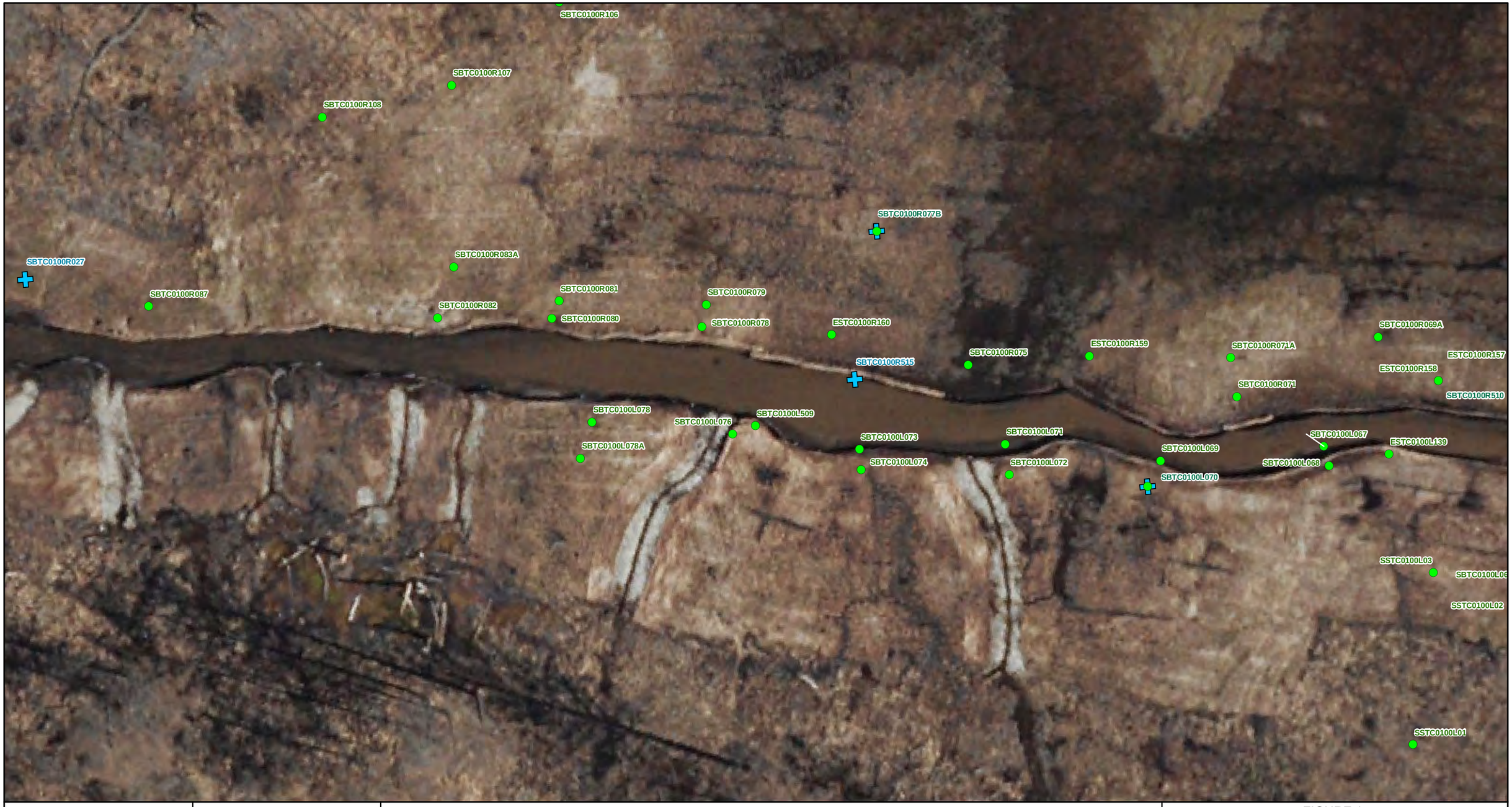
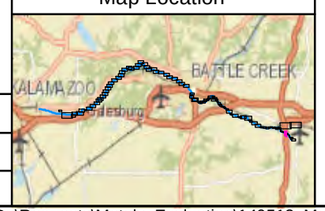
Aerial Photography Date: April 2011 over August 2010



ENBRIDGE

Drawn:	NS	5/28/2014
Approved:	JC	5/28/2014
Project #:	60313732	

Map Location



Legend

Metals Evaluation Sample

- Soil
- Temporary Well
- Soil and Temporary Well
- Monitoring Well
- Soil and Monitoring Well

Quarter Mile Grid Segment

N

0 10 20 40

Scale in Feet

FIGURE 1
UNSATURATED SOIL AND GROUNDWATER SAMPLE LOCATIONS WITH METALS ANALYTICAL DATA
METALS EVALUATION
SHEET 25 OF 159

ENBRIDGE LINE 6B MP 608
MARSHALL, MI PIPELINE RELEASE
ENBRIDGE ENERGY, LIMITED PARTNERSHIP

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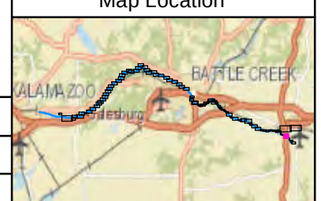
Aerial Photography Date: April 2011 over August 2010

ENBRIDGE

Drawn:	NS	5/28/2014
Approved:	JC	5/28/2014
Project #:	60313732	

Map Location



Legend

Metals Evaluation Sample

- Soil
- Temporary Well
- Soil and Temporary Well
- Monitoring Well
- Soil and Monitoring Well

Quarter Mile Grid Segment

N

0 10 20 40

Scale in Feet

FIGURE 1
UNSATURATED SOIL AND GROUNDWATER SAMPLE LOCATIONS WITH METALS ANALYTICAL DATA
METALS EVALUATION
SHEET 26 OF 159

ENBRIDGE LINE 6B MP 608
MARSHALL, MI PIPELINE RELEASE
ENBRIDGE ENERGY, LIMITED PARTNERSHIP

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Aerial Photography Date: April 2011 over August 2010

ENBRIDGE

Drawn:	NS	5/28/2014
Approved:	JC	5/28/2014
Project #:	60313732	

Map Location

Legend

Metals Evaluation Sample

- Soil
- Temporary Well
- Soil and Temporary Well
- Monitoring Well
- Soil and Monitoring Well

Quarter Mile Grid Segment

N

0 10 20 40

Scale in Feet

FIGURE 1
UNSATURATED SOIL AND GROUNDWATER SAMPLE LOCATIONS WITH METALS ANALYTICAL DATA
METALS EVALUATION
SHEET 27 OF 159

ENBRIDGE LINE 6B MP 608
MARSHALL, MI PIPELINE RELEASE
ENBRIDGE ENERGY, LIMITED PARTNERSHIP

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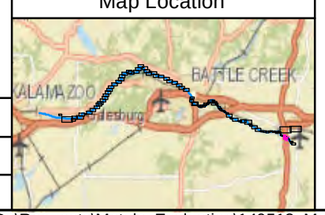
Aerial Photography Date: April 2011 over August 2010

ENBRIDGE

Drawn:	NS	5/28/2014
Approved:	JC	5/28/2014
Project #:	60313732	

Map Location



Legend

Metals Evaluation Sample

- Soil
- Temporary Well
- Soil and Temporary Well
- Monitoring Well
- Soil and Monitoring Well

Quarter Mile Grid Segment

N

0 10 20 40

Scale in Feet

FIGURE 1
UNSATURATED SOIL AND GROUNDWATER SAMPLE LOCATIONS WITH METALS ANALYTICAL DATA
METALS EVALUATION
SHEET 28 OF 159

ENBRIDGE LINE 6B MP 608
MARSHALL, MI PIPELINE RELEASE
ENBRIDGE ENERGY, LIMITED PARTNERSHIP

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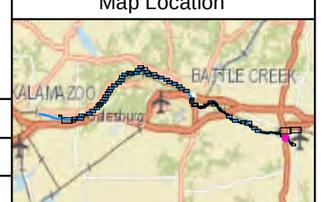
Aerial Photography Date: April 2011 over August 2010

ENBRIDGE

Drawn:	NS	5/28/2014
Approved:	JC	5/28/2014
Project #:	60313732	

Map Location



Legend

Metals Evaluation Sample

- Soil
- Temporary Well
- Soil and Temporary Well
- Monitoring Well
- Soil and Monitoring Well

Quarter Mile Grid Segment

N

0 10 20 40

Scale in Feet

FIGURE 1
UNSATURATED SOIL AND GROUNDWATER SAMPLE LOCATIONS WITH METALS ANALYTICAL DATA
METALS EVALUATION
SHEET 29 OF 159

ENBRIDGE LINE 6B MP 608
MARSHALL, MI PIPELINE RELEASE
ENBRIDGE ENERGY, LIMITED PARTNERSHIP

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Aerial Photography Date: April 2011 over August 2010

ENBRIDGE

Drawn:	NS	5/28/2014
Approved:	JC	5/28/2014
Project #:	60313732	

Map Location

Legend

Metals Evaluation Sample

- Soil
- Temporary Well
- Soil and Temporary Well
- Monitoring Well
- Soil and Monitoring Well

Quarter Mile Grid Segment

N

0 10 20 40

Scale in Feet

FIGURE 1
UNSATURATED SOIL AND GROUNDWATER SAMPLE LOCATIONS WITH METALS ANALYTICAL DATA
METALS EVALUATION
SHEET 30 OF 159

ENBRIDGE LINE 6B MP 608
MARSHALL, MI PIPELINE RELEASE
ENBRIDGE ENERGY, LIMITED PARTNERSHIP

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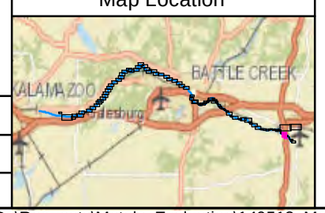
Aerial Photography Date: April 2011 over August 2010

ENBRIDGE

Drawn:	NS	5/28/2014
Approved:	JC	5/28/2014
Project #:	60313732	

Map Location



Legend

Metals Evaluation Sample

- Soil
- Temporary Well
- Soil and Temporary Well
- Monitoring Well
- Soil and Monitoring Well

Quarter Mile Grid Segment

N

0 10 20 40

Scale in Feet

FIGURE 1
UNSATURATED SOIL AND GROUNDWATER SAMPLE LOCATIONS WITH METALS ANALYTICAL DATA
METALS EVALUATION
SHEET 31 OF 159

ENBRIDGE LINE 6B MP 608
MARSHALL, MI PIPELINE RELEASE
ENBRIDGE ENERGY, LIMITED PARTNERSHIP

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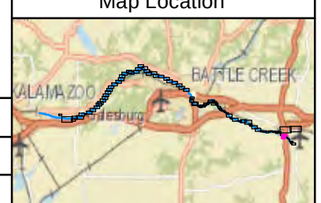
Aerial Photography Date: April 2011 over August 2010

ENBRIDGE

Drawn:	NS	5/28/2014
Approved:	JC	5/28/2014
Project #:	60313732	

Map Location



Legend

Metals Evaluation Sample

- Soil
- Temporary Well
- Soil and Temporary Well
- Monitoring Well
- Soil and Monitoring Well

Quarter Mile Grid Segment

N

0 10 20 40

Scale in Feet

FIGURE 1
UNSATURATED SOIL AND GROUNDWATER SAMPLE LOCATIONS WITH METALS ANALYTICAL DATA
METALS EVALUATION
SHEET 32 OF 159

ENBRIDGE LINE 6B MP 608
MARSHALL, MI PIPELINE RELEASE
ENBRIDGE ENERGY, LIMITED PARTNERSHIP

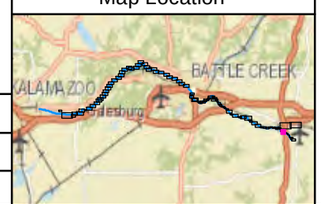
Z:\Work\GIS\Kalamazoo_River_RI\MXDs\Requests\Metals_Evaluation\140513_Metals_Evaluation_Unsaturated_Samples_SA_TC_KR.mxd

Aerial Photography Date: April 2011 over August 2010

ENBRIDGE

Drawn:	NS	5/28/2014
Approved:	JC	5/28/2014
Project #:	60313732	

Map Location



Legend

Metals Evaluation Sample

- Soil
- Temporary Well
- Soil and Temporary Well
- Monitoring Well
- Soil and Monitoring Well

Quarter Mile Grid Segment

N

0 10 20 40

Scale in Feet

FIGURE 1
UNSATURATED SOIL AND GROUNDWATER SAMPLE LOCATIONS WITH METALS ANALYTICAL DATA
METALS EVALUATION
SHEET 33 OF 159

ENBRIDGE LINE 6B MP 608
MARSHALL, MI PIPELINE RELEASE
ENBRIDGE ENERGY, LIMITED PARTNERSHIP

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Aerial Photography Date: April 2011 over August 2010

ENBRIDGE

Drawn:	NS	5/28/2014
Approved:	JC	5/28/2014
Project #:	60313732	

Map Location

Legend

Metals Evaluation Sample

- Soil
- Temporary Well
- Soil and Temporary Well
- Monitoring Well
- Soil and Monitoring Well

Quarter Mile Grid Segment

N

0 10 20 40

Scale in Feet

FIGURE 1
UNSATURATED SOIL AND GROUNDWATER SAMPLE LOCATIONS WITH METALS ANALYTICAL DATA
METALS EVALUATION
SHEET 34 OF 159

ENBRIDGE LINE 6B MP 608
MARSHALL, MI PIPELINE RELEASE
ENBRIDGE ENERGY, LIMITED PARTNERSHIP

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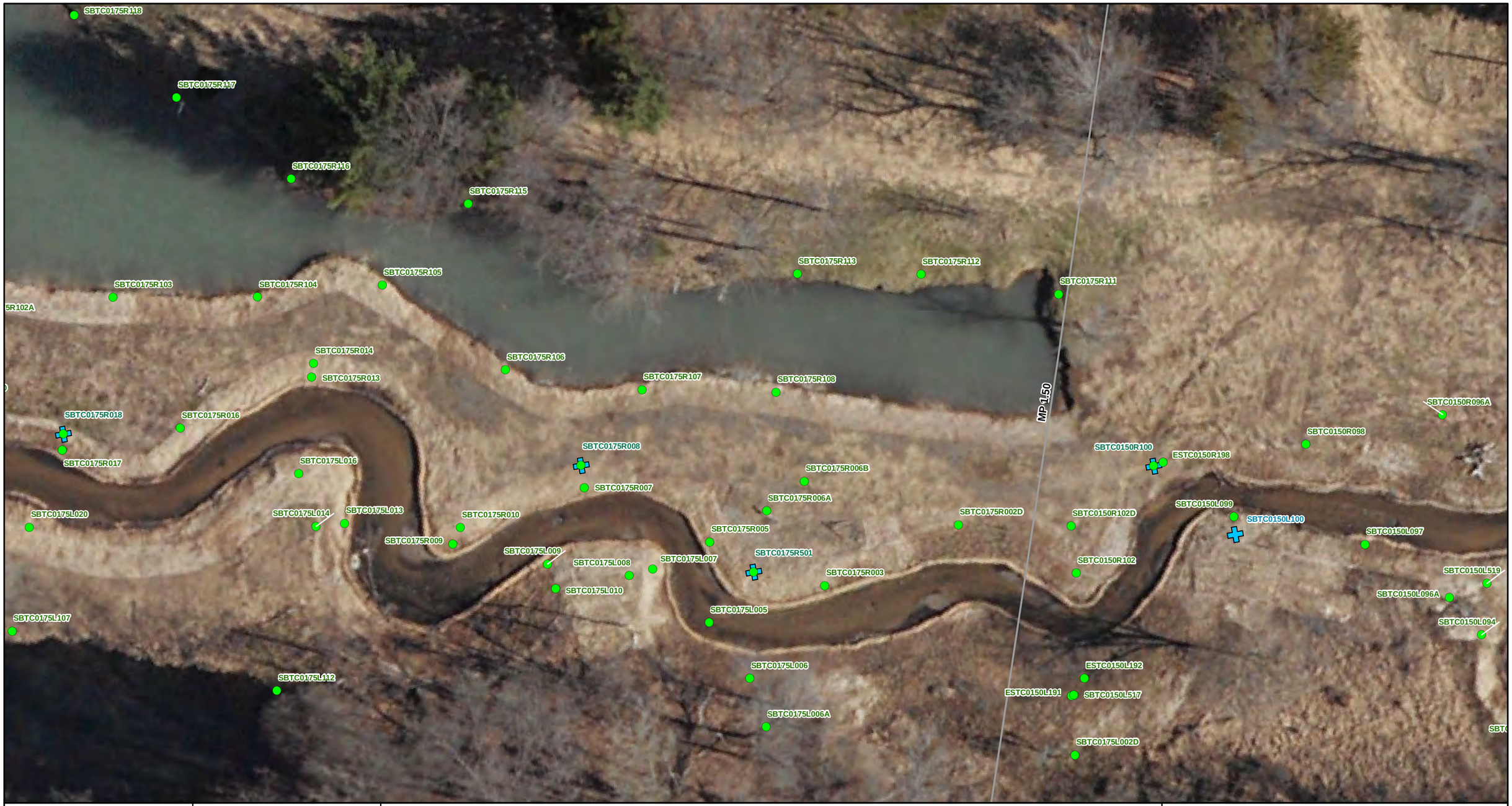
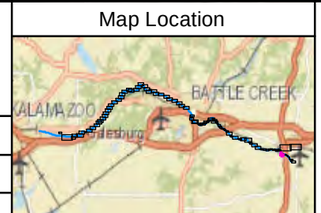
Aerial Photography Date: April 2011 over August 2010



ENBRIDGE

Drawn:	NS	5/28/2014
Approved:	JC	5/28/2014
Project #:	60313732	

Map Location



Legend

Metals Evaluation Sample

- Soil
- Temporary Well
- Soil and Temporary Well
- Monitoring Well
- Soil and Monitoring Well

Quarter Mile Grid Segment

N

0 10 20 40

Scale in Feet

FIGURE 1
UNSATURATED SOIL AND GROUNDWATER SAMPLE LOCATIONS WITH METALS ANALYTICAL DATA
METALS EVALUATION
SHEET 35 OF 159

ENBRIDGE LINE 6B MP 608
MARSHALL, MI PIPELINE RELEASE
ENBRIDGE ENERGY, LIMITED PARTNERSHIP

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Aerial Photography Date: April 2011 over August 2010

ENBRIDGE

Drawn:	NS	5/28/2014
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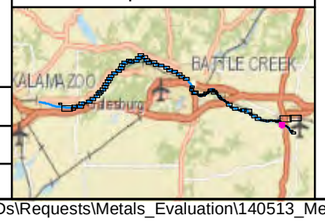
Map Location



Legend

Metals Evaluation Sample

- Soil
- Temporary Well
- Soil and Temporary Well
- Monitoring Well
- Soil and Monitoring Well

Quarter Mile Grid Segment

N

0 12.5 25 50

Scale in Feet

FIGURE 1
UNSATURATED SOIL AND GROUNDWATER SAMPLE LOCATIONS WITH METALS ANALYTICAL DATA
METALS EVALUATION
SHEET 36 OF 159

ENBRIDGE LINE 6B MP 608
MARSHALL, MI PIPELINE RELEASE
ENBRIDGE ENERGY, LIMITED PARTNERSHIP

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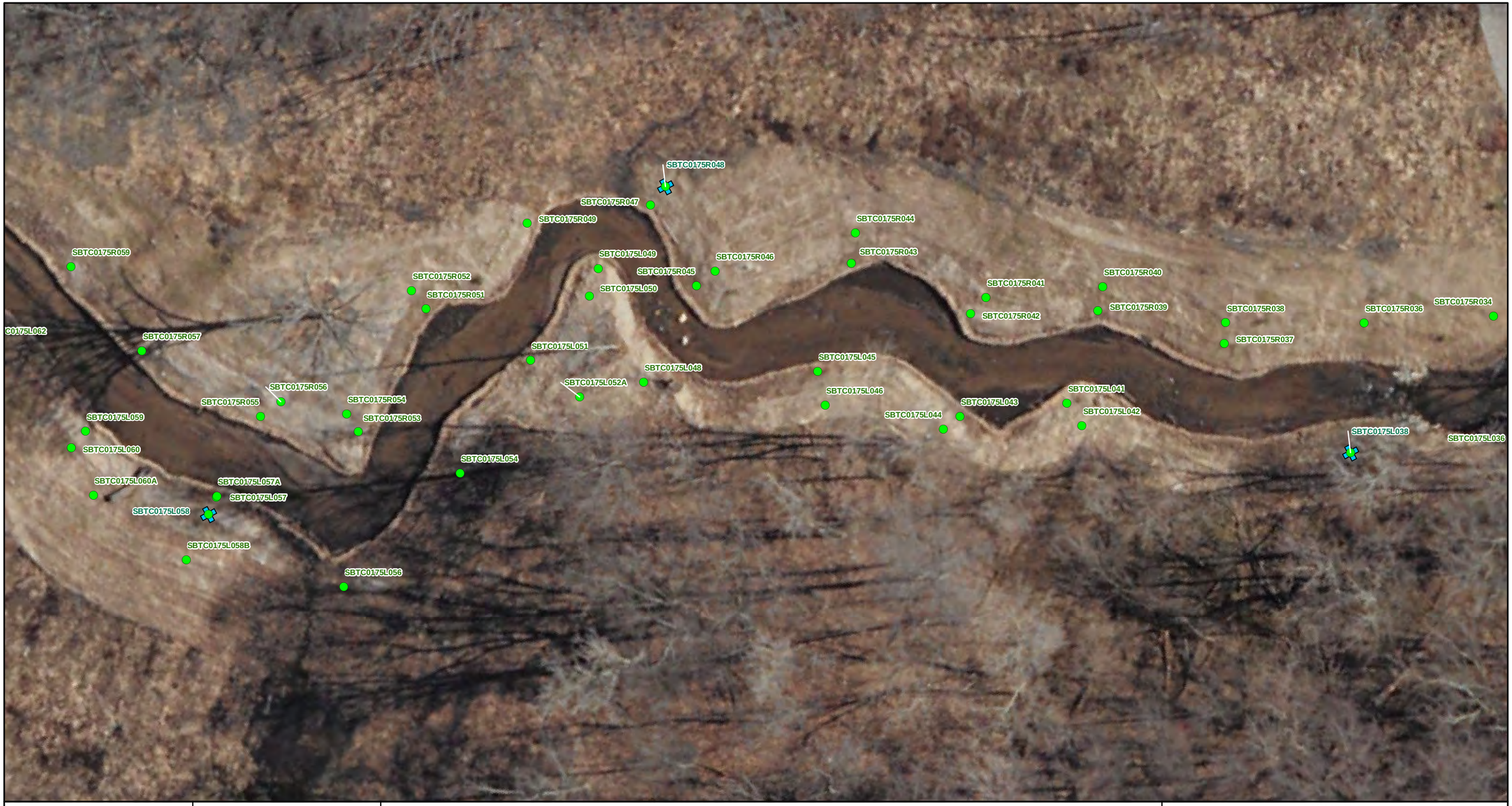

ENBRIDGE

Drawn:	NS	5/28/2014
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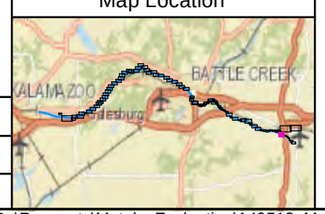
Map Location



Legend

Metals Evaluation Sample

- Soil
- Temporary Well
- Soil and Temporary Well
- Monitoring Well
- Soil and Monitoring Well

Quarter Mile Grid Segment

N

0 10 20 40

Scale in Feet

FIGURE 1
UNSATURATED SOIL AND GROUNDWATER SAMPLE LOCATIONS WITH METALS ANALYTICAL DATA
METALS EVALUATION
SHEET 37 OF 159

ENBRIDGE LINE 6B MP 608
MARSHALL, MI PIPELINE RELEASE
ENBRIDGE ENERGY, LIMITED PARTNERSHIP

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Aerial Photography Date: April 2011 over August 2010

ENBRIDGE

Drawn:	NS	5/28/2014
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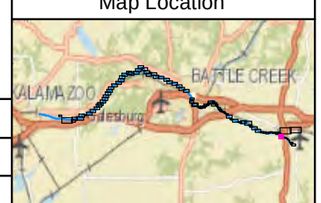
Project #:	60313732	

Map Location



Legend

Metals Evaluation Sample

- Soil
- Temporary Well
- Soil and Temporary Well
- Monitoring Well
- Soil and Monitoring Well

Quarter Mile Grid Segment

N

0 10 20 40

Scale in Feet

FIGURE 1
UNSATURATED SOIL AND GROUNDWATER SAMPLE LOCATIONS WITH METALS ANALYTICAL DATA
METALS EVALUATION
SHEET 38 OF 159

ENBRIDGE LINE 6B MP 608
MARSHALL, MI PIPELINE RELEASE
ENBRIDGE ENERGY, LIMITED PARTNERSHIP

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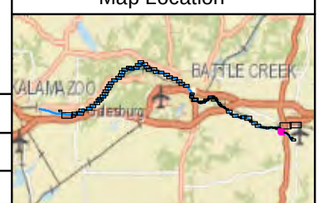

Legend

Metals Evaluation Sample

- Soil
- Temporary Well
- Soil and Temporary Well
- Monitoring Well
- Soil and Monitoring Well

Quarter Mile Grid Segment

N

0 10 20 40

Scale in Feet

FIGURE 1
UNSATURATED SOIL AND GROUNDWATER SAMPLE LOCATIONS WITH METALS ANALYTICAL DATA
METALS EVALUATION
SHEET 39 OF 159

ENBRIDGE LINE 6B MP 608
MARSHALL, MI PIPELINE RELEASE
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