# Listing Methodology for Determining Water Quality Impairments from Petroleum Hydrocarbons, Oils and Grease

## GUIDANCE

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Alaska Department of Environmental Conservation
Division of Water

## Contents

## Tables

# Acronyms

| | |
|---|---|
| µg/L | micrograms per liter |
| AAC | Alaska Administrative Code |
| BTEX | benzene, toluene, ethylbenzene, and xylenes |
| DEC | Alaska Department of Environmental Conservation |
| CWA | Clean Water Act |
| DNR | Alaska Department of Natural Resources |
| EPA | U.S. Environmental Protection Agency |
| NOAA | National Oceanic and Atmospheric Administration |
| PAH | polynuclear or polycyclic aromatic hydrocarbons |
| PEL | probable effects level |
| QAPP | quality assurance project plan |
| SPAR | DEC's Division of Spill Prevention and Response |
| SQuiRT | NOAA Screening Quick Reference Tables (http://response.restoration.noaa.gov/sites/default/files/SQuiRTs.pdf) |
| TEL | threshold effects level |
| TAH | total aromatic hydrocarbons |
| TAqH | total aqueous hydrocarbons |
| TH | total hydrocarbons |
| WQS | Water Quality Standards |

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# 1 Purpose and Background

This listing methodology is intended to be used by Alaska Department of Environmental Conservation (DEC) staff as guidance for listing or delisting a waterbody on the Clean Water Act §303(d) list as impaired from petroleum hydrocarbons, oils and grease. The methodology includes information on the quantity and characteristics of data needed to be deemed sufficient and credible for these decisions. The methodology presents the applicable regulations as adopted in the Alaska Water Quality Standards (WQS) in 18 AAC 70, and discusses challenges to making listing and delisting determinations based on sampling data for volatile and semi-volatile chemicals. These guidelines are designed to assure that sufficient data are gathered to determine if a waterbody is impaired or attaining WQS, and to characterize the areal extent of the impairment (if necessary).

## 1.1 Parameter-Specific Regulations and Criteria

Alaska water quality criteria for petroleum hydrocarbons, oils and grease are specified in 18 AAC 70.020(b)(5) for fresh water uses and in 18 AAC 70.020(b)(17) for marine water uses. Petroleum hydrocarbons, oils and grease criteria are established for seven fresh water and seven marine water designated uses. The designated uses and criteria applicable to the waterbody of interest need to be identified before applying the criteria. Generally, a waterbody is designated either for fresh water designated uses or marine water designated uses, including the corresponding criteria with the exception of a waterbody that has been reclassified (18 AAC 70.230) or a waterbody subject to site-specific criteria (18 AAC 70.236). The designated uses for fresh water and marine water may differ (e.g., water supply for drinking, culinary, and food processing for fresh waters versus harvesting for consumption of raw mollusks or other raw aquatic life for marine waters).

Table 1.1. Petroleum hydrocarbon, oils and grease criteria for fresh water uses

| **(5) PETROLEUM HYDROCARBONS, OILS AND GREASE, FOR FRESH WATER USES** | |
|---|---|
| (A) Water Supply<br>(i) drinking, culinary, and food processing | May not cause a visible sheen upon the surface of the water. May not exceed concentrations that individually or in combination impart odor or taste as determined by organoleptic tests. |
| (A) Water Supply<br>(ii) agriculture, including irrigation and stock watering | May not cause a visible sheen upon the surface of the water. |

| **(5) PETROLEUM HYDROCARBONS, OILS AND GREASE, FOR FRESH WATER USES** | |
|---|---|
| (A) Water Supply<br>(iii) aquaculture | Total aqueous hydrocarbons (TAqH) in the water column may not exceed 15 µg/l (see note 7)[1]. Total aromatic hydrocarbons (TAH) in the water column may not exceed 10 µg/l (see note 7)[1]. There may be no concentrations of petroleum hydrocarbons, animal fats, or vegetable oils in shoreline or bottom sediments that cause deleterious effects to aquatic life. Surface waters and adjoining shorelines must be virtually free from floating oil, film, sheen, or discoloration. |
| (A) Water Supply<br>(iv) industrial | May not make the water unfit or unsafe for the use. |
| (B) Water Recreation<br>(i) contact recreation | May not cause a film, sheen, or discoloration on the surface or floor of the waterbody or adjoining shorelines. Surface waters must be virtually free from floating oils. |
| (B) Water Recreation<br>(ii) secondary recreation | Same as (5)(B)(i). |
| (C) Growth and Propagation of Fish, Shellfish, Other Aquatic Life, and Wildlife | Same as (5)(A)(iii). |

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[1] Note 7. Samples to determine concentrations of total aromatic hydrocarbons (TAH) and total aqueous hydrocarbons (TAqH) must be collected in marine and fresh waters below the surface and away from any observable sheen; concentrations of TAqH must be determined and summed using a combination of: (A) EPA Method 602 (plus xylenes) or EPA Method 624 to quantify monoaromatic hydrocarbons and to measure TAH; and (B) EPA Method 610 or EPA Method 625 to quantify polynuclear aromatic hydrocarbons listed in EPA Method 610; use of an alternative method requires department approval; the EPA methods referred to in this note may be found in Appendix A of 40 C.F.R. 136, Appendix A, as revised as of July 1, 2003 and adopted by reference.

Table 1.2. Petroleum hydrocarbon, oils and grease criteria for marine waters uses

| **(17) PETROLEUM HYDROCARBONS, OILS AND GREASE, FOR MARINE WATER USES** | |
|---|---|
| (A) Water Supply<br>(i) aquaculture | Total aqueous hydrocarbons (TAqH) in the water column may not exceed 15 µg/l (see note 7)[1]. Total aromatic hydrocarbons (TAH) in the water column may not exceed 10 µg/l (see note 7)[1]. There may be no concentrations of petroleum hydrocarbons, animal fats, or vegetable oils in shoreline or bottom sediments that cause deleterious effects to aquatic life. Surface waters and adjoining shorelines must be virtually free from floating oil, film, sheen, or discoloration. |
| (A) Water Supply<br>(ii) seafood processing | May not cause a film, sheen, or discoloration on the surface or floor of the waterbody or adjoining shorelines. Surface waters must be virtually free from floating oils. May not exceed concentrations that individually or in combination impart odor or taste as determined by organoleptic tests. |
| (A) Water Supply<br>(iii) industrial | May not make the water unfit or unsafe for the use. |
| (B) Water Recreation<br>(i) contact recreation | May not cause a film, sheen, or discoloration on the surface or floor of the waterbody or adjoining shorelines. Surface waters must be virtually free from floating oils. |
| (B) Water Recreation<br>(ii) secondary recreation | Same as (17)(B)(i). |
| (C) Growth and Propagation of Fish, Shellfish, Other Aquatic Life, and Wildlife | Same as (17)(A)(i). |

| **(17) PETROLEUM HYDROCARBONS, OILS AND GREASE, FOR MARINE WATER USES** | |
|---|---|
| (D) Harvesting for Consumption of Raw Mollusks or Other Raw Aquatic Life | May not exceed concentrations that individually or in combination impart undesirable odor or taste to organisms as determined by bioassay or organoleptic tests. |

The petroleum hydrocarbons, oils and grease criteria are multi-pronged in that they address different parts of a waterbody. The criteria for a given designated use contain one or more of the following provisions from 18 AAC 70.020:

Water Surface, Floor, and Adjoining Shoreline

- May not cause a visible sheen on the surface of the water.
- Surface waters and adjoining shorelines must be virtually free from floating oil, film, sheen, or discoloration.
- May not cause a film, sheen, or discoloration on the surface or floor of the waterbody or adjoining shorelines.
- Surface waters must be virtually free from floating oils.

Bottom sediments

- There may be no concentrations of petroleum hydrocarbons, animal fats, or vegetable oils in shoreline or bottom sediments that cause deleterious effects to aquatic life

Water column

- Total aromatic hydrocarbons (TAH)[2] in the water column may not exceed 10 µg/L.
- Total aqueous hydrocarbons (TAqH)[3] in the water column may not exceed 15 µg/L.
- May not make the water unfit or unsafe for the use.

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[2] TAH means the sum of the following volatile monoaromatic hydrocarbon compounds: benzene, ethylbenzene, toluene, and the xylenes isomers, commonly called BETX [sic]. 18 AAC 70.990(60).

[3] TAqH means those collective dissolved and water-accommodated monoaromatic and polynuclear aromatic petroleum hydrocarbons that are persistent in the water column; "total aqueous hydrocarbons" does not include floating surface oil or grease. 18 AAC 70.990(59).

- May not exceed concentrations that individually or in combination impart undesirable odor or taste to organisms as determined by bioassay or organoleptic tests.

The analytical methods used to determine levels of TAH and TAqH are defined in Note 7[1]. The analytical methods for "Oils and grease" are defined in 18 AAC 70.990(43).[4]

Criteria for individual petroleum hydrocarbons pollutants (i.e., human health criteria for benzene, toluene, ethylbenzene and xylenes (BTEX)) can be found in the 2008 *Alaska Water Quality Criteria Manual for Toxic and Other Deleterious Organic and Inorganic Substances* (Alaska Toxics Manual, 2008), which can be accessed at the following website: https://dec.alaska.gov/media/11546/alaska-water-quality-criteria-manual-for-toxic-and-other-deleterious-organic-and-inorganic-substances.pdf.

An impairment determination can only be based on anthropogenic sources of petroleum hydrocarbons, oils and grease. For example, impairment determinations shall not be based on naturally occurring oils, animal fats, or sheens.

### 1.1.1 Alaska's Numeric Aquatic Life Criteria for Petroleum Hydrocarbons

Alaska's numeric aquatic life criteria for petroleum hydrocarbons were adopted in 1979 and continue to be the most stringent in the nation at approximately three orders of magnitude lower than any other state's criteria (Tetra Tech, Inc., 2008). The numeric aquatic life criteria for TAH and TAqH are protective for two fresh water and marine water designated uses: (1) water supply for aquaculture, and (2) growth and propagation of fish, shellfish, other aquatic life and wildlife. The 2008 Alaska Toxics Manual contains no additional numeric aquatic life criteria for acute or short-term chronic toxicity for petroleum hydrocarbons, oils and grease. Although not explicitly stated in the TAH and TAqH criteria narratives, examination of several DEC development documents for the petroleum hydrocarbons criteria indicate that TAH and TAqH are chronic criteria for fresh water and marine water as described below.

Obtaining representative samples over a chronic averaging period is challenging due to the volatility of the pollutants, intermittent sources and seasonal activity levels (e.g., motorized watercraft during three-week salmon fishery periods). The characteristics of petroleum hydrocarbons and the need for data that support chronic exposure averaging periods have led to unique challenges in implementing this standard in Alaska.

The EPA guidance on aquatic life criteria are provided in the 1985 *Guidelines for Deriving Numerical National Water Quality Criteria for the Protection of Aquatic Organisms and Their Uses*. Water quality criteria are composed of three components: magnitude, duration and frequency. The 4-day average

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[4] Oils and grease as defined by the procedure used under *Standard Methods for the Examination of Water and Wastewater*, 18th edition, 1992; 19th edition, 1995; or 20th edition, 1998 published jointly by the American Public Health and American Water Works Associations and the Water Environment Federation. 18 AAC 70.990(43) and 18 AAC 70.020(c)(1).

concentration of a chronic criterion may not be exceeded more than once every three years. Specifically, the guidelines state:

> "Except possibly where a locally important species is very sensitive, aquatic organisms and their uses should not be affected unacceptably if the **four-day average** concentration does not exceed the **chronic criterion** more than **once every three years** on the average, and if the one-hour average concentration does not exceed the acute criterion more than once every three years on the average" (EPA 1985).

Because of the volatility of petroleum constituents and the possibility of intermittent sources, these EPA guidelines for developing water quality criteria were used to aid in the thresholds used for impairment determinations discussed in Section 2.3.3.

### 1.1.2 Magnitude

TAH Criterion

Two approaches were evaluated and compared to establish the TAH criterion: (1) a review of acute toxicity for Alaskan species at various life stages and (2) a review of laboratory and field literature on chronic, sub-lethal effects for aromatic hydrocarbons.

Acute toxicity thresholds were reported as the concentration lethal to 50% of the test organisms or lethal concentration, 50% (LC50). The LC50 values for Alaskan species ranged from 300 to 1,400 µg/L depending on the species and life stage tested. Larval crustaceans were determined to be one of the most sensitive Alaskan marine groups with an average LC50 for TAH of 1,000 µg/L.

A chronic TAH criterion of 10 µg/L was derived multiplying the acute value of 1,000 µg/L TAH by a 0.01 safety factor. The chronic TAH criterion of 10 µg/L was also compared with published chronic toxicity test results for petroleum hydrocarbons. The TAH criterion was found to be more conservative (DEC 1976). In 1979, DEC adopted the chronic TAH criterion into Alaska Water Quality Standards.

The derivation of TAH criteria implements EPA's recommended narrative criteria in their 1976 *Quality Criteria for Water,* as well as the 1986 recommended criteria in the "Gold Book", and is EPA's current nationally recommended 304(a) water quality criteria for oil and grease, as of April 2015 (see http://water.epa.gov/scitech/swguidance/standards/criteria/current/index.cfm).

> "For aquatic life, 0.01 of the lowest continuous flow 96 hour LC50 to several important freshwater and marine species, each having a demonstrated high susceptibility to oils and petrochemicals."

This approach is somewhat different from current EPA guidelines for deriving other aquatic life criteria for toxic substances (Stephen, et al. 1985) in which a chronic value is calculated based on a final acute-chronic ratio by taking the geometric mean of the appropriate acute-chronic ratios measured for the same species. The DEC last reviewed the TAH criterion in 1989 (DEC 1989). The original toxicity test data used to derive the TAH criteria was not retained, so recalculation of the criteria using current criteria methodology is not possible without new toxicity testing of Alaska species from at least 8 taxonomic families as required by the EPA methodology and/or a search for scientific literature containing the required data.

TAqH Criterion

The DEC originally adopted the TAqH criterion in 1979 as a total hydrocarbon (TH) criterion. TH in the water soluble phase is generally proportional to the TAH present with a measured TH to TAH toxicity ratio of 1.5:1 for various fish exposed to crude oil (DEC 1989). Applying this toxicity ratio to the chronic TAH criterion (10 µg/L) results in a chronic TH criterion of 15 µg/L. In 1996, the DEC conservatively converted the chronic TH criterion to a chronic TAqH criterion, as TAqH is the largest fraction of soluble TH. The DEC last reviewed the TAqH criterion in 2005 to incorporate scientific literature published since 1995 (Weber-Scannell, *et al.* 2005).

### 1.1.3 Persistence and Frequency of Exceedance

Exceedances from TAH and TAqH vary based on many factors. Exceedances can vary by time of day and time of week due to the sources and volatility of the parameter. Factors affecting volatility include: water flow and turbulence, temperature, and solar irradiation. Factors affecting pollutant source loading include characteristics of the pollutant source (i.e. numerous, intermittent nonpoint sources such as motorized watercraft compared to continuous point source wastewater discharge), and hydrological flow conditions.

TAH Persistence

TAH is the sum of the concentrations of individual aromatic BTEX compounds and these compounds are extremely volatile. As a result, TAH concentrations are likely to have pronounced short-term fluctuations in the water column.

TAqH Persistence

TAqH is the sum of BTEX and polycyclic aromatic hydrocarbons (PAHs). PAH compounds are less volatile and also less soluble than BTEX compounds. Due to various factors including dilution, volatilization, photolysis, and biodegradation, these petroleum hydrocarbon fractions are unlikely to persist in the water column for an extended period of time.

PAHs are more likely to accumulate in sediments where they can remain for decades under some conditions. As a result PAHs are frequently used to implement the narrative criterion for sediment in the petroleum standard, which is discussed in more detail in Section 2.2. In addition, BTEX compounds are readily volatile and biodegradable and therefore, less likely to accumulate and remain in sediments for extended periods.

### 1.1.4 Duration of Exposure

The duration of exposure to a pollutant in exceedance of a chronic criterion is based on a 4-day average, which also corresponds to the duration of a chronic toxicity test. The duration of acute exposure is 1-hour or 24-hours depending on the parameter. For most pollutants (especially when part of a relatively consistent and continuous wastewater discharge), weekly or even monthly sampling is sufficient to establish whether or not there has been sustained exposure exceeding the duration period of the criterion.

TAH Exposure

The volatility of TAH can result in exposure durations that are very short, particularly if the source is intermittent as from a passing motorized watercraft. For this type of pollution source, chronic exposure to elevated TAH concentrations is only likely in certain instances such as when watercraft are numerous and in a particular area for sustained periods. Due to both the volatility of the pollutants, when there are intermittent sources more frequent sampling may be necessary for TAH than is necessary for sampling for other toxic pollutants to establish the average concentration during the critical exposure period.

TAqH Exposure

TAqH compounds are less volatile and therefore exposure duration is easier to demonstrate. However, TAqH, like TAH, may be rapidly diluted when in the water column, so sustained exposure is more likely to occur in bottoms sediments where the same types of compounds are measured as PAH.

# 2 Implementing Methods

DEC recommends using current data (within five to ten years old) to determine impairment, but may consider the use of older documentation or data when the number of recent data points is limited or seasonality is not well captured. Older data are generally given less significance unless circumstances that would lead to impairment have not changed. In addition, DEC recognizes that data collected prior to development of this listing methodology may not be as comprehensive as newly collected data. Data collected prior to this methodology and from independent sources not using this protocol should be considered in impairment decisions after evaluating the data to determine similarities to and applicability with a more recent data set. Furthermore, additional sampling:

- May need to be conducted for all portions of the waterbody that may be affected by suspected impairments (i.e., water surface, floor, adjoining shoreline, water column, and bottom sediments) to establish the spatial extent of the suspected impairment.
- May need to be conducted more over a longer time period and more frequently to satisfy the requirements outlined in this guidance.
- Must be performed and observations conducted under a Quality Assurance Project Plan (QAPP) written in accordance with DEC guidance or under a DEC-approved QAPP.

## 2.1 Sampling and Laboratory Analysis Methods

The authorized sampling and analysis methods for TAH and TAqH in the water column are found in 18 AAC 70.020(b) Note 7 found in Section 1.1 of this document.

However, for the purposes of ascertaining an impairment determination EPA Method 624 and EPA Method 625 are strongly recommended instead of the older EPA Methods 602 and 610.

## 2.2 Sediment Sampling

DEC has not promulgated numeric sediment quality standards; however, the DEC Contaminated Sites Program has issued the technical memorandum *Sediment Quality Guidelines* (DEC 2013), which states the Department recommends the use of Probable effect levels (PELs) and threshold effect levels (TELs) from the most current NOAA SQuiRT (http://response.restoration.noaa.gov/sites/default/files/SQuiRTs.pdf) to evaluate sediment quality. PELs represent the concentration above which adverse effects are expected to occur frequently. TELs represent the concentration below which adverse effects are expected to occur rarely. DEC uses SQuiRTs to implement narrative criteria for petroleum hydrocarbons, oils and grease in fresh water and marine water sediments. The guidelines recommend a weight of evidence approach and additional information must be considered when it is available.

If TEL/PEL values are not listed for a contaminant of concern (COC), alternative published screening levels may be proposed and reviewed by the department on a site specific basis. The guidelines recommend a weight of evidence approach.

## 2.3 Sample-Specific Methods

Sampling guidelines for specific provisions within the criteria are included in the following subsections.

### 2.3.1 Water Surface, Floor, and Adjoining Shoreline

The following guidelines apply to observing films, sheens, or floating oils on the water surface, floor, and adjoining shorelines for the fresh water and marine water designated uses of water supply and recreation.

(a) Sample Observation: Establish that the film, sheen, or floating oils is a result of anthropogenic origins and is not a naturally occurring film or sheening event (e.g., Langmuir streaks, pollen, natural foam, algae, or algal blooms). Naturally occurring events should be documented but not considered when assessing a waterbody for potential Section 303(d) listing as impaired from petroleum hydrocarbons, oils and grease.

(b) Observation Reporting: Contact the DEC Division of Spill Prevention and Response (SPAR) regional emergency response section (phone (800) 478-9300) to confirm if petroleum films or sheens have been reported. On-going DEC SPAR emergency response and clean-up efforts may obviate the need for Section 303(d) listing. Information from SPAR may also be useful in the impairment determination.

(c) Frequency/Number of Samples: To determine impairment or attainment of the standard for films, sheens or floating oil, a listing determination should evaluate at least 30 independent sampling events representing at least a two year assessment period to establish the statistical significance and persistence of the impairment. Sampling must be representative of the waterbody and address the spatial extent and temporal (seasonal) periods of concern (normally not less than a three week annual interval).

A sampling plan may consider a two-phased approach, with phase one used for screening purposes and phase two for more intensive sampling to confirm impairment or attainment.

Phase one: A minimum of 10 visual observations of oil film, sheen, or floating oils are needed during the first year of assessment. More than 10% of these observations should identify a petroleum film, sheen or floating oils to warrant a second year of more intensive observations.

Phase two: 10-20 visual observations of oil film, sheen, or floating oils during the second year of assessment. A minimum of 30 observations over at least two years must be collected to determine impairment or attainment status.

Observations must be spaced such that they are not tied to a single, isolated event (such as would occur with a spill), an isolated source (such as a single motor boat), or a single year. Sampling plans should be designed to be temporally and spatially representative of the waterbody and the sampling period and to capture the persistence of the sheen for a significant period of time during each observation.

Observations should be conducted by a trained and knowledgeable person. As with all sampling, a QAPP should be developed and, where possible, reviewed by DEC. The plan should incorporate testing to demonstrate that sheens are not biological in nature. In the absence of EPA approved standard methods, standard operating procedures for sheen observations can be found in Appendix A and should be followed. Additional information on differentiating oil and biological sheens can be found in the USGS Introduction to Microbes publication (http://pubs.usgs.gov/gip/microbes/intro.html).

(d) Documentation: Field sheets should be developed as a part of the sampling plan enabling different observers to capture consistent information and should be included with the assessment report. For example, the field sheets should document the percent of area observed, the area of the sheen, length of time the sheen persists, and other relevant information describing observations.

(e) Impairment Determination: The waterbody will be considered for impairment if more than 10% of the total observations, reveal the presence of petroleum hydrocarbons, oils and grease over an assessment period of at least two years. There should not be consideration of an impairment listing based solely on short term intermittent sheening that does not meet the minimum data requirements.

The 10% impairment threshold and sample size of 30 is consistent with EPA listing methodology guidance (EPA, 2002). “Sample size is an important element of data quality. In general, statistical tests have good power for detecting exceedances if they are based on data from samples composed of 30 or more sampling units. Smaller sample sizes are prone to yield erroneous attainment decisions because they have a low probability of detecting WQS exceedances unless they are large and pervasive.”

If a waterbody is under consideration as being impaired from oil film or sheening, then water column and/or sediment sampling should be considered, but is not required, to evaluate the extent of petroleum hydrocarbons contamination (Sections 2.3.2 and 2.3.3).

### 2.3.2 Bottom Sediments

The following guidelines apply to monitoring petroleum hydrocarbons, oils and grease in bottom sediments for the fresh water and marine water designated uses of water supply.

(a) Sample Collection: Collect discrete sediment samples for PAH. Consider initially collecting samples using a grid pattern encompassing the area of concern. Subsequent follow-up sampling can be limited to the area where contamination has been found. The sampling program should ensure enough samples have been collected (minimum of 20) to accurately assess the areal extent of the petroleum hydrocarbons, oils and grease. Core sampling may also be conducted to determine the depth of contamination. Sampling near creosote pilings should be avoided.

(b) Frequency/Number of Samples: Collect a minimum of 20 different bottom (surface sediment) samples encompassing the area of concern per year. Collect samples over two different years within a five-year period.

(c) Documentation: At a minimum, laboratory results should be included with the waterbody assessment report.

(d) Impairment Determination: If any surface sediment sampling location exceeds the PEL in the NOAA SQuiRTs for two years, then that area is considered impaired. If a PEL value is not available, the next more conservative guideline value should be used. An evaluation of both the individual constituents and the combined PAH levels should be conducted. Core sample results can be used to establish a historical impairment.

### 2.3.3 Water Column

The following guidelines apply to monitoring petroleum hydrocarbons, oils and grease in the water column for the fresh water and marine water designated uses of water supply; and growth and propagation of fish, shellfish, other aquatic life, and wildlife.

(a) Sample Collection: Collect representative samples at multiple sample sites to establish the spatial and temporal extent of the impairment (e.g., thalweg, horizontal, and vertical samples).

Collect at least one sample near the surface (at elbow depth to avoid any sheen) and one sample near the bottom. Sampling at multiple depths is not necessary in shallow waters, which are defined as less than three meters. Compare sample results (vertically and horizontally) to establish the degree and extent of mixing in the water column. After the degree of mixing is established, multiple depth sampling may cease. Future sampling should only occur in locations where petroleum hydrocarbon results have exceeded water quality criteria.

Sampling should be conducted (1) during periods and in areas of suspected on-going impairment when sources of pollutants are present and (2) during periods or in areas of low pollutant loading to the surface water, adjoining shoreline, and water column. Sampling during both times will help define the temporal extent of contamination.

(b) Frequency/Number of Samples: Initial samples should be taken daily to determine periods of suspected impairment and the spatial extent of the waterbody that has been contaminated by petroleum. Subsequent sampling should then verify the magnitude, exposure duration and frequency of the exceedance of petroleum hydrocarbons criteria in the potential impairment area. Once the spatial and temporal extent of the area of concern has been identified, the magnitude, duration and frequency of impairment should be verified at one or two sampling sites that best represent the impaired condition of the waterbody.

At the selected site(s) a minimum of 20 samples should be collected over four 24-hour consecutive cycles (i.e. a total of 96 hours) in the area and during periods in which initial sampling showed the highest exceedance(s). Samples collected during periods of suspected on-going impairment should be collected no more than 5 to 7 hours apart from each other. The sample results should be used to calculate a 4-day average and represent diurnal fluctuations. The requirement to collect at least 20 samples may be reduced if the source of contamination is a continuous source (e.g., effluent discharge). At least 20 samples are needed when the source is intermittent (e.g., motorized, non-stationary source) to establish an exceedance of the TAH or TAqH criteria.

A single sample is sufficient to establish the duration of an exceedance of the acute criteria (see impairment determination below).

(c) Impairment Determination: If the 4-day average exceeds the TAH or TAqH criteria (10 μg/l and 15 μg/l respectively) more than once in a 3-year period, then the waterbody will be considered impaired for aquatic life related uses due to chronic toxicity. In addition, if the 1-hour average exceeds 1,000 μg/L for TAH or 1,500 μg/L for TAqH more than once in a 3-year period, then the waterbody will be considered impaired for aquatic life uses due to acute toxicity. Impairment based on the acute criterion would need to be verified as having occurred during two years and should not be considered an impairment based only on an isolated event (e.g., active oil spill that can be cleaned up in less than one year).

The spatial and seasonal extent of the impairment may be based on independent sampling events consisting of single and/or duplicate samples from multiple sites during the same day. For example, consider a monitoring plan with five monitoring locations. Assume two 4-day averages from monitoring location number 1 (ML1) exceed WQS. If individual sample results from sites ML2 through ML5 also exceed WQS during both of the two 4-day ML1 sampling events, then those additional sites with two exceedances can be used to define the spatial extent of the impairment.

## 2.4 Other Methods

Laboratory analytical testing is the preferred methodology to inform listing or delisting a waterbody for the water column or sediment. However, DEC recognizes the significant cost and resources necessary to fulfill these data requirements. Therefore, impairment decisions and subsequent restoration monitoring may be based on surrogate information (i.e., statistical modeling or other method agreed upon by DEC). For example, initial petroleum sampling may be paired with observation of the number, type and size of motors on boats in a river to create a petroleum loading model that then allows boat motor count as a surrogate for petroleum sampling. Provided sufficient data (at a minimum 20 samples) is available, a regression analysis of surrogates may be considered given a strong correlation (example: $R^2$ more than 0.85) exists between the actual water quality data and the surrogate.

# 3 Removal of a Waterbody from the Section 303(d) List for Petroleum Hydrocarbons, Oils and Grease

The basic direction for listing determinations used by Alaska and outlined in the Integrated Reports dictate that removing a waterbody from the Section 303(d) list requires a level of data equivalent to that used in the initial Section 303(d) listing determination. Sampling plans for removing a waterbody should be designed to capture whether changes have occurred that have resulted in the waterbody meeting WQS. Sampling should be specifically designed to determine if the documented impairment still exists.

The minimum number of samples depends on the number needed to document that the criteria are not exceeded during periods of highest risk (e.g., greatest number of sources, low flow). Data from at least two years must show that criteria have not been exceeded in order to demonstrate consistent attainment of the WQS.

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# Appendix A – Visible Oil Sheen Standard Operating Procedure

## 1.0 SCOPE AND METHOD SUMMARY

Not all sheens are caused by petroleum oil. Sheens with iridescent or silvery appearance are often observed on water in ditches, wetlands, and on other areas with stagnant, standing water. In some cases, there are reddish precipitates associated with the sheen. Such sheens may not be oil related sheens, but actually natural sheens from masses of bacteria. These bacteria include iron and manganese reducing bacteria such as Leptothrix spp. that also produce the reddish or blackish precipitates seen in some stagnant waters (Robbins and Norden, 1994). Natural bacterial or biogenic sheens are often confused with oil sheens.

This Standard Operating Procedure (SOP) describes the basic methods and testing methodology to differentiate oil sheen from biogenic sheen in the field. The sheen differentiation methods are referred to in this document as 'Stick Test' and 'Jar Shake Test' (see sections 5.1 and 5.2 below)

Procedures outlined in this SOP should be followed to document presence of sheen for the purposes of making an impairment determination. Procedural modifications may be warranted depending on equipment limitations or limitations imposed by the procedure. Substantive modification to this SOP will be noted in a project-specific Quality Assurance Project Plan (QAPP) and advance approval by the DEC Quality Assurance Officer should be requested. Deviations from the SOP will be documented in the project records and in subsequent reports. Observations will be recorded in a field log.

It should be recognized that in some cases the amount of sheen present may preclude application of all the tests described in this SOP. To address this issue, field personnel shall, after initial observation of the sheen, determine if full implementation of the process is practicable. A decision to eliminate one or more steps of the process based on this issue shall be fully documented in the field log.

## 2.0 PERSONNEL QUALIFICATIONS

Sheen identification via these methods can be a relatively involved process requiring training. It is recommended that initial sampling be supervised by more experienced personnel. Similar to the other tests, the same observers will visually rate the sample.

It is the responsibility of the field personnel to be familiar with the sheen testing procedures outlined within this SOP, a sampling and analysis plan (SAP), an approved QAPP and work plans under which the sampling/testing will be conducted. Field personnel are responsible for sheen testing of samples, decontamination of equipment, disposal of waste, and proper documentation in a field log, and/or electronic data collector.

## 3.0 HEALTH AND SAFETY

The health and safety considerations for the work associated with this SOP, including both potential physical and chemical hazards, are addressed in the site specific work plan.

Sheen differentiation testing may involve physical and/or chemical hazards associated with exposure to water, sediment, and petroleum related materials in contact with either water and/or sediment. Contact with oil and sheen should be minimized, and proper personal protective equipment should be worn throughout the sheen collection and testing.

## 4.0 EQUIPMENT AND SUPPLIES

The following equipment list contains materials that may be needed to carry out the procedures contained in this SOP:

- Nitrile gloves,
- Stick or rock,
- 8 ounce glass jar for the Jar Shake Test,
- Tetrafluorocarbonethylene-fluorocarbon polymer (Teflon®) sampling nets cut in 2.5 inch squares,
- Waterproof marker pens (Sharpie® or similar),
- Field log or electronic data collector,
- Equipment decontamination supplies, and
- Health and safety supplies.

## 5.0 METHODS

### 5.1 Stick Test

Using a stick or stone, break up the sheen. A biogenic sheen will often break into small platelets that stay separate and fail to re-coalesce, or entirely dissipate. Oil sheen will tend to swirl and quickly re-coalesce. Sheen will react differently according to the temperature. At colder or freezing temperatures, sheen may not reform as quickly as at warmer temperatures.

If sheen type is clearly evident from observations from the Stick Test, then stop. If sheen type is unclear or concurrence with oversight from United States Environmental Protection Agency or Alaska Department of Environmental Conservation, as applicable, cannot be achieved, perform the Jar Shake Test, as described below in Section 5.2.

### 5.2 Jar Shake Test

The premise of this test is that petroleum oil sheen will remain visible or shortly re-coalesce on the water surface, while biogenic sheen will disperse or dissipate. The continued presence of sheen is a positive indicator of petroleum oil sheen. The key factor in this test is to collect sheen in sufficient quantities to be observable.

Collect as much sheen as possible into a clean, 8-ounce glass jar. To collect sheen, submerge the jar lip and gently "scoop up" the sheen. Multiple scoops may be collected if needed. The surface area of sheen collected should be recorded. Carefully seal the jar, vigorously shake it, and allow the water to settle. Allow sufficient observation time (at least 30 seconds after shaking) for water to stop moving enough that potential oil sheen can re-accumulate on the surface of the water. Remove the lid and observe the condition of the surface of the water. Biogenic sheen will disperse or dissipate into the water and not re-coalesce on the surface, while oil sheen in sufficient quantities will shortly re-coalesce on the surface. If sheen type is evident from observation in this test, stop.

Observations should be made by the same observers as in the Stick Test. Note presence or absence of sheen. Jars and their contents will be discarded in accordance with approved disposal plans for oily wastes. Note results in appropriate field log.

## 5.3 Equipment Decontamination

All investigation derived waste generated from the sampling effort (e.g., gloves, disposable sampling equipment, decontamination water, etc.) shall be appropriately containerized and transported to the onsite collection area for appropriate disposal.

# 6.0 DATA AND RECORDS MANAGEMENT

The data associated with sheen differentiation will be contained within the following:

- Field logbook and/or electronic data collection,
- Field modification documentation (used prior to field work, when required), and/ or
- Nonconformance records (used after field work, when required).

During testing relevant notes will be recorded and will include the following information:

- Testing personnel,
- Type of equipment used,
- Location ID,
- General observations regarding oil/sheen on the water surface present, prior to, and during the Sheen Test,
- Color of sheen (e.g., rainbow, silver, metallic, black, etc.),
- Area of sheen collected,
- Test type and conclusion of test, and
- Concurrence by applicable oversight.

All information will be logged in the appropriate field documentation.

## 7.0 REFERENCES

ASTM D4489-95 (2006): D4489-95 (2006) Standards and Practices for Sampling of Waterborne Oils. ASTM International, 2006 Edition.

Enbridge, 2011. Enbridge Line 6B MP 608 Pipeline Release; Marshall, Michigan; Sheen Differentiation Methods – SOP. Prepared for Michigan Department of Environmental Quality. http://www.michigan.gov/documents/deq/wrd-enbridge-residual-oil-10_464696_7.pdf

Robbins and Norden, 1994. Robbins, E.I. and Nordern, A.W., 1994. Microbial oxidation of iron and manganese in wetlands and creeks of Maryland, Virginia, Delaware, and Washington, D.C. in Chiang, S.-H., ed., Pittsburgh Coal Conference Proceedings, Coal—Energy and the Environment, Volume 2, p. 1154 – 1159.