

US EPA ARCHIVE DOCUMENT



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

February 20, 2012

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**Re: Sampling Plans Prepared by the Scientific Support Coordination Group (SSCG)  
for Aquatic Toxicity Testing and Oil Fingerprinting  
Enbridge Line 6B MP608 Release, Marshall, MI**

Dear Ron and Faith:

I have reviewed the above-referenced Sampling Plans and accompanying memos that were prepared in response to Charges 1, 2, and 3 submitted to the SSCG:

Charge 1

- a) Provide an evaluation of viable analytical approaches, including benefits and draw backs for each, to quantify the amount of submerged oil in the Kalamazoo River sediments attributable to the Enbridge Oil pipeline Release.

Charge 2

- a) Identify and evaluate viable procedures for assessing the toxicity of remaining submerged oil.
- b) Provide a recommendation for the best procedure to accomplish this goal.

Charge 3

- a) Provide an evaluation of viable procedures, including benefits and draw backs for each, to assess whether remaining submerged oil will biodegrade over time.
- b) Provide a recommendation for the best approach to accomplish this goal.

I hereby accept the group's recommendations on these issues. Our Environmental Unit and Enbridge have already initiated its implementation. Field work will begin on Monday February 20, 2012 to collect these sediment samples.

I am very pleased with the ability of your SSCG subgroups to coordinate their efforts and produce a unified approach that will address the near-term data needs for this project. Please extend my regards to all members of the subgroups for their valued participation.

In my review of the Plans I see that there is discussion of potential “next steps” beyond the February/March timeframe, and I will be thinking about these concepts and will discuss them soon with both of you. In addition my preference is that we continue to consider that chronic toxicity testing may yet be useful to our evaluation of potential ecological impacts and will not necessarily fall to MDEQ for implementation.

I am glad to hear that the SSCG is energized and actively advancing our collaborative effort.

Once again I must extend my sincere appreciation for the level of professionalism and diligence displayed by the SSCG members. I know that our overall project will be more successful because of their efforts.

Sincerely,



Ralph Dollhopf  
Federal On-Scene Coordinator and Incident Commander  
U.S. EPA, Region 5

cc: L. Kirby-Miles, U.S. EPA, ORC  
Sonia Vega, U.S. EPA, Deputy Incident Commander  
John Sobojinski, Enbridge  
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February 16, 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

Subject: Sampling Plan - Enbridge Line 6B MP 608, Marshall, Mich., Pipeline Release

Dear Mr. Dollhopf,

With this memorandum, the Chemistry, Fingerprinting, and Biodegradation Subgroup of the SSCG transmits recommendations as part of its responses to three of the FOOSC's charges to the Science Support Coordination Group:

1. (a) Provide an evaluation of viable analytical approaches, including benefits and draw backs for each, to quantify the amount of submerged oil in the Kalamazoo River sediments attributable to the Enbridge Oil pipeline Release.

2. (a) Identify and evaluate viable procedures for assessing the toxicity of remaining submerged oil. (b) Provide a recommendation for the best procedure to accomplish this goal.

3. (a) Provide an evaluation of viable procedures, including benefits and draw backs for each, to assess whether remaining submerged oil will biodegrade over time. (b) Provide a recommendation for the best approach to accomplish this goal.

The evaluations and recommendations included in our attached response fall into several categories:

- Submittal of fresh and weathered samples of oil for fingerprinting analysis of targeted analytes that are petroleum-specific, to ensure adequate characterization of important constituents that comprise petroleum;
- Submittal of samples split from the bulk samples of bed sediment collected for aquatic toxicity assessments;
- Similarly, submittal of samples split from the bulk samples of bed sediment collected for biodegradability assessments; and
- Collection and submittal of samples of the fine-particulates settling within cylindrical sedimentation-trap samplers to be deployed in geomorphic sediment-deposition areas.

Based on subgroup members' experience working on oil spill related issues for the past 20 years, we recommend the adoption of this technical approach in completing the response to the Enbridge Line 6B MP 608 Marshall, Michigan, Pipeline Release.

On behalf of the SSCG sub-group, very sincerely yours,

/s/

Ronald B. Zelt, P.HWQ.  
U.S. Geological Survey

# Recommendations to FOSC for Submerged Oil Sampling Plan Addendum

## Summary

**Goals, Scope, and Background.** The goals of sampling and analysis of crude oil and associated sediment are to:

- (1) characterize the chemical composition (fingerprint) of the spilled and weathered Line 6B crude oils and that of background sediment and its contaminants;
- (2) quantify the crude oil remaining as residuals in the impacted environment;
- (3) distinguish Line 6B oil from other hydrocarbon background and organics interference;
- (4) assess toxicity exposure and effects from various possible response actions; and
- (5) assess the biodegradability of residual oil through specific chemical evidence of biodegradation.

The scope of sampling planned for February-March 2012 will address goals 1, 2, 3, and 5 herein (table 1); goal 4 is being addressed by a separate sampling plan prepared by the “ecological risk and aquatic toxicity” subgroup. Regarding goal 2, quantification of residual submerged oil in designated sediment trap areas (Enbridge Energy, 2012a) is within the present scope, but the Spring 2012 reassessment of impacted-area quantity of residual submerged oil is outside the present scope and is to be addressed with subsequent evaluations and recommendations. Subsequent activity periods are expected to include a late-Spring 2012 reassessment period, Summer 2012 monitoring period, Fall 2012 reassessment period, and, if the results from Fall 2012 allow the transition from response activity to remedial activity, the final activity period envisioned might be a long-term phase for investigating the biogeochemical processes and rates affecting ultimate fates of the residual submerged oil. The sampling recommendations contained herein build upon the evaluations, discussions, and recommendations for chemical analysis and fingerprinting (i.e., the *Analytical & QA Plan*, or AP; SSCG, written commun., Feb. 10, 2012) through careful application of state-of-the-art laboratory determinations of metals, PIANO analytes, PAHs, including alkylated homologues, and petroleum biomarkers. Moreover, these evaluations and recommendations were undertaken in response to the FOSC charge to the SSCG:

1. a) Provide an evaluation of viable analytical approaches, including benefits and draw backs 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 approach to accomplish this goal.
2. a) Identify and evaluate viable procedures for assessing the toxicity of remaining submerged oil.  
b) Provide a recommendation for the best procedure to accomplish this goal.

3. a) Provide an evaluation of viable procedures, including benefits and draw backs for each, to assess whether remaining submerged oil will biodegrade over time.
- b) Provide a recommendation for the best approach to accomplish this goal.
4. Identify viable procedures to assess the potential for adverse ecological effects resulting from further oil recovery using sediment agitation (“toolbox”) techniques.

**Recommendations.** Actions recommended by the SSCG subgroup for FOSC consideration include the collection and analytical chemistry analysis of the following types of samples.

#### 1. Crude Oil Samples

- a) Source oil and samples of freshly spilled crude oil – four (4) samples of each source crude oil type (from Enbridge Energy’s sample archive); and four (4) subsamples of the DS02 sample of freshly spilled oil collected by USEPA on July 27, 2010, and archived at U.S. Coast Guard, Marine Safety Lab. Three source oil samples should be analyzed at the fingerprinting contract lab retained by Enbridge Energy, by the methods as detailed in the Analytical Plan, except that AVS, TOC and grain-size determinations are not needed. Source oil samples also should be provided to the U.S. EPA-ERT lab for analysis in support of biodegradability studies.
- b) Weathered crude oil -- four (4) samples from the 2010 recovered oil (from Griffith, Indiana), and three (3) subsamples from adequately preserved samples of well-weathered oil should be collected for chemical characterization of degradation states. Weathered oil samples should be analyzed at the fingerprinting contract lab retained by Enbridge Energy, by the methods as detailed in the *Analytical Plan*, except that AVS, TOC and grain-size determinations are not needed.

#### 2. Bed Sediment Samples

- a) Coordinate with the Toxicity Assessments sampling plan to ensure that subsamples of the bulk sediment samples collected for those assessments are split and submitted for analyses of targeted compounds at the fingerprinting contract lab retained by Enbridge Energy, by the methods as detailed in the *Analytical Plan*.
- b) Presumably, the protocols for biodegradation studies will specify collection of bulk samples of bed sediment, similar to those for the initial study of biodegradability. A subsample should be collected from each sample intended for biodegradability studies, by homogenizing and splitting in the field laboratory. Presuming that at least two samples will be collected for each study, then two homogenized subsamples would be collected as splits. These samples should be analyzed at the fingerprinting contract lab retained by Enbridge Energy, by the methods as detailed in the *Analytical Plan*, except that AVS, metals and VOCs are not needed.
- c) Sediment trap areas (geomorphic traps) that have been designated per Enbridge Energy’s work plan should have sampling devices deployed to collect the vertically accreting fine sediment that settles onto the streambed, to verify and quantify whether the trap areas’ vertical accretion includes Line 6B oil, in what quantities that oil is trapped, and whether the trapped material poses an exposure hazard for

aquatic biota. An average of three (3) sampling devices should be deployed at all designated geomorphic trap areas; and trapped sediment collected monthly, with subsequent redeployment of samplers. These samples should be analyzed at the fingerprinting contract lab retained by Enbridge Energy, by the methods as detailed in the *Analytical Plan*, except that AVS, metals and VOCs are not needed.

### **Fresh Oil from Talmadge Creek Source Area**

Two blends of crude oil (diluted bitumen) released by the Line 6-B spill (CLB and WCS) were sampled and are expected to represent the source of the spill. The Cold Lake Blend was sampled from “behind the isolation valve” prior to the re-opening of pipeline 6-B; whereas the sample of Western Canadian Select blend was collected from a covered storage tank at Stockbridge, Mich. (R. Steede, oral commun., 2012). Given that residual oil in the impacted environment could represent examples of either source type (or a mixture of both) in various states of weathering, and given that the chemical fingerprinting methods allow quantitative distinction among the source types and approximation of the mixture ratio, as well as biomarker-based characterization of the relative degree of weathering—in relation to the source oil biomarkers and hopanes fingerprint—it is important to develop a detailed characterization of the source-oil chemistry. These two crude oil blends are hereafter referred to as source oil (i.e., two source oil types), as distinguished from other samples of freshly spilled oil (fresh oil) that were collected near the release point, but for which there is no physical identifier that would allow samplers to know which source oil type was being sampled.

In addition to those Enbridge samples of source oil, U.S. EPA personnel collected 3 grab samples on July 27, 2010, from the freshly spilled oil flowing down the channel of Talmadge Creek: the sample closest to the release point was collected adjacent to the culvert passing under Division Drive (MP 0.5); whereas the third sampling point was adjacent to “A” Drive (MP 2.0) and just upstream from where the spill entered the Kalamazoo River (fig. 1). These fresh oil samples were analyzed by and archived in refrigerated storage at the U.S. Coast Guard Marine Safety Laboratory, New London, Conn.

Members of the subgroup evaluated the importance of these two available sources of archived source or fresh oil samples. The source oil samples are expected to show no effects of environmental exposure (weathering, mixture with non-petroleum materials), and also would be used as reference materials for analytical determinations in the primary fingerprinting laboratory and for the U.S. EPA-ERT lab doing initial tests of biodegradability of the oil. Whereas all three of the Talmadge Creek fresh-oil samples are expected to show similar oil-chemistry profiles, because they were separated by only a small distance in time and space, the third sample (DS02) was from the preferred location, just before the oil flowed into the river.

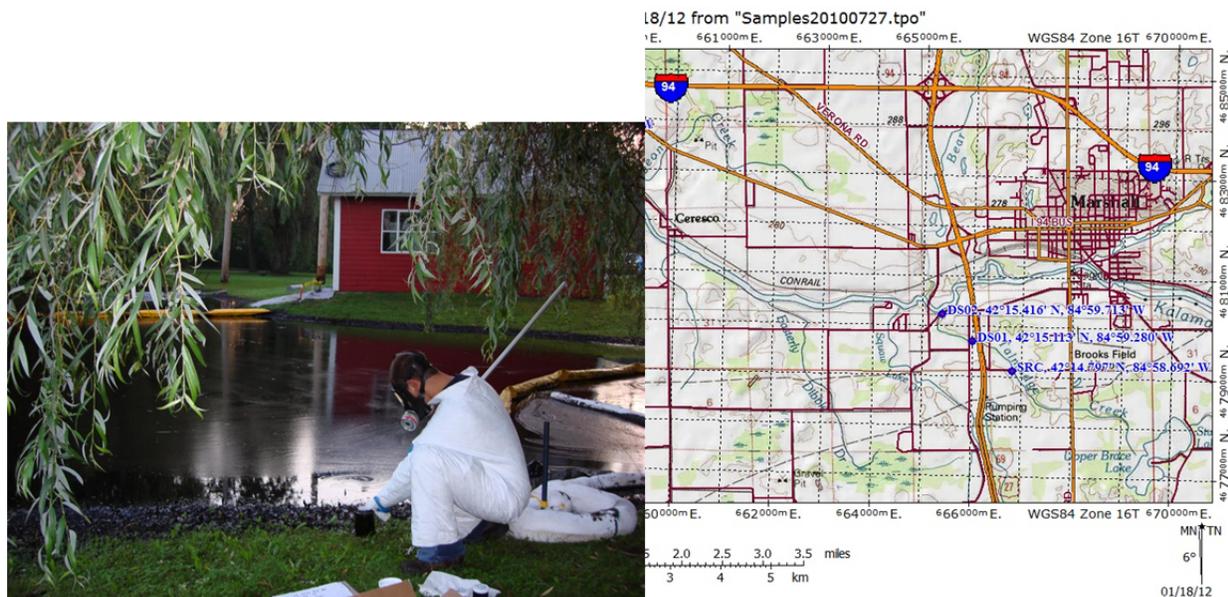


Figure 1. – (a) Collection of sample DS02 from spilled oil flow on Talmadge Creek; and (b) location of sampling points where oil samples were collected by U.S. EPA on July 27, 2010.

**Recommendations:** Obtain 4 samples (~40 mL each) of each source oil type. Obtain 3 subsamples (~40 mL each) of the DS02 sample of freshly spilled oil collected by USEPA from Talmadge Creek on July 27, 2010, 0636 hr. By analyzing three samples, the Fingerprint Lab could evaluate the source-oil variability and estimate 95%-confidence intervals for the target compounds. Oil samples should be preserved (see *Sample Processing and Preservation for Laboratory Analysis* section) and shipped promptly to the primary fingerprinting lab (3 samples of each source type; 3 subsamples of DS02) and to the ERT lab (1 sample of each source type). The source oil samples should be analyzed by the following methods, as detailed in the *Analytical Plan*:

- Polycyclic Aromatic Hydrocarbons (PAHs) and Sulfur Heterocyclic Compounds including alkyl homologues by gas chromatography with low resolution mass spectrometry using selected ion monitoring;
- Saturate hydrocarbons by gas chromatography with flame ionization;
- Total Extractable Hydrocarbons (TEH) representing the total aromatic and aliphatic hydrocarbon content of sample extracts after silica gel clean-up and analysis by GC/FID;
- Pre- and post-silica column gravimetric analysis;
- Petroleum biomarkers by GC/MS-SIM;
- Metals by ICP/MS;
- Extended list of volatile organic compounds (PIANO compounds) by GC/MS.

## Weathered Crude Oil

Sealed drums of recovered oil that previously had been stored at Griffith, Indiana, were recently

relocated to the Marshall area. This oil is a mixture of that recovered during July through September 2010; samples would presumably represent partially weathered heavy crude oil, probably lacking the much lighter diluent and much of the light-molecular weight components of the source oil.

Samples collected from this partially weathered, recovered oil could provide insight on weathering and degradation pathways that occurred during the first several weeks following the spill. Given that the samples would include oil from a mixture of points along the weathering/degradation timeline, the results may not provide a very clear understanding of processes and pathways.

A small sample of submerged oil was collected in Fall 2011 during recovery operations at the Ceresco power plant, just below Ceresco Dam. Another sample of subsurface oil was collected in February 2012 from the MP 13.4-LDB overbank excavation site; the oil was encountered in a soil void about 2 ft below land surface (possibly a burrow). Presumably, these recent samples represent well-weathered crude oil. Other well-weathered samples of submerged oil masses of sufficient volume (>~100 mL) that either have been adequately preserved (securely sealed and chilled) since collection, or are newly collected during the remainder of the response period, would also have potentially a high priority for analysis.

Recommendations: Obtain 3 samples (~40 mL each) from the 2010 recovered oil (from Griffith drums). More importantly, obtain 3 subsamples (~40 mL each) from adequately preserved samples of well-weathered oil. Ideally, at least 10 oil samples with varying levels of weathering would be obtained to evaluate the weathering pathway and develop a weathering model to estimate the percentage degradation over time; however, the existence of additional samples of weathered oil beyond a couple recently identified samples is unclear. Oil samples should be preserved and shipped promptly to the primary fingerprinting lab. The weathered oil samples should be analyzed by the following methods, as detailed in the *Analytical Plan*:

- Polycyclic Aromatic Hydrocarbons and Sulfur Heterocyclic Compounds including alkyl homologues by gas chromatography with low resolution mass spectrometry using selected ion monitoring;
- Saturate hydrocarbons by gas chromatography with flame ionization;
- Total Extractable Hydrocarbons (TEH) representing the total aromatic and aliphatic hydrocarbon content of sample extracts after silica gel clean-up and analysis by GC/FID;
- Pre and post silica column gravimetric analysis;
- Petroleum biomarkers by GC/MS-SIM;
- Metals by ICP/MS;
- Extended list of volatile organic compounds (PIANO compounds) by GC/MS.

## **New Samples of Bed Sediment**

After discussion of a larger range of different types of sampling purposes and site groups, the subgroup converged on three sampling purposes as the scope for the February-March activity period (table 1). First, bulk samples of bed sediment should be collected in support of the aquatic toxicity studies, as

described in the separate sampling plan developed by that subgroup. Second, bulk samples of bed sediment should be collected in support of submerged-oil biodegradability studies. Third, time-integrating samplers (cylindrical sedimentation traps) should be deployed to collect samples of sediment settling onto the river bottom in the designated sediment trap areas (geomorphic traps). The second and third sampling purposes and protocols are discussed and evaluated in this section.

### ***Biodegradability Studies***

Protocols for this suite of studies are still in formulation; however, one study is already in progress. The study of biodegradability under optimal conditions has prepared for testing the samples of bed sediment collected in January from a designated geomorphic trap (MP 10.75-LDB) known as a location where submerged oil has repeatedly been deposited. U.S. EPA-ERT has subsampled the bulk sediment samples and completed in-house analyses of PAHs, biomarkers, and (TEH).

There are questions about whether the oil content of the samples from MP 10.75-LDB is high enough to allow a reliable measurement of biodegradation during the test period, and thus whether a definitive conclusion on the oil degradability question will be attained from this initial study.

Additional studies of biodegradability will be planned once SSCG recommendations are finalized. For the immediate need to identify groups of sampling sites, it is reasonable to suggest that at least one additional study will focus on laboratory testing of samples from a site demonstrating residual oil presence at the heaviest levels still found in the impacted area, e.g., from one of the natural or historically effective sediment traps, such as Ceresco impoundment or the Morrow Lake delta. An additional study of *in situ* biodegradation has also been discussed, but since bulk sampling would not occur for *in situ* testing, a different sampling protocol (coring is likely) would likely be used for that study plan (not yet in preparation). *In situ* biodegradation studies would not be started during the February-March period that is the scope of this report. They would best be conducted in seasons of warmer water temperatures (most important since both abiotic chemical reactions and microbial activity are sensitive to temperature) and are more likely to succeed in a period with higher probability of lower and more stable river flows (i.e., June-September).

Typically, bulk samples of sediment are collected using clam-shell dredges for studies of biodegradability (or sediment toxicity). Initial sample volumes often exceed 4 liters. Then the sediments are sieved, typically through a 500-micron mesh, to remove coarse organic matter and other coarse particles, as well as any organisms which were entrained in the sample.

Recommendations: A bulk subsample should be collected from each sample intended for biodegradability studies, by splitting in the field laboratory. Minimum volume needed for sediment chemistry analyses is 250 g (8 oz). These homogenized split samples should be preserved and shipped promptly to the primary fingerprinting lab. Details of the biodegradation studies are not yet developed, but the sampling plan (QAPP Addendum) should include a substantial amount of QC sampling: if applicable, split samples for interlab comparison (~10%); matrix spikes (with duplicates); and field duplicates (> 5%). The bed sediment samples should be analyzed by the following methods, as detailed in the Analytical Plan:

- Polycyclic Aromatic Hydrocarbons and Sulfur Heterocyclic Compounds including alkyl homologues by gas chromatography with low resolution mass spectrometry using selected ion monitoring;
- Saturate hydrocarbons by gas chromatography with flame ionization;
- Total Extractable Hydrocarbons (TEH) representing the total aromatic and aliphatic hydrocarbon content of sample extracts after silica gel clean-up and analysis by GC/FID;
- Pre and post silica column gravimetric analysis;
- Petroleum biomarkers by GC/MS-SIM;
- TOC and grain size distribution.

### ***Sediment Trap Areas (geomorphic traps)***

A work plan has been submitted by Enbridge Energy (2012b) designating geomorphic sediment trap areas (either actively enhanced or taking advantage of passive/natural trapping at reduced current velocities) to be monitored and maintained for enhancing the retention of submerged oil and associated fine sediment within the riverine sections of the impacted area. The intended benefits of this plan are to (a) minimize the transport of these materials into the open water part of Morrow Lake, and (b) reduce the risk of their transport beyond Morrow Dam.

Trap areas will have routine monitoring of sediment accretion provided by standard surveying and/or geomorphologic methods. Thus, the primary use of sediment samples would be to verify and quantify whether the trap areas' vertical accretion includes Line 6B oil, in what quantities that oil is trapped, and whether the trapped material poses an exposure hazard for aquatic biota. This information should be the basis for guidance on how the trap areas could be effectively maintained without impairment to aquatic health.

Although sediment samples could be collected by coring, it might prove difficult to ascertain the bottom of the interval that contains the newly accreted deposits. Similarly, bulk samples of the bed in the trap area would not be definitive for these purposes. Potentially suitable sediment sampling devices have been deployed in previous studies (Scrudato et al. 1988; Hedrick et al. 2007) to collect samples of the fine sediment that settles out in slow- or no-velocity habitats. Gardner (1980) studied sediment traps in moving water, and suggested these traps not be thought to simply catch particles falling nearly vertically through a water column; rather sediment particles are carried into the trap by eddies and are trapped if their fall velocity allows them to settle or reach a stagnant zone in the trap before being carried out of the trap. For fine sediment ( $d_{95} < 25 \mu\text{m}$ ) in slow current ( $< 9 \text{ cm/s}$ ), the dominant control of fluid residence time in the trap is its geometry; the trapping efficiency of a container for a given current velocity is a function of fluid residence time but not of particle concentration; cylindrical traps gave a measurement of sediment accumulation rate similar to what collected on a flume bed (Gardner 1980). A suitable trap design presently in use in Wisconsin is shown in figure 2.



Fig. 2 – Cylindrical sampling device for collecting time-integrated sample of sedimentation in slowly moving or stagnant water (USGS photos by F.A. Fitzpatrick).

**Recommendations:** An average of three (3) cylindrical sampling devices (oriented so axis of rotation is vertical; open end facing up) should be deployed on the streambed at all designated geomorphic trap areas; apportion the samplers among trap areas in proportion to the spatial size (length or area) of trap areas. Positioning of samplers longitudinally along the trap is advised; e.g., one near inlet, one near outlet; however, carefully avoid zones where higher velocity or turbulence seem possible. Samplers should be located in the channel cross section where maximum rates of deposition are expected.

After deployment, trapped sediment should be collected about monthly, and the sampler immediately redeployed in the same location. All collected sediment samples should be labeled and preserved until a sufficient mass has been accumulated for a specific sampling point, and then sent to the selected primary lab. Minimum mass needed for sediment chemistry analyses is 3-5 g (5-10 g is optimal). Special care is needed with these samples to reduce the final extract pre-injection volume from 1 mL to not more than 0.1 mL (10x) because of the smaller maximum sediment sample size. The sampling plan (QAPP Addendum) should include a substantial amount of QC sampling: split samples for interlab comparison (~10%); matrix spikes (with duplicates); and field duplicates (> 5%). The bed sediment samples should be analyzed by the following methods, as detailed in the *Analytical Plan*:

- Polycyclic Aromatic Hydrocarbons and Sulfur Heterocyclic Compounds including alkyl homologues by gas chromatography with low resolution mass spectrometry using selected ion monitoring;
- Saturate hydrocarbons by gas chromatography with flame ionization;
- Total Extractable Hydrocarbons (TEH) representing the total aromatic and aliphatic hydrocarbon content of sample extracts after silica gel clean-up and analysis by GC/FID;
- Petroleum biomarkers by GC/MS-SIM;
- TOC and grain size distribution.

Based on results for decalins and sesquiterpanes, a subset of samples may be additionally analyzed for the extended list of volatile organic compounds (PIANO compounds) by GC/MS.

## Sample Processing and Preservation for Laboratory Analysis

Oil samples. Samples of crude oil media (source, fresh, or weathered) should be collected in tightly sealed vials, taped with teflon tape, and labeled with sample identifier, collecting agency code, date/time of collection, sample location, and sampler's name or initials. Follow established QAPP for completion of appropriate documentation of sample collection, preservation, and analytical requests. Preserve samples by maintaining as chilled at 4°C.

Sediment samples. Depending upon the purpose of sampling, samples of sediment-oil mixtures may be collected as bulk samples using either dredge or clam-shell type samplers; as complete contents of a trapping device (either Walling-type sampling tube or vertical-cylinder type settling trap); or as complete cores of submerged bottom material to a prescribed target depth below the water-sediment interface. It is critical to ensure that the surface floc layer is retained when collecting sediment samples from cores or settling traps to accurately represent the hydrocarbon content in the targeted interval, including that in the fine-grained interface between bed and water column. For bulk samples collected with dredges, sample containers should be filled to the top (minimize head space), sealed securely, labeled just as for oil samples, and documented per the established QAPP. Preserve samples either by chilling at 4°C or freezing, in accordance with analysis type, planned holding time, and the "advisory" holding times guidance included in the *Analytical Plan* (sect. 3.1).

## **Appendix – Sediment Site Groups not included in present recommendations for February-March Sampling Plan**

The appendix is included only to document some of the discussion or evaluations contributing to the deferral of site or sample groups until after the February-March time period that is the scope of the body of this document.

For 2012 reassessment and impacted area-wide sub-oil quantification purposes, plans will await the consideration and recommendations from the SSCG at a later date. An associated set of background samples also is expected to be recommended, but until plans and protocols for primary, impacted-area samples are known, those background samples and site selection are postponed.

Core samples collected from sediment trap areas (geomorphic traps) are envisioned for chemistry analysis to quantify toxics content of accumulated sediment in trap areas prior to maintenance.

Passive samplers of suspended sediment. If deployed during February-March 2012, samples collected are not expected to provide a very different picture than results from the initial deployment period in late 2011. These samples should be collected during late Spring 2012 (runoff period) when higher flows might re-suspend and transport sediment-associated sub oil.

Passive samplers within bed sediment have been mentioned as an option to consider for monitoring hydrocarbon levels both in pore water and adsorbed to solid phase materials. The SSCG has not yet discussed or evaluated the varieties and options related to this sampler class in enough detail to offer recommendations at this time.

### ***Archival Samples of Bed Sediment***

Using the inventory of sediment core samples previously analyzed for PAHs (standard priority pollutant suite), GIS processing is in progress to identify available analytical-laboratory extracts from the previously analyzed samples. Specifically, the processing will identify characteristics of the sampled location: type of geomorphic surface; location relative to areas previously classified as to Fall 2011 visible response to poing disturbance of bed (sheening category: light, moderate, heavy); and coarseness of surface sediment.

Further data processing will stratify the available locations to cover: (1) the important depositional habitats where submerged oil has remained detectable during 2011: impoundments, deltas, sediment fans, oxbows, backwaters, island margins, and overbank wetlands; and (2) the silt, silty sand, and sandy silt substrates where sub oil has been detected most frequently. A subset of the cores will be selected from across the range of sheening categories, and for those cores the uppermost sample (where that uppermost unit is not thicker than 0.6 ft) will be selected as a candidate. For candidate samples from across a broad range of the TPH concentrations (analyzed previously in those samples), the suitability of the archived extract will be evaluated; e.g., preserved and monitored appropriately for viable reanalysis (i.e., transferred to 4-mL vial, topped with solvent to prevent evaporative loss, meniscus marked on vial, capped securely, and stored frozen).

Selected extracts should be transferred from archival location to analyzing laboratory in accordance with SOP for inter-lab transfer (document not yet prepared). The analyzing laboratory will require copies of the original sample preparation records to provide quantitative re-analysis of the archived extracts.

Table 1. Summary of sampling plan and site groups for Winter-early Spring sampling

[Goals: goal numbers refer to those in Summary section; Y, goal supported; P, potentially adds some support for goal; N, not intended to support goal;]

Row	Medium	Samp.type	Sampler	Site group	Geomorph.setting	Sample.interval	Goal(s) supported					Sample.purpose	Number of samples recommended					Comments
							1	2	3	4	5		Environ (primary)	QC (split)	QC (field dup.)	QC (blank)	QC (ref. mat'l)	
1	sediment	bed sed	split from bulk (clam shell)	Toxicity	coordinate with Toxicity study plan	inexact (dredge or clam shell sampler)	Y	N	Y	Y	Y	toxicology/ exposure hazard	16	3	5	0	2	[4 geomorph categ] x [4 sub oil categ]
2	sediment	bed sed	split from bulk (clam shell)	Toxicity	background (per Toxicity study plan)	inexact (dredge or clam shell sampler)	Y	P	Y	Y	N	toxicology/ background fingerprint	9	1	1	0	2	[3 background areas] x [2 to 3 samples per area]
3	sediment	bed sed	split from bulk (clam shell)	Biodegrad	coordinate with Biodegrad study plan (in preparation)	inexact (dredge or clam shell sampler)	Y	N	N	N	Y	support Biodegrad study needs; sampled from "heavy" oil area	4	1	1	0	2	2 samples per Biodegrad study site
4	sediment	bed sed	anchored cylindrical sedimentation trap	Geomorphic sed trap area	coordinate with Operations' Monitoring & Maintenance Plan	full interval accumulated between deployment and retrieval; retrieve monthly and composite sampling-point sediment until mass meets analytical requirements	Y	Y	Y	N	Y	monitor quantity and fingerprint of SO accumulation in designated geomorph trap area	39	2	4	0	2	avg of 3 fixed-trap devices per geomorphic trap area, apportioned per size (length or area) of geomorphic trap.