August 8, 2012

Mr. Ralph Dollhopf
Federal OSC and Incident Commander
U.S. EPA, Region 5
Emergency Response Branch
801 Garfield Avenue, #229
Traverse City, MI 49686

Re: Submerged Oil Spring 2012 Volume Quantification
Enbridge Line 6B MP 608, Marshall, MI Pipeline Release

Dear Mr. Dollhopf,

Attached is my recommendation for methodologies to define methods of estimating the quantity of submerged oil present as a result of the Enbridge Line 6B Oil Spill based on the scientific opinions that I have received. The attached document represents additional response to the Federal On-Scene Coordinator’s (FOSC) Charge No. 1 to the SSCG (as amended in your letter of March 21, 2012):

> 1. (a) Provide an evaluation of viable analytical and sampling approaches (such as sampling design, sample collection and sample processing/handling) including benefits and disadvantages for each, to quantify the amount of submerged oil in the Kalamazoo River sediments attributable to the Enbridge Oil pipeline Release.
>
> b) Provide a recommendation for the best analytical and sampling approach to accomplish this goal.

Further, the evaluations and recommendations included in the attachments are consistent with the FOSC's charge #1 to SSCG (listed above):

- To quantify the volume of submerged oil, and Line 6B oil fraction thereof, remaining in riverine sediment of the impacted area (cf. CWP, p. 15).
- To quantify the change in oil volume since Fall 2011 sampling (cf. CWP, sec. 3.2.1, p. 11).
- To identify implications of the remaining oil volume for USEPA FOSC's tactical operations plan and Incident response end points, SSCG - Concept white paper, Nov. 17, 2011 [p. 2, Objectives]).

The individual members of the SSCG have provided me with their recommendations for the Spring 2012 submerged oil volume quantification around the following key components of the study design:

- Stratification of impacted area for sampling to quantify Line 6B residual oil.
- Characterization of background hydrocarbons.
- Spatial distribution of sample locations.
- Methods for collecting sample cores.

- Methods for selecting core-layer samples for analytical chemistry, geotechnical testing, logging, or preservation for potential future use.
- Methods for processing sample cores and core-layer samples.

The attached document represents my synthesis (as a Scientific Support Coordinator) of the applicable opinions and recommendations received from individuals involved with the Chemistry, Fingerprinting and Biodegradation Subgroup of the Scientific Support Coordination Group (SSCG). The individual scientific opinions provided to me are based on each scientist’s prior experiences in addressing issues related to oil spill recovery and potential effects of recovery. Opinions expressed by individuals from the SSCG and its subgroup are included in the attached document, or are otherwise documented in supporting documents maintained in the response files.

I recommend adoption of this technical approach to further develop the understanding of the quantity and sources of submerged oil for the purposes of oil recovery from the Kalamazoo River.

Sincerely yours,

/s/

Thomas Graan, Ph.D.
Scientific Support Coordinator to the FOSC for Enbridge Line 6B Oil Spill
Weston Solutions, Inc., Region 5 S.T.A.R.T. Contractor

RECOMMENDATION TO THE FOSC

SUBMERGED OIL VOLUME QUANTIFICATION SAMPLING DESIGN AND METHODS FOR SEDIMENT SAMPLING, PROCESSING, AND ANALYSIS

ENBRIDGE LINE 6B MP 608 MARSHALL, MI PIPELINE RELEASE
AUGUST 8, 2012

BACKGROUND

The Federal On-Scene Coordinator-approved Consolidated Work Plan (*CWP; Enbridge Energy, 2011*) recognizes the need for at least two additional studies to re-quantify the volume of residual submerged oil in the impacted area and to attempt to distinguish the oil volume that originated from the Enbridge Line 6B Incident release from unrelated oil. The timing for these studies corresponds to conditions in Spring 2012, following a spring flood but prior to commencement of any submerged-oil recovery efforts, and in Fall 2012 (CWP, p. 21). The quantification of submerged oil is discussed in the CWP as part of the Submerged Oil Characterization, and was described as being critical to understanding submerged oil fate and transport (CWP, sec. 4.0, p. 14). While the Submerged Oil Quantification section of the CWP does call for sediment cores to be collected (CWP, sec. 4.5), the coring methods, core sampling, and associated plans are discussed separately, in the plan's Hydrodynamic Assessment section (CWP, sec. 4.2.4). Collection of new cores in 2012 was explained as a help to not only the effort to quantify submerged oil, but also to determine submerged-oil transport rates and depositional patterns.

The evaluations and recommendations conveyed herein will follow the pattern of the CWP by separating submerged oil quantification and sediment sampling into distinct sections of the document outline. Linkages to both the CWP and the Federal On-Scene Coordinator's (FOSC) charges to the Science Support Coordination Group (SSCG) will be made clear wherever applicable. The overall purposes of the recommendations are to improve upon the methods used to quantify submerged oil in 2011, and to refine the existing protocols for sediment sampling (Enbridge, 2011, SOP EN-202, Nov. 2011) and core processing.

The following principal objectives (linked to the CWP and the FOSC's charge #1 to SSCG) of the planned submerged oil reassessment and re-quantification studies are recommended to remain essentially unchanged:

- To quantify the volume of submerged oil, and Line 6B oil fraction thereof, remaining in riverine sediment of the impacted area (cf. CWP, p. 15).
- To quantify the change in oil volume since Fall 2011 sampling (cf. CWP, sec. 3.2.1, p. 11).

This document represents a synthesis of the applicable opinions and recommendations received from individual scientists and engineers of the SSCG.

SCOPE

Individuals of the SSCG evaluated the protocols used to collect sediment cores and sediment-layer samples for the Fall 2011 submerged oil quantification task. Beyond that evaluation, the FOSC explicitly requested a review of the oil quantification study of Fall 2011 to demonstrate the potential value of incorporating a statistically based design, together with recommendations (FOSC USEPA, written communication, Mar. 21, 2012). The third aspect of the evaluations was to review the previously recommended, general Analytical QA Plan (USEPA-SSCG, 2012). Fourth, the analytical results from the February 2012 sediment samples collected for aquatic acute-toxicity studies were considered.

Out of the findings of these evaluations, individuals of the SSCG developed recommendations for the Spring 2012 submerged oil quantification study. These recommendations have implications for key components of the study design:

- Stratification of impacted area for sampling to quantify Line 6B residual oil.
- Characterization of background hydrocarbons.
- Spatial distribution of sample locations.
- Methods for collecting sample cores.
- Methods for selecting core-layer samples for analytical chemistry, geotechnical testing, logging, or preservation for potential future use.
- Methods for processing sample cores and core-layer samples.

STRATIFICATION OF IMPACTED AREA

The application of distinct, mappable geomorphic settings was recognized in the CWP to have value for such tasks as testing the cohesion and erodibility of streambed sediment (CWP, sec. 4.2.2), mapping the extent of areas categorized to have “light” submerged oil (CWP, sec. 4.5.3.3), measurement of current-velocity profiles (CWP, sec. 4.2.3), and monitoring of suspended sediment and associated hydrocarbons being actively transported (CWP, sec. 4.2.5).

Potential calculation of submerged oil volumes within specific geomorphic strata was discussed in the CWP (sec. 4.5.2.1) and an evaluation of various geomorphic surface types as part of the statistical evaluation of TPH results was proposed (sec. 4.5.4). Moreover, up to 10 distinct geomorphic settings were described for the riverine section of the impacted area (CWP, Figure 7.2). Thus, the use of geomorphic mapping information to stratify the impacted area for the purpose of developing an objective, balanced sampling design is not only appropriate but a logical progression from the discussion of options in the CWP.

Evaluations

The statistical value of stratifying a target population for sampling is to reduce the amount of random variation by accounting for a significant fraction of total variance of the primary variable under study that is systematically associated with a supporting characteristic, e.g., spatial or categorical variable. For stratification to be effective, the within-stratum variance should be less than the between-stratum differences. The primary variable under study is the quantity of submerged oil from the Line 6B release that is present in streambed sediment of the impacted area.

Forensic data should help to separate the background hydrocarbon content from the oil. Until forensic chemistry approaches were first applied to this Incident in February 2012, there were no samples for which analysis had attempted to differentiate Line 6B oil content from total hydrocarbon content. However, the February 2012 samples did not include a sufficient number of oil droplet/globule/sheen samples to allow reliable analysis of the Line 6B oil concentration per unit mass of sediment. Subsequently developed protocols for collecting samples of sheen and globules to document the oil's chemical signatures are being applied to archived samples and have been applied to samples from cores collected in Spring 2012 so that the mass of oil (TPH plus non-chromatographed compounds) may be determined and its source identified with confidence.

In review of Fall 2011 submerged oil quantification (Appendix 1), Zach Nixon (RPI) used GIS overlay analysis with a digital map of geomorphic strata (modified from Enbridge/TetraTech's geomorphic surfaces map) to identify the geomorphic unit type from which each Fall 2011 sediment core was collected. Despite 100 of 110 cores being from areas that, prior to oil recovery work, had shown indications of having "moderate" to "heavy" submerged oil, the uppermost layer of the cores had TPH concentrations that tended to differ among geomorphic strata, although results were not statistically significant overall (ANOVA, $p = 0.20$).

TPH concentrations in Fall 2011 appeared highest on average for four geomorphic strata that are typified as low-gradient and low-velocity environments (impoundments, cutoff/oxbows, backwaters, and anthropogenic channelized reach). These results, together with the recognition that analytical methods used in Fall 2011 did not allow for any within-sample adjustments for level of background hydrocarbons present in the TPH concentration, offer some additional rationale for applying a geomorphic stratification approach to design the Spring 2012 submerged oil quantification. The correspondence of TPH concentration with low-gradient and low-velocity environments was not unexpected, to the extent that both background TPH and submerged oil are preferentially associated with fine sediment (silt / clay) and organic matter, both would be expected to be strongly affected by geomorphic setting. These associations can be exploited during data analysis by normalizing the concentration data to factors (i.e., particle size, organic matter content and bulk density) known to affect sediment-associated organic contaminants.

A second approach to stratification also was evaluated: the use of the surrogate, point-screening results from poling, as generalized and mapped to form polygonal areas, to define two or more strata of expected sediment-oiling intensity. There is available information to suggest this would be an effective stratification approach: the SSCG review of Fall 2011 SO quantification (Appendix 1) reported that the uppermost layer of the cores had TPH concentrations that significantly differed (t-test, $p=0.002$) between two strata, i.e., cores collected from within the polygons delineating area of moderate to heavy poling results, and cores collected from outside those areas.

The recommended alternative for stratification of the impacted area is to use a two-way stratification where ten (10) fluvial geomorphic strata by two (2) Spring 2012 poling categorical strata are applied in combination to define up to 19 total strata as a framework for sampling (table 1). Because the poling results are based only on response from the upper layer(s) of the streambed sediment, samples of deeper layers of sediment should be apportioned using the geomorphic strata alone (table 1). Note that table 1 shows hypothetical scenario for number of cores by stratum that includes only tier-1 counts, i.e., makes the assumption that oil concentration variance within each stratum calculated from the tier-1 core-sample results will be small enough to achieve desired precision in confidence interval for each stratum-average concentration. Large hypothetical count for Impoundment stratum is, in part, an expectation that this geomorphic stratum may be expanded to include deeper parts of Morrow Lake, west of the sediment fan (Lake stratum).

[Values are counts allocated to stratum-category combination; NA, none allocated because combination did not occur within impacted area.]

		Geomorphic stratum										
Count units	Submerged oil screening category	Impoundment	Cutoff / oxbow	Depositional bar	Backwater	Channel deposit	Delta	Sediment fan in lake	Lake (beyond fan)	Tributary mouth	Anthropogenic channel	Total
Cores	Heavy to moderate	10	5	5	5	3	8	5	NA	5	5	51
Cores	Light to none	5	5	4	5	3	3	5	7	5	4	46
Cores	**Subtotal**	15	10	9	10	6	11	10	7	10	9	97
Additional samples from cores included above	Sediment layer >1 ft below water-sediment interface	8	5	4	5	3	6	5	4	5	4	49
Samples	**Total**	38	25	22	25	15	28	25	18	25	22	243

Table 1. Two-way stratification for allocating spatially balanced statistically based sample of streambed sediment across area impacted by Enbridge Line 6B incident. (Core counts are hypothetical tier-1 counts, and do not include cores from upstream reference sampling nor quality-control duplicates. Two samples were assumed would be collected per core from the uppermost 1-ft thickness of sediment. Also, some stratum-category combinations may not actually occur, and core count value then would be "NA")

Whatever analytical chemistry method is selected for quantifying oil in sediment cores in 2012, it is likely that a spatial interpolation method involving strata means/medians and strata dimensions will be used to estimate total amount of oil. Given this expectation, it is important that sampling effort is balanced appropriately to minimize bias and maximize precision.

This section addresses neither the analytical methods proposed for use in oil quantification (see *Analytical Scope* section) nor methods for distinguishing oil in sediments from background (see *Background and Upstream Reference Samples* section), but focuses on spatial sampling design for use with whatever oil chemistry analytical methods are selected. Present understanding of factors affecting the differences in submerged oil concentrations across the impacted area guided the evaluation of sampling strata. Relations between TPH concentration and poling methods informed only the sampling design, and are not a proposed method for Spring 2012 quantification of submerged oil. In all designs proposed for 2012, it is assumed that the selected analytical method will measure oil concentrations separate from background regardless of the relative concentrations of these two values.

A ***model-based approach*** would use existing data to predict oil presence and quantity based on other variable(s) – like space (geostatistical model), geomorphic surface, depth, hydrodynamics, etc. Sampling could be random, but this is not required. To produce a sensitive model, existing data should represent a wide range of possibly related covariates, and sampling often is designed to span the gradient of values for potential predictive covariates. Model-based methods are often best when: (1) it is desired to map the property of interest; and (2) a strong correlation exists between the property of interest and covariates.

The total amount of submerged oil is the primary quantity of interest – suggesting a survey-based approach. Understanding how such oil is distributed across space would also be of interest, but the distribution of submerged oil is strongly spatially patterned and appears to be clearly affected by known spatially distributed covariates. The review of 2011 oil quantification efforts (Appendix 1) demonstrated evidence that the amount of submerged oil in 2012 is likely to be strongly related to poling results and to geomorphic surface types. Further, spatial variogram analysis indicated that oil concentrations vary widely over small (<10 m) spatial scales. This result means that pure interpolation approaches would require unrealistically large numbers of samples. To make best use of known covariates to sample efficiently, a hybrid approach known as ***model-assisted survey sampling*** is recommended. The recommended hybrid approach is a ***spatially balanced, stratified Generalized Random Tesselation survey (GRTS) design*** (Stevens and Olsen, 2004). Such a survey design has the advantages of:

- Likely being more efficient than simple random sampling
- Being spatially balanced across the area of interest in the event that geostatistical models (interpolation) are required/helpful
- Leveraging known information about the relationship between covariates and submerged oil presence and quantity
- Having most of the advantageous statistical properties of a simple random sample
- Can include an oversample to accommodate non-response or no-access issues in the field
- Generating data useable for design-based estimates of total submerged oil properties via a variety of frequentist or Bayesian methods

RECOMMENDED STRATIFIED SEDIMENT SAMPLING DESIGN

This approach involves the following two-step process for determining stratification: collecting Spring 2012 Reassessment poling data as per previous years, and generating a stratified GRTS spatial sample using strata based on a combination of (1) 2012 poling results (or spatially interpolated products thereof—e.g., mapped polygons of similar submerged-oil response), and (2) mapped geomorphic surfaces reclassified to better manage the number of two-way strata resulting from the combination. Following the collection of sediment cores at the indicated sampling locations, and use of the selected analytical quantification method to determine hydrocarbon concentrations, the previously approved method (i.e., “calculator”) would be applied to estimate median or mean contaminant concentrations (separate from background) within these strata.

Advantages: This approach uses data collected at a stratified sample of all potentially affected locations, so results can be used to derive a more precise and unbiased estimate of remaining subsurface oiling. This approach is also spatially balanced.

Disadvantages: If a method for quantifying oil in sediments directly from poling results is derived, the poling results cannot be considered a sample of all locations. Poling results may be used, but only to stratify sediment sampling for other analysis. Sampling must be performed after poling because sediment sampling is dependent upon poling results. This approach is somewhat logistically complex.

BACKGROUND AND UPSTREAM REFERENCE SAMPLES

Previous rounds of submerged oil quantification, as well as the preliminary results from samples collected in 2012 for toxicity tests, suggest that concentrations of Enbridge Line 6B oil remaining in the streambed sediment of the impacted area may be of the same order of magnitude as that of background and other anthropogenic hydrocarbons. Possible sources of the background oil include historical industrial releases in the watershed, spills or natural seepage of oil from geologic formations upstream, and runoff containing oil and grease from roads or other surfaces. Atmospheric sources include both local and distant combustion of wood and hydrocarbon fuels that result in release of PAHs and other hydrocarbon emissions that are subsequently deposited on water bodies or other surfaces from which they become entrained by runoff and eventually reach streams.

To achieve the objectives of the submerged oil quantification, distinguishing Line 6B oil from that originating from other sources is necessary. Forensic chemistry-based approaches can be applied to mixing models when the chemical signature of each significant source is sufficiently resolved, and should be able to allocate quantitatively the mixed signature seen in samples from streambed cores among the several sources. Work has already begun using archived samples to address the source signatures, but additional samples may be needed if variation of the chemical signature within a source(s) is large relative to its difference between sources. To better ensure robust resolution of source chemical signatures, it is recommended that (1) duplicate cores be collected at each sampling location, and (2) one of the duplicates be frozen in the vertical position promptly after collection for processing the next day in the field, whereas the other be opened unfrozen at a field processing station, where one-half of that core would be used for core description (protocol enhancements discussed below) and subsequently processed to collect a sample of oil globules, if present, which would be frozen and archived for possible later analysis if needed for the source-resolution purpose; and from the other half of the core a sample would be collected for determinations of total organic carbon (TOC) and particle-size distribution (PSD).

An independent line of evidence for characterizing the background sources' contribution of oil in streambed sediment is possible through sampling of cores representative of analogous riverine environments outside the impacted area and unaffected by the Enbridge Line 6B release. This approach was attempted during the Fall 2011 SO quantification study, but has not previously been used to submit core-interval samples for the high-resolution analyses recommended in the Analytical QA Plan (USEPA-SSCG, 2012).

During the spring 2012 sampling, the effectiveness of the forensic analytical methods with the highly disturbed sediment from impacted areas is being validated, and direct comparison to reference sites (where any hydrocarbons present would be from other sources) is an important aspect of the validation. Therefore, it is recommended that cores be collected for the 2012 SO quantification in about equal numbers from each of the unaffected areas—i.e., Battle Creek and the Kalamazoo River upstream from the impacted area. If this were the primary approach for quantifying background concentrations, it would be important to represent as many of the Table 1 geomorphic strata as occur in the unaffected areas; however, as a secondary line of evidence, and in view that a few previously archived samples might also contribute evidence, a less intensive effort could suffice. Collection of 4 or 5 cores from each of two depositional geomorphic strata, and including some from each stream, is suggested—i.e., a total of 8 to 10 cores from unaffected areas. The uppermost 2.5-cm interval from each core would be submitted for analytical chemistry, whereas other layers of each core could be archived frozen. Core collection and processing of these “background” cores should be the same as for cores collected from the impacted area. The purpose of these background cores is independent validation that hydrocarbons in non-impacted areas have a signature of alkylated PAHs and biomarkers that is distinct from Line 6B oil. Previously archived samples that potentially could also assist with the purpose of background cores include three samples from each stream collected by Ponar sampler in February 2012; but since those samples are mixtures of the upper 5 to 6 inches, the oil signatures in the initial bulk sediment samples analyzed were less distinct.

SPATIAL DISTRIBUTION OF IMPACTED-AREA SAMPLES

Draft maps of the geomorphic strata developed by USGS and USEPA/START personnel from the previously mapped geomorphic surfaces (Enbridge/TetraTech) are shown as Figure 1 below. The maps show a reclassification of the numerous categories of geomorphic surfaces to produce a set of 13 categories; however, the three categories without a color symbol (Engineered channel, Exclude, and Island) are not within the sampling domain for the Spring 2012 oil quantification study. Thus, there are 10 categories that serve as the geomorphic strata for the two-way stratification of the study area. The concrete-lined Engineered Channel is a reach unsuited for this study and contains few, if any, sediment deposits. Island areas are not submerged at the flow conditions during which cores are collected, and their deposits do not fall within the operational definitions for submerged oil. Neither the Island nor Engineered Channel areas were sampled as part of the 2011 studies undertaken for the purpose of quantification of submerged oil. With the expansion of the impacted area in Spring 2012 to include all of Morrow Lake, additional areas that also were not sampled as part of the 2011 oil-quantification studies are now included in the study design for 2012. As the geomorphic surfaces map units that cover those areas were evaluated and reclassified, one polygon that encompasses an island was identified as not quite fitting into any of the 10 categories. It had been mapped as an Island Deposit with sand and gravel substrate in the geomorphic surfaces map. Clearly it lies beyond the sediment fan which occupies the east end of the lake, but its substrate texture contrasts strongly with the soft sediment of the central and western areas of the lake. Rather than have a single such polygon comprise an eleventh geomorphic stratum, we elected to exclude this unit from the study area.

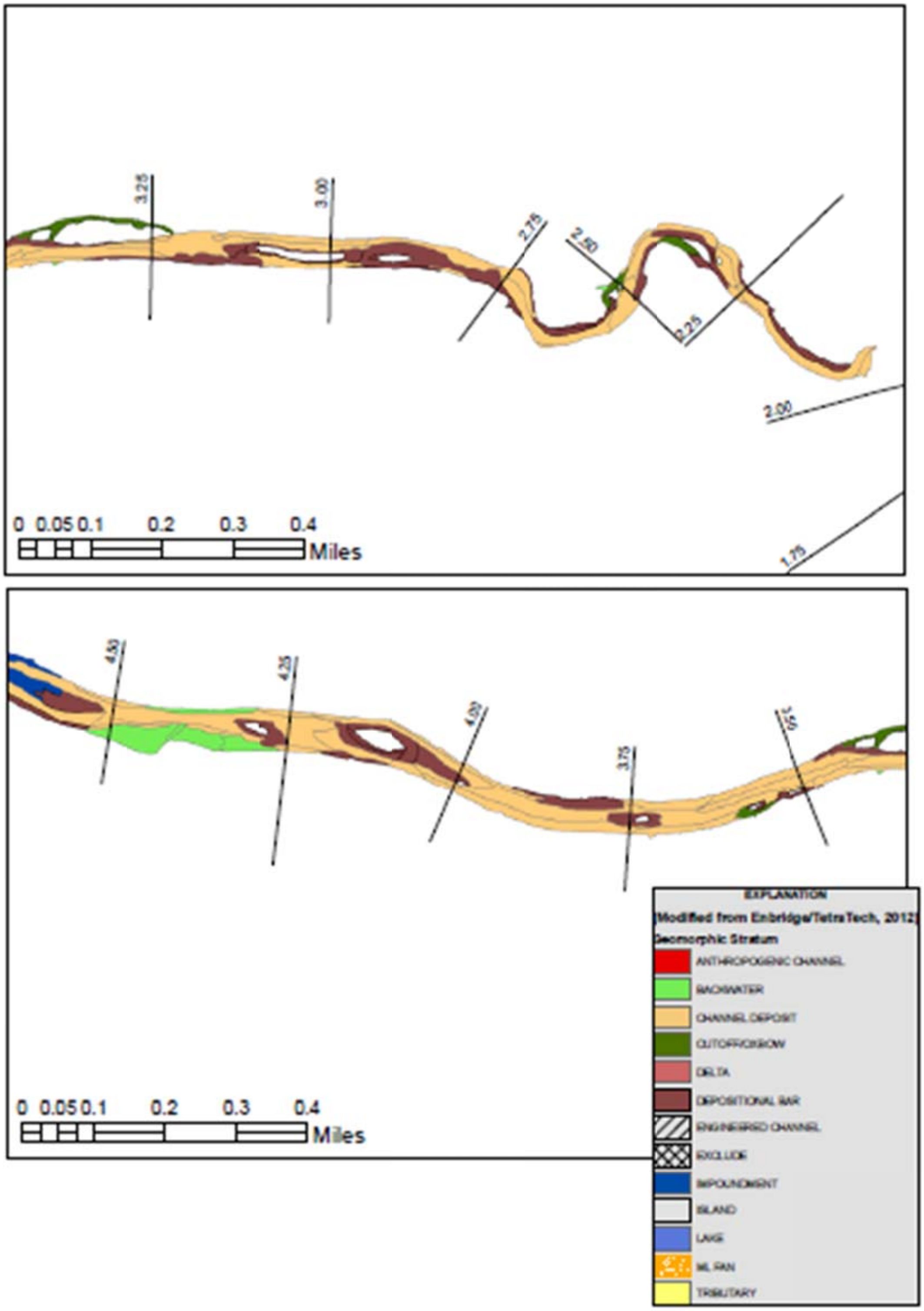

Figure 1. Draft maps of the geomorphic strata developed by USGS and USEPA/START personnel from the previously mapped geomorphic surfaces (Enbridge/TetraTech).

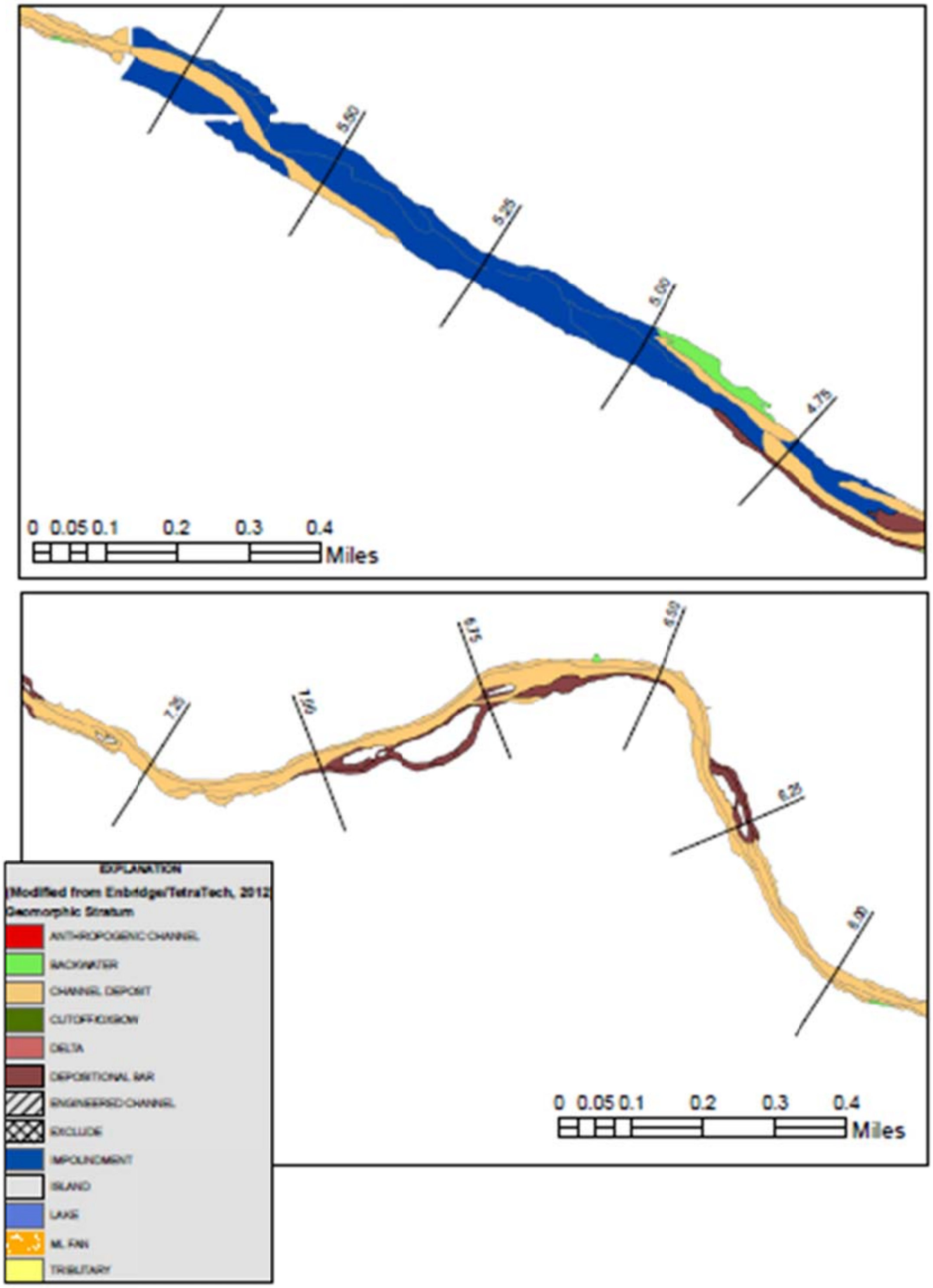

Figure 1 (continued). Draft maps of the geomorphic strata developed by USGS and USEPA/START personnel from the previously mapped geomorphic surfaces (Enbridge/TetraTech).

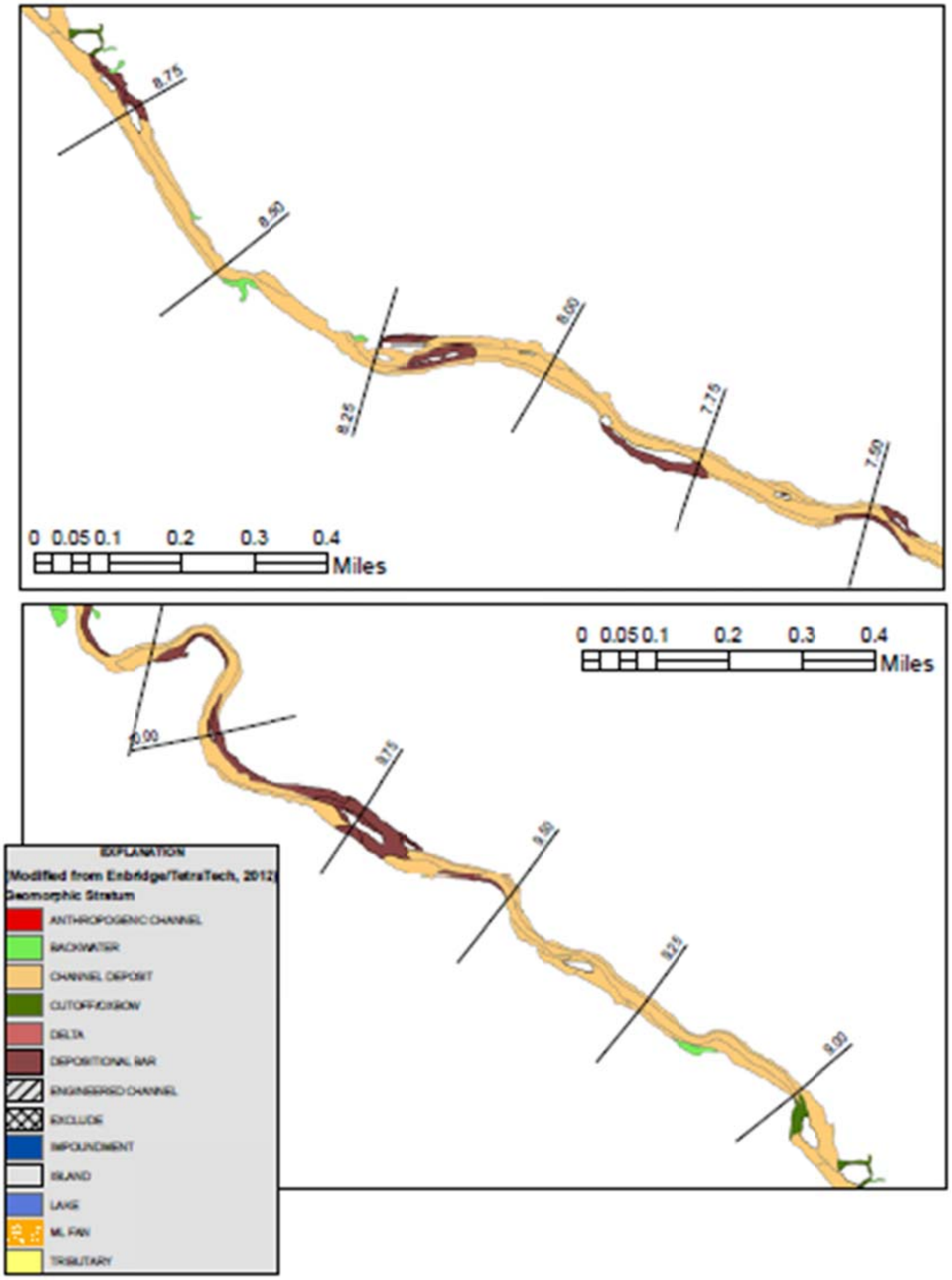

Figure 1 (continued). Draft maps of the geomorphic strata developed by USGS and USEPA/START personnel from the previously mapped geomorphic surfaces (Enbridge/TetraTech).

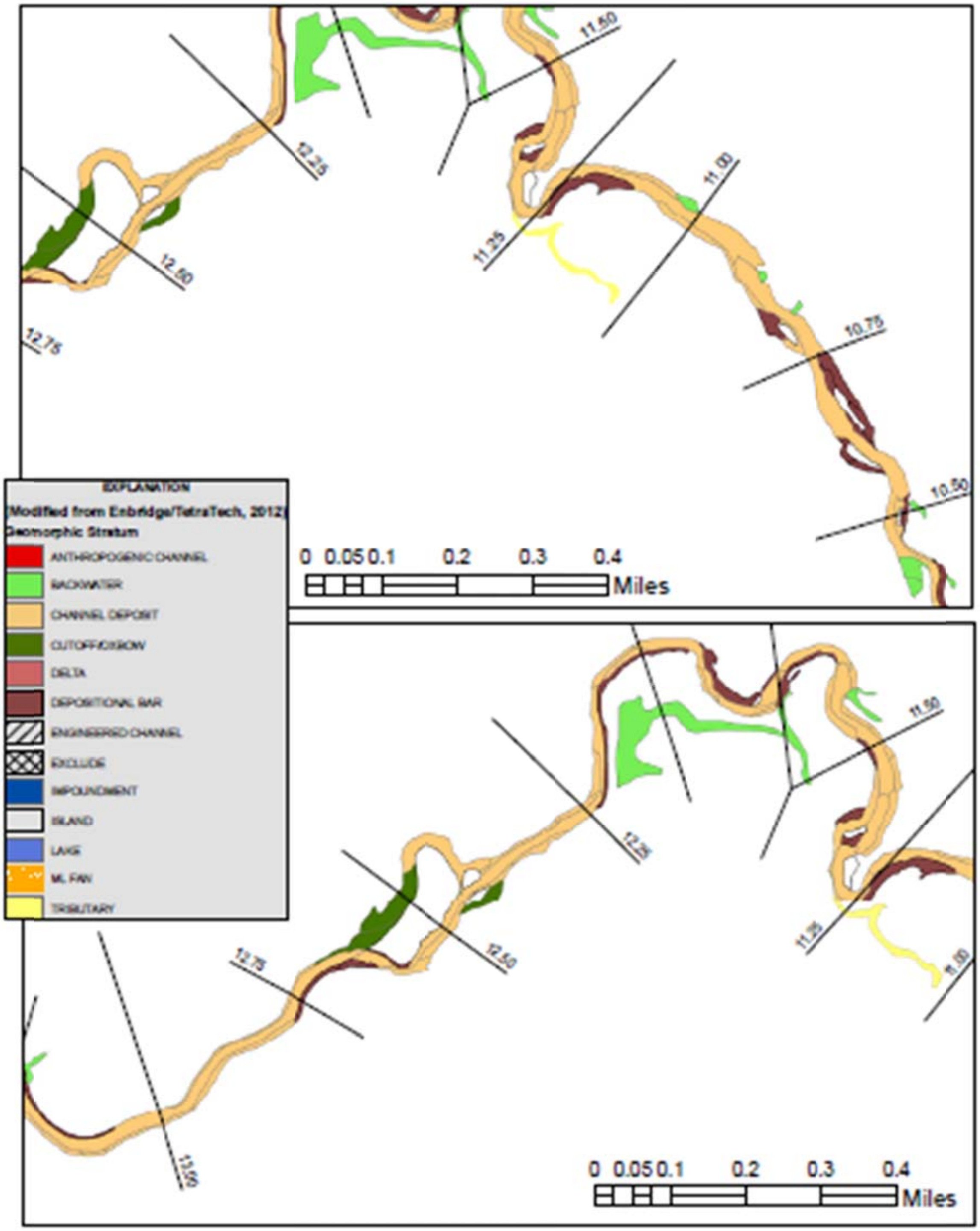

Figure 1 (continued). Draft maps of the geomorphic strata developed by USGS and USEPA/START personnel from the previously mapped geomorphic surfaces (Enbridge/TetraTech).

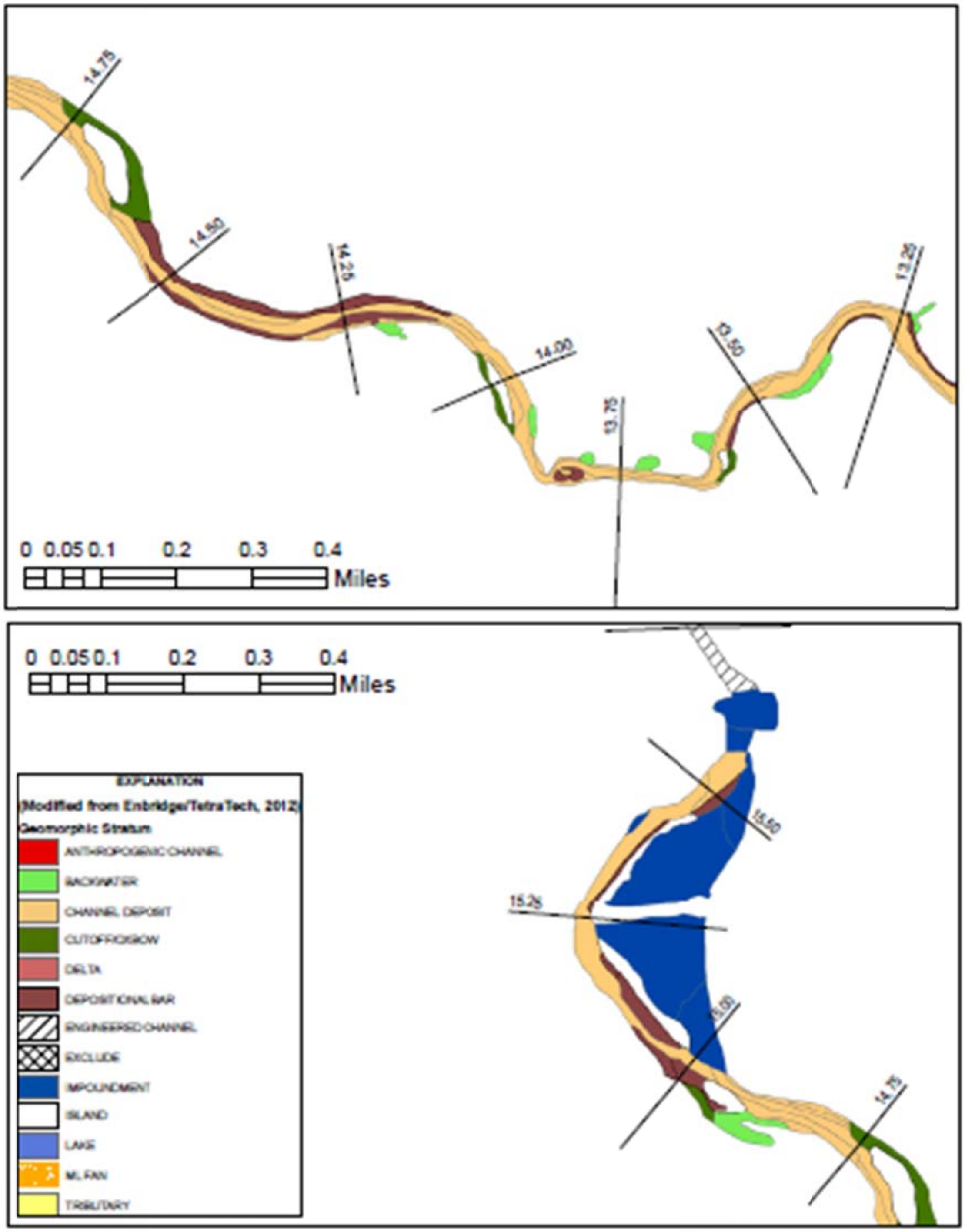

Figure 1 (continued). Draft maps of the geomorphic strata developed by USGS and USEPA/START personnel from the previously mapped geomorphic surfaces (Enbridge/TetraTech).

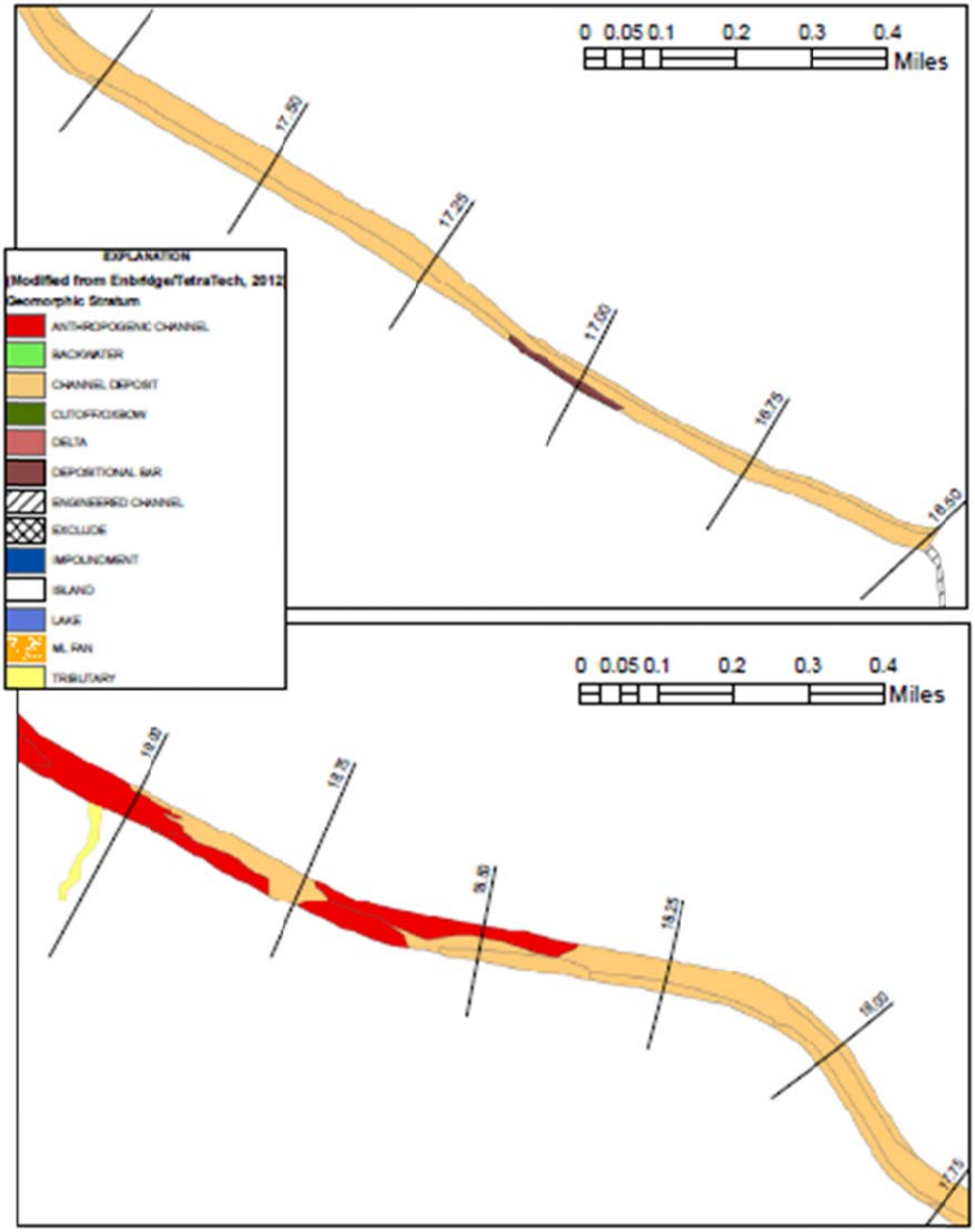

Figure 1 (continued). Draft maps of the geomorphic strata developed by USGS and USEPA/START personnel from the previously mapped geomorphic surfaces (Enbridge/TetraTech).

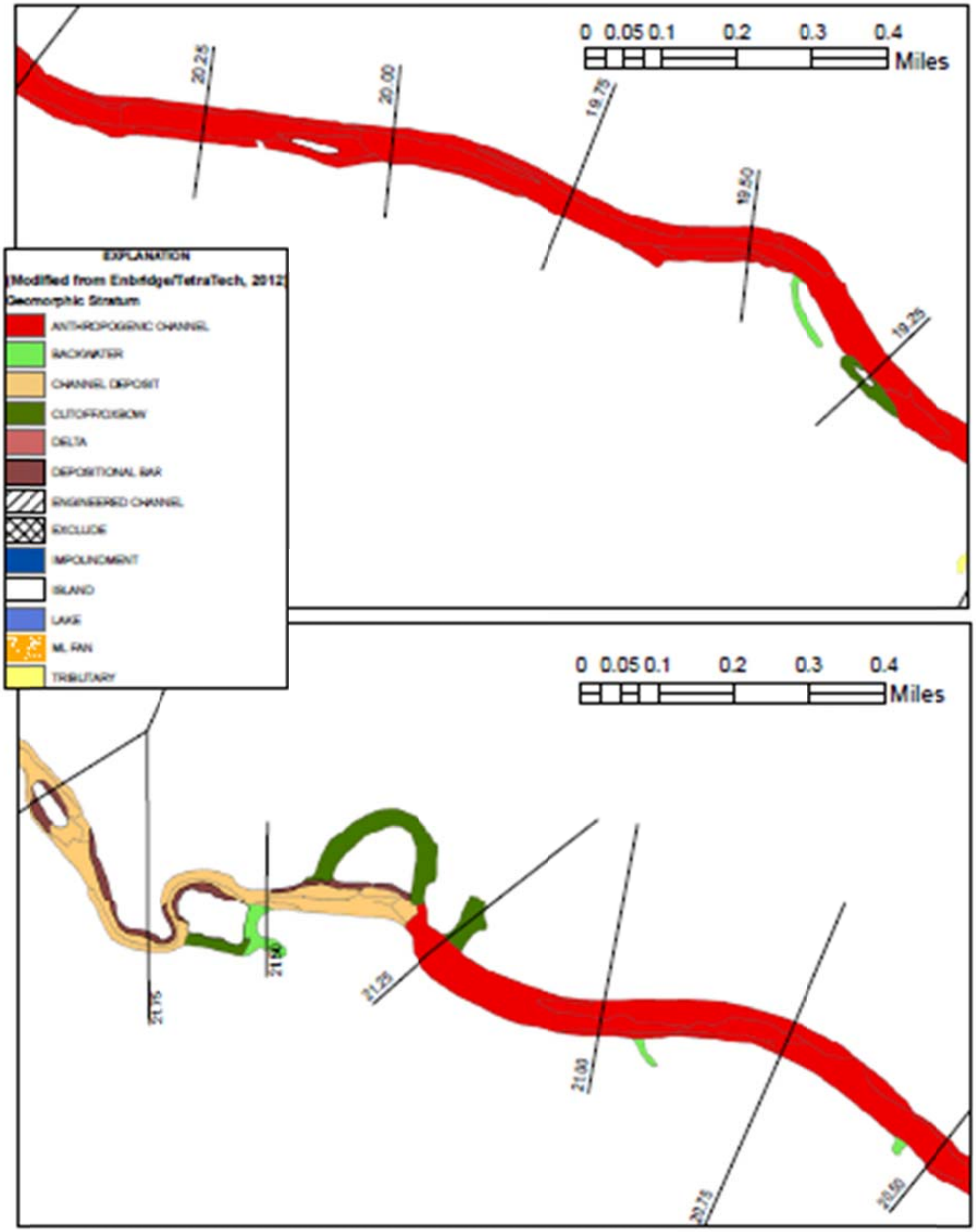

Figure 1 (continued). Draft maps of the geomorphic strata developed by USGS and USEPA/START personnel from the previously mapped geomorphic surfaces (Enbridge/TetraTech).

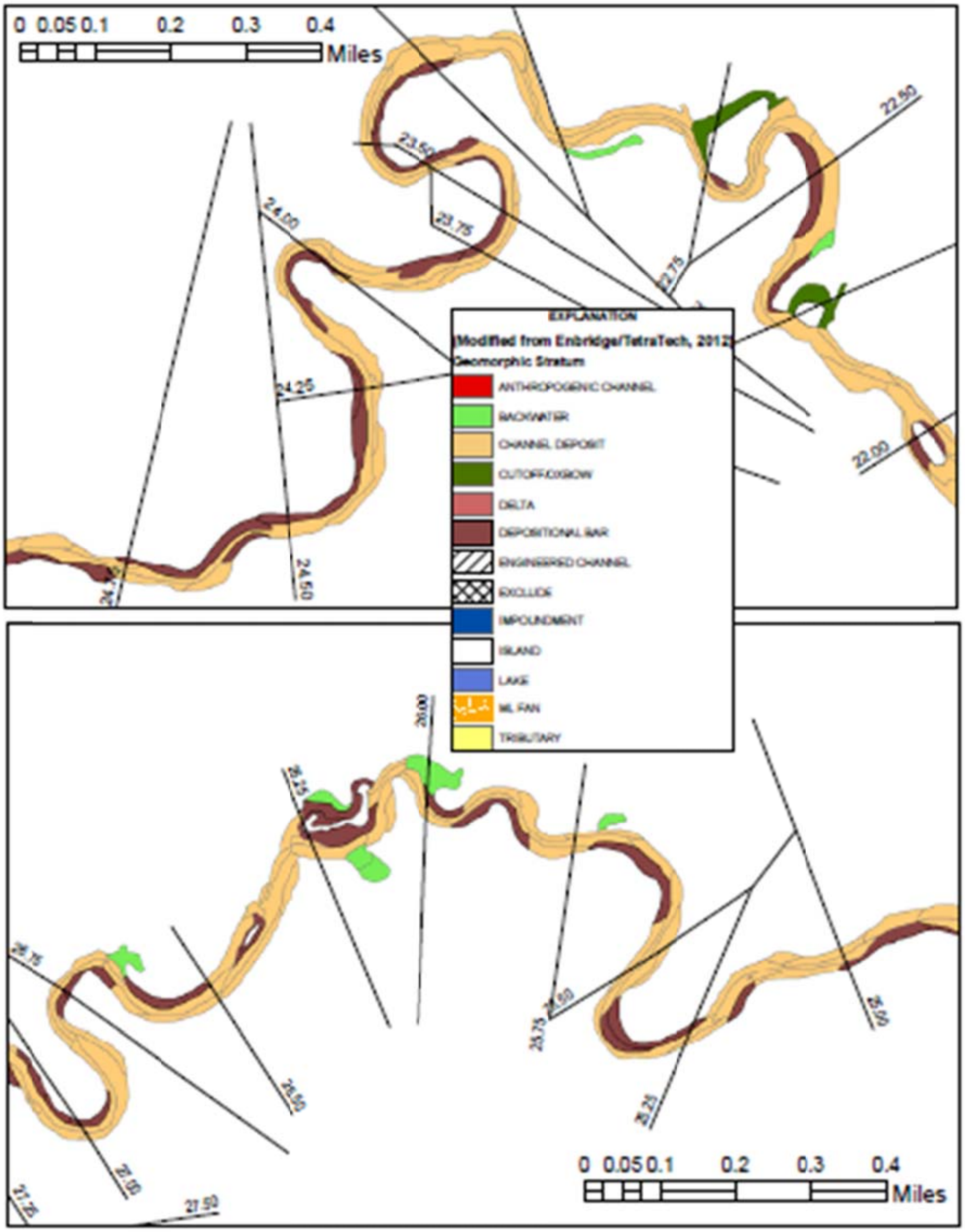

Figure 1 (continued). Draft maps of the geomorphic strata developed by USGS and USEPA/START personnel from the previously mapped geomorphic surfaces (Enbridge/TetraTech).

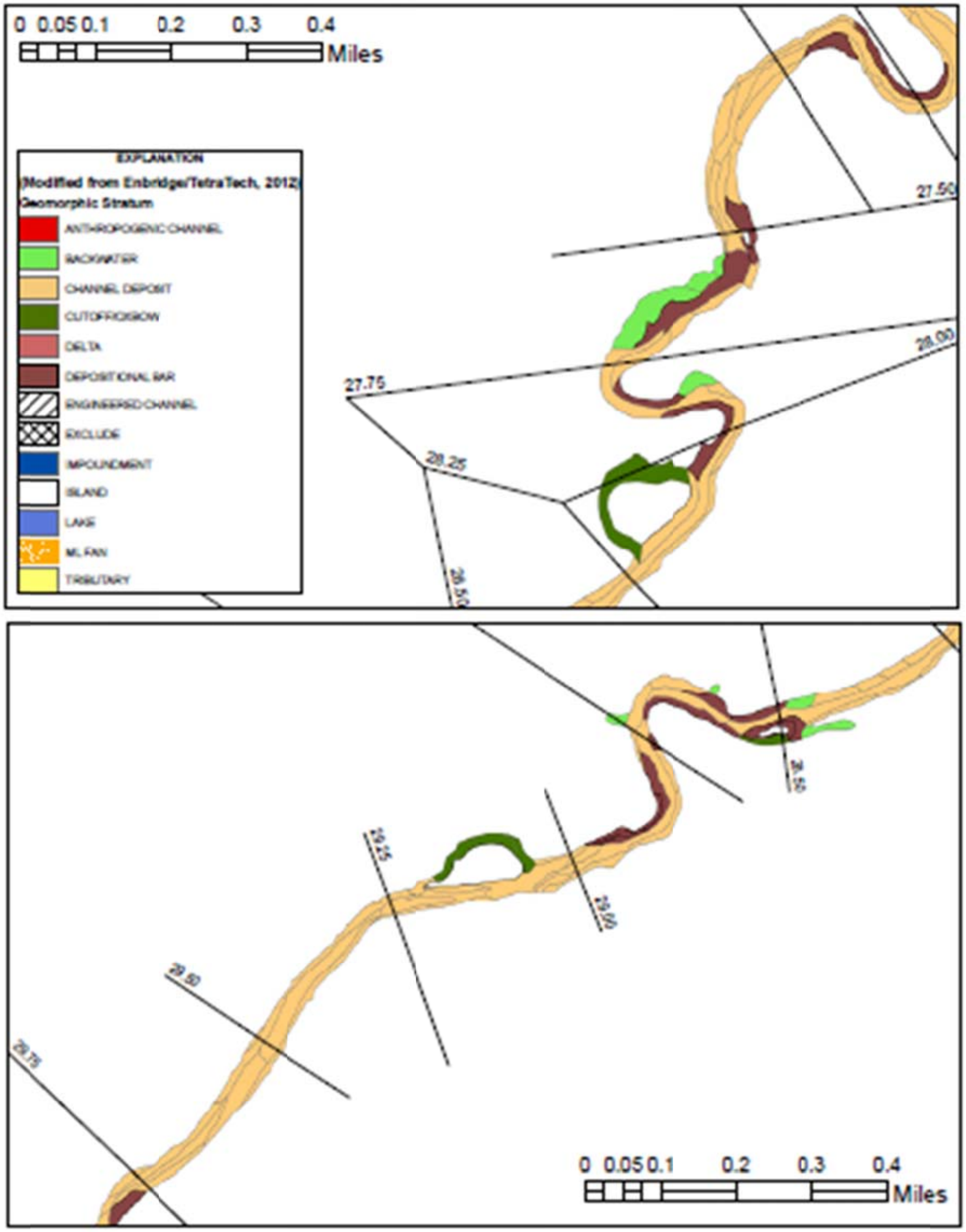

Figure 1 (continued). Draft maps of the geomorphic strata developed by USGS and USEPA/START personnel from the previously mapped geomorphic surfaces (Enbridge/TetraTech).

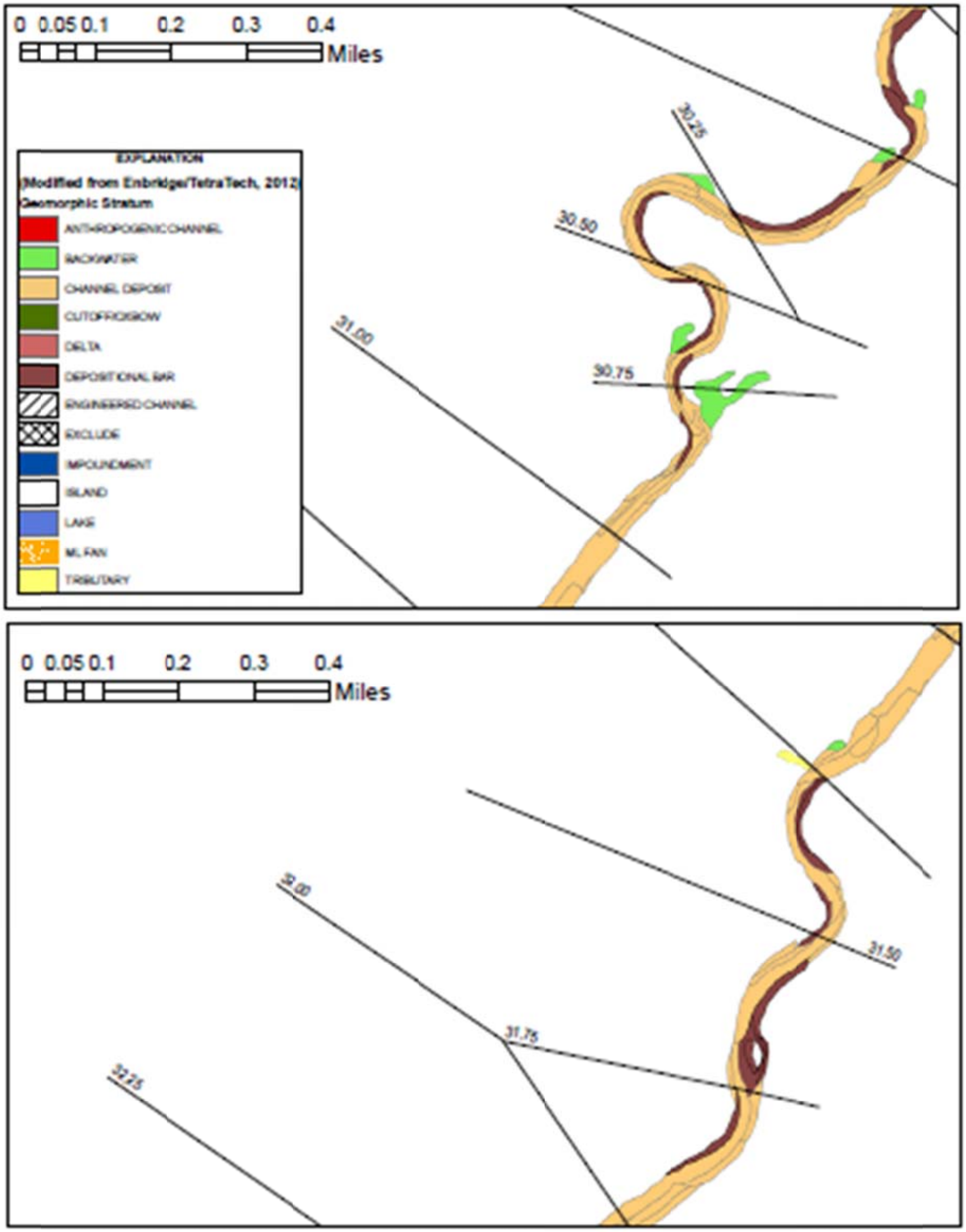

Figure 1 (continued). Draft maps of the geomorphic strata developed by USGS and USEPA/START personnel from the previously mapped geomorphic surfaces (Enbridge/TetraTech).

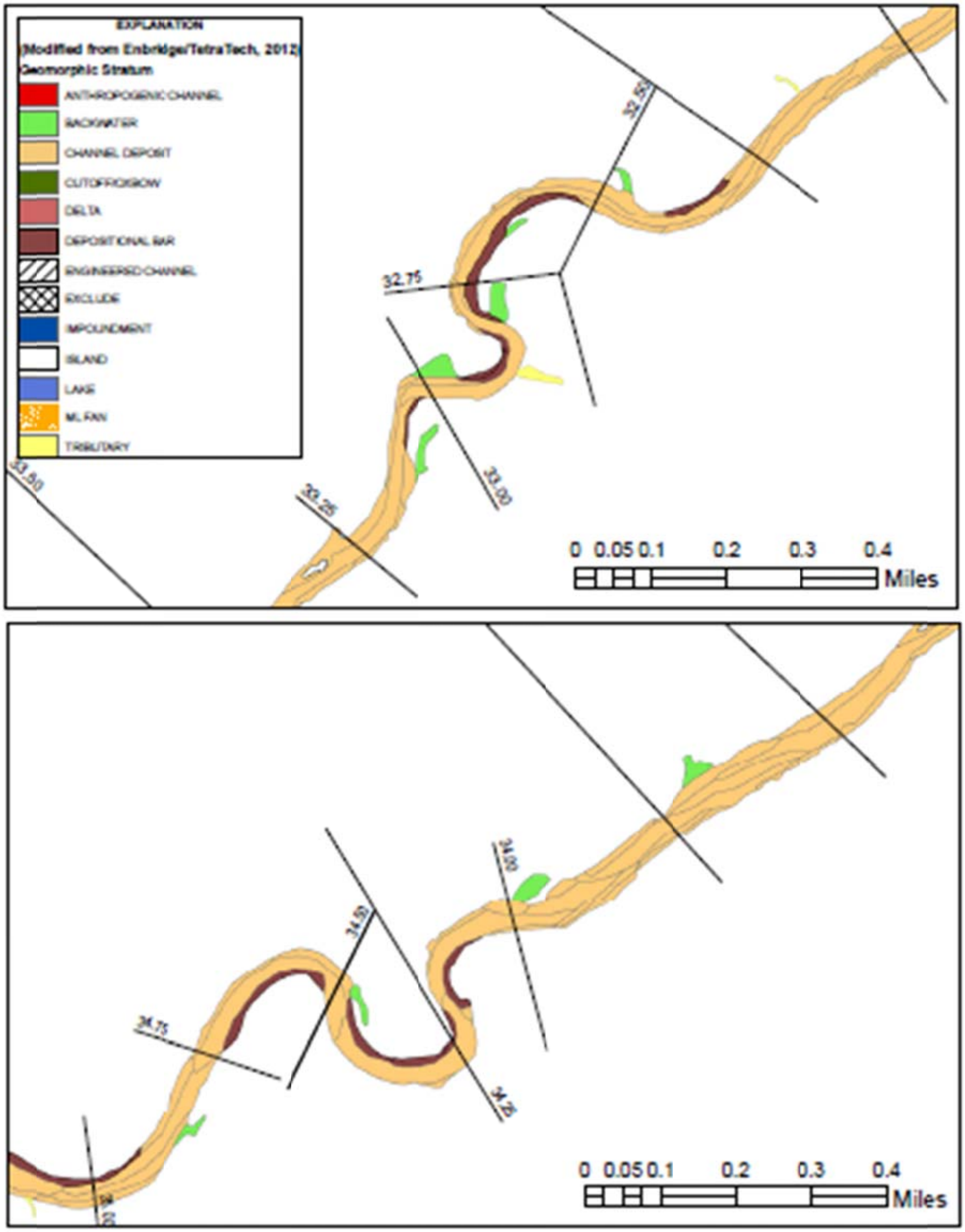

Figure 1 (continued). Draft maps of the geomorphic strata developed by USGS and USEPA/START personnel from the previously mapped geomorphic surfaces (Enbridge/TetraTech).

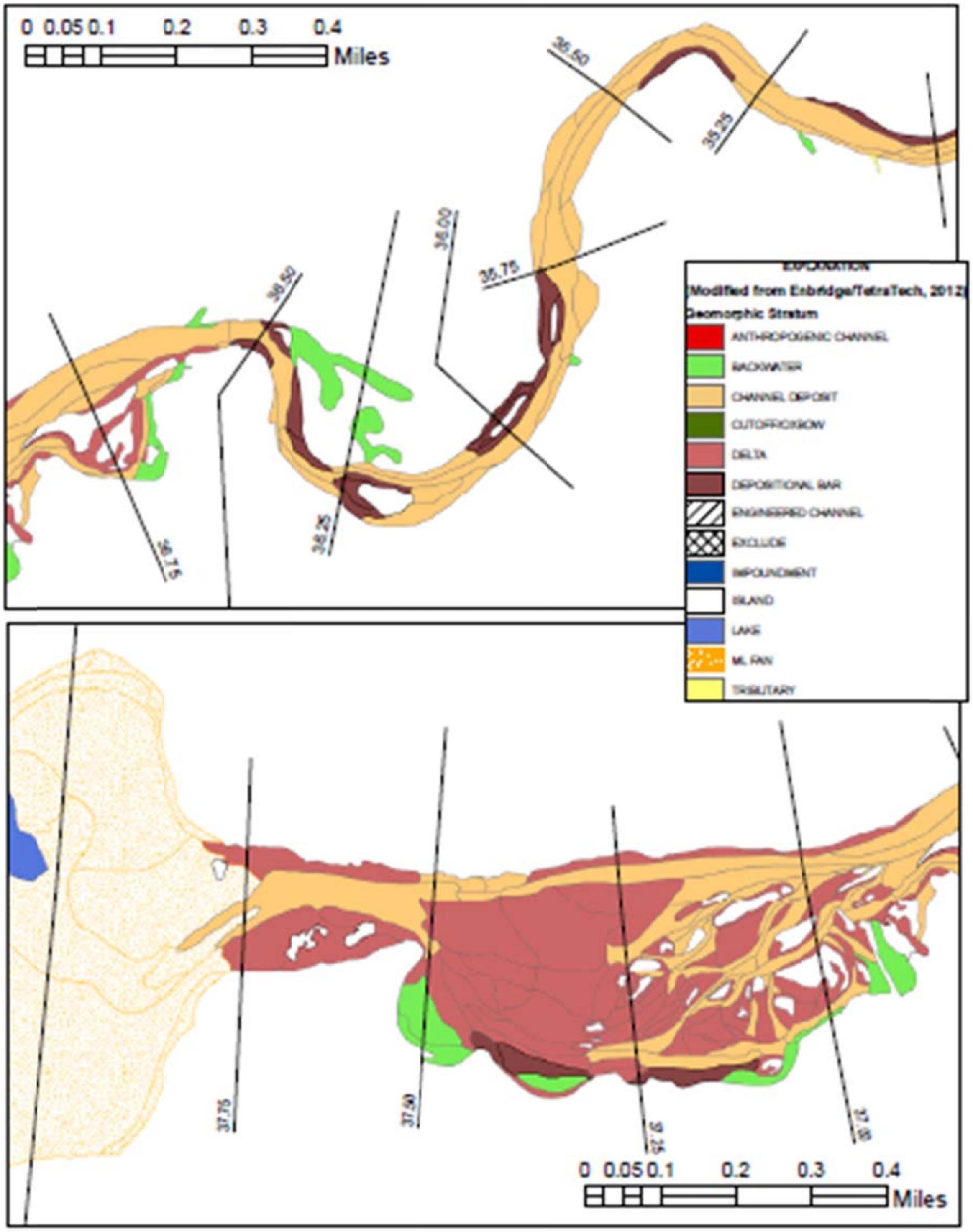

Figure 1 (continued). Draft maps of the geomorphic strata developed by USGS and USEPA/START personnel from the previously mapped geomorphic surfaces (Enbridge/TetraTech).

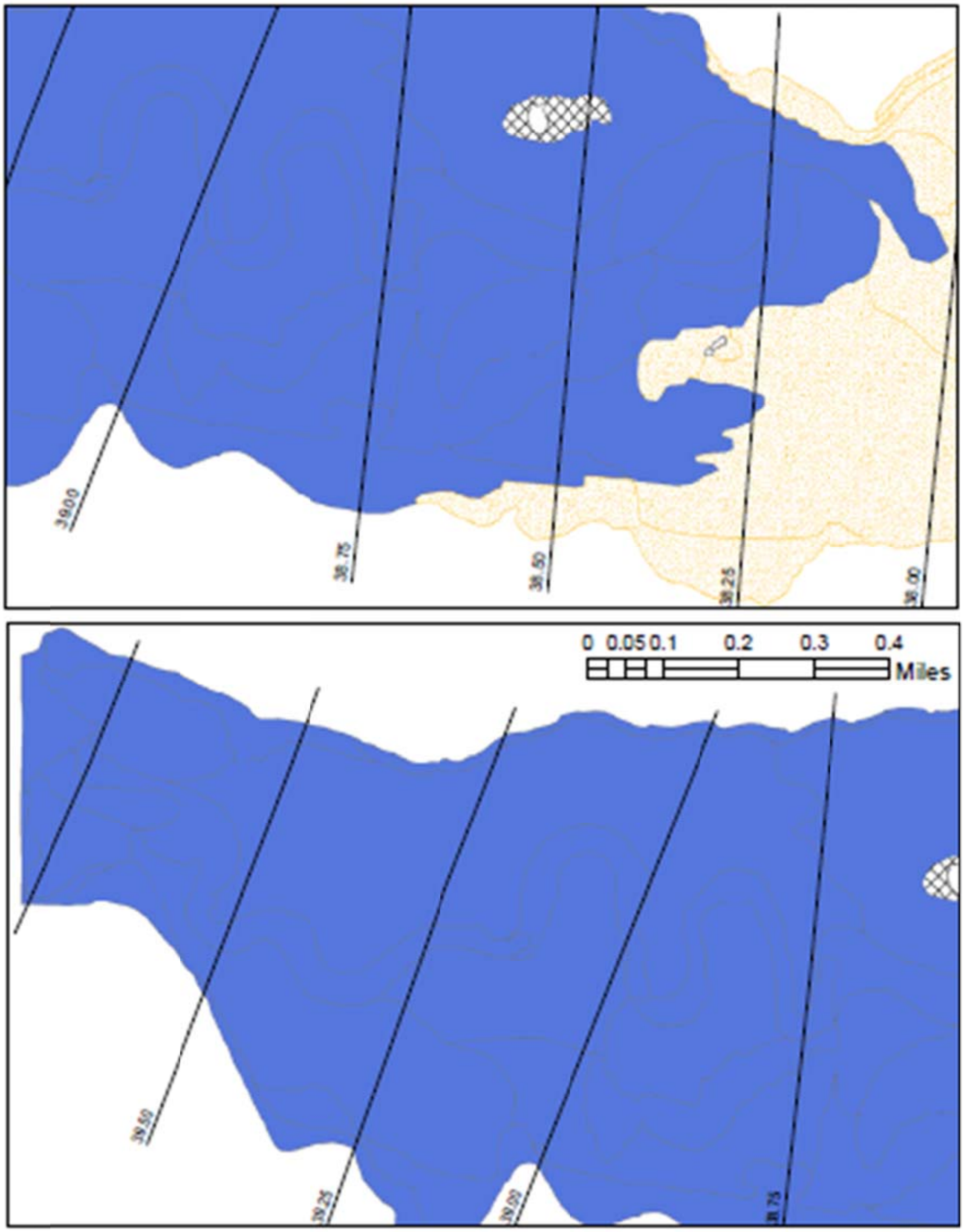

Figure 1 (continued). Draft maps of the geomorphic strata developed by USGS and USEPA/START personnel from the previously mapped geomorphic surfaces (Enbridge/TetraTech).

Draft maps of the submerged-oil poling categories (heavy, moderate, and light) will be made available following completion of the 2012 Spring Reassessment poling. Those poling categories comprise the second layer of the two-way stratification. Once finalized, the poling categories and geomorphic strata will be processed together using GIS overlay analysis to define up to 19 combinations between the 10-category geomorphic layer and the 2-category submerge oil layer (heavy and moderate poling being combined into a single category, and light and 'absent' poling results comprising the second category).

Each of the 19 or so combination categories comprises one sampling stratum, and from the area corresponding to each, the GRTS software will be used to select a sample of coring locations, with a list of alternates; e.g., perhaps 20-30 locations will be listed per sampling stratum. Maps and tables of the map coordinates and category attributes of each sampling/coring location will be deliverables from the use of the GRTS software. As field teams visit the first tier of sampling/coring locations, if a location is determined in the field to not actually belong to the indicated geomorphic stratum, and a small horizontal offset (say, 10-15 ft) would not permit the location to be shifted into the targeted stratum, then to avoid subjective selection of a replacement, it is recommended that the field team replace the site with the next alternate location from the GRTS-generated list.

ENHANCEMENT OF SAMPLING PROCEDURES

The existing protocols that were used for Fall 2011 coring of streambed sediment and subsequent processing to collect samples for chemical analyses were approved by USEPA for SO quantification prior to compilation of experts within the SSCG. Wherever they do not introduce cause for technical concern, it is accepted that, for consistency and comparability, those methods remain unchanged for the Spring 2012 SO quantification. There are a number of aspects, however, that did raise concerns during evaluation and those are discussed in this section along with recommended alternative methods.

1. *Verification of Sampling Location*

When the field crew arrives at the projected sampling location, a suitably qualified and experienced fluvial geomorphologist with the U.S. EPA or USGS oversight should verify that the point is "on target" with respect to the study design's stratification categories. That is, the actual observed geomorphic setting, hydraulics and sediment surface should provide mutual agreement with the projected geomorphic stratum; and the presence/absence of sheen and/or globules observed just downstream of the "on target" location should confirm the projected submerged-oil category.

2. *Collection of Sediment Cores*

2.1 Recommendations

After decontamination, the corer (e.g., check-valve corer head) should be dried, and the core-tube-receiving end then wrapped in foil and kept isolated in clear plastic bags for transport to the sampling site. At the coring site, the corer should be thoroughly rinsed with ambient stream water prior to use. The interior of coring tubes also should be isolated from atmospheric contamination during transport to the coring site.

Field data to be collected for each core should be expanded from the Fall 2011 SOP to include water temperature and sediment temperature at 1 and 2 ft below the sediment surface, both measured *in situ*. Other field measured parameters from the existing 2011 protocol should remain mandatory data elements for the 2012 protocol.

Cores should be collected with either a check-valve corer or a piston corer; dredge-type samplers should not be used. The bottom end of the core-collection tube should be placed into contact with the sediment surface using a slow descending transit rate to avoid disturbance to any floc layer at the water-sediment interface. For purposes of quantifying submerged oil, the target depth for coring should extend beyond the estimated depth of maximum scour that has occurred since the Line 6B release, whether that scour was introduced by riverine hydraulics or by submerged-oil recovery methods. However, given that collected cores would likely be sub-sampled to even greater depths to acquire particle-size distribution parameters to support data needs of the hydrodynamic assessment and hydrodynamic modeling components of the CWP, the primary recommendation is that recovered material in the primary core be containerized, frozen, and intervals not selected for chemical analysis be archived at the analytical laboratory at -20°C for an indefinite period. The primary core should, in any case, include at least the uppermost 2 ft of the bed sediment profile, unless coring refusal is encountered above that depth.

At each location, it is suggested (at least) two (2) side-by-side cores should be collected. One core would be used for field analysis and sub-sampled for TOC, PSD and oil globules, whereas the other core would be sub-sampled for forensic chemistry in the field with concurrence from an oversight geologist/observer. Because the designation of cores as to destination would not be made until they are inspected at the field processing station, both cores should receive identical treatment at the sampling location and be chilled to 4^{o}C immediately following collection. Additional cores may be collected as dictated by quality-control or other project objectives.

Sheen sampling also is critical to achieve study objectives, because it provides an integrated signature of the oil and degree of environmental weathering and (or) biodegradation at each sampling site without the sediment background interference. Therefore, the field protocol should be revised to specify that immediately after core collection is completed, record a paired observation of sheening response to poling agitation of the streambed adjacent to coring location. Additionally, collect the sheen so produced using a Teflon sheen sampler and following the ***Recommended Oil Globule Sample Collection Procedure*** (4/26/2012).

2.2 Evaluations

Clam-shell-type dredge samplers cause rotation and mixing within the sampled volume of sediment, both as the clam-shell halves close and commonly again as the sample material is emptied from the sampler into an open container of some type. Other types of dredges impose similar hazards of mixing among the layers of sediment. In addition, dredge samplers typically do not collect equal volumes of sediment from each vertical fraction of the streambed material; rather, a sampler-shape induced bias is introduced, typically collected more material from the sediment surface and less from the lowest layers included in the sample. Either the Universal-type push-corer (i.e., check-valve corer) or piston corer are expected to provide a reliable method of collecting undisturbed sediment cores at almost all sampling locations along the impacted section of the river, as long as sampling techniques follow guidance for collecting "acceptable" sediment samples (fig. 2; NewFields, written communication, 2012):

The following sample-collection guidelines describe a recommended sediment sampling technique.

1) The sampler is lowered at a slow, controlled velocity to minimize the bow wake of the sampler.
2) The sampler is inserted and retrieved at a slow steady rate
3) A minimum sediment depth of 60 cm is recovered in the sample chamber.
4) The core-head check valve closes completely to create a tight seal at the bottom of the sample chamber
5) The sampler is maintained vertically while retrieving and processing activities are conducted
6) A minimum of 1 cm of standing water remains atop the sediment collection chamber.
7) No water is leaking from the sediment collection chamber while the sampler is inspected on the boat
8) The sediment sampler did not over-penetrate the sediments causing sediments to squeeze out of the top of the collection chamber or contact the corer head.
9) The maximum potential volume of standing water is removed from the sample collection chamber without affecting the flocculent material atop the sample.
    - Flocculent material is allowed to settle for a minimum of 1 hour until supernate is clear.
    - Water is removed via a suction bulb turkey baster or small-diameter (~1/4" ID) siphon tubing.
    - Removal of standing water does not remove the flocculent material.
    - Removal of the standing water does not disturb the flocculent material via mixing or mobilization.
    - Potentially 1/8 to 1/4 inch of standing water will remain atop the sample after surface water removal.
10) The sample collection & handling equipment are properly decontaminated.
    - Decontamination activities shall be conducted between each sample attempt.
    - All equipment that contacts sediment surfaces must be decontaminated between each sample attempt.
11) The sample is collected and processed in a "clean environment"
    - Such as maintaining position upwind of any exhaust and with any boat motor turned off.

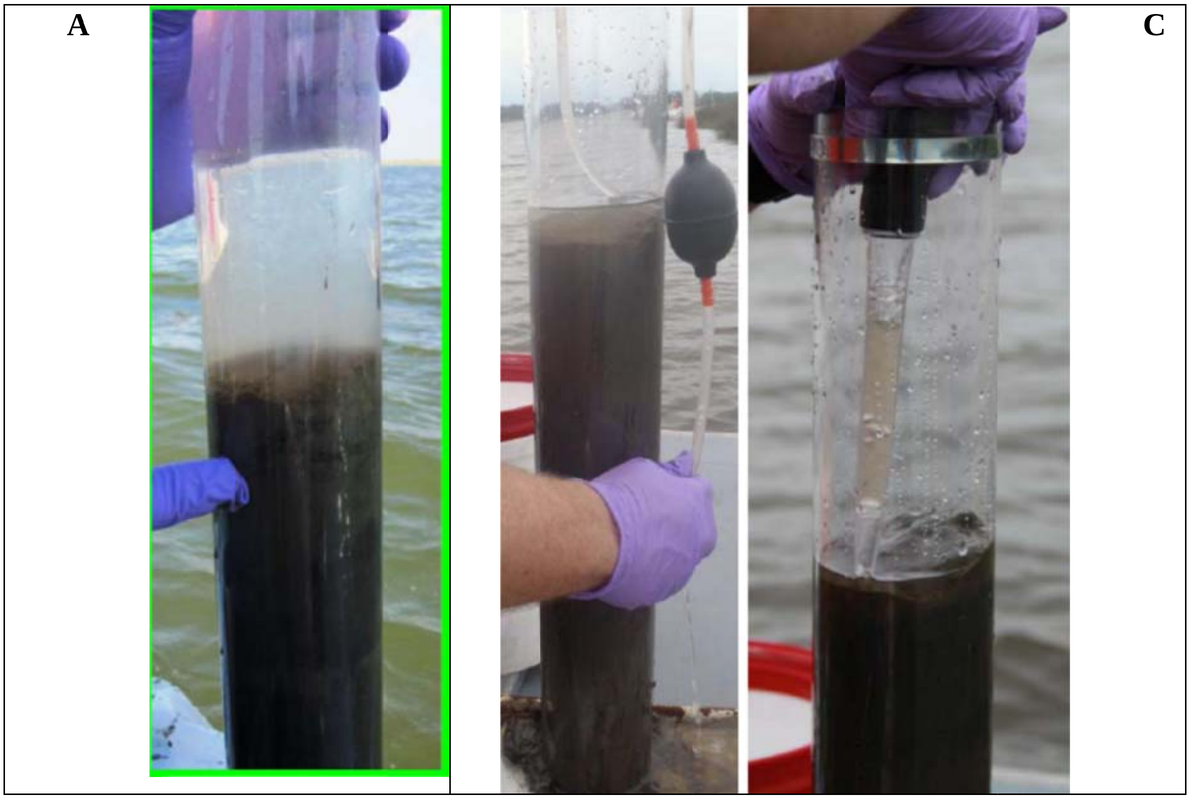

Figure 2. – Photographs showing (A) an acceptable sample that preserved undisturbed the surface flocculent material; and removal of supernatant water by (B) siphoning and (C) suctioning with turkey baster. Note that the technician was cautious not to disturb the flocculent material, and may acceptably leave a shallow depth of supernatant water (1/8 to ¼ inch). Photo source: NewFields.

The sediment deposited since submerged-oil recovery commenced upstream is likely to be present as a low-density layer on the sediment surface. In areas where agitation-based recovery occurred locally, the re-depositing, vertically settling sediment that was suspended by the recovery efforts is expected to occur as an upward-fining sequence. In either situation, the uppermost layer of sediment encountered during core collection could be the most enriched in sediment-associated submerged oil. Thus, a sampling technique that avoids disturbance to that uppermost layer of sediment or floc is strongly preferred.

A 3-inch-diameter piston corer is commonly used by the USGS to collect core samples and paired with a core tube composed of Lexan™ polycarbonate. The corer head is composed of steel. After decontamination, the corer is air dried, covered in foil and transported in clear plastic bags to the sampling site. At the coring site, the corer is thoroughly rinsed with ambient stream water (F.A. Fitzpatrick, USGS, written communication [QAPP for Neopit Millpond], 2004).

Core length. The scour depth of streambed sediment in the Kalamazoo River generally would be field identifiable using streambed cores, or could be estimated from hydrodynamic simulation of specific hydrologic events. The Fall 2011 thickness of oil impacted sediment generally ranged up to 1.9 ft[1], with a reported average thickness of 0.7 to 0.8 ft for cores with field-detected oil. Previous attempts to quantify the submerged oil volume remaining in the impacted area have used calculation methods that neglected hydrocarbon content below the average thickness of the oil-impacted layer of sediment. Thus, for the objectives only of Spring 2012 oil quantification, there would be little value in collecting cores much longer than the 2-ft maximum expected thickness of the oil-impacted layer. However, collected cores would have uses for other objectives, e.g., they are likely to be sub-sampled to greater depths (perhaps at expected scour depth from 100-year flood) to acquire particle-size distribution parameters for use in the hydrodynamic assessment and hydrodynamic modeling components of the CWP.

3. Processing of Sample Cores

3.1 Recommendations

It is important to preserve undisturbed the uppermost, often “sloppy” or “soupy” *floc* layer at the water-sediment interface (approximately the upper 2.5 cm). Cores collected for field observations and chemical analysis should be maintained in a vertical orientation throughout handling, and transport, except when frozen. Document the quality of each core based on floc thickness, vertical sediment features and sediment recovery. The highest quality core should be reserved for chemical analysis (Core #1), and the remaining core (Core #2) should be used first for collection oil globules and then making the field observations (half A) and collection of PSD and TOC samples (half B). Transport all cores to the core processing station—a “clean” area—while maintaining cores in the vertical position. Allow any sediment in the overlying water settle (approximately one hour), then siphon off the water from both cores *without removing the visible flocculent layer.* Measure and record the sediment thickness in both cores.

Place the chemistry core (Core #1) in the freezer overnight, in a vertical position, to partially freeze the sediment. Process the chilled**,** non-frozen Core #2 by splitting the core liner and laying each half out on a table for processing. Process this core according to the recommendations provided in *Section 3.1.1-Screening method for selecting core subsamples for analytical chemistry***.**

Take photographs of Core #2 under white light and UV illumination (use a specialty camera or film that has particular sensitivity to UV fluorescence is recommended for the latter). The 2012 protocol should give clear instructions on photo documentation of the described core; e.g., prior to any further processing or subsampling, intervals of the opened core should be photographed at an explicit scale (scale/ruler in photo) and under illumination such that sediment general texture and color are well distinguished in the digital image. Then perform a UV-aided visual analysis of the undisturbed exposed sediment, as follows. For each 2-cm interval along the core, record on a core-logging form the presence and relative intensity or frequency of petroleum indicators (i.e.,

---

[1] Exceptions being 2.5 ft for core SEKR2225C01, and four cores composited from discrete-interval samples collected using a different coring apparatus (Russian peat borer).

sheen, and number of oil globules, droplets, or tar flecks observed along with size range of the point-type indicators).

The field-analysis core[2] (Core #2) will be opened[3] at a field processing station and one of the core halves would be examined (as in existing 2011 SOP) for field determinations of color (Munsell Color, 1975), UV fluorescence, texture by rubbing sediment between the fingers to classify according to the Unified Soil Classification System (ASTM D-2488-09a), and major stratigraphic units. This half-core also would be processed to collect oil globules (discussed below; see also USEPA-SSCG, ***Recommended Oil Globule Sample Collection Procedure*** [4/26/2012]). Sub-samples of the remaining, undisturbed half of the field-analysis core would be collected for determinations of total organic carbon (TOC) and PSD at a high categorical resolution to support the requirements of the hydrodynamic modeling component of the CWP (see ***Sediment Particle-Size Distribution*** section), as per the existing SOP.

Prior to sub-sampling either core, the sub-sampling equipment should be decontaminated by washing with soapy water, rinsed with tap water and rinsed again with de-ionized water. The sub-sampling equipment is allowed to air dry and stored in aluminum foil. At the core-processing site, the sub-sampling equipment should be thoroughly rinsed, just prior to use, with ambient stream water.

3.1.1 Screening method for selecting core subsamples for analytical chemistry

Selection of the core intervals that will be submitted for chemical analysis should be performed at the field station, with decisions made by qualified personnel knowledgeable about site-specific conditions. The following procedure is recommended: On the day following core collection, remove the partially frozen Core #1 from the freezer. Split the core lengthwise and place each half on a table for observation. Photograph the core under UV illumination, using a specialty camera or film that has particular sensitivity to UV fluorescence. Each subsample of the core selected for chemical analysis should additionally be photographed (at similar scale and illumination) before removal of the core sample from the core.

For all cores, the highest priority sample interval will be the uppermost one-inch (2.5 cm) thick layer, including any flocculent and the most recent deposition. Collect from Core #1 the upper 2.5-cm layer and place into pre-cleaned wide-mouth 8 oz jars (larger if needed). Based on the observations performed on Core #2, collect two additional samples from the chemistry core for analysis/archival (Figure 3).

Additional samples would be selected based on results of a core screening process that depends on both sediment stratigraphy and visible indications of oil presence—data collected as they have been previously under the existing 2011 protocol. The recommended change is that, rather than submitting all distinct sediment strata for laboratory analysis, the SSCG recommends that two additional 4-cm-thick intervals of the primary core would be selected as samples, but only one of those is automatically submitted for chemical analyses. The lowermost 4 cm of the oiled

---

[2] This sample will be used to define the forensic chemistry sampling intervals.

[3] The core tube is cut on opposite sides, and split in half with the entire length of the sediment core exposed for examination by the field team.

layer will be selected as the second core interval to be sampled; but if the maximum depth of oil indications is from 2.5 to 6.5 cm beneath the sediment surface, the sampled interval will be less than 4 cm thick. The third interval would be of intermediate depth within the oiled layer, and up to 4 cm in thickness. If maximum depth of oil indications is at least 10.5 cm below the sediment surface, select a 4-cm interval that showed greatest amount of visible indications of oil presence. If oil indications are uniform along the oil-impacted interval, select the interval 2.5 to 6.5-cm from top of core (i.e., the interval immediately below the uppermost, first layer selected). If the described core showed no visible indications of oil presence, or if the maximum depth of those indications did not extend below the bottom of the 2.5-cm thickness of the uppermost interval, then collect as the second and third sub-samples the 2.5 to 6.5-cm and 6.5 to 10.5-cm intervals for archiving—neither is automatically submitted for analysis.

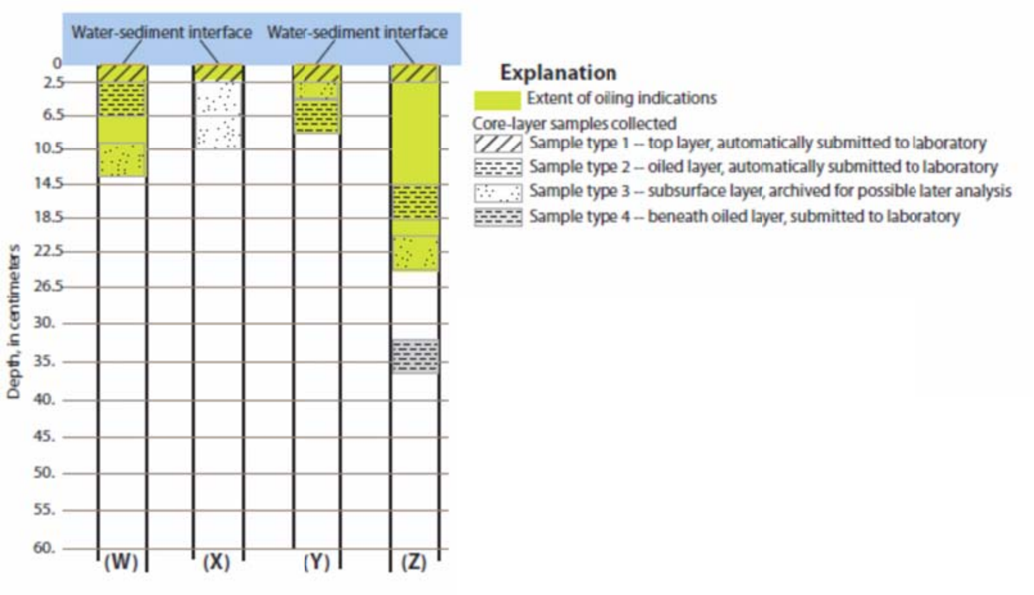

Figure 3.—Diagram illustrating four contrasting scenarios defined by combinations of oil indications depth and consequent intervals that were identified for sample collection [Note that any of the samples not submitted for immediate analysis would be archived (frozen at -20^{o}C); and all extra core material would be archived frozen in core containers that preserve the vertical-position relations intact.] :

Location W has oil indications extending beyond 10.5-cm depth (below water-sediment interface) and the middle sample was designated for initial chemical analysis, along with the top layer that is automatically to be submitted for analysis in all cases; deepest sample would have had less intense visible indication of oil and is to be archived frozen.

Location X has oil indications limited to the top 2.5 cm of the core, and consequently only the top layer is submitted initially; whereas, the two deeper layer samples are archived frozen for possible later analysis.

Location Y has oil indications extending to less than 10.5-cm depth and consequently one of the deeper layer samples is less than 4 cm thick; based on the visible indications of oil, the 4-cm thick deeper layer selected for initial submittal might be either the bottom 4 cm of the oiled layer (as shown) or the 4 cm immediately beneath the top 2.5-cm thick layer. The other deeper layer (not selected for initial submittal) would be archived frozen.

Location Z has oil indications extending well beyond 10.5-cm depth, and additionally was one of the subset of locations selected *a priori* for collection of a deeper sample from below the oiled layer; in the scenario shown, the oiled sample at middle depth was selected for initial analysis based on visible indications of oil, whereas the sample from below the oiled layer was selected from a fine-grained, organic-rich stratigraphic unit. The sample collected at bottom of the oiled interval (not selected for initial submittal) would be archived frozen.

A fourth interval of the primary core would be submitted for analysis if the sample location is one of those designated for confirming that deeper sediment contains only hydrocarbons that lack the distinctive chemical signature of the Enbridge Line 6B oil. This sample should be collected from the uppermost stratigraphic layer having fine-grained sediment (i.e., predominantly silt or clay), enriched in organic matter, and below the stratigraphic layer that contains the maximum depth of oil indicators (visible sheen or globules under UV illumination). If no deeper layer is both enriched in organic matter and fine-grained sediment, the alternative would be to sample the uppermost deeper interval of fine-grained sediment. If no such deeper layer exists, then the sample would be collected below the maximum depth of oil indicators, but from within the layer that contained the maximum depth of oil indicators. If this, too, is not available, then a pre-determined alternate coring location within the same geomorphic stratum should become the source for this deeper sediment sample.

The intervals to be sampled are determined from logging stratigraphy and indications of oil presence on the non-frozen core examined at the field station. This core is presumed to be representative of the frozen core collected adjacent to the logged core. All samples for forensic chemistry analysis are collected from the semi-frozen core that has been split and opened for visual examination and sample collection. The subsample is removed with a clean stainless steel spoon (wooden tongue depressors may also be used and discarded after each subsample) and placed into a pre-cleaned 8 oz jar. Core subsamples are kept frozen for shipment to the analyzing laboratory. Subsamples may be assigned field identifiers according to the conventions of the existing 2011 protocol, which encodes core location and depth interval information. The remaining intervals of the frozen core should be archived frozen at -20°C for an indefinite period to allow further samples and analysis of any core that chemistry results indicate as challenging to interpret or unusually high in variability along the vertical profile of streambed sediment.

Label each selected subsample of core with sample ID, location identifier, date/time of core collection, and depth interval. Maintain responsible chain-of-custody possession and documentation per applicable EPA-approved SOP.

Evaluations

Vertical orientation of all non-frozen cores is essential to preserve the flocculent or low-density layer at the water-sediment interface. Cores for chemical analysis should no longer be laid in horizontal orientation while they are cut open (unless they are frozen), to prevent the otherwise unavoidable mixing of the flocculent/surface layer with lower layers of sediment within the core. Piston-type incremental core-extruder apparatus is readily available optional equipment for several of the check-valve corers presently available. For the primary sample (to be analyzed for organics), the frozen-core method was considered by SSCG to be the preferred approach.

Sample contamination of sediment samples during collection and subsampling of a core, either by smearing of sediment along the walls of the core tube or by ineffective cleaning of equipment has been shown to be minimal.

Field measurements required by existing SOP include measurement of water depth and core penetration. Sediment temperature, conductivity, and dissolved oxygen or ORP are variables that might be useful to understand environmental controls on degradation. Similarly, nutrients in pore water would be another supporting variable to consider, though more likely determined at a lab. A third core could be used for both bulk density and pore-water concentration of nutrients;

consider trying this for a subset of sampled locations. NewFields (written communication, 2012) consider it essential for the sampling field crew to note and record any of the following: Any sheens, oil droplets, flecks/specks, or discolorations observed (a) on the water surface within the immediate area of sampling, (b) within the sample-collection chamber (core tube), (c) or within sample compositing/processing container, if used.

Disturbance to extensive parts of the impacted area caused by submerged-oil recovery methods argues against the need to look at very thin intervals of sediment cores. The upper 2 cm is a typical interval selected for chemical analysis of recently deposited oiled-sediment mixture. But for purposes of oil volume quantification, it is recommended to characterize more than the top 2 cm to represent full oiled interval of core; select in addition a middle sample and a bottom sample. Use core logging information to determine bottom of oiled layer, which has frequently been 1 ft or less.

QUALITY-ASSURANCE PROCEDURES

Decontamination

There are numerous sources of hydrocarbon contamination in the field environment, including fuels from boat motors and portable engines, exhaust from boats and vehicles, lubricating oils, cross contamination between sample locations, and vertical cross contamination between shallow and deeper layers of sediment. Thus, field decontamination procedures are crucial to sample/data integrity (NewFields, written communication, 2012).

Prior to each field trip, all sampling equipment will be washed with soapy water, rinsed with tap water and finally rinsed with de-ionized water. At the sampling location, rinse sampling equipment with native water. In the field, the any re-used sampling or sample-processing equipment will be washed between samples with soapy water and rinsed with native water. All non-disposable sampling equipment will be decontaminated after each sample in order to avoid cross contamination between samples or sites. Store sampling equipment in a secure, isolated container during transport to next sampling location (e.g., equipment cooler, tubs or garbage bags). Field crew will wear nitrile gloves whenever there is potential for contact with any sampling equipment or collected sample of sediment or water.

Quality-Control Samples

Equipment Blanks and Blank-Source Water Blank(s)

Prior to beginning environmental sampling for the Spring 2012 study, one (1) equipment blank should be collected with each check-valve coring head to be used in the study. Attach a clean core tube to the coring head. The interior of the tube and check-valve should be rinsed with organic-free blank water, and rinse water collected into a 1-liter glass water-sample bottle. The first 1-liter volume of rinse water is to be submitted as the equipment blank sample. Analyze the equipment blank for PAHs (parent and alkylated homologues) and biomarkers using GC/MS-SIM, and total extractable hydrocarbons using GC/FID at the same laboratory that analyses the core samples. Repeat the equipment blank sample collection at the conclusion of the seasonal study, again collecting one (1) equipment blank per coring head used in the study.

In addition, collect a 1-liter sample of the blank water from each distinct source lot used for blank sampling (either equipment or trip blanks) during the seasonal study. Collect blank-source water sample in glass bottle and submit

Trip Blanks

A trip blank coring tube should be collected by each field crew daily; the trip blank tube's interior should be exposed to the atmosphere whenever a primary sampling tube is exposed. At the end of the day, the interior of the trip blank tube should be rinsed with organic-free blank water into a water-sample bottle. The collected rinse water becomes the trip blank sample for that day-crew combination, and should be analyzed for PAHs (parent and alkylated homologues) at the same laboratory that analyses the core samples.

Field Duplicate Core Collection

Field duplicates will consist of separate side-by-side cores taken at the same sampling site, one immediately after the other. Duplicates will be contained and labeled separately. A minimum of 10 duplicate cores should be collected. Processing and laboratory analysis for duplicate core should be identical to its paired primary chemistry core.

Opportunistic Duplicate Core Subsample Collection

Additional replicate samples (not cores) should be collected opportunistically when it is evident that more than typical vertical heterogeneity (of oil indications) exists within the oil-enriched interval, if present. Process and analyze a duplicate sediment sample identically as its same-core primary samples.

Sampling Method Quality Performance

An analysis and discussion of data quality assurance shall be included in the final report on Spring 2012 submerged oil volume. The scope of the analysis should include information derived from results of blank samples on contamination sources and how effectively the sampling protocol minimized contamination, and information on sources and magnitude of uncertainty in laboratory determinations that, based on QC replicate sample results, appears attributable to sampling procedures or equipment.

ANALYTICAL SCOPE

Recommendations

The previously recommended Analytical QAP (USEPA-SSCG, 2012) contains the bulk of recommended protocols and evaluations concerning analytes for determining oil content and source identifications. The primary sediment core subsamples will be sent to the Alpha Analytical Laboratory.

Ship to:
Sue O'Neil
Alpha Analytical Laboratory
320 Forbes Blvd
Mansfield, MA 02048
Phone (508-844-4117)

Primary sediment samples should be analyzed per the Analytical QAP, except that analyses of PIANO compounds and metals may be omitted. An aliquot of each primary sample should be kept frozen and archived for possible later analysis of nutrient, reducible iron, and/or sulfide concentrations in sediment—an aliquot mass of 40 g should be sufficient.

Samples collected from Core #1 (analytical chemistry core from each sampling location) should be analyzed for both wet and dry mass. Together with the core interval thickness and diameter, bulk densities and sediment sample porosity will be calculated. The specific gravity of the various particle types (oil, other organic and inorganic) should be measured using an inert gas (helium) pycnometer (ASTM D5550-94). This method requires an order of magnitude less amount of material (~5 g) than alternate methods of direct measure.

Sediment Particle-Size Distribution

Improved Particle-Size Distribution (PSD) data are needed to support improvements in the hydrodynamic model development as well as to understand and interpret the hydrocarbon chemistry results for sediment-core samples. Organic contaminants in streams are well known to adsorb to the fine-grained fraction of the suspended PSD (Domagalski and Kuivila, 1993). PSD parameters are measurable in many ways, ranging from using sieves, to x-rays, to laser beams. Because a large number of core samples are being proposed for analysis, and improved resolution of the PSD is needed beyond the percentages of sand, silt, and clay fractions (as were determined for previous core samples collected for the Line 6B incident response), the use of an optical laser-diffraction based particle-size analyzer is recommended. The optical Mastersizer (Malvern Instruments, 2012, Mastersizer Particle Size Analyzer) has been suggested (J. Hamrick, TetraTech, oral communication, 2012). However, rather than measuring all particles in a sample, this instrument analyzes a small aliquot (an advantage when sample mass is small), but one that could be biased depending on presence of coarser, fast-settling particles that escape inclusion. Minimum recommended data resolution includes five (5) sand size classes, four (4) silt size classes, and four (4) clay size classes; the total range in phi-scale units is from -1 to 12. A combination approach using sieve analysis for the sand size classes, followed by optical instrument analysis for smaller size fractions, is another option.

Alternative to GC-Based Methods for Screening and Trends Monitoring

A third suggested objective for sediment-core sampling, beyond oil quantification using precise and reliable GC and GC/MS methods (i.e., Analytical QAP) and obtaining needed physical and supporting parameters (bulk density, PSD, TOC, etc.), is to examine the possibility for fluorometry to objectively indicate the extent of the oil-affected layer (and potentially relative concentration of oil) based on oil within the fine-grained pore spaces that is not visible by macroscopic observation. If such a technique is sensitive to and correlates strongly with total extractable hydrocarbons or total PAHs in the fraction of oil from Line 6B, it could potentially be adapted for field application to (a) determine the interval of oil-affected sediment; and (b) track the temporal trend of oil concentrations. If it were successful, such a technique might allow future re-quantifications to be achieved with only a subset of cores needing to have the Analytical QAP suite of laboratory analyses. Because the oil-quantification objectives can be achieved without adoption of this suggested objective, this element of suggested work as optional.

To test the fluorometry-based approach and validate its use as an acceptable alternative, the SSCG recommends that a first phase be conducted in a laboratory under controlled conditions. If successful, a second phase would be needed to adapt the procedure to a field station and portable fluorometer.

The first phase would be conducted using a subset of core samples (say, 30 or 40 samples), selected to represent a wide range of TEH or TPAH concentrations, and should ideally include replication of this range for more than one level each of sediment coarseness and organic-matter content. Test samples could be selected from archived excess sample material once the initial GC/MS and GC/FID results are known for the core samples. In the analytical laboratory, the pore water contained within an aliquot of each selected sample should be collected and oil extracted using techniques that also could be done at a field laboratory, e.g., extraction by shaken flask with hexane solvent. The extract would then be analyzed by fluorometer (e.g., Kim et al., 2010). Phase I should continue, analyzing pore water from aliquots of selected core sub-samples, until 95% confidence interval for the response curve to oil and/or PAH concentration is accepted as validated as a useful alternative to GC results for trend monitoring by the USEPA, with SSCG advisement.

Evaluations

If the aliquot of each sample sent for chemical fingerprinting analysis is not sieved, there is the potential that sediment samples with large amounts of leaf litter or other plant material may contribute substances (e.g., plant waxes or alkanes) that might interfere with the analysis of petroleum hydrocarbons. To determine whether this plant material was affecting the analysis of PAHs, biomarkers, TEH, and other hydrocarbons, it was previously recommended (letter dated March 2, 2012), and FOSC approved and implemented, a comparative experiment, whereby ten (10) sediment samples were split (from a homogenized composite), and one aliquot sieved using a stainless steel 10-mm mesh sieve. The sieving and analyses were performed at Alpha Analytical laboratory. Results of the comparison (G. Douglas, NewFields, oral communication, 2012) indicated that routine sieving of sediment samples from the Kalamazoo River would not be necessary.

Fluorescence spectroscopy has been widely used for the routine monitoring or characterization of oils, source identification of oil spills, and oil weathering. Fluorometric detection techniques measure the fluorescence intensity from both dissolved and emulsified oil. It has been used as a field-determined surrogate for TPH by GC analysis, particularly in applications where the relative magnitude is sufficient, e.g., for time series monitoring or spatial mapping of relative contamination. Portable fluorometers have been applied to monitor the decline of oil concentrations in pore water of beach sand (Kim et al., 2010).

Laser fluorosensors also have been used for detection of oil (Karpicz et al., 2005), and are able to discriminate remotely between non-fluorescing biogenic oil and petroleum oils (Brown et al., 1996), thus allowing real-time measurement, immediate results, and increased detection ranges.

High-resolution digital photography under UV illumination followed by automated image processing to quantify the amount of fluorescence could be a third approach to using fluorescence as a field-determined surrogate for TPH.

Fluorescence microscopy is another method that may be suitable and valuable for understanding oil-sediment associations and interactions, but may not be as suitable as a field screening technique.

> *Strengths:* The fluorescence spectroscopy technique is very sensitive to aromatic concentrations (Eastwood, 1981; He et al., 2003). Pore-water samples analyzed by fluorometer will need to be filtered, but have the advantage of relatively short turnaround time (< 1 day) and should be more cost effective than the traditional GC or GC/MS technique, which requires a large amount of solvents, meticulous sample preparation and chromatographic separation (Maher, 1983; Li et al., 2004; Christensen and Tomasi, 2007). By measuring the fluorescence of aromatic compounds using a portable fluorometer, one can obtain insight into the concentrations of TPH. Fluorometric detection of oil can be a good alternative to GC/MS analysis for rapid decision making. Thus, it should provide an objective surrogate measure of TPH that would allow delineation between core intervals that would be submitted for laboratory chemical analyses versus retained intervals.
>
> *Limitations:* Fluorometric oil analysis may not be a reliable direct surrogate for GC/MS oil measurement because of the complex relation between the chemical composition of oil and its fluorescence signal and because the relative proportion of aromatic hydrocarbons changes as oil degrades (Lambert et al., 2003). In one oil-spill monitoring study (Kim et al., 2010), some samples had high GC–TPH content but low fluorometric oil content, probably because of the preferential loss of relatively labile fluorescent compounds during weathering of oil, while more refractory compounds were still contributing to the GC TPH contents. GC TPH includes extractable fractions of the unresolved complex mixture, especially abundant in highly weathered samples, whereas fluorometric analysis measures only fluorescent aromatic compounds. In addition, the fluorescence response is not linear and increases almost exponentially with increasing number of rings on the PAH molecule. The presence of high TOC may also result in some quenching of the fluorescence response. Generally, this approach is used for screening purposes only.

For fluorometric measurements to be effectively related to GC or GC/MS concentrations and reliably used for quantitative applications (e.g., volume estimation, or comparison with environmental criteria), the fluorometric sensor shall be continuously recalibrated as the condition of oil weathering or oil composition change. Without appropriate recalibration, oil concentrations could be underestimated in heavily weathered samples (Kim et al., 2010).

Finally, fluorometric measurements provide no information regarding identification of the oil source.

Comparison to Fall 2011 protocols. Ultraviolet fluorescence of sheen, globules and flecks was observed visually as part of the routine processing protocol at the field lab. However, there was no use of a fluorometer or fluoresensing instrumentation; thus, the measurement typically was limited to counting the individual fluorescing particles exposed on the plane of core section, and noting the maximum depth at which sheen or globules were observed on the exposed plane. Photographic documentation under UV illumination was part of the protocol, but images were not processed further as a measurement technique.

REFERENCES

Agency for Toxic Substances and Disease Registry, 1995, Toxicological profile for polycyclic aromatic hydrocarbons (PAHs): U.S. Dept. Health and Human Serv., Public Health Service, 458 p., accessed May 5, 2012, at http://www.atsdr.cdc.gov/toxprofiles/tp69.html.

ASTM International, 1994, ASTM D5550-94: Standard test method for specific gravity of soil solids by gas pycnometer. West Conshohocken, Pa., ASTM International.

ASTM International, 2009, ASTM D2488-09a: Standard practice for description and identification of soils (Visual-manual procedure). West Conshohocken, Pa., ASTM International.

Brown, C.E., Fingas, M.F., 2003. Review of the development of laser fluorosensors for oil spill application. Marine Pollution Bull. 47, p. 477–484.

Brown, C.E., Nelson, R.D., Fingas, M.F., Mullin, J.V., 1996. Laser fluorosensor overflights of the Santa Barbara oil seeps. Spill Science & Technology Bull. 3, p. 227–230.

Christensen, J.H., Tomasi, G., 2007. Practical aspects of chemometrics for oil spill fingerprinting. J. Chromatography A 1169, p. 1–22.

Domagalski, J.L., and Kuivila, K.M., 1993, Distributions of pesticides and organic contaminants between water and suspended sediment, San Francisco Bay, California: Estuaries 16, p. 416-426.

Eastwood, D., 1981. Use of luminescence spectroscopy in oil identification. ***in***: Wehry, E.L. (ed.), Modern Fluorescence Spectroscopy, vol. 4. New York, Plenum Press, p. 251–275.

Enbridge Energy, 2011, [CWP] Consolidated Work Plan from Fall 2011 through Fall 2012—Addendum and Supplement to [various] —Enbridge Line 6B MP 608, Marshall, Mich., pipeline release: Enbridge, Dec. 21, 2011, 70 p.

Enbridge Energy, 2011, Sediment sampling—SOP EN-202—Enbridge Line 6B MP 608, Marshall, Mich., pipeline release: Enbridge, August 29, 2011, 12 p.

Enbridge Energy, 2012, Quantification of submerged oil report—Supplement to the response plan for downstream impacted areas-- Enbridge Line 6B MP 608, Marshall, Mich., pipeline release [approval pending]: Enbridge, Febr. 8, 2012, 63 p. [updated May 4, 2012]

Fitzpatrick, F.A., and Peppler, M.C., 2003, Sedimentation and sediment chemistry, Neopit Mill Pond, Menominee Indian Reservation, Wisconsin, 2001: U.S. Geological Survey Open-File Report 03-23, 58 p.

He, L.M., Kear-Padilla, L.L., Lieberman, S.H., Andrews, J.M., 2003. Rapid ***in situ*** determination of total oil concentration in water using ultraviolet fluorescence and light scattering coupled with artificial neural networks. Analytica Chimica Acta 478, p. 245–258.

Karpicz, R., Dementjev, A., Gulbinas, V., Kuprionis, Z., Pakalnis, S., Westphal, R., Reuter, R., 2005. Laser fluorosensor for oil spot detection. Lithuanian J. Physics 45, p. 213–218.

Kim, Moonkoo, Yim, U.H., Hong, S.H., Jung, J.H., Choi, H.W., et al., 2010, ***Hebei Spirit*** oil spill monitored on site by fluorometric detection of residual oil in coastal waters off Taean, Korea : Marine Pollution Bull. 60, p. 383-389.

Lambert, P., 2003. A literature review of portable fluorescence-based oil-in-water monitors. J. Hazardous Materials 102, p. 39–55.

Lambert, P., Fingas, M., Goldthorp, M., 2000. An evaluation of field total petroleum hydrocarbon (TPH) systems. J. Hazardous Materials 2577, p. 1–17.

Lambert, P., Goldthorp, M., Fieldhouse, B., Wang, Z., Fingas, M., Pearson, L., Collazzi, E., 2003. Field fluorometers as dispersed oil-in-water monitors. J. Hazardous Materials 102, p. 57–79.

Li, J., Fuller, S., Cattle, J., Way, C.P., Hibbert, D.B., 2004. Matching fluorescence spectra of oil spills with spectra from suspect sources. Analytica Chimica Acta 514, p. 51–56.

Maher, W.A., 1983. Use of fluorescence spectroscopy for monitoring petroleum hydrocarbon contamination in estuarine and ocean waters. Bull. Environmental Contamination and Toxicology 30, p. 413–419.

Munsell Color, 1975. Munsell soil color charts. Baltimore, Munsell Color.

Sansalone, John, Hong Lin, and G. Ying. 2009. Experimental and field studies of type I settling for particulate matter transported by urban runoff. J. Environmental Engineering 135(10), p. 953-963.

Stevens, D.L., Jr., and A.R. Olsen. 2004. Spatially-balanced sampling of natural resources. J. American Statistical Assoc. 99, p. 262-278.

U.S. Environmental Protection Agency, Science Support Coordination Group, 2012, Analytical quality assurance plan, Enbridge Line 6B MP 608, Marshall, Mich., pipeline release (ver. 2.1). U.S. Environmental Protection Agency, unpublished draft, February 10, 2012, 32 p.

APPENDIX 1
REVIEW OF FALL 2011 SUBMERGED OIL QUANTIFICATION SAMPLING PLAN

ENBRIDGE LINE 6B MP 608 MARSHALL, MI PIPELINE RELEASE
JUNE 11, 2012

INTRODUCTION

This document describes the results of the review of the fall 2011 Submerged Oil Sampling Plan for the Enbridge Line 6B release. Specifically, experts evaluated sample locations and results for the 2011 poling and sediment cores used or potentially used in the Fall 2011 submerged oil quantification task. The results of this initial review were then evaluated to complete the following tasks relative to potential approaches for the spring 2012 Submerged Oil Sampling Plan:

- Discussion of pros and cons of various alternative sampling approaches.
- Ranking of recommended alternatives with benefits of each.
- Comparison of recommended alternative to the plan implemented in fall 2011. Identify pros and cons: include discussion of what will be gained in terms of reduced uncertainty, better representation, more applicability to modeling, etc., with the new approaches; and what those gains would cost in terms of additional sampling sites, samples, schedule, or other limitations imposed thereby.

These results are presented below.

The details of the methods used for submerged oil quantification in 2011 can be found in other documents. The following discussion focuses on sampling design recommendations to quantify the submerged oil. . In essence, the quantification method used thus far multiplies the average Total Petroleum Hydrocarbon (TPH) concentration adjusted for sediment bulk density by the planimetric area and thickness of various areal units (areas). These areas are defined by spatial analysis of the poling data wherein areas of “Heavy” and “Moderate” submerged oil sheening or surface-observed globules are manually delineated based upon poling locations and assigned “Heavy” or “Moderate” categorical descriptors; whereas “Light” and “None” areas are delineated via a process of creating and editing Thiessen polygons around “Light” and “None” poling locations. Whatever analytical chemistry method is selected for quantifying oil in sediment cores in 2012, it is likely that a spatial interpolation method involving strata means/medians and strata dimensions will be used to estimate total amount of oil. Given this expectation, it is important that sampling effort is balanced appropriately to minimize bias and maximize precision.

This work does not address analytical methods proposed for use in oil quantification or methods for distinguishing oil in sediments from background, but focuses on spatial sampling design for use with whatever suite of analytical methods is selected. While previous quantification efforts used both TPH and Oil and Grease (O&G) results, alternate or supplemental methods will be used in 2012. Differences in TPH concentrations across areas are evaluated, and the relationship between TPH concentration and poling methods only to inform sampling design, and not as a proposed method for quantification. In all designs proposed for 2012 it was assumed that the selected analytical method will measure concentrations separate from background regardless of the relative concentrations of these two values.

INVESTIGATION OF 2011 SAMPLING PLAN

Fall 2011 Submerged Oil Sampling Plan Description – Poling Results

A total of 7,443 locations on the Kalamazoo River downstream from the release were investigated using a screening assessment of subsurface oil via agitation/poling (hereafter referred to as “poling”) in fall 2011 prior to fall remediation activities. These data were collected generally between August and October 2011 with a few supplemental data points from June of 2011 (Enbridge, 2011). A variety of semi-quantitative and quantitative metrics are collected at each screening location (observations of sheen, globules, water depth, etc.), and each location is characterized by a single categorical class describing relative amounts of subsurface oil present at that location: Heavy, Moderate, Light, or None. Statistically speaking, the sampling plan for sediment poling locations can be described as directed sampling in that the poling locations were selected by field practitioners and were not, to our knowledge, a probability sample of all sample locations. Nonetheless, there are evident correlations between the poling results and the geomorphic strata that are proposed for use in 2012.

The poling locations (Figure 1) are spatially widely distributed and cover the Kalamazoo River from the confluence with Talmadge Creek to Morrow Lake. In the area of coverage, poling results are typically collected at points along cross-channel transects with higher densities of poling locations in areas of known current or past subsurface oiling.

These results were evaluated to examine the relationships between the subsurface descriptor and proposed geomorphic strata, as well as the collocated current velocity and sediment type categorical variables also collected at the time of screening for subsurface oil. Results are depicted graphically in mosaic plots (e.g., Friendly, 1994) in Figure 2 below. Chi-squared tests of the relationship between categorical descriptor and these three categorical variables indicate strongly significant ($p < 0.0001$) correlations.

These results indicate that, as expected, categorical descriptor of subsurface oil at poling locations in 2011 are strongly correlated with the proposed geomorphic strata for sampling in 2012 – with heavier oiling generally found in more depositional strata, as well as at locations with lower current velocities and finer sediments.

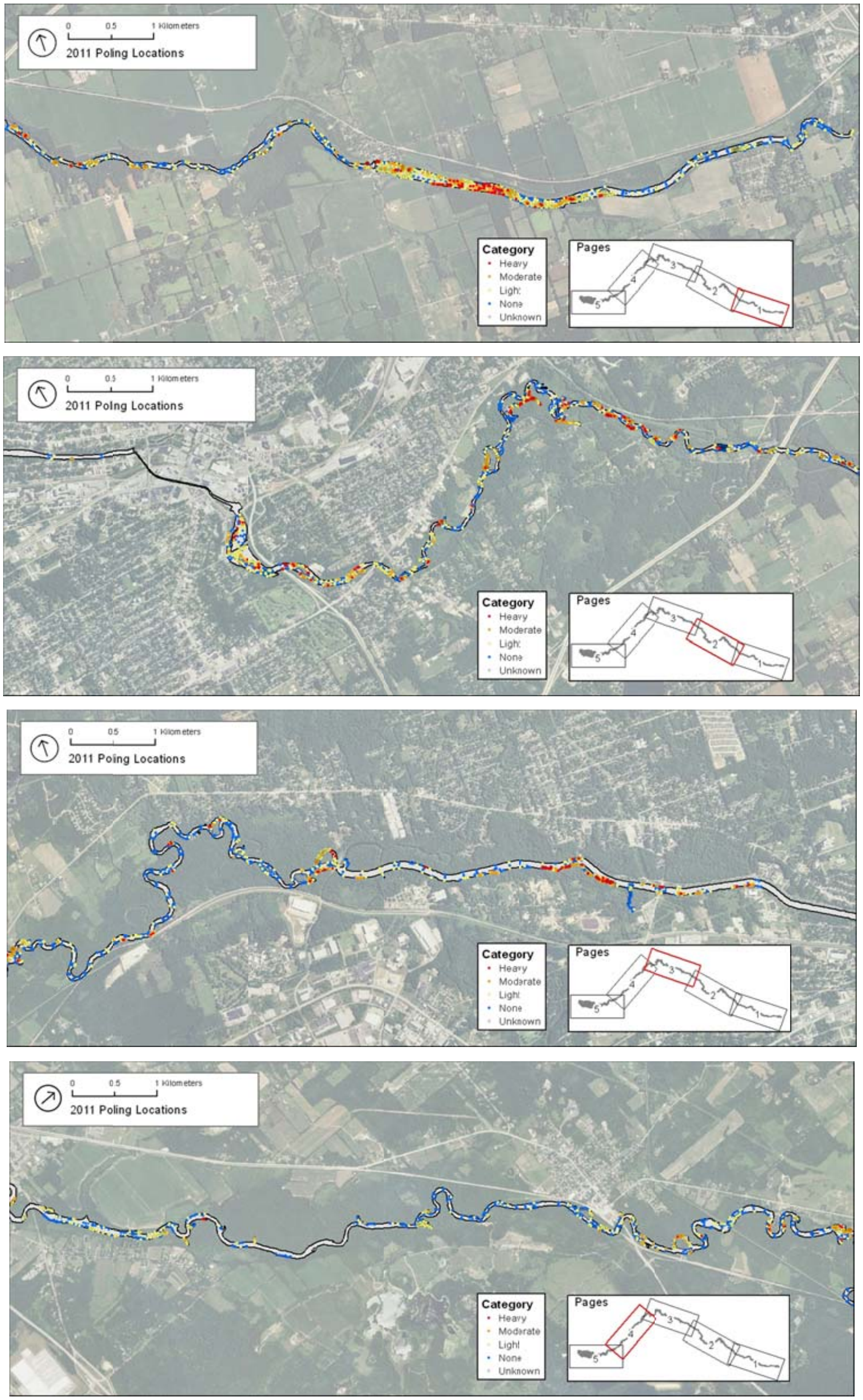

Figure 1. Maps of fall 2011 sediment poling locations by categorical descriptor of subsurface oil

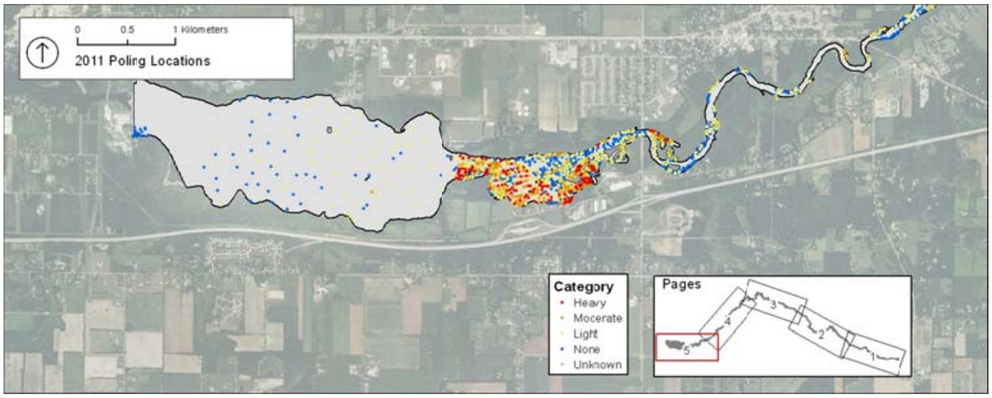

Figure 1 (continued). Maps of fall 2011 sediment poling locations by categorical descriptor of subsurface oil

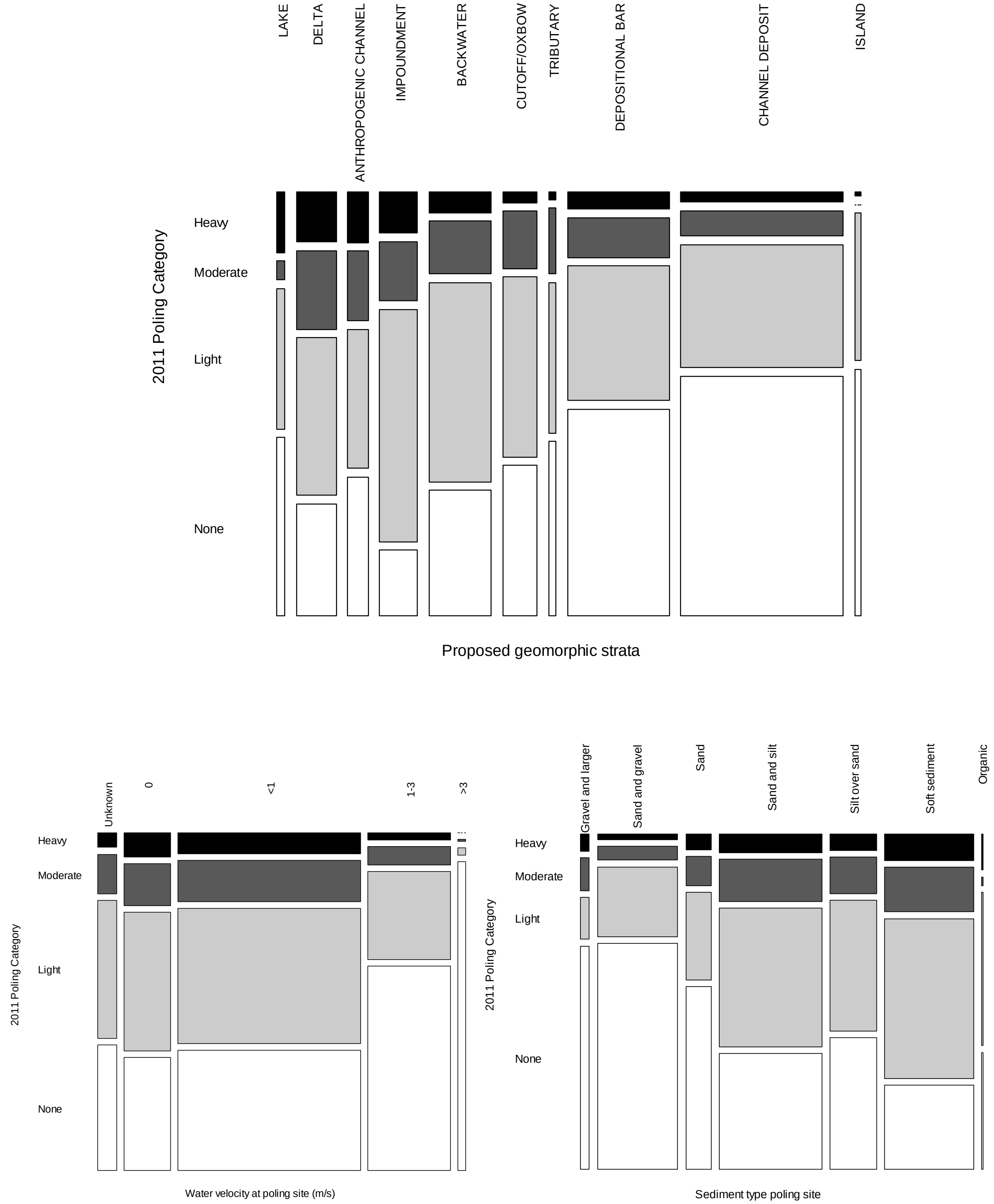

Figure 2. Mosaic plots of contingency tables for categorical descriptor of subsurface oil at poling locations in 2011 proposed geomorphic strata, current velocity and sediment size descriptors. (Dimensions of plotted rectangle correspond to number of samples in the indicated category combination.)

Fall 2011 Submerged Oil Sampling Plan Description – Sediment Core Surface Total Petroleum Hydrocarbon (TPH) Results

A total of 110 sediment cores were collected from depositional areas located on the Kalamazoo River downstream from the release in 2011. These cores were largely collected within previous oil recovery work areas, and only within depositional areas. Of these, 100 were collected within areas characterized as having “heavy” or “moderate” subsurface oiling via poling at any time in the past. Of these 100 locations, 36 were within areas characterized as having “heavy” or “moderate” subsurface oiling via poling in fall 2011. The remaining 10 cores were collected in areas characterized as “light”. These 110 sediment core locations were not co-located with concurrent screening via poling.

Statistically speaking, the sampling plan for sediment samples collected via coring in 2011 can be described as directed sampling, in that the core locations were selected by field practitioners and were not, to our knowledge, a probability sample of all sample locations. Similarly, while the sediment core locations were grouped into categories for the purposes of oil quantification one cannot describe these as sampling strata per se.

The coring locations (Figure 3) are spatially widely distributed and cover most of the Kalamazoo River from the confluence with Talmadge Creek to Morrow Lake. Because the coring locations were intended to be primarily located in areas of previous heavy or moderate poling results, the locations appear clustered at coarse scales within the main stem of the river, and irregularly spaced but spatially balanced in the delta and lake.

The results of the sediment sampling were examined to evaluate the relationships between the surface TPH concentrations (defined as the sum of the oil range and diesel range organics [ORO and DRO] analytical values for the uppermost vertical layer at each core location) and proposed geomorphic strata, as well as the categorical submerged oil descriptor at the nearest 2011 poling location, and whether that sediment core location was inside or outside the Heavy/Moderate polygons as delineated by the 2011 poling data. Each coring location was associated with the nearest poling location. All coring locations were within 500 meters of an adjacent poling location and the median distance between coring location and poling location was 26.5 meters. This analysis was carried out primarily to ensure that quantitative sediment chemistry results display similar relationships to the strata proposed for 2012 as the more descriptive poling results discussed above.

Results are depicted graphically as box plots in Figure 4 below. T-test results indicate evidence for significant ($p=0.069$) differences in log surface TPH concentration between core locations inside and outside the Heavy/Moderate polygons as delineated by the 2011 poling data. Analysis of Variance (ANOVA) results yield significant evidence for differences between log surface TPH concentration by nearest categorical poling result ($p=0.03$) but no real evidence for differences across proposed geomorphic strata ($p=0.21$). There is visual evidence of trends present in both cases, however, with higher TPH values found in more depositional strata as well as at locations with heavier nearby poling categories.

It was also noted that previous work carried out in 2010 has noted similar, and statistically significant, correlations between collocated poling-based categorical oiling descriptor and sediment core TPH values (Enbridge, 2011).

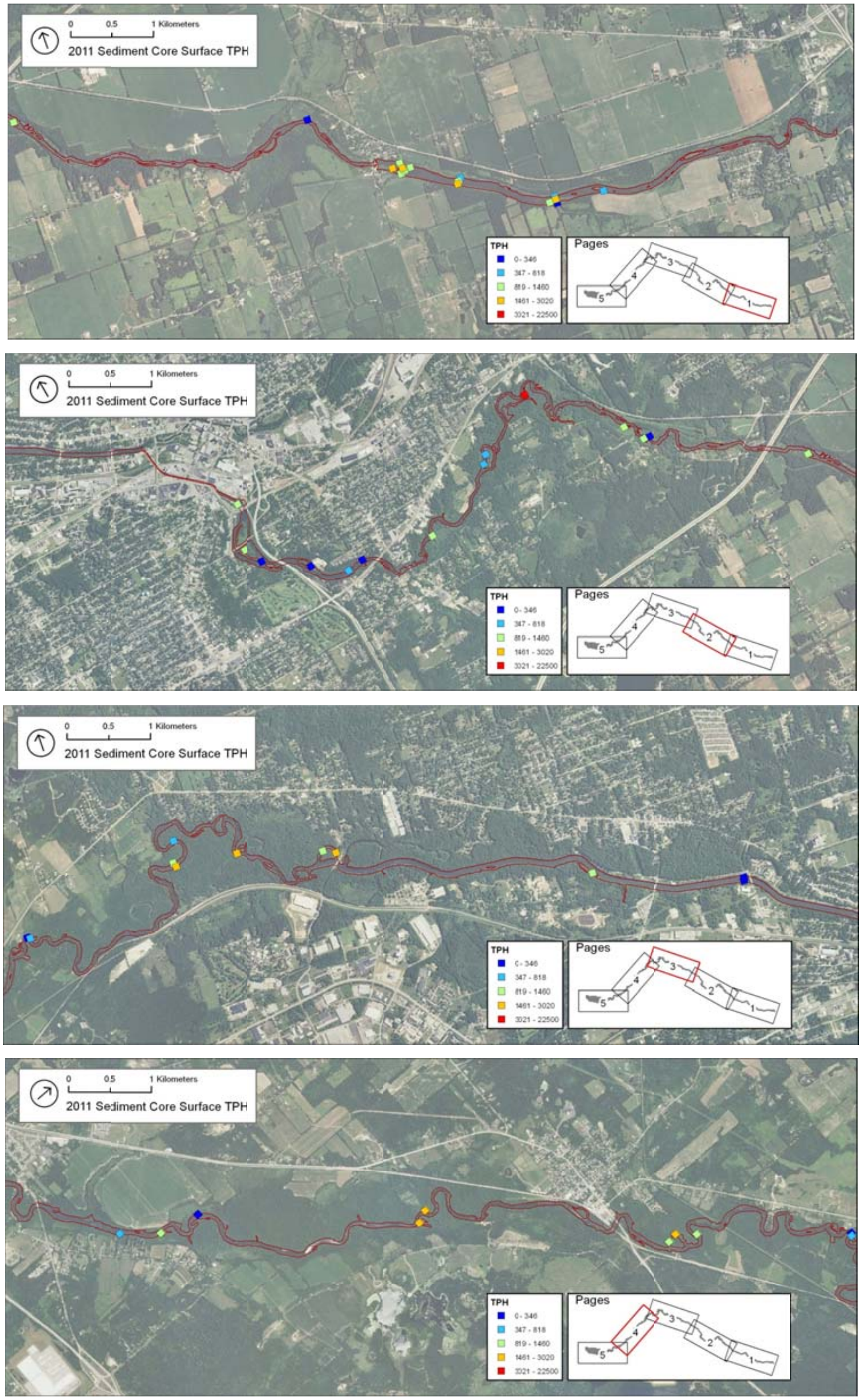

Figure 3. Maps of uppermost sediment-layer TPH concentration ranges (mg/kg) at 2011 sediment coring locations.

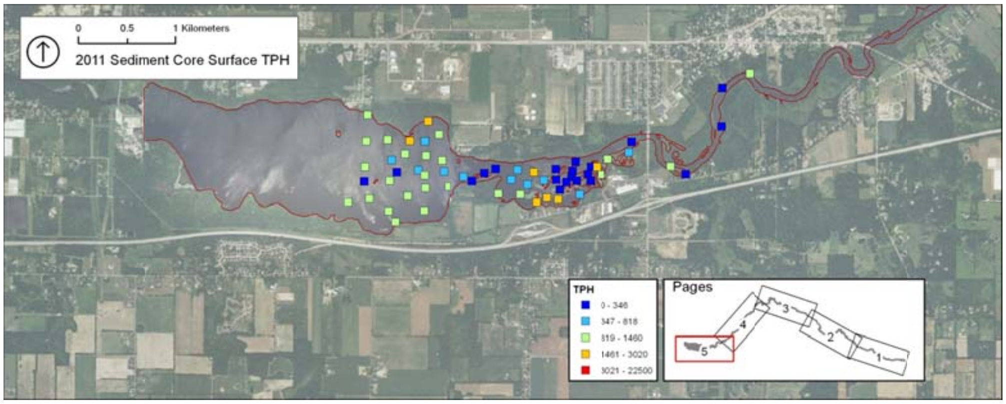

Figure 3 (continued).Maps of uppermost sediment-layer TPH concentration ranges (mg/kg) at 2011 sediment coring locations.

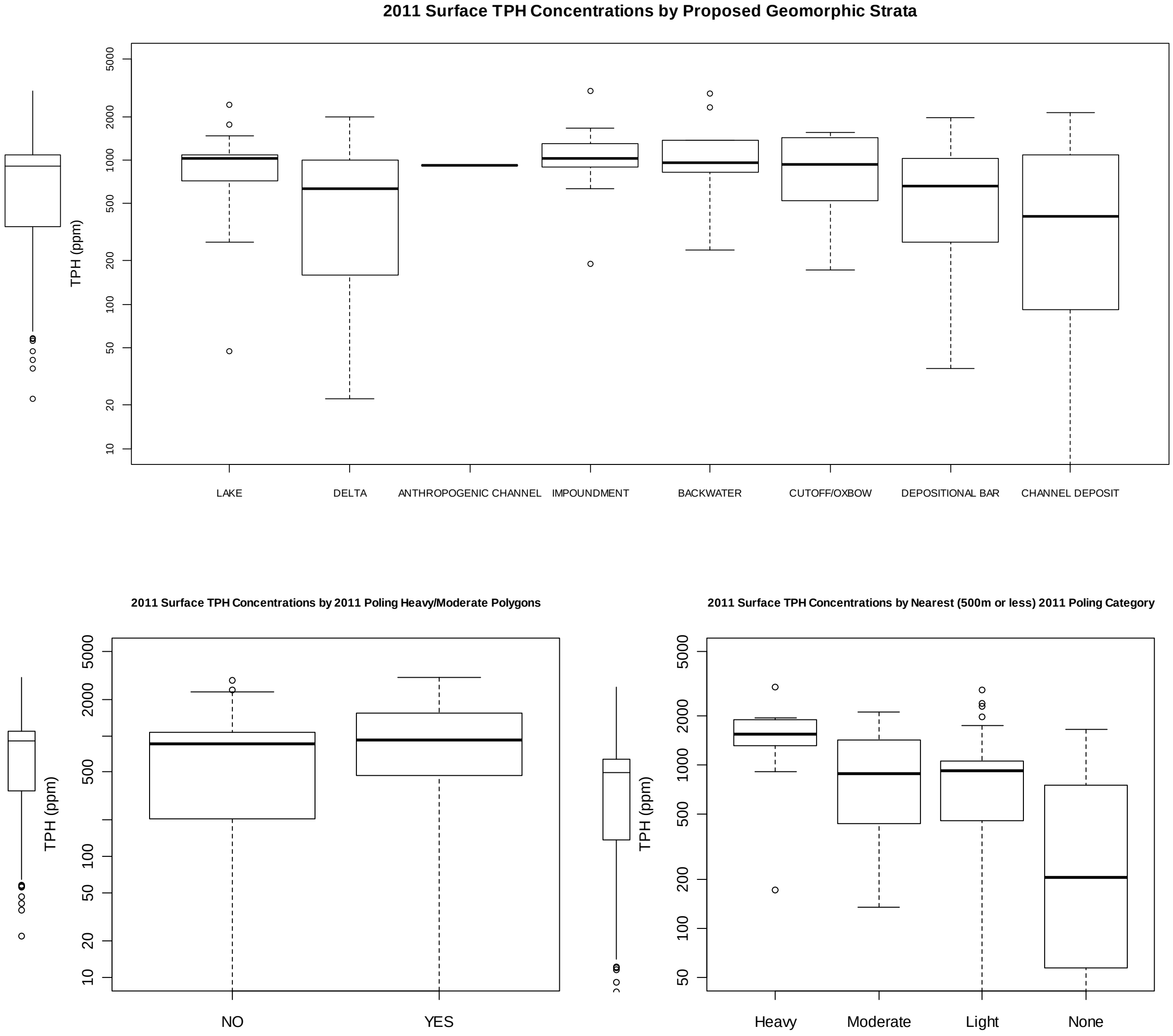

Figure 4. Box plots of surface TPH values (log scale) at 2011 sediment core locations categorized by proposed geomorphic strata (top), Heavy/Moderate poling polygon presence (bottom left) and nearest categorical poling result (bottom right).

ALTERNATIVE APPROACHES

This document identifies alternative spatial approaches for sample designs for sampling in 2012. The analytical method to be used to quantify oil from the Enbridge Line 6B release in subsurface sediments is unknown at this time. While raw TPH results were analyzed above as part of the investigation of the 2011 sampling design and its relationship to proposed approaches for 2012, it should be stressed that the below-considered approaches involving probability samples, stratification, or leveraging of existing screening results can be applied to any analytical method used to quantify all oil, or oil specifically from the Enbridge Line 6B release, in subsurface sediments. It is assumed that the selected analytical method will measure concentrations separate from background regardless of the relative concentrations of these two values.

There are generally two primary methods for estimation: survey-based and model-based. In this context, a survey-based approach would be to generate a probability sample of the entire domain (river and associated water-bodies), sample these, then estimate the total amount of oil remaining. The design could be a simple random sample or more complex – involving stratification, clustered sampling, or multi-stage or adaptive designs. Design-based methods are often best when: (1) one wants to rigorously estimate statistics of the population (e.g. the mean, median, etc.) and/or conduct hypothesis tests against these statistics; (2) a relatively large number of samples can be afforded, and (3) random sampling is feasible. A model-based approach would be use existing data to predict the relationship of oil presence and quantity based on other variable(s) – like space (geostatistical model), geomorphic surface, depth, hydrodynamics, etc. Sampling could be random, but this is not required. One wants to sample across the range of possibly related covariates so often directed sampling is used to span the gradient of values for potential predictive covariates. Model-based methods are often best when: (1) we want to map the property of interest; and (2) a strong correlation exists between the property of interest and covariates.

The total amount of submerged oil is the primary quantity of interest – suggesting a survey-based approach. Understanding how such oil is distributed across space would also be of interest and that the distribution of submerged oil is strongly spatially patterned and driven by known spatially distributed covariates. The above investigations demonstrate that there is good evidence that the amount of submerged oil in 2012 is likely to be very strongly related to poling results and the geomorphic surface. Further, variogram analysis indicates that oil concentrations vary widely over small (<10 m) spatial scales indicating that pure interpolation approaches would require unrealistically large numbers of samples. In order to make best use of known covariates and sample efficiently, a hybrid approach known as model-assisted survey sampling is recommended. The recommended hybrid approach is a spatially balanced, stratified Generalized Random Tesselation (GRTS) survey design (Stevens and Olsen, 2004). Such a survey design has the advantages of:

- Likely being more efficient than simple random sampling
- Being spatially balanced across the area of interest in the event that geostatistical models (interpolation) are required/helpful
- Leveraging known information about the relationship between covariates and submerged oil presence and quantity
- Having most of the advantageous statistical properties of a simple random sample
- Can include an oversample to accommodate non-response or no-access issues in the field

- Generating data useable for design-based estimates of total submerged oil properties via a variety of frequentist or Bayesian methods

The approaches considered below (except alternative 1) would involve GRTS sample designs. These designs may or may not be stratified, as detailed below. Potential alternative approaches are summarized and evaluated in the following subsections.

Alternative 1 - Directed sediment sampling:

This approach involves field practitioners collecting spring 2012 poling data as per previous years, collecting sediment cores at locations selected by field practitioners as per previous years, and using a soon-to-be-selected analytical quantification method to estimate median or mean contaminant concentrations separate from background for all locations.

Advantages: Logistically simple. Sampling potentially could be performed within heavy/moderate areas essentially immediately once poling delimits those areas, because the two data collection efforts are not dependent.

Disadvantages: This approach does not constitute a sample of all potentially affected areas, so results cannot be used validly to estimate remaining subsurface oiling in an unbiased way.

Alternative 2 - Sediment sampling design:

This approach involves field practitioners collecting Spring 2012 poling data as per previous years, generating a GRTS spatial sample for sediment coring across all river, delta, and lake areas independent of the 2012 poling results, collecting sediment cores at these sampling locations, and using a selected analytical quantification method to estimate median or mean contaminant concentrations separate from background for all locations.

Advantages: This approach uses data collected at a sample of all potentially affected locations, so results can be used to derive an unbiased estimate of remaining subsurface oiling. This approach is also spatially balanced, and relatively logistically simple. Sampling can be performed at the same time as poling because the two data collection efforts are not dependent.

Disadvantages: This approach ignores other factors known to be correlated with submerged-oil presence and quantity, such as poling results, sediment texture or geomorphic strata.

Alternative 3 - Stratified sediment sampling design (strata from poling only)

This approach involves field practitioners collecting spring 2012 poling data as per previous years, generating a stratified spatial sample using 2012 poling results (or spatial products thereof) after poling is complete, collecting sediment cores at these locations, and using selected analytical quantification method to estimate median or mean contaminant concentrations separate from background within these strata.

Advantages: This approach uses data collected at a stratified sample of all potentially affected locations, so results can be used to derive a more precise and unbiased estimate of remaining subsurface oiling. This approach is also spatially balanced.

Disadvantages: This approach ignores geomorphic information known to be correlated with subsurface presence and quantity. Sampling must be performed after poling because sediment sampling is dependent upon poling results. This approach is somewhat more logistically complex.

Alternative 4 - Stratified sediment sampling design (poling and geomorphology)

This approach involves field practitioners collecting Spring 2012 poling data as per previous years, generating a stratified GRTS spatial sample using strata based on a combination of 2012 poling results (or spatial products thereof) and geomorphic surface reclassification, collection of sediment cores at these locations, and use of a selected analytical quantification method to estimate median or mean contaminant concentrations separate from background within these strata. For this alternative and the alternatives below, the 2012 poling data would be used to generate polygonal strata within the, either using methods from previous years as described above, a more automated method (interpolation), or some hybrid approach. These polygons would be used as stratum boundaries.

Advantages: This approach uses data collected at a stratified sample of all potentially affected locations, so results can be used to derive a more precise and unbiased estimate of remaining subsurface oiling. This approach is also spatially balanced.

Disadvantages: If a method for quantifying oil in sediments directly from poling results is derived, the poling results cannot be considered a sample of all locations. Poling results may be used, but only to stratify sediment sampling for other analysis. Sampling must be performed after poling because sediment sampling is dependent upon poling results. This approach is somewhat more logistically complex.

Alternative 5 – Two-phase stratified poling and sediment sampling design

This approach involves generating a stratified GRTS spatial sample for 2012 poling locations using geomorphic surface reclassification and 2011 poling results, collecting Spring 2012 poling data at these locations, then generating a second-phase stratified random sample using geomorphic surface reclassification and 2012 first-phase poling sample, collecting sediment cores at these locations, and using selected analytical quantification method to estimate median or mean contaminant concentrations separate from background within these strata.

Advantages: If a method for quantifying oil in sediments directly from poling results is derived, the poling results can be considered a sample of all locations and can be used directly to derive a more precise and unbiased estimate of remaining subsurface oiling. If not, sediment sampling data are collected at a stratified sample of locations, so these results can also be used to derive a precise and unbiased estimate. This approach is also spatially balanced.

Disadvantages: This approach is significantly more logistically complex than other alternatives because it is a two-phase design. A design must be generated and implemented for spring 2012 poling in a short time. Sediment sampling must be performed after poling because sediment sampling is dependent upon poling results.

OTHER DESIGN CONSIDERATIONS

There are a few other design options for consideration, detailed below.

Sample Number

It is assumed that overall sampling effort will remain approximately the same or less than that available for fall 2011. In 2011, some 340 samples were analyzed from different vertical strata within sediment cores collected at the 110 sampling locations. It is proposed that samples collected in 2012 be apportioned evenly across strata, or proportional to stratum size with a minimum number per stratum. If one assumes 10 geomorphic strata and 2 different poling polygon strata this would yield up to 20 strata, with n representing either a fixed sample size (e.g., 5 to 10 cores) being the same across strata, or a fixed percentage if samples are apportioned by stratum size.

The sampling potentially could be done in two tiers or phases, where an initial phase collects the minimum number of cores per stratum (e.g., 3-5), these cores are processed to provide oil chemistry results (e.g., for 2 samples per core, or 6-10 samples per stratum), and the variance among the tier 1 results becomes the basis for estimating the number of remaining cores needed to achieve statistical confidence intervals of acceptable width to provide useful estimates of oil volume for each stratum. Tier two would consist of the collection and processing of the remaining number of cores to implement the estimate from tier 2.

Collocation of Poling or Other Screening Techniques

For all of these approaches, sediment coring locations may be collocated with poling locations from 2012. This can be done by re-occupying poling locations if sediment coring is performed after poling, or by field teams performing poling screening at the same time and location as sediment coring.

While the results above relating sediment surface TPH to nearest poling location category indicate some relationships, earlier data from 2010 indicated an even stronger relationship between sediment chemistry and collocated poling category. Collection of collocated data will allow quantification of this relationship and possible development of a poling-based model to refine estimates of amount of remaining subsurface oil.

Timing of Sample Design

Because time is limited and the sampling design for sediment core sampling in impacted areas is dependent upon completion of 2012 poling prior to completion of the design, it is so noted in the following. Some geomorphic types are not widely distributed across the entire impacted area (e.g. the delta) and poling is likely to be completed within them in short time frames. Other geomorphic types (e.g. channel deposits) occur along the entire main-stem of the river and will likely have been surveyed completely via poling only at the end of the entire poling effort. Given this, it is possible to phase the generation of sample locations, with a sample for a given geomorphic stratum generated as soon as poling for that stratum is complete and the poling-derived category boundaries have been mapped.

PREFERRED ALTERNATIVE APPROACH

I recommend Alternative 4. The primary advantage of the proposed alternative approach is that it constitutes a representative sample of all the sediments within the designated strata, so that estimation of median and mean contaminant concentrations separate from background may be estimated without bias. These unbiased estimates of contaminant concentration, or concentrations above background, may be used to generate an unbiased estimate of the total volume of remaining subsurface oil. Further, there is evidence that analytical sediment chemistry results (or TPH results, in any case) are related to both poling results and proposed geomorphic strata. As such, allocation of sampling effort across strata defined by both poling results and geomorphic class should result in smaller within-strata variances and greater precision in mean or median contaminant concentrations, and resultant total oil quantities.

While it is evident that the poling is valuable as a screening technique and as a method to define strata for sediment sampling, the logistic disadvantages and additional complexity required to implement a two-phase sampling plan for poling and sediment sampling outweigh the potential gains in precision that may be possible with such a design if a suitable technique is devised to relate poling categorical results to subsurface oil quantity.

It is recognized that the conceptual model of subsurface sediment oil contamination source and distribution since the spill may be complex. Specifically, there may be a gradient of contamination as one moves downstream from source areas, and this may have been compounded by subsequent redistribution and removal. However, use of the 2012 poling results as sampling strata essentially allows the system to be considered as static for the purposes of sampling for quantification in 2012. There is ample evidence from 2010 and 2011 that poling, and derivative analysis products, are well correlated with spatially adjacent and contemporaneous sediment chemistry results, and as such provide the best way to account for gross spatial heterogeneity in present-day oil contamination.

It is also recommended to collocate poling at all sediment sample collections. We recommend processing an initial tier of 3 to 5 cores (>10 samples) from each stratum. Given the probable large variations in areas across strata (Table 1), it is likely that additional sample processing in subsequent tiers will take place preferentially in larger strata, or mid-size strata with large variances, resulting in larger sample numbers for larger and more variable strata. Figure 5 depicts a hypothetical GRTS sample generated using the strata defined as in Table 1, by proposed geomorphic classification and 2011 poling-derived Heavy/Moderate delineation areas. A fixed sample size of 20 coring locations was generated for each stratum, regardless of size. The first 5 sample locations in each stratum were assumed to be the first tier of sample processing.

	Heavy/Moderate Area	**Light or None Area**
Strata	**Acres**	**Acres**
Anthropogenic Channel	6.0	72.6
Backwater	9.8	44.5
Channel Deposit	12.4	501.3
Cutoff/Oxbow	3.6	22.3
Delta	29.5	163.3
Depositional Bar	8.4	132.2
Impoundment	15.2	52.1
Lake	4.3	643.2
Tributary	0.8	2.4
Totals	90.1	1633.9

Table 1. Areas of strata as defined by one possible geomorphic classification and 2011 poling-derived Heavy/Moderate delineation areas. Note that strata for sampling in 2012 will be spatially defined by 2012 poling-derived delineation areas, but 2011 areas provide an estimate of areal extent.

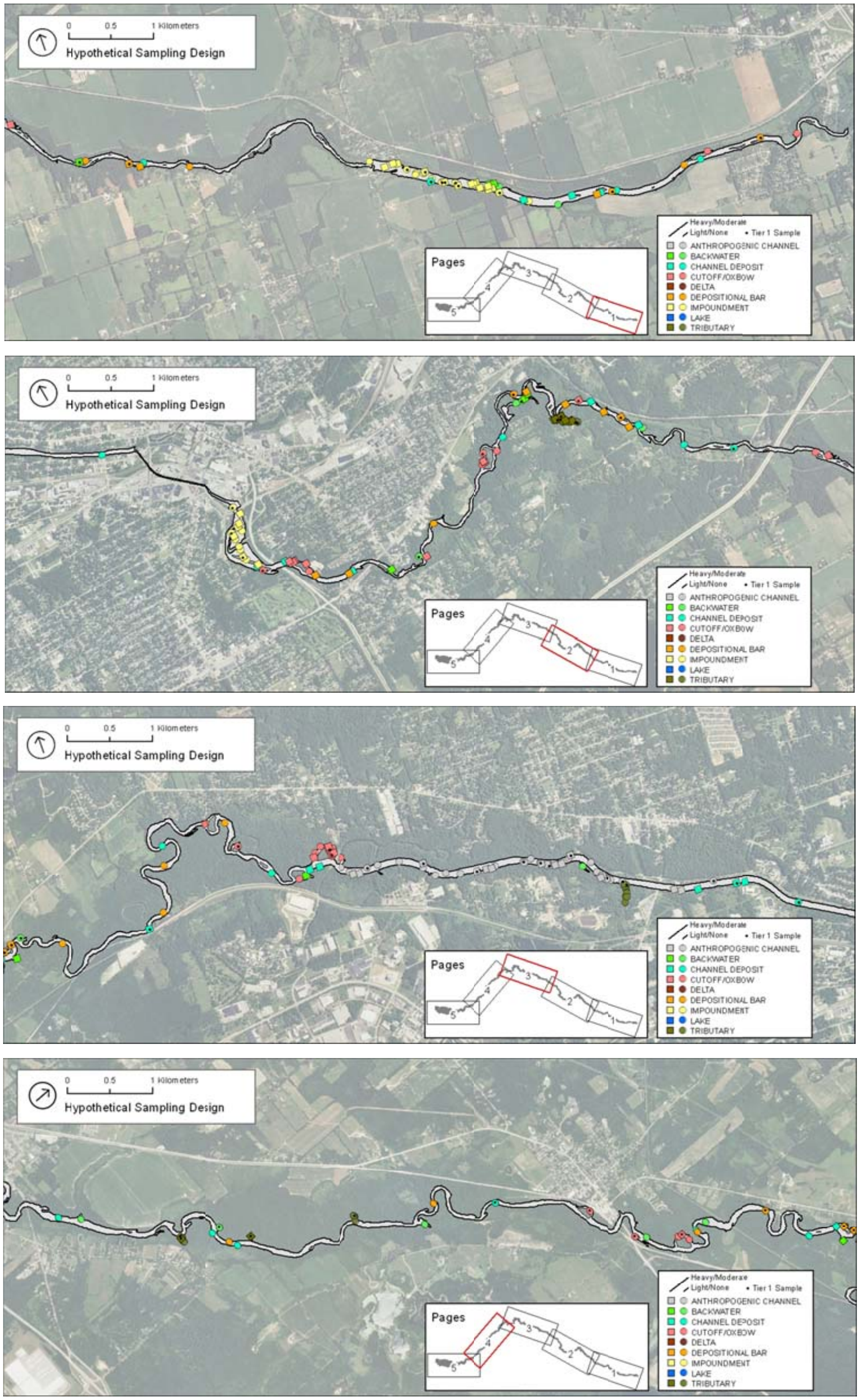

Figure 5. Hypothetical GRTS sample generated using example strata defined as one possible geomorphic classification (9 categories) and 2011 poling-derived submerged-oil indications (2 categories). Note that color indicates geomorphic strata and shape indicates poling derived submerged oil indicators. Tier 1 samples identified with dot.

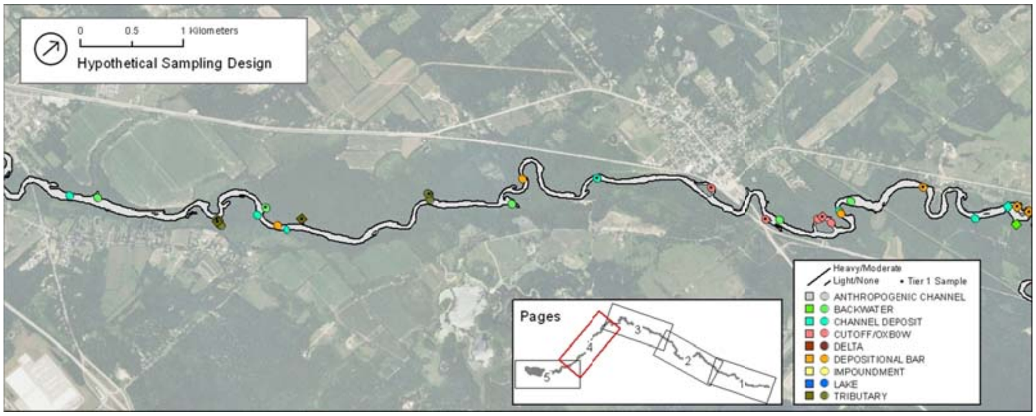

Figure 5 (continued). Hypothetical GRTS sample generated using example strata defined as one possible geomorphic classification (9 categories) and 2011 poling-derived submerged-oil indications (2 categories). Note that color indicates geomorphic strata and shape indicates poling derived submerged oil indicators. Tier 1 samples identified with dot.

REFERENCES

Enbridge, 2011. Enbridge Line 6B Pipeline Release, Marshall, Michigan; Supplement to the Response Plan for Downstream Impacted Areas Commonly Referred to as the "Quantification of Submerged Oil Work Plan." Resubmitted on May 4, 2012.

Friendly, Michael. 1994. Mosaic displays for multi-way contingency tables. Journal of the American Statistical Association 89:190-200.

Stevens, D.L., Jr., and A.R. Olsen. 2004. Spatially-balanced sampling of natural resources. Journal of the American Statistical Association 99:262-278.