h) All wells should be clearly marked and include well name(s) or identification numbers

i) Groundwater elevation information

j) Depths and locations of any active and inactive UIC wells showing their zones of injection

k) At least one cross-section shall include construction detail for an upgradient groundwater monitoring well, and one or more downgradient monitoring wells

l) Well construction details, where available, for water supply wells located within 1,000 feet of the line(s) of cross section

m) For each protected water aquifer, indicate any available hydraulic conductivity data (in meters per second) and the source of the data (e.g., hydraulic test)

n) Any available geophysical logs (e.g., spontaneous potential, resistivity, and any porosity logs

o) Depths of low-permeability zones and the strata that contain them that will function to hydraulically isolate the protected waters or the surface from any fluids injected or produced during or following the well stimulation

p) Map legend

q) Elevation reference, preferably normalized to mean sea level elevation, with scale clearly shown

6. Information, including methods and supporting data, used for the determination of TDS in groundwater along the stratigraphic section between the water table and zone of stimulation.
7. The locations, depths, screened intervals, and justification for each existing and new groundwater monitoring well(s) shall be included in the groundwater monitoring plan, including well completion reports for existing wells.
8. If any water wells identified within 0.5 mile of individual stimulation stages are not to be used for groundwater monitoring, a technical justification for their exclusion shall be included.
9. A detailed description of the well(s) to be stimulated, and any wells within two times the ADSA for any stage, including all of the following:

    a) American Petroleum Institute (API) identification numbers

    b) Any available geophysical logs (e.g., including spontaneous potential, resistivity, and any porosity logs), and any other logs or tests that can provide information about the integrity of annular seals, including past mechanical integrity tests.

    c) Casing diagrams, including the following:

        - Depths of perforation intervals
        - Diameter and depth of borehole
        - Cement plugs inside casings, including top and bottom of cement plug, with indication of method of determination
        - Cement fill behind casings, including top and bottom of cement fill, with indication of method of determination

- Depths and names of the formations, zones, and markers penetrated by the well, including the top and bottom of the zone where well stimulation treatment will occur
- Wellbore path giving both inclination and azimuth for directionally drilled wells

10. For any geologic features within or intersecting five times the ADSA of any stage that have the potential to constitute a leakage pathway (including faults, fractures, and changes in stratigraphy), the operator shall identify the potential risk where the geologic feature may act as a conduit and impact protected water.
11. For all existing wells to be used for monitoring, the operator shall submit well construction details and any lithologic information collected during well installation.
12. For all proposed water wells that will be used for monitoring, the operator shall submit well construction details.
13. For all drinking water wells located within one mile and downgradient of the surface projection of the zone(s) of stimulation, the operator shall submit well construction details, where available.
14. A list of chemical additives and tracers anticipated to be used in the well stimulation, including:
    a) A complete list of the names, Chemical Abstract Service (CAS) numbers, and estimated concentrations, in percent by mass, of each chemical constituent of the well stimulation fluids anticipated to be used in the treatment (if a CAS number does not exist for a chemical constituent, another unique identifier may be used, if available), and
    b) Radiological components or tracers to be used during the well stimulation treatment.
15. Details regarding sampling and testing procedures to be used that are consistent with the methods outlined in Section 2.1.3.
16. Details regarding reporting procedures to be used that are consistent with the methods outlined in Section 2.1.4.
17. A contingency plan outlining actions taken by the operator in the event of a well failure or breach, consistent with applicable DOGGR well stimulation regulations, is to be included in the groundwater monitoring plan. The contingency plan shall include a conceptual framework for monitoring well locations, depths, and well construction details to detect potential impacts of a well failure or breach.
18. The proposed plan is to be signed and stamped by a California registered professional geologist or engineer.

Addendum to an Approved Groundwater Monitoring Plan

An area-specific groundwater monitoring plan applies only to the stimulation well(s) identified by the operator in its proposal and approved by Water Boards staff. Where an operator proposes to stimulate additional wells in an area that has been approved by Water Boards staff for area-specific groundwater monitoring based on these Model Criteria, the operator is required to submit an addendum to the approved area-specific groundwater monitoring plan that includes, at a minimum, the following:

1. A map of the area-specific groundwater monitoring network, including a one mile buffer zone, that shows the following:
    a) Administrative boundary of the oil field
    b) DOGGR-defined oil and gas production limits
    c) Active or inactive produced water ponds
    d) Water supply wells (public, private domestic, irrigation, and industrial)
    e) All oil and gas well(s) proposed to be stimulated
    f) Estimated extent and orientation of the planned stimulation
    g) Active, inactive, or abandoned UIC wells
    h) Proposed groundwater monitoring wells
    i) Where available, contours showing the potentiometric surface for each protected water aquifer, showing arrows indicating groundwater flow direction. The operator shall document whether the water levels were measured during pumping or non-pumping conditions
    j) Line(s) of cross section
    k) Surface features displayed on a topographic map
    l) Legend, north arrow, and bar scale
2. A detailed description of the well(s) to be stimulated, and any wells within two times the ADSA for any stage, including all of the following:
    a) API numbers
    b) Any available geophysical logs (e.g., including spontaneous potential, resistivity, and any porosity logs) and any other logs or tests that can provide information about the integrity of annular seals, including past mechanical integrity tests.
    c) Casing diagrams, including the following:
        - Depths of perforation intervals
        - Diameter and depth of borehole
        - Cement plugs inside casings, including top and bottom of cement plug, with indication of method of determination
        - Cement fill behind casings, including top and bottom of cement fill, with indication of method of determination

- Depths and names of the formations, zones, and markers penetrated by the well, including the top and bottom of the zone where well stimulation treatment will occur
- Wellbore path giving both inclination and azimuth for directionally drilled wells

2.1.3 Sampling and Testing Requirements

For area-specific groundwater monitoring, the operator shall sample the groundwater monitoring wells as follows:

- Collect samples before well stimulation. Following well stimulation, area-specific groundwater monitoring wells shall be placed on a semi-annual monitoring schedule.
- The quarter selected for semi-annual sampling shall alternate each year. For example, the first year, the operator will collect samples during the first and third quarter; the following year, samples will be collected during the second and fourth quarters.

All groundwater sampling, analytical testing, and monitoring conducted pursuant to these monitoring methods shall be done in accordance with all of the following:

1. All groundwater sampling is to be performed by a qualified person.
    a) A qualified person is any person with the knowledge and training in proper sampling methods, chain of custody, and quality assurance/quality control protocols.
    b) Any person conducting groundwater sampling, other than personnel from an approved laboratory, shall consult with the laboratory to ensure that the sampler understands and follows the proper sample collection procedures and protocols.
2. All procedures to sample groundwater monitoring wells shall be consistent with US EPA Groundwater Sampling Guidelines for Superfund and RCRA Project Managers (May 2002). All procedures to sample water supply wells shall be consistent with US EPA Science and Ecosystem Support Division Operating Procedure for Groundwater Sampling (March 2013). Alternative sampling methods may be used if approved by Water Boards staff.
3. Groundwater level and field parameters including pH, temperature, electrical conductivity, hydrogen sulfide, dissolved oxygen, and oxidation-reduction potential shall be measured and recorded before sample collection.
4. All analytical testing shall be performed by a laboratory that is certified by the State Water Board Environmental Laboratory Accreditation Program (ELAP).
5. Groundwater samples shall be analyzed for the analytes listed in Table B1 of Appendix B using current applicable U.S. EPA-approved analytical methods. Based on analytical results, the State Water Board may modify the list of required analytes.
6. If analytical results indicate potential impact(s) from a stimulation treatment (based on interpretation of baseline water quality conditions) Water Boards staff may require testing of the additional analytes listed in Table B2 of Appendix B.

7. Water Boards staff may request aquifer testing at monitoring wells if data are needed to evaluate aquifer conditions in the area of stimulated well(s).
8. All purge water, soil cuttings, debris and other investigation derived materials are to be sealed and secured in clearly and properly labeled containers and shall be properly managed (removed, and/or disposed of) in accordance with all pertinent regulatory agency requirements, including permitting.

2.1.4 Reporting Requirements

All groundwater monitoring data collected in accordance with an area-specific groundwater monitoring plan shall be compiled in a groundwater monitoring report. The groundwater monitoring report and associated water quality data shall be submitted to the State Water Board in an electronic format and uploaded to the online GeoTracker groundwater information system following the guidelines detailed in California Code of Regulations, title 23, division 3, chapter 30 (commencing with section 3890).

Data collected prior to commencement of the well stimulation treatment and public disclosures required under California Code of Regulations, title 14, section 1788, shall be submitted in the first semi-annual groundwater monitoring report.

Data collected prior to commencement of the well stimulation request for water testing required under California Code of Regulations, title 14, section 1783.3, shall be submitted in the first semi-annual groundwater monitoring report.

Semi-annual groundwater monitoring reports shall include, at a minimum:

1) Site map clearly labeling and showing the location of all oil and gas wells that have or will undergo stimulation, all groundwater monitoring and water supply wells (public, private domestic, irrigation, and industrial), sample location(s) requested for water testing required under California Code of Regulations, title 14, section 1783.3, active or inactive UIC wells, active or inactive oil and gas wells, any oil and gas wells that have been previously stimulated, and active or inactive produced water ponds:
    a) Within one mile of any vertical well(s) that underwent stimulation, or
    b) Within one mile of the surface projection of the portion of the well that underwent stimulation in directionally drilled horizontal wells.
2) Table(s) of analytical results, with both recent and historical data in chronological order and tabulated by monitoring well number or other identification.
3) Potentiometric map(s) for each protected water aquifer and at least one cross-section displaying groundwater analytical results for TDS by depth.
4) Description of field activities, including well installation, groundwater sampling, and decontamination procedures.
5) Copies of analytical laboratory reports, including quality assurance/quality control procedures and analytical test methods.
6) Well completion reports for all new water wells that will be used for monitoring.
7) A detailed description of any additional wells installed within two times the ADSA for any stage, including all of the following:
    a) American Petroleum Institute (API) identification numbers

b) Any available geophysical logs (e.g., including spontaneous potential, resistivity, and any porosity logs), and any other logs or tests that can provide information about the integrity of annular seals, including past mechanical integrity tests

c) Casing diagrams, including the following:

- Depths of perforation intervals
- Diameter and depth of borehole
- Cement plugs inside casings, including top and bottom of cement plug, with indication of method of determination
- Cement fill behind casings, including top and bottom of cement fill, with indication of method of determination
- Depths and names of the formations, zones, and markers penetrated by the well, including the top and bottom of the zone where well stimulation treatment will occur
- Wellbore path giving both inclination and azimuth for directionally drilled wells

8) Changes, if any, to the scope of work, and rationale for the changes.

9) Waste management and disposal procedures, including associated documentation, permits, manifests, and bills of lading.

10) The report is to include a detailed description, which should include at a minimum a summary of groundwater flow patterns, gradients, known velocities, and analysis and interpretation of data collected to date and any potential impacts from well stimulation activities for each monitored aquifer zone.

11) The report is to include an analysis of data collected to date and an identification of potential impacts. If potential impacts are identified, proposed actions necessary to protect water quality must be included.

12) The report is to be signed and stamped by a California registered professional geologist or engineer.

Water Boards staff will evaluate data and statistical test results to determine changes in water quality and whether additional monitoring requirements or corrective actions are necessary.

2.2 Requests for Exclusion from Area-specific Groundwater Monitoring Requirement Based on Absence of Protected Water

Area-specific groundwater monitoring related to well stimulation treatment on oil or gas wells is required, unless an operator has received written concurrence from Water Boards staff for an exclusion from the monitoring requirement (written concurrence).

Water Code section 10783 provides that groundwater monitoring is not required if the wells to be stimulated do not penetrate groundwater of beneficial use, or solely penetrate aquifers exempted under section 146.4 of title 40 of the Code of Federal Regulations.

An operator may seek written concurrence from Water Boards staff where the operator can demonstrate the absence of protected water. Written concurrence may relate to a single proposed well to be stimulated, a group of proposed wells to be stimulated, or a geographic area.

As previously stated, protected water for current and future beneficial use is defined as:

- Water with less than 10,000 mg/L TDS, and
- Outside an exempt aquifer (meeting the criteria of Code of Federal Regulations, title 40, part 146.4).

To seek written concurrence that groundwater monitoring is not required, an operator shall submit information to Water Boards staff that clearly indicates the absence of protected water in the vicinity of the well to undergo stimulation. If the technical submittal provided by the operator clearly indicates the absence of protected water, Water Boards staff will issue written concurrence. However, if future information indicates the presence of protected water, the State Water Board will reevaluate its determination. Written concurrence issued prior to the date of adoption of the Model Criteria will remain in effect unless future information indicates the presence of protected water.

Operator requests for written concurrence shall be in a defined geographic area that is generally no larger than a map section (one-square mile). To demonstrate the absence of protected water, an operator shall provide the information as outlined below (Water Boards staff may also request additional information as warranted):

1. Oil field site map clearly labeled to show the location of all oil and gas wells (with legend, north arrow, and bar scale) that have or will undergo stimulation, active or inactive UIC, oil and gas wells, active or inactive produced water ponds, all water wells (public, private domestic, irrigation, industrial, and monitoring), and all abandoned wells of any type.
2. A map of the subject area where the operator is proposing absence of protected water displaying the location (with legend, north arrow and bar scale) of the following:
    a) All oil and gas wells that have or will undergo stimulation, all UIC wells, and all active, abandoned, or inactive oil and gas wells within the subject area where the operator is proposing absence of protected water,
    b) All existing water supply wells (public, private domestic, irrigation, and industrial) and any groundwater monitoring wells within one mile of the subject area where the operator is proposing absence of protected water, and
    c) Any additional applicable information.
3. Geologic cross-sections through each well to undergo stimulation, showing the well construction details from the surface (outcrop) to total depth, depicting all geologic units, geologic structure, fluid-bearing formations, extent of oil and gas production zones, and depth to first encountered fluid for each well (oil and water). At a minimum, two cross-sections: one across the strike, one across the dip (where available, at least 5 wells per cross-section).
4. Applicable geophysical well log information, including digital copies of well logs.
5. Proposed stimulation depth(s) for each well.
6. Laboratory analysis from an ELAP certified laboratory for any water samples that demonstrate the proposed well to be stimulated does not penetrate protected waters.
7. Detailed analysis and methods used to estimate TDS concentrations using geophysical log data.
8. Any available detailed borehole logs.
9. Distance to the nearest water supply well(s).

10. Aquifer exemption documentation per Code of Federal Regulations, title 40, part 146.4, as applicable.
11. Any additional documentation and evidence that supports the operator's assertion that there are no protected waters in the area.
12. Submittal signed and stamped by California registered professional geologist or engineer.

3.0 Requirements for Designated Contractor Sampling and Testing

This section describes standards and protocols to perform property owner requested water sampling and testing as described in Public Resources Code section 3160, subdivision (d)(7). These requirements include:

- How to become a designated contractor for water sampling, and
- Water quality testing standards, protocols, and data submittal.

3.1 How to Become a Designated Contractor for Water Sampling

The State Water Board is required to designate one or more qualified independent third-party contractors (designated sampler) to perform property owner requested water quality sampling and testing. All parties interested in becoming a designated sampler shall complete and submit the "Application to be a Designated Third-Party Contractor for Property Owner Requested Water Sampling and Testing" found at the State Water Board's website. All water sampling and analytical testing conducted pursuant to this section, shall be performed by an independent third-party contractor that meets the following requirements:

1) A person representing a corporation, sole proprietorship, partnership, or any other business entity, not owned in whole or part, by the oil or gas well owner or operator, or any of their parent companies, subsidiaries or contractors, for the well stimulation project for which water sampling and analytical testing is to be performed.
2) Not an employee or contractor of the oil or gas well owner or operator, or any of their parent companies, subsidiaries or contractors, for the well stimulation project for which water sampling and analytical testing is to be performed.
3) A person with the knowledge and training in proper sampling methods, chain of custody, and quality assurance/quality control protocols.

3.2 Water Quality Testing Standards, Protocols, and Data Submittal

1) A designated sampler conducting water sampling, other than personnel from an approved laboratory, shall consult with the laboratory to ensure that the sampler understands and follows the proper sample collection and chain-of-custody procedures and protocols.
2) A designated sampler shall notify the State Water Board at least two working days prior to water sampling.
3) A designated sampler shall retain all records associated with designated contractor property owner requested water sampling for three calendar years following sampling and analytical testing, and to submit copies of these records to the State Water Board upon request.
4) All procedures to sample water supply wells shall be consistent with US EPA Science and Ecosystem Support Division Operating Procedure for Groundwater Sampling U.S. EPA (March 2013), including pre-sampling purge methods and purge volumes consistent with Detection Monitoring protocol.
5) All procedures to sample surface water shall be in accordance with the State Water Board's Surface Water Ambient Monitoring Program Quality Assurance Project Plan.
6) All analytical testing shall be performed by a laboratory that is ELAP certified.

7) All water quality data and water monitoring reports shall be submitted to the State Water Board in an electronic format that follows the guidelines detailed in California Code of Regulations, title 23, division 3, chapter 30 (commencing with section 3890).

8) Groundwater level and field parameters including pH, temperature, electrical conductivity, dissolved oxygen, and oxidation-reduction potential shall be measured and recorded before sample collection.

9) For all water sampling and analytical testing conducted pursuant to this section, water samples shall be analyzed using the analytes listed in Table B1 of Appendix B using current applicable U.S. EPA-approved analytical methods.

4.0 Regional Monitoring Program

Factors considered for the Regional Monitoring Program design include well stimulation treatments, among other events or activities that have the potential to contaminate groundwater, such as an oil and gas well failure or breach. The volume of fluid used in well stimulation activities while small compared to other oil and gas production generated fluids (e.g., water flood, wastewater disposal), still becomes part of the overall waste stream in oil production. As a result, all fluids produced or introduced in the well stimulation process will be examined in the Regional Monitoring Program including, but not limited to, produced water ponds and UIC wells.

Due to the large scale associated with the Regional Monitoring Program, it will take a considerable amount of time before an appropriate level of data is collected and the density of the groundwater monitoring well network is fully established. The program with be conducted in a phased approach, with the first phase anticipated to take approximately five years to accomplish. Details of the Regional Monitoring Program and the implementation approach are discussed in the following sections.

4.1 Interim Period – Preliminary Surveys and Pilot Studies

Since there is a lack of sufficient groundwater data and information related to oil and gas fields, State Water Board staff worked with the United State Geological Survey (USGS) to develop a conceptual model for a Regional Monitoring Program starting in 2014. Assessment of existing information, as well as collection of new information, was conducted through reconnaissance-level vulnerability assessments, and detailed characterization of two oil fields.

Reconnaissance-level vulnerability assessments were conducted at two oil fields in Kern County. The proximity of oil and gas production zones to groundwater resources in these areas was assessed. The preliminary results indicated one field had a higher number of oil and gas wells screened at similar depths or located in close proximity to screened intervals of nearby water supply wells. In contrast, the other field indicated a higher degree of separation between oil and gas wells and screened intervals of nearby water supply wells. The results from this assessment were used to inform the development of characterizing groundwater risk zones.

The USGS also evaluated TDS concentrations in three dimensions by analyzing water quality information in the Wilmington and Santa Maria Field areas. Preliminary results indicate that high TDS waters within oil and gas production zones have greater vertical separation from lower TDS groundwater in the Santa Maria Field than in the Wilmington Field. This assessment suggests oil fields that show a smaller separation between oil and gas production zones and higher quality, lower TDS groundwater, may be a higher priority for groundwater monitoring.

Accurately identifying the location of protected waters relative to current and past well stimulation, among other activities that have the potential to impact groundwater, is critical. A preliminary review identified the location of domestic water supply wells in relation to oil and gas wells, including UIC wells. This well survey identified several areas that have significant horizontal and vertical well overlap that indicates groundwater resources may be at risk (Figure 1).

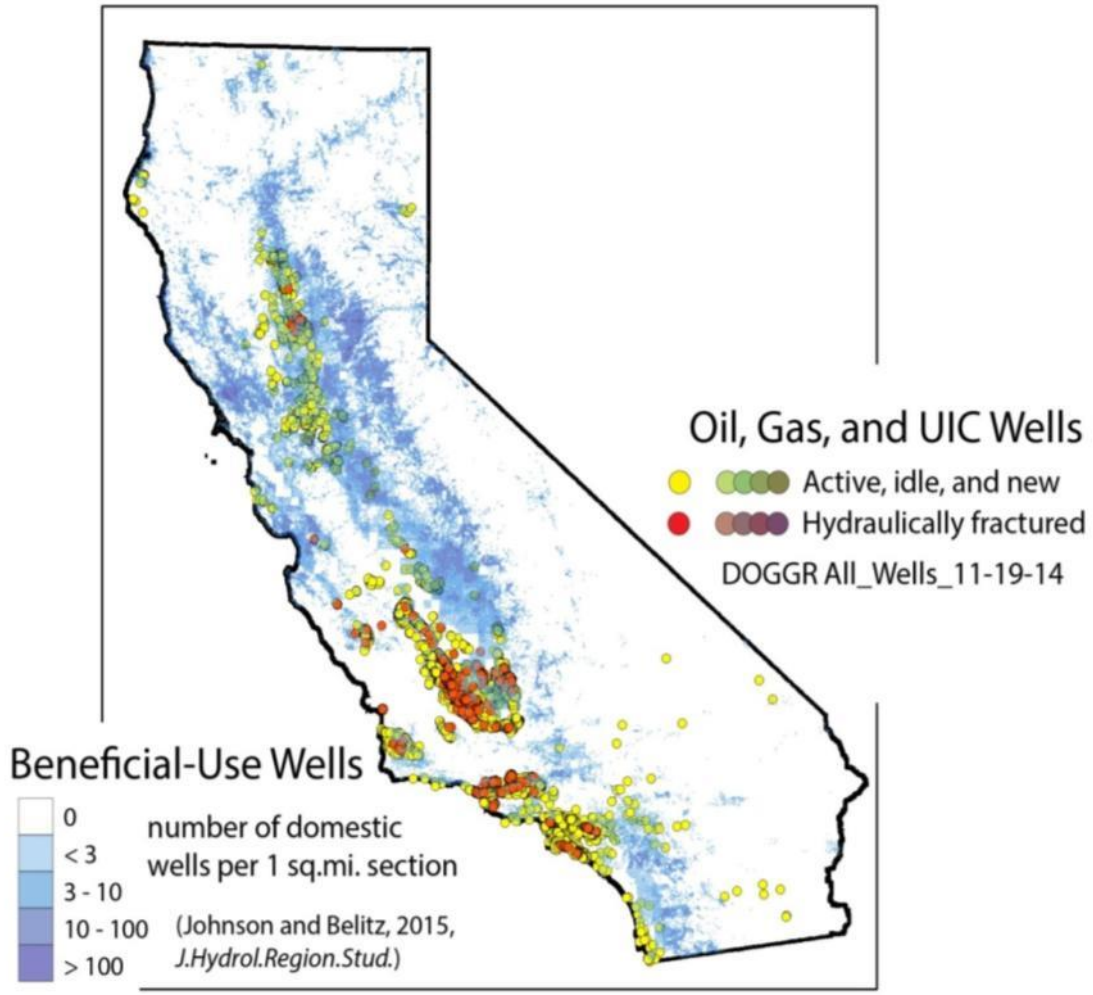

Figure 1. Comparison of Locations of Water Supply Wells (Beneficial Use Wells) and Oil, Gas, and Underground Injection Control Wells. (USGS, Johnson and Belitz, 2015)

4.2 Components of the Regional Monitoring Program

Information collected during the exploratory background surveys have been used to develop an initial approach for the Regional Monitoring Program. Three main components of the Regional Monitoring program will include:

- Characterizing and Monitoring Groundwater Risk Zone,
- Surface activity effects, and
- Well integrity.

Assessing potential water quality impacts related to these three components will help to systematically and comprehensively collect and interpret information that will support management and protection of waters designated for any beneficial use, while prioritizing the monitoring of groundwater that is or has the potential to be a source of drinking water.

Characterizing and Monitoring Groundwater Risk Zones

To identify groundwater risk zones, the Regional Monitoring Program will include the following actions:

- Characterizing the risk of any fluid related to well stimulation migrating into waters of beneficial use, while prioritizing monitoring of water that is or has the potential to be a source of drinking water, and
- Establishing monitoring networks to provide early warning in higher risk zones.

This will be achieved by mapping the extent, in three dimensions, of beneficial use water resources near oil and gas fields, and performing assessments to determine if fluids related to well stimulation, or other events or activities that have the potential to contaminate groundwater (e.g., well failure or breach), have migrated into these groundwater resources. These assessments require geochemical, hydrogeological, geological, and geophysical tools and the development of integrated conceptual models of transport potential for each oil field under investigation. Other events or activities associated with well stimulation that have the potential to contaminate groundwater may include underground injection and surface releases.

Surface Activity Effects

To assess surface activity effects, the Regional Monitoring Program will include the following actions:

- Characterizing the effect of legacy and currently regulated surface activities, including sumps and spills, and
- Characterizing risks to shallow water users from chemical constituents associated with well stimulation.

Near-surface contamination associated with well stimulation activities may pose a risk to groundwater resources, specifically shallower groundwater resources that are typically used for beneficial use such as drinking water. The State Water Board GAMA Program design applied to an area with a history of surface activities may be an appropriate approach. This component would require sampling and analyses of produced water ponds, oil and gas formation water, and groundwater under produced water ponds.

Well Integrity

The Regional Monitoring Program will also analyze potential risks to water quality from well bore integrity and inadequate seals. There is a limited amount of information regarding the age of an oil well, standards of well construction, well material degradation, improper well abandonment, and whether external forces (e.g., subsidence) correspond to well failure or breach, and groundwater degradation. Evaluation methods are best carried out after the fate and transport of fluids are determined in an oil field. This sequence will ensure that enough detailed information is available to differentiate between well integrity and other pathways for groundwater contamination.

4.3 Regional Monitoring Program Approach

The first phase of the Regional Monitoring Program will focus on identifying where vulnerable beneficial use water resources are located. Part of that effort will systematically delineate aquifer zones containing less than 3,000 mg/L TDS and between 3,000 and 10,000 mg/L TDS to help create a tiered approach for the regional monitoring.

Establishing a baseline of water quality is a critical step of the Regional Monitoring Program and likely will require years of data gathering and analysis. Establishing a vulnerability model is necessary to rank levels of relative risk to groundwater resources. Risk parameters may include, but are not limited to, oil and gas field proximity (vertically and horizontally) to beneficial use water with an emphasis on those areas used for drinking water purposes. Over the course of time, these approaches may be modified to best make use of time and resources.

The Regional Monitoring Program well network will be designed using shallow, mid-depth, and deep monitoring wells along multiple flow paths in and adjacent to a given oil field. Initially, well types to be used will rely on existing wells using depth dependent sampling techniques. New monitoring wells will be installed in areas as necessary. Options include a cluster of single wells, each screened at discrete depths in separate aquifers, or a depth-discrete multilevel monitoring system in a multiple screened well casing. For deeper zones, converting idle oil and gas production-related wells into monitoring wells will also be investigated as an alternative to installing new monitoring wells.

Due to the number and density of monitoring wells necessary to properly assess the potential effects of well stimulation treatments, it is expected that the Regional Monitoring Program well network will need to be supplemented with additional monitoring wells installed as part of an area specific groundwater monitoring plan. Water quality monitoring will also leverage the use of wells from other groundwater monitoring programs, where available, for the Regional Monitoring Program.

Monitoring wells must be constructed properly, developed, and permitted in accordance with applicable local well ordinances. If there are no applicable local well ordinances, they will be constructed in accordance with the California Well Standards. Waste management and disposal procedures, including associated documentation, permits, manifests, and bills of lading will also be documented.

4.3.1 Sampling and Testing Parameters

Regional Monitoring Program groundwater monitoring wells will be sampled frequently enough to establish baseline conditions and to detect changes in water quality. Water quality data associated with the Regional Monitoring Program will be uploaded to the online GeoTracker groundwater information system.

Groundwater sampling and analytical testing conducted pursuant to the Regional Monitoring Program will consist of the chemical constituents analyzed in samples collected for the operator area-specific monitoring and additional constituents that may be useful for identifying and understanding constituent sources and transport processes. These additional chemical constituents may include, but may not be limited to:

- Hydrocarbon gas concentrations and isotopic compositions,
- Noble gas concentrations and isotopic compositions,
- A broader suite of volatile and semi-volatile organic compounds,
- Groundwater age dating tracers,

- Isotopic compositions of water and dissolved inorganic constituents (e.g., lithium, boron, sulfur, and strontium), and
- Concentrations of additional inorganic constituents.

4.3.2 Pilot and Special Studies

Understanding of the impact of oil and gas development on groundwater resources in California and how to best monitor for potential impacts is limited. To help address these and other data gaps, focused field or pilot studies will be conducted in parallel with other activities. These focused studies are to include investigations of:

- The use of inactive oil and gas production or injection wells as monitoring wells,
- Tracking the movement (fate and transport) of chemicals associated with oil and gas production in groundwater,
- Various monitoring methods,
- Ways to define potential contamination pathways, and
- Potential risks associated with well failure or breach.

4.4 Regional Monitoring Program Review

The implementation of the Regional Monitoring Program is the first of its type in the United States. The State Water Board will periodically review data associated with well stimulation and groundwater monitoring to assure quality results and assessments. Data, information and status reports will be made publicly available on a regular basis. Formal reports on the status and findings of the Regional Monitoring Program are anticipated to be prepared on a biennial basis starting January 2018. Adjustments to the Regional Monitoring Program elements may be necessary periodically as data and information are evaluated.

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APPENDIX A

Text of Water Code Section 10783

Water Code Section 10783

(a) The Legislature finds and declares that protecting the state's groundwater for beneficial use, particularly sources and potential sources of drinking water, is of paramount concern.

(b) The Legislature further finds and declares that strategic, scientifically based groundwater monitoring of the state's oil and gas fields is critical to allaying the public's concerns regarding well stimulation treatments of oil and gas wells.

(c) On or before July 1, 2015, in order to assess the potential effects of well stimulation treatments, as defined in Article 3 (commencing with Section 3150) of Chapter 1 of Division 3 of the Public Resources Code, on the state's groundwater resources in a systematic way, the state board shall develop model groundwater monitoring criteria, to be implemented either on a well-by-well basis for a well subject to well stimulation treatment or on a regional scale. The model criteria shall address a range of spatial sampling scales from methods for conducting appropriate monitoring on individual oil and gas wells subject to a well stimulation treatment, to methods for conducting a regional groundwater monitoring program. The state board shall take into consideration the recommendations received pursuant to subdivision (d) and shall include in the model criteria, at a minimum, the components identified in subdivision (f). The state board shall prioritize monitoring of groundwater that is or has the potential to be a source of drinking water, but shall protect all waters designated for any beneficial use.

(d) The state board, in consultation with the Department of Conservation, Division of Oil, Gas, and Geothermal Resources, shall seek the advice of experts on the design of the model groundwater monitoring criteria. The experts shall assess and make recommendations to the state board on the model criteria. These recommendations shall prioritize implementation of regional groundwater monitoring programs statewide, as warranted, based upon the prevalence of well stimulation treatments of oil and gas wells and groundwater suitable as a source of drinking water.

(e) The state board shall also seek the advice of stakeholders representing the diverse interests of the oil- and gas-producing areas of the state. The stakeholders shall include the oil and gas industry, agriculture, environmental justice, and local government, among others, with regional representation commensurate with the intensity of oil and gas development in that area. The stakeholders shall also make recommendations to the state board regarding the development and implementation of groundwater monitoring criteria, including priority locations for implementation.

(f) The scope and nature of the model groundwater monitoring criteria shall include the determination of all of the following:

(1) An assessment of the areas to conduct groundwater quality monitoring and their appropriate boundaries.

(2) A list of the constituents to measure and assess water quality.

(3) The location, depth, and number of monitoring wells necessary to detect groundwater contamination at spatial scales ranging from an individual oil and gas well to a regional groundwater basin including one or more oil and gas fields.

(4) The frequency and duration of the monitoring.

(5) A threshold criteria indicating a transition from well-by-well monitoring to a regional monitoring program.

(6) Data collection and reporting protocols.

(7) Public access to the collected data under paragraph (6).

(g) Factors to consider in addressing subdivision (f) shall include, but are not limited to, all of the following:

(1) The existing quality and existing and potential use of the groundwater.

(2) Groundwater that is not a source of drinking water consistent with the United States Environmental Protection Agency's definition of an Underground Source of Drinking Water as containing less than 10,000 milligrams per liter total dissolved solids in groundwater (40 C.F.R. 144.3), including exempt aquifers pursuant to Section 146.4 of Title 40 of the Code of Federal Regulations.

(3) Proximity to human population, public water service wells, and private groundwater use, if known.

(4) The presence of existing oil and gas production fields, including the distribution, physical attributes, and operational status of oil and gas wells therein.

(5) Events, including well stimulation treatments and oil and gas well failures, among others, that have the potential to contaminate groundwater, appropriate monitoring to evaluate whether groundwater contamination can be attributable to a particular event, and any monitoring changes necessary if groundwater contamination is observed.

(h) (1) On or before January 1, 2016, the state board or appropriate regional board shall begin implementation of the regional groundwater monitoring programs based upon the model criteria developed under subdivision (c).

(2) In the absence of state implementation of a regional groundwater monitoring program, a well owner or operator may develop and implement an area-specific groundwater monitoring program, for the purpose of subparagraph (D) of paragraph (3) of subdivision (d) of Section 3160 of the Public Resources Code, based upon the model criteria developed under subdivision (c), subject to approval by the state or regional board, and that meets the requirements of this section.

(i) The model criteria for either a well-by-well basis for a well subject to well stimulation treatment, or for a regional groundwater monitoring program, shall be used to satisfy the permitting requirements for well stimulation treatments on oil and gas wells pursuant to Section 3160 of the Public Resources Code. The model criteria used on a well-by-well basis for a well subject to a well stimulation treatment shall be used where no regional groundwater monitoring plan approved by the state or regional board, if applicable, exists and has been implemented by either the state or regional board or the well owner or operator.

(j) The model criteria shall accommodate monitoring where surface access is limited. Monitoring is not required for oil and gas wells where the wells do not penetrate groundwater of beneficial use, as determined by a regional water quality control board, or solely penetrate exempt aquifers pursuant to Section 146.4 of Title 40 of the Code of Federal Regulations.

(k) (1) The model criteria and groundwater monitoring programs shall be reviewed and updated periodically, as needed.

(2) The use of the United States Environmental Protection Agency's definition of an Underground Source of Drinking Water as containing less than 10,000 milligrams per liter total dissolved solids in groundwater (40 C.F.R. 144.3) and whether exempt aquifers pursuant to Section 146.4 of Title 40 of the Code of Federal Regulations shall be subject to groundwater monitoring shall be reviewed by the state board through a public process on or before January 1, 2020.

(l) (1) All groundwater quality data collected pursuant to subparagraph (F) of paragraph (1) of subdivision (d) of Section 3160 of the Public Resources Code shall be submitted to the state board in an electronic format that is compatible with the state board's GeoTracker database, following the guidelines detailed in Chapter 30 (commencing with Section 3890) of Division 3 of Title 23 of the California Code of Regulations.

(2) A copy of the reported data under paragraph (1) shall be transferred by the state board to a public, nonprofit doctoral-degree-granting educational institution located in the San Joaquin Valley, administered pursuant to Section 9 of Article IX of the California Constitution, in order to form the basis of a comprehensive groundwater quality data repository to promote research, foster interinstitutional collaboration, and seek understanding of the numerous factors influencing the state's groundwater.

(m) The adoption of criteria required pursuant to this section is exempt from the rulemaking provisions of the Administrative Procedure Act (Chapter 3.5 (commencing with Section 11340) of Part 1 of Division 3 of Title 2 of the Government Code). The adoption of criteria pursuant to this section shall instead be accomplished by means of a public process reasonably calculated to give those persons interested in their adoption an opportunity to be heard.

APPENDIX B

List of Required Analytes

Tables B1 and B2

Table B1 – List of Required Analytes for Area-specific and Designated Contractor Water Sampling

Analyte	Area-Specific	Designated Contractor
Total dissolved solids (TDS)	x	x
Major and minor cations, including sodium, potassium, magnesium, calcium, and ammonium	x	x
Major and minor anions, including nitrate, chloride, fluoride, sulfate, bromide, iodide, and total inorganic carbonate (bicarbonate + carbonate)	x	x
Trace elements, including iron, manganese, lithium, strontium, barium, and boron	x	x
All metals and metalloids listed in California Code of Regulations, title 22, section 66261.24, subdivision (a)(2)(A), including arsenic, barium, cadmium, chromium, lead mercury, and selenium (excluded from the Title 22 list are asbestos and fluoride salts)	x	x
Radionuclides listed under California Code of Regulations, title 22, Table 64442 (includes Ra-226, Ra-228, and uranium)	x	x
Methane, ethane, propane	x	x
Dissolved organic carbon (DOC)	x	x
BTEX (benzene, toluene, ethylbenzene, and xylenes) and tentatively identified compounds (TICs)	x	x
Trimethylbenzene, acetone, methylene chloride	x	x
Total petroleum hydrocarbons for crude oil, gasoline, and diesel ranges	x	x
PAH (polynuclear aromatic hydrocarbons) including the 16 priority pollutant PAHs (acenaphthene, acenaphthylene, anthracene, benz[*a*]anthracene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, benzo[*ghi*]perylene, chrysene, dibenzo[*a,h*]anthracene, fluoranthene, fluorene, indeno[1,2,3-*cd*]pyrene, naphthalene, phenanthrene, and pyrene) and (TICs)	x	x
Stable carbon isotopes in dissolved methane (if present)	x	
Stable isotopes of oxygen and hydrogen in water	x	
Guar gum sugars (if guar gum is used in the well stimulation)	x	
At least two additional analytes selected by the operator, to be reviewed by Water Boards staff. The analytes chosen shall be well stimulation chemical additives or their degradation products. One chemical constituent shall be chosen based on large soluble mass used during well stimulation; the other chemical constituent will be chosen based on high persistence in the subsurface. Availability of a laboratory analytical method shall also be considered. For instance, if there are several chemical constituents of high persistence, then the constituent with a combination of greatest injected mass and persistence shall be monitored, if there is an accepted laboratory analytical method available.	x	

Note: Analytes are to be tested using available EPA-approved analytical methods, using drinking water detection limits.

Table B2 - Additional Analytes for Area-specific Sampling That May Be Required

Cationic, anionic, and nonionic surfactants used during well stimulation
Alcohols and glycols used during well stimulation
Biocides used during well stimulation, including any of the following compounds and their known harmful or persistent degradation products: – Glutaraldehyde, – DBNPA (2,2-dibromo-3-nitrilopropionamide) and its degradation products dibromoacetonitrile, dibromoacetic acid, and dibromoacetamide, and – Isothiazolinones (e.g., 2-methyl-3-isothiazolinone, 5-chloro-2-methyl-3-isothiazolinone).
Tracers used during well stimulation

Note: Analytes are to be tested using available EPA-approved analytical methods, using drinking water detection limits.

PERMITTING REQUIREMENTS ASSOCIATED WITH OFF-CHANNEL CONTAINMENT PITS

October 12, 2002

Background

This document was developed as an interagency cooperative effort to provide guidance to the CBM industry on the permitting requirements associated with the development and construction of off-channel reservoirs, ponds or pits. This guidance is applicable to any man-made reservoirs, ponds or pits created to contain CBM discharge water that are located in upland areas outside of natural waterways. This guidance is not applicable to reservoirs and ponds constructed within the channels of natural waterways. This document is also intended to implement a companion document titled Off-Channel, Unlined CBM Produced Water Pit Siting Guidelines for the Powder River Basin, attached hereto. Representatives of the Wyoming Department of Environmental Quality (DEQ), the Wyoming Oil and Gas Conservation Commission (WOGCC), the Bureau of Land Management (BLM) and the Office of the State Engineer (SEO) jointly developed these recommendations. These guidelines were heard and approved by the DEQ Water and Waste Advisory Board on October 1, 2002.

Purpose

This document will briefly describe the permitting requirements of four separate regulatory entities that have some level of jurisdiction over the discharge to and the construction of off-channel containment pits. These structures, referred to as "pits" in this document may also be called ponds, containment units, or reservoirs by the SEO and DEQ.

Wyoming DEQ Permitting Requirements

1. If there are designated uses of the water discharge to or contained in the off-channel containment pit, an NPDES discharge permit must be obtained before discharge begins. This permit authorizes the discharge and ensures the quality of the discharge will protect the designated uses and other waters of the state. Designated uses may include livestock watering, wildlife use, irrigation, etc. The NPDES permit is not for the construction of the off-channel containment pit, although the permit limits rely on the discharge water being fully contained in the containment pit and not entering other surface waters of the state. The discharge can be authorized through a general permit created specifically for this unique type of discharge or through an individual permit which is site-specific. Authorization under the general permit should take less than 45 days for approval, while an individual permit may take 60 to 90 days for approval. These ponds must be designed and constructed so that there is no direct subsurface hydrologic connection to other surface waters of the state.

2. If there is a threat that the containment pit may degrade higher quality groundwater aquifers, DEQ may require a Chapter 3 construction permit. Generally, however, DEQ will rely on the WOGCC and BLM siting and permitting requirements to ensure that groundwater resources are adequately protected. See the later discussions under WOGCC and BLM and the attached Off-channel, Unlined CBM Produced Water Pit Siting Guideline for the Powder River Basin document.

Wyoming SEO Permitting Requirements

1. If there are beneficial uses of the water contained in the off-channel containment pit, a reservoir permit is required from the State Engineer's Office before construction of the off-channel containment pit begins. Beneficial uses can include inactive uses such as stock, wildlife, and/or wetlands and/or active uses such as land application, leach fields, irrigation, and/or dust abatement.

2. If the reservoir/pit is constructed with an embankment which is 20 feet or higher or more than 50 acre-feet will be stored against a man-made embankment, then safety-of-dams requirements may apply.

Wyoming Oil and Gas Commission Permitting Requirements

1. Form 14A must be submitted and approved prior to construction of off-channel produced water pits built on fee or state leases. The Supervisor may request information in addition to what is required on Form 14A. Pits proposed to be constructed in the Powder River Basin for percolation of water produced in association with recovery of coalbed methane gas into shallow sands or aquifers may be considered if the applicant can demonstrate their operation will comply with water quality standards of the DEQ. A siting guideline for off-channel, unlined CBM produced water pits has been drafted to assist operators. Approval for pit construction is handled administratively and Commission staff routinely pre-sites pit locations prior to taking action on applications.

2. The Commission may require a bond from the owner/operator of a pit conditioned for the workmanlike operation of the pit and that its closure be done in accordance with the agency's rules. Separate bonding amounts for the pits are set by the Supervisor following evaluation of site-specific conditions and circumstances. The owner/operator should provide a written cost estimate prepared by a Wyoming registered professional engineer with expertise in surface pit remediation for closure of the pit and reclamation of the surface and access areas closely adjacent to the pit. The surface landowner must receive a copy of the cost estimate from the owner/operator.

   Because the produced water retention pits used by the methane industry in the Powder River Basin may be of use to the landowner, the Supervisor may waive bonding and allow such pits

to remain open after the cessation of production. In this instance, a notarized statement of acceptance signed by the landowner must accompany the Form 14A when it is submitted to the agency. Specifics of that letter of acceptance are included in Chapter 3, Section 4.

Bureau of Land Management Approval Requirements

1. The Bureau of Land Management (BLM) Buffalo Field Office will approve, bond, inspect, and enforce compliance on all off-channel pits resulting from a federal action for the discharge of produced water from a CBM well into these containment structures. The off-channel pits must meet the attached siting criteria and BLM's guidance as referenced in BLM's updated Coal Bed Methane Well APD and POD Preparation Guide Book.

2. Information required in the application for an off-channel pit approval, includes but is not limited to, a representative onsite standard water analysis (DEQ'S NPDES analytical suite) for CBM produced water, size of containment pit, freeboard capacity, method of disposal of produced fluids (i.e., land application, etc.), maximum fluid level above cut (native soil) on downgradient side, % compaction, slope of inside and outside face of berm/dam, distance to nearest drainage, soil characteristics, and depth to shallow groundwater (with collection of shallow groundwater sample during subsurface investigation). The subsurface investigation will provide adequate information to insure that the shallow aquifer will not be degraded below its existing class of use and that infiltration will be primarily downward and not migrate laterally entering "surface waters of the state". Off-channel pits are designed to be full containment with water loss only to infiltration and evaporation, which precludes the use of a drop-pipe or spillway.

Recommended Permitting Process

The following figure is a decision tree to help the reader understand which permits must be obtained based upon site-specific conditions. It is recommended that the operator first obtain the authorization for construction of the off-channel pit before obtaining the NPDES permit, so that when the operator seeks the DEQ discharge permit, he can be confident that the siting of the off-channel pit is acceptable.

Dennis Stenger, BLM

Date: 10/15/02

Dennis Hemmer, DEQ

Date: 10-22-02

Don Likwartz, WOGCC

Date: 10-16-02

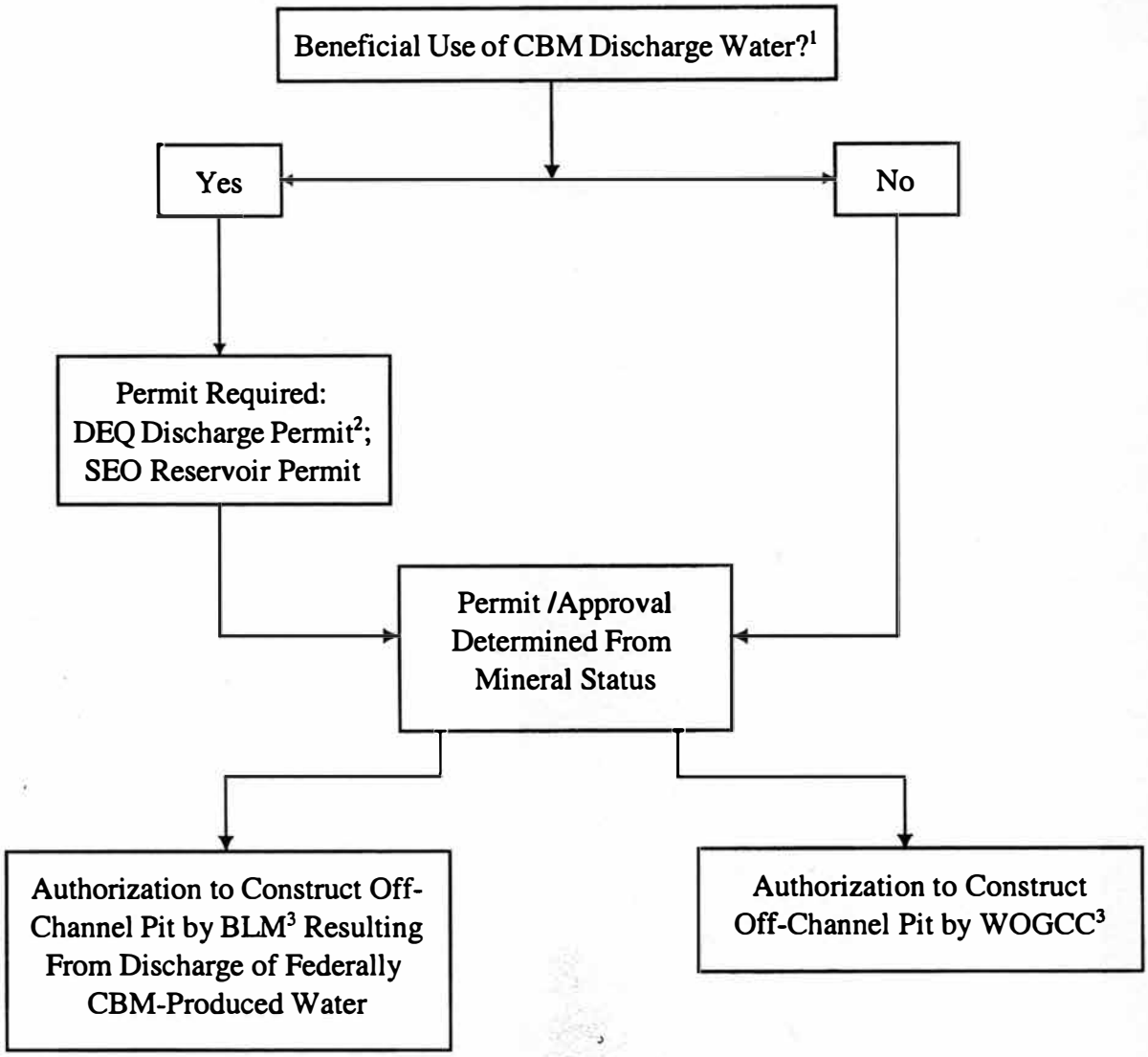
Pat Tyrrell, SEO

Date: 10-17-02

Attachment, Off-channel, Unlined Produced Water CBM Pit Siting Guideline for the Powder River Basin, August 16, 2002.

/pjb
2-2489-doc

Figure 1
CBM OFF-CHANNEL CONTAINMENT / INFILTRATION PITS
PERMITTING DECISION TREE



1 Will CBM water in the containment pit be used for livestock watering, wildlife, irrigation or other beneficial uses?

2 May be authorized through General Permit for discharges to off-channel containment pits.

3 May request DEQ to review proposed location if there are questions concerning potential for adverse impacts to the groundwater.

Wyoming Department of Environmental Quality
CBM Permitting Guideline for Discharges to Irrigated Drainages of the Powder River Basin

May 2011

Scope:

The permitting requirements below apply to drainages with existing irrigation uses, located within the structural Powder River Basin of Wyoming, including the hydrologic basins of the Tongue, Powder and Little Powder Rivers. Existing irrigation uses are defined by WDEQ as follows:

Artificially Irrigated Lands: Artificially irrigated lands are those where water is intentionally applied for agricultural purposes. Artificially irrigated lands will be identified by the presence of canals, ditches, spreader dikes, spray irrigation systems or any other constructed mechanism intended to divert water from a stream channel for application on adjacent lands.

Naturally Irrigated Lands: Naturally irrigated lands are areas of land along stream channels that have enhanced vegetative production due to periodic natural flooding or sub-irrigation. Naturally irrigated lands are those lands where a stream channel is underlain by unconsolidated material and on which the combination of stream flow and channel geometry provides for enhanced productivity of agriculturally significant plants. Naturally irrigated lands may be identified by an evaluation of infra-red aerial photography, surficial geologic maps, wetland mapping, landowner testimony or any combination of that information. For permitting purposes, naturally irrigated lands are subject to water quality protection when they total 20 acres or more within a drainage, and are generally at least 50 feet wide.

General Requirements For Irrigation Protection:

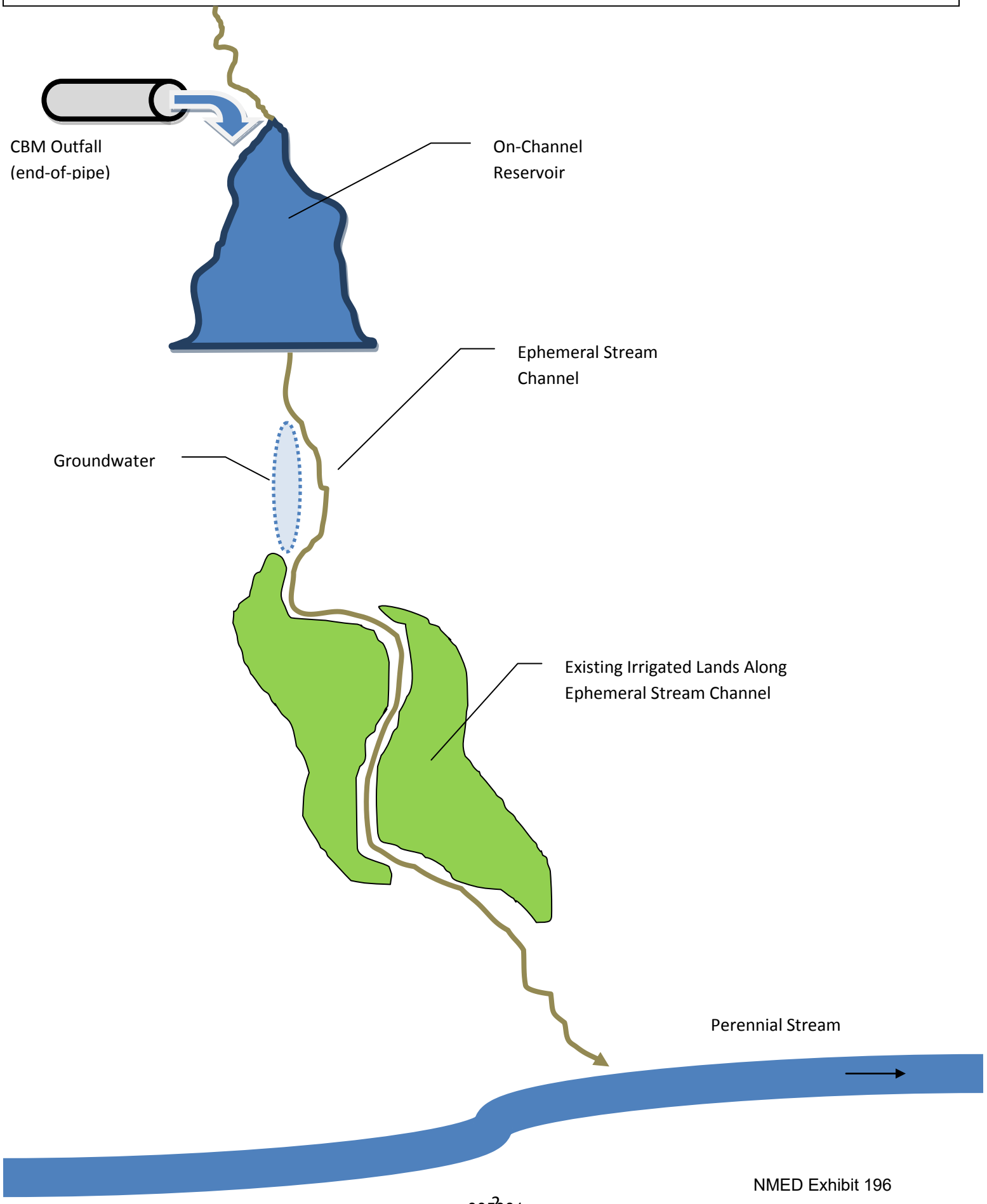
Planning: Prior to issuing new or renewed CBM discharge permits within an irrigated drainage area, WDEQ will confer with the permittees and affected landowners to select accessible long-term monitoring sites. Affected landowners will be those landowners who own or control irrigated acreage (as defined above), located downstream of CBM discharges.

Ongoing Review: Permittees will be required to meet the conditions outlined below. WDEQ will assess collected data annually. Upon review, adjustments may be made to permit conditions as necessary, including monitoring and reporting requirements, effluent limits and water management, in order to ensure that the permits remain adequately protective of the downstream irrigation uses.

Basic CBM permitting scenarios within the Powder River Basin:

See below.

Scenario 1: Discharge to On-Channel Reservoir; Above Irrigated Lands on Ephemeral Stream



NMED Exhibit 196

Scenario 1: Permit Requirements

Outfall: 

Monitoring: For first twelve months, monthly sampling for Electrical Conductivity (EC), sodium adsorption ratio (SAR), pH, bicarbonate (HCO_3), flow. Quarterly sampling thereafter if constituents are below threshold levels.

Threshold: Effluent limits to protect livestock and wildlife. EC = 7500 micromhos/cm, pH = 6.5 – 9.0. Plus effluent limits for protection of downstream class 3 and class 2 waters.

Corrective Action (If threshold exceeded): WDEQ enforcement action.

Reservoir: 

Monitoring: For first twelve months, monthly sampling for EC, SAR, pH, bicarbonate , sulfates (SO_4). Quarterly sampling thereafter if constituents are below threshold levels. Sample at least 5 feet from shoreline and at least 50 feet from CBM inlet. On select reservoirs, install staff gage. Monthly measurement of water elevation and stored volume within those reservoirs. Water volume data to be used for detailed water budgets within each drainage. Check for water re-surfacing below reservoir (flowing seeps).

Threshold: Flowing seep visible. Excessive salt build-up within reservoir = reservoir EC at 150% of average outfall EC or higher. Water release permitted if EC meets default crop threshold (USDA soil EC threshold / 1.5), and SAR meets Hanson 2006 formula. Additional SAR restrictions may apply if irrigated lands contain smectitic clays (clay fraction is 50% or greater smectite content).

Corrective Action (If threshold exceeded): If flowing seep appears below reservoir, then cease discharge at outfall, repair or close reservoir. If reservoir EC reaches or exceeds 150% of average outfall EC, then cease discharge and modify permit to eliminate outfall or require 50-year containment in reservoir.

Scenario 1: Permit Requirements (continued)

Ephemeral Channel: 

Monitoring: Locate surface water monitoring stations below each reservoir series and near irrigated lands. Monitor flow daily near irrigated lands. Monthly flow measurements at stations higher in the watershed. At all flowing stations, sample monthly for pH, EC, Ca, Mg, Na, K, SO_4, HCO_3, carbon isotopes.

Threshold: N/A

Corrective Action (If threshold exceeded): N/A

Groundwater: 

Leakage From Ponds:

Site Selection: Selective reservoir sampling, prioritize by highest risk (evaluate proximity of reservoir to fields, size of reservoir, underlying geology).

Monitoring: Monthly static water level year-round. Monthly water quality sampling during May, June July; Quarterly the rest of the year. Always sample and analyze for pH, EC, Ca, Mg, Na. Additional sampling for K, SO_4, HCO_3, Cl, carbon isotopes if under intensified monitoring. Groundwater monitoring wells subject to WDEQ guideline specifications for siting, installation, instrumentation, sampling and reporting.

Threshold: Evidence of lateral migration into stream channels, with groundwater flow toward irrigated fields.

Corrective Action (If threshold exceeded): Initiate continuous water level monitoring, using pressure transducer. Investigate source of groundwater flow, using intensified groundwater monitoring. Add monitoring wells if necessary; increase water quality sampling frequency if necessary. If CBM water is contributing to problematic groundwater elevations in downstream irrigated fields (see below), cease discharges from contributing outfalls.

Scenario 1: Permit Requirements (continued)

Shallow Groundwater Near Fields:

Monitoring: Quarterly static water level year-round. At least one continuous water level monitoring station per site, using pressure transducer. Quarterly water quality sampling. Always sample and analyze for pH, EC, Ca, Mg, Na. Additional sampling for K, SO_4, HCO_3, Cl, carbon isotopes if under intensified monitoring. Groundwater monitoring wells subject to WDEQ guideline specifications for siting, installation, instrumentation, sampling and reporting.

Threshold: First threshold = depth to groundwater less than 6 feet. Second threshold = depth to groundwater less than 3 feet.

Corrective Action (If threshold exceeded): If first threshold is triggered (depth to groundwater less than 6 feet), then investigation is needed to detect cause and corrective action. Evaluate upstream monitoring well data, intensify sampling in upstream monitoring wells and irrigated field monitoring wells, evaluate surface hydrology conditions in fields. If second threshold is triggered (depth to groundwater less than 3 feet), and the groundwater has a CBM water contribution, then cease contributing discharges.

Soils: 

Site Selection: Segment fields according to differences in soil characteristics or depth to groundwater. Look for distinct differences in EC (if using ground-based electromagnetic survey), texture, pH or vegetation. For each identified segment, minimum of one subsample per acre, but not less than 5 and not more than 15 subsamples per segment.

Monitoring (initial): 4 feet deep in grass fields. 6 feet deep if alfalfa present. Increments = 0-6", 6-12", then 12" each to depth. **Analyze for texture, clay mineralogy, exchangeable sodium percent (ESP), pH, EC, SAR, SO_4, HCO_3, lime, organic carbon (OC), N, P, K.** Composite within each identified soil segment, using co-located composited samples. On initial sampling, do not composite analysis for EC and pH. Analyze EC and pH on each individual subsample before compositing subsamples to run other analytes.

Monitoring (ongoing): 4 feet deep in grass fields. 6 feet deep if alfalfa present. Increments = 0-6", 6-12", then 12" each to depth. **Analyze for pH, EC, SAR, SO_4, HCO_3, chlorides (Cl).** Composite within each identified soil segment, using co-located composited samples. Annual fall sampling.

Scenario 1: Permit Requirements (continued)

Threshold: Greater than 40% increase in EC or SAR in one year, or greater than 15% over two years or more. Regardless of trend, ESP greater than 10% or EC greater than 4,000 micromhos/cm at 0 -12" triggers corrective action below.

Corrective Action (If threshold exceeded): If any of the above thresholds is triggered, increase soil monitoring to twice per year (spring / fall). Initiate detailed study to identify cause of salt / sodium increase. If damage to soil is identified that is expected to impair crop / forage production, and damage is due to CBM discharges, then proceed with one or more of: curtailing contributing CBM discharges, changing discharge locations, providing improved drainage to fields, adding chemical amendments to fields.

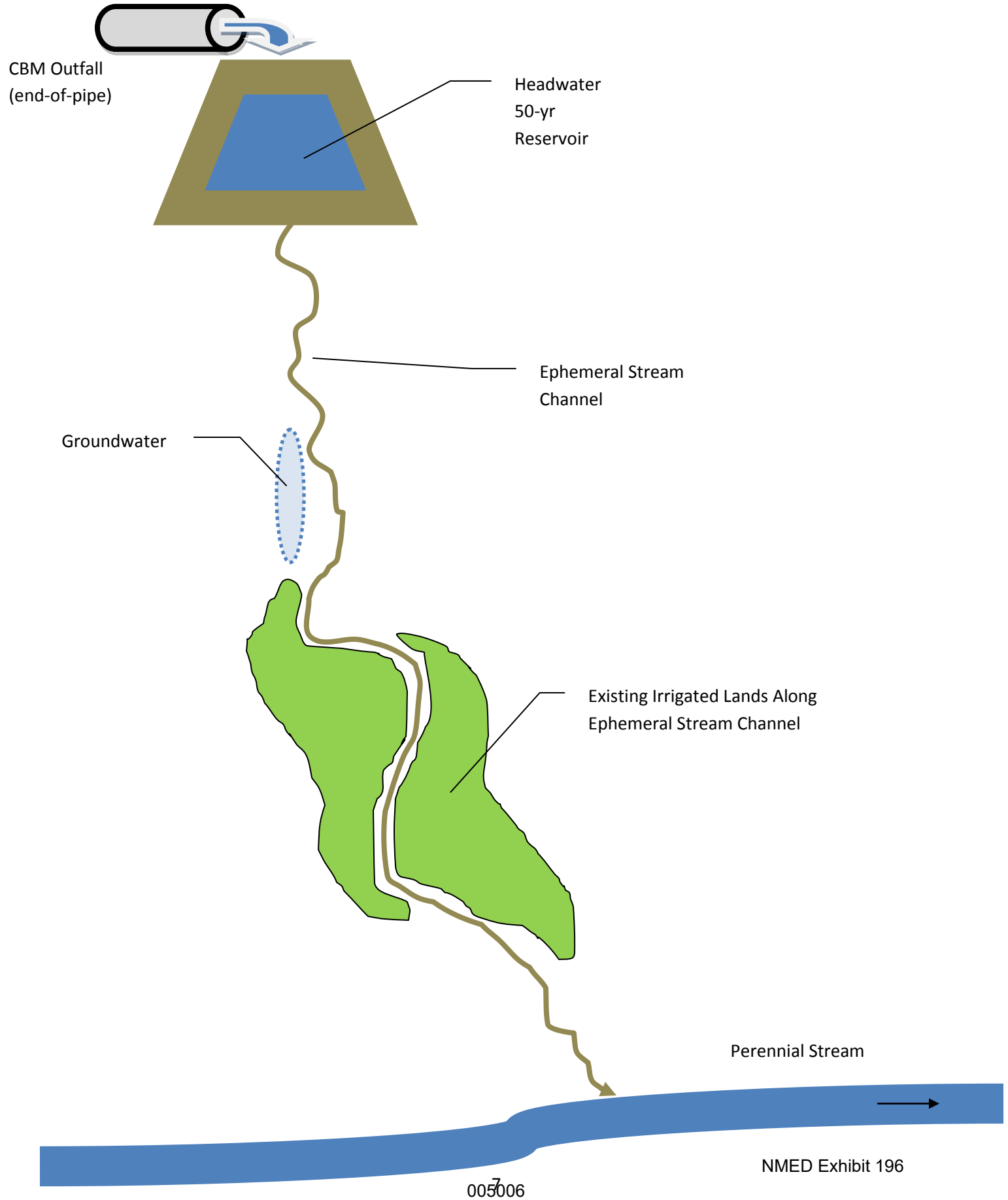
Crops / Forage: 

Monitoring: Vegetation sampling to occur in same areas as soil sampling. One square meter sample cuttings. Sample annual peak standing crop (late June – early July) or pre-cutting for hayed fields. Measure annually: yield (tons/acre), crude protein (CP), Ca, P, K; plus Selenium bi-annually. Can use field harvest data for hay yield if available.

Threshold: Statistically significant decrease in yield or quality that correlates with causative mechanism such as soil water or groundwater impacts.

Corrective Action (If threshold exceeded): Reclamation of any damaged fields.

Scenario 2: Discharge to Headwater 50-yr Reservoir; Above Irrigated Lands on Ephemeral Stream



Scenario 2: Permit Requirements

Outfall: 

Monitoring: Annual sampling for Electrical Conductivity (EC), sodium adsorption ratio (SAR), pH, bicarbonate (HCO_3), flow.

Threshold: Effluent limits to protect livestock and wildlife. EC = 7500 micromhos/cm, pH = 6.5 – 9.0. Plus effluent limits for protection of localized class 3 stream as needed.

Corrective Action (If threshold exceeded): WDEQ enforcement action.

Headwater 50-yr Reservoir: 

Monitoring: For first twelve months, monthly sampling for EC, SAR, pH, bicarbonate , sulfates (SO_4). Quarterly sampling thereafter if constituents are below threshold levels. Sample at least 5 feet from shoreline and at least 50 feet from CBM inlet. Install staff gage within all 50-yr reservoirs. Monthly measurement of water elevation and stored volume within the reservoirs. Water volume data to be used for detailed water budgets within each drainage. Check for water re-surfacing below reservoir (flowing seeps).

Threshold: Flowing seep visible below reservoir.

Corrective Action (If threshold exceeded): If flowing seep appears below reservoir, then cease discharge at outfall, repair or close reservoir.

Scenario 2: Permit Requirements (continued)

Groundwater: 

Leakage From Ponds:

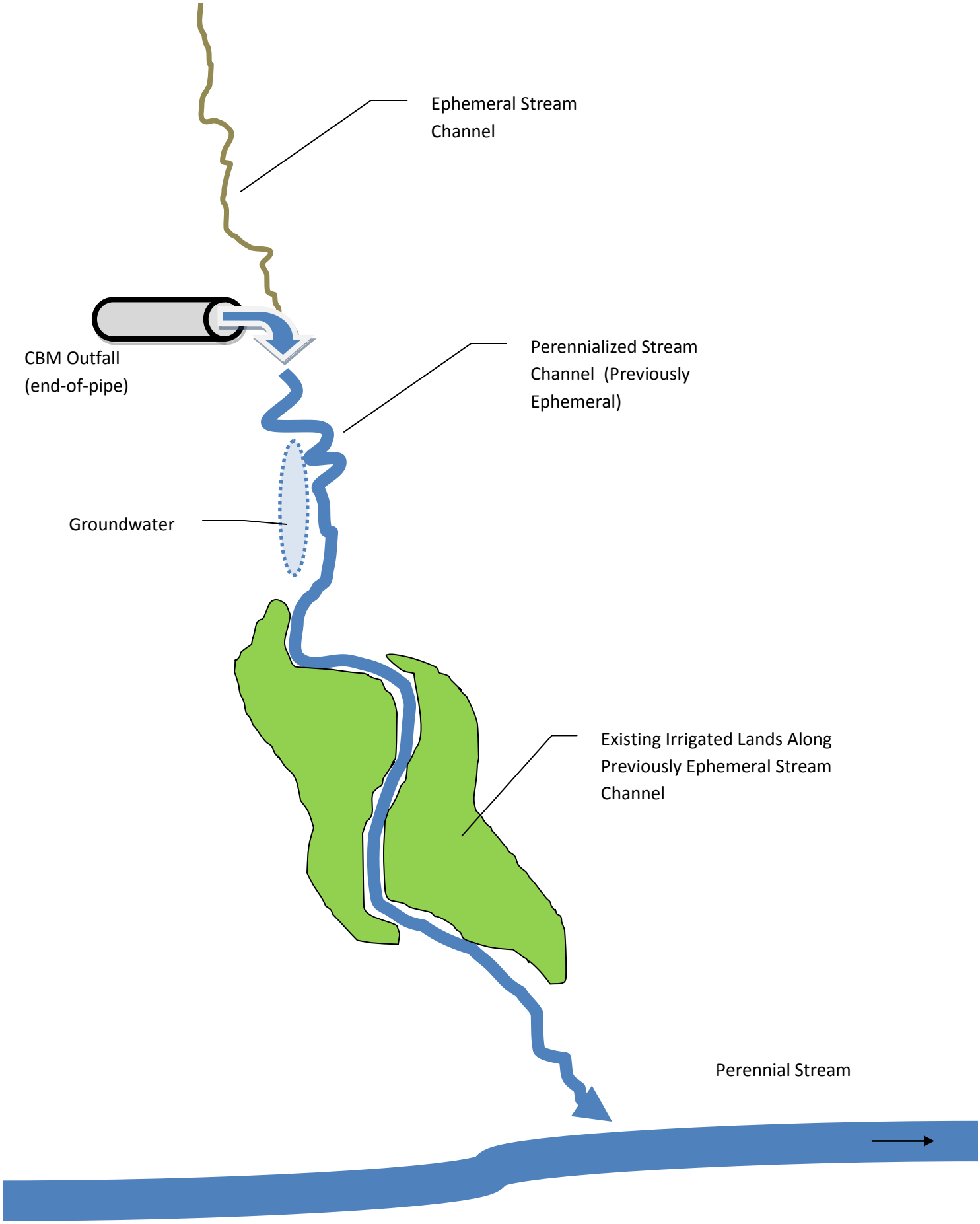
Site Selection: Selective reservoir sampling, prioritize by highest risk (evaluate proximity of reservoir to fields, size of reservoir, underlying geology).

Monitoring: Monthly static water level year-round. Monthly water quality sampling during May, June July; Quarterly the rest of the year. Always sample and analyze for pH, EC, Ca, Mg, Na. Additional sampling for K, SO_4, HCO_3, Cl, carbon isotopes if under intensified monitoring. Groundwater monitoring wells subject to WDEQ guideline specifications for siting, installation, instrumentation, sampling and reporting.

Threshold: Evidence of lateral migration into stream channels, with groundwater flow toward irrigated fields.

Corrective Action (If threshold exceeded): Initiate continuous water level monitoring, using pressure transducer. Investigate source of groundwater flow, using intensified groundwater monitoring. Add monitoring wells if necessary; increase water quality sampling frequency if necessary. If CBM water is contributing to problematic groundwater elevations in downstream irrigated fields, cease discharges from contributing outfalls.

Scenario 3: Direct Discharge; Ephemeral Stream Becomes Perennialized



NMED Exhibit 196

Scenario 3: Permit Requirements

Outfall: 

Monitoring: For first twelve months, monthly sampling for Electrical Conductivity (EC), sodium adsorption ratio (SAR), pH, bicarbonate (HCO_3), flow. Quarterly sampling thereafter if constituents are below threshold levels. Continuous flow measurement.

Threshold: Default EC effluent limit for protection of downstream crop; EC limit to be derived from USDA salt tolerance database thresholds. EC limit will be calculated by dividing the published soil EC threshold value by 1.5. Where the published soil EC threshold is presented as a range of values, the median value of the range will serve as the published soil EC threshold. Limit SAR to < 6.67 x EC (dS/m) – 3.33, where EC = actual measured EC of the sample. Limit SAR to a value between 3 and 10. Under circumstances where smectitic soils are present in the downstream irrigated lands (clay fraction is 50% smectite or greater), then additional restrictions may apply on SAR. EC and SAR effluent limits at outfall are subject to modification based upon results of downstream surface water monitoring. Limit discharge quantity to prevent inadvertent flooding of fields.

Corrective Action (If threshold exceeded): WDEQ enforcement action for exceedence of EC or SAR limits. Curtail direct discharge quantity if current discharges are causing inadvertent flooding of downstream fields.

Perennialized Stream Channel

(Previously Ephemeral): 

Monitoring: Locate surface water monitoring stations below outfall and near irrigated lands. Measure flow continuously near irrigated lands. Monthly flow at stations higher in the watershed. At all stations, sample monthly for pH, EC, Ca, Mg, Na, K, SO_4, HCO_3, carbon isotopes.

Threshold: Instream threshold for EC to protect downstream crop; Instream EC threshold to be derived from background EC (where known), or USDA salt tolerance database thresholds. When using USDA salt tolerance values, instream EC threshold will be calculated by dividing the published soil EC threshold value by 1.5. Where the published soil EC threshold is presented as a range of values, the median value of the range will serve as the published soil EC threshold. Limit SAR to < 6.67 x EC (dS/m) – 3.33, where EC = actual measured EC of the sample. Set instream SAR threshold between 3 and 10. Under circumstances where smectitic soils are present in the downstream irrigated lands (clay fraction is 50% smectite or greater), then

additional restrictions may apply on SAR. Limit discharge quantity to prevent inadvertent flooding of fields.

Corrective Action (If threshold exceeded): If instream EC or SAR threshold is exceeded over multiple months, then adjust outfall limits downward on contributing outfalls to account for instream increases; or eliminate contributing discharges.

Shallow Groundwater Near Fields:

Monitoring: Quarterly static water level year-round. At least one continuous water level monitoring station per site, using pressure transducer. Quarterly water quality sampling. Always sample and analyze for pH, EC, Ca, Mg, Na. Additional sampling for K, SO_4, HCO_3, Cl, carbon isotopes if under intensified monitoring. Groundwater monitoring wells subject to WDEQ guideline specifications for siting, installation, instrumentation, sampling and reporting.

Threshold: First threshold = depth to groundwater less than 6 feet. Second threshold = depth to groundwater less than 3 feet.

Corrective Action (If threshold exceeded): If first threshold is triggered (depth to groundwater less than 6 feet), then investigation is needed to detect cause and corrective action. Evaluate all available data from upstream surface water and groundwater monitoring locations, intensify sampling in irrigated field monitoring wells, possible add new wells to study subsurface connectivity of stream channel and groundwater below fields, evaluate surface hydrology conditions in fields. If second threshold is triggered (depth to groundwater less than 3 feet), and the groundwater has a CBM water contribution, then cease contributing discharges.

Scenario 3: Permit Requirements (continued)

Soils: 

Site Selection: Segment fields according to differences in soil characteristics or depth to groundwater. Look for distinct differences in EC (if using ground-based electromagnetic survey), texture, pH or vegetation. For each identified segment, minimum of one subsample per acre, but not less than 5 and not more than 15 subsamples per segment.

Monitoring (initial): 4 feet deep in grass fields. 6 feet deep if alfalfa present. Increments = 0-6", 6-12", then 12" each to depth. **Analyze for texture, clay mineralogy, exchangeable sodium percent (ESP), pH, EC, SAR, SO_4, HCO_3, lime, organic carbon (OC), N, P, K.** Composite within each identified soil segment, using co-located composited samples. On initial sampling, do not composite analysis for EC and pH. Analyze EC and pH on each individual subsample before compositing subsamples to run other analytes.

Monitoring (ongoing): 4 feet deep in grass fields. 6 feet deep if alfalfa present. Increments = 0-6", 6-12", then 12" each to depth. **Analyze for pH, EC, SAR, SO_4, HCO_3, chlorides (Cl).** Composite within each identified soil segment, using co-located composited samples. Annual fall sampling.

Threshold: Greater than 40% increase in EC or SAR in one year, or greater than 15% over two years or more. Regardless of trend, ESP greater than 10% or EC greater than 4,000 micromhos/cm at 0 -12" triggers corrective action below.

Corrective Action (If threshold exceeded): If any of the above thresholds is triggered, increase soil monitoring to twice per year (spring / fall). Initiate detailed study to identify cause of salt / sodium increase. If damage to soil is identified that is expected to impair crop / forage production, and damage is due to CBM discharges, then proceed with one or more of: curtailing contributing CBM discharges, changing discharge locations, providing improved drainage to fields, adding chemical amendments to fields.

Crops / Forage: 

Monitoring: Vegetation sampling to occur in same areas as soil sampling. One square meter sample cuttings. Sample annual peak standing crop (late June – early July) or pre-cutting for hayed fields. Measure annually: yield (tons/acre), crude protein (CP), Ca, P, K; plus Selenium bi-annually. Other constituents annually. Can use field harvest data for hay yield if available.

Threshold: Statistically significant decrease in yield or quality that correlates with causative mechanism such as soil water or groundwater impacts.

Corrective Action (If threshold exceeded): Reclamation of any damaged fields.

Scenario 4: Permit Requirements

Outfall: 

Monitoring: For first twelve months, monthly sampling for Electrical Conductivity (EC), sodium adsorption ratio (SAR), pH, bicarbonate (HCO_3). Quarterly sampling thereafter if constituents are below threshold levels. Continuous flow measurement.

Threshold: Outfall effluent limits for EC and sodium to be calculated using waste load allocation. EC and sodium limits at outfall will be calculated based on historic median stream flow during the irrigation season, and shall apply during the irrigation season. Effluent limits for EC and sodium at outfall will be calculated to achieve instream targets outlined below.

Corrective Action (If threshold exceeded): WDEQ enforcement action.

Perennial Stream Channel: 

Monitoring: Monthly sampling upstream and downstream of outfall, plus at first point of irrigation diversion for pH, EC, Ca, Mg, Na, flow. If necessary for additional investigation, sample for K, SO_4, HCO_3, Cl, carbon isotopes.

Threshold: Instream target EC will be derived using USDA salt tolerance database thresholds. When using USDA salt tolerance values, instream target EC will be calculated by dividing the published soil EC threshold value by 1.5. Where the published soil EC threshold is presented as a range of values, the median value of the range will serve as the published soil EC threshold. Where historic background EC in the perennial stream exceeds the above USDA crop threshold, the historic background EC will serve as the instream target. Instream SAR target will be < 6.67 x EC (dS/m) – 3.33, where EC = actual measured EC of the instream sample. Set instream SAR target between 3 and 10. Under circumstances where smectitic soils are present in the downstream irrigated lands (clay fraction is 50% smectite or greater), then additional restrictions may apply on SAR and sodium.

Corrective Action (If threshold exceeded): If persistent exceedences of the instream thresholds for EC or SAR occur, investigate cause(s), including examination of non-point sources, stream flow data, other point sources within the basin. If CBM discharges are determined to be contributing to the exceedence of instream threshold(s) and crop/forage production is adversely affected, then modify EC and/or sodium limits downward to correct the problem, or curtail discharge quantity.

Scenario 4: Permit Requirements (continued)

Soils: 

Site Selection: Segment fields according to differences in soil characteristics or depth to groundwater. Look for distinct differences in EC (if using ground-based electromagnetic survey), texture, pH or vegetation. For each identified segment, minimum of one subsample per acre, but not less than 5 and not more than 15 subsamples per segment.

Monitoring (initial): 4 feet deep in grass fields. 6 feet deep if alfalfa present. Increments = 0-6", 6-12", then 12" each to depth. **Analyze for texture, clay mineralogy, exchangeable sodium percent (ESP), pH, EC, SAR, SO_4, HCO_3, lime, organic carbon (OC), N, P, K.** Composite within each identified soil segment, using co-located composited samples. On initial sampling, do not composite analysis for EC and pH. Analyze EC and pH on each individual subsample before compositing subsamples to run other analytes.

Monitoring (ongoing): 4 feet deep in grass fields. 6 feet deep if alfalfa present. Increments = 0-6", 6-12", then 12" each to depth. **Analyze for pH, EC, SAR, SO_4, HCO_3, chlorides (Cl).** Composite within each identified soil segment, using co-located composited samples. Annual fall sampling.

Threshold: Greater than 40% increase in EC or SAR in one year, or greater than 15% over two years or more. Regardless of trend, ESP greater than 10% or EC greater than 4,000 micromhos/cm at 0 -12" triggers corrective action below.

Corrective Action (If threshold exceeded): If any of the above thresholds is triggered, increase soil monitoring to twice per year (spring / fall). Initiate detailed study to identify cause of salt / sodium increase. If damage to soil is identified that is expected to impair crop / forage production, and damage is due to CBM discharges, then proceed with one or more of: curtailing contributing CBM discharges, changing discharge locations, providing improved drainage to fields, adding chemical amendments to fields.

Crops / Forage: 

Monitoring: Vegetation sampling to occur in same areas as soil sampling. One square meter sample cuttings. Sample annual peak standing crop (late June – early July) or pre-cutting for hayed fields. Measure annually: yield (tons/acre), crude protein (CP), Ca, P, K; plus Selenium bi-annually. Can use field harvest data for hay yield if available.

Threshold: Statistically significant decrease in yield or quality that correlates with causative mechanism such as soil water or groundwater impacts.

Corrective Action (If threshold exceeded): Reclamation of any damaged fields.

IMPLEMENTATION GUIDANCE FOR RECLAMATION AND BONDING OF
ON –CHANNEL RESERVOIRS THAT STORE
COALBED NATURAL GAS PRODUCED WATER

Wyoming Department of Environmental Quality
Water Quality Division
November, 2009

Section 1 - Need and Authority

The rapid development of coalbed natural gas (CBNG) in the greater Powder River Basin (PRB) of Wyoming has resulted in the construction of large numbers of produced water retention reservoirs. These reservoirs are constructed "on-channel" by damming natural drainages or "off-channel" by excavating pits or ponds.

Reclamation and bonding of the off-channel reservoirs is required by the Wyoming Oil and Gas Conservation Commission (WOGCC), the Office of State Lands and Investments (OSLI), and the US Bureau of Land Management (BLM). The BLM will require bonding and reclamation of on-channel reservoirs located over federal oil and gas leases. However, there is concern that there is no mechanism for bonding and reclamation of on-channel reservoirs where there is no federal nexus.

Reclamation of the reservoirs, once the CBNG produced water is no longer being discharged, is important for the long term environmental health of the area. Un-reclaimed reservoirs cause fragmentation and isolation of drainages. This fragmentation will have an adverse impact on the natural biota as well as an adverse impact on agricultural uses of the land. Dry reservoir bottoms that are not re-vegetated may result in fugitive dust, may promote the spread of noxious weeds, and may expose salts and sediments that could contain toxic constituents such as selenium.

The purpose of this document is to describe how the Water Quality Division (WQD) of the Wyoming Department of Environmental Quality (DEQ) will implement the requirements of section 35-11-102 of the Wyoming Environmental Quality Act (EQA) as they pertain to reclamation of on-channel CBNG ponds. Section 35-11-102 of the EQA states, in part, that "it is the policy and purpose of this act to enable the state to prevent, reduce, and eliminate pollution; to preserve and enhance the air, water, and reclaim the land of Wyoming ….". Sections 35-11-109(a)(i) and (iii) of the EQA give the Director of the DEQ the authority to carry out and implement the purposes of the act. Section 35-11-109(a)(xiii) of the EQA gives the Director the authority to hold bonds to ensure reclamation of disturbed lands. Sections 35-11-110(a)(ii) and (x) give similar authority to the division Administrators.

Section 2 - Applicability

This guidance applies to any CBNG operator who has or will construct dams across natural drainages to store and manage CBNG produced water. The resultant reservoirs, because of their location, may hold natural runoff in addition to CBNG produced water. To avoid duplication, off-channel reservoirs that are bonded by the WOGCC, OSLI, or BLM are excluded from the requirements of this guidance. This guidance envisions that all on-channel reservoirs constructed or modified after August 2005 must be bonded by the BLM or DEQ effective immediately. On-channel CBM reservoirs in existence prior to August 2005, must be bonded by the BLM or DEQ as their WYPDES permits are renewed or modified to the extent that public notice is required.

Section 3 - Definitions

The following terms are defined for purposes of this Guidance:

(a) "Administrator" means the Administrator of the Water Quality Division.

(b) "Approximate original contours" means the surface configuration achieved after removal of the embankment, backfilling and grading so that the reclaimed land resembles the general surface configuration of the land prior to construction of the reservoir as it blends into and complements the drainage pattern of the surrounding terrain.

(c) "Director" means the Director of the Wyoming Department of Environmental Quality.

(d) "Existing reservoir" is a reservoir that existed on the original date of this guidance and was not constructed or modified for the purpose of managing produced water from coal bed natural gas operations.

(e) "Reservoir" means any on-channel, man-made water detention structure created primarily to manage produced water from coalbed natural gas operations and which is designated as a receiving water in a WYPDES permit.

(f) "WQD" means the Water Quality Division of the Department of Environmental Quality.

(g) "WYPDES" means the Wyoming Pollution Discharge Elimination System.

Section 4 - Implementation

The requirements of this guidance shall be implemented through the issuance of WYPDES permits. After the original date of this guidance, no CBNG operation with an on-channel CBNG reservoir will receive a new, renewed, or modified WYPDES permit unless the requirements of this guidance have been met.

Section 5 - General Reclamation and Bonding Requirements

(a) During reservoir construction, topsoil shall be salvaged and stockpiled. Topsoil stockpiles shall be separate from the dam embankment and marked in the field with a sign. Such stockpiles shall be protected from erosion through temporary seeding and containment berms, and/or other approved means. A Topsoil covering may be used on dams, but topsoil may not be used for the dam core. This requirement shall not apply to reservoirs in existence on the original date of adoption of this guidance.

(b) Each reservoir must have a sign showing the WYPDES permit and outfall number and that sign must be retained until bond release.

(c) For all reservoirs that will not be retained by the landowner, the permittee shall perform the following reclamation requirements once the discharge of CBNG produced water to the reservoir permanently ends:

(i) At the time of reservoir closure:

(A) Sample and analyze the soil on the floor of the reservoir and submit the results of sampling to the WQD using the form provided as Appendix C to this document. Further reclamation may not proceed until the WQD reviews the soil quality data and gives permission to proceed;

(B) Excavate layers of salts and mineral residue that may exceed acceptable concentrations. Isolate this material so it will not leach into surface or groundwater. Appendix A to this document shall be used by the WQD to determine acceptable soil quality;

(C) Backfill, contour and grade the disturbed area of the reservoir to the approximate original contours and stabilize all surface drainage channels that flow through the disturbed area.

(D) Replace topsoil, seed and mulch the area with a native grass and shrub seed mixture, unless the landowner specifies some other seed mixture consistent with the land use. If the area is open to active grazing, the permittee shall make arrangements to protect the reclaimed area to ensure successful re-vegetation.

(d) For reservoirs where only a portion of the impoundment is authorized for retention by the landowner under the Waiver of Reclamation requirements in section 7 of this guidance, the permittee shall perform the reclamation requirements of subsection (a) of this section for those portions of the reservoir to be reclaimed, except that the disturbed area is not required to be reclaimed to the approximate original contours. However, the disturbed area above the authorized reservoir level, including the remaining embankment, spillway and outlet structures must be stabilized to provide for long-term low maintenance care.

(e) Provide to the Administrator an acceptable performance security, or a federally insured certificate of deposit, other government security or cash, or a self-bond to cover the estimated cost of reclamation per the requirements of this subsection. This security is to ensure that funds are available to the department if the permittee fails to perform the reclamation requirements of this guidance. The Administrator shall prescribe the forms and conditions of the security.

(i) If the applicant desires to use a letter of credit as the performance security, the applicant shall meet the requirements of Chapter 12 of the LQD's rules for non-coal operations.

(ii) If the applicant desires to utilize self-bonding for some or all of the security, the applicant shall provide the information required in LQD Non-coal Rules, Chapter 6, Section 2, subsections (a)(i) through (xii), excluding (v) and (xiii)(D). For purposes of application of this guidance to CBNG operations, "mining operation" and "non-coal operator" shall mean "CBNG operations". The Administrator shall render a decision on the self-bonding application in accordance with Sections 3 and 4, of LQD's Non-coal Rules, Chapter 6.

(f) The size of the performance security required by this guidance shall be determined as follows:

(i) Where excavation, backfilling and topsoiling to meet the requirements of this section involves 5,000 cubic yards of earthwork or less, the security shall be $7,500 during the first calendar year of this guidance. This amount shall escalate by 3 percent on January 1 of each year. The amount of the security will be recalculated whenever the WYPDES permit for the reservoir is renewed or has a modification requiring public notice.

(ii) Where the excavation, backfilling and topsoiling to meet the requirements of this section involves between 5,000 cubic yards and 10,000 cubic yards of earthwork, the security shall be $12,500 during the first calendar year of this guidance. This amount shall escalate by 3 percent on January 1 of each year. The amount of the security will be recalculated whenever the WYPDES permit for the reservoir is renewed or has a modification requiring public notice.

(iii) Where the excavation, backfilling and topsoiling to meet the requirements of this section exceeds 10,000 cubic yards of dirt work, the security amount shall be based upon a certified professional engineer's estimate that quantifies the reclamation costs including associated costs to remove pipes, concrete and other structural components. This amount shall escalate by 3 percent on January 1 of each year. The amount of the security will be recalculated whenever the WYPDES permit for the reservoir is renewed or has a modification requiring public notice. For purposes of this subsection, the security amount shall be at least $13,000.00 and this amount shall escalate by 3 percent on January 1 of each year.

(g) The applicant may request that one security instrument be held for multiple reservoirs.

Section 6 – Well Reclamation

(a) All monitoring or other wells associated with any reservoir bonded under this guidance document shall be reclaimed in accordance with the provisions of Appendix B.

Section 7 - Waiver of the Bond and Reclamation Requirements

(a) If the permittee provides a letter from the landowner indicating the landowner's desire that an existing reservoir (see definition) be retained after the CBNG operations are complete, and provides certification from the SEO that the reservoir may be left permanently, no bond is required from DEQ and the reservoir does not have to be reclaimed.

(b) Once a permittee has ceased discharge to a reservoir (see definition) the permittee may request that the bond for that reservoir be released without reclamation. Such request must include:

(i) A signed statement from the landowner requesting retention of the reservoir; and

(ii) Certification from the SEO that the reservoir may be left permanently;

(iii) Submission of proof that the well reclamation requirements of Section 6 above have been met.

(c) If a landowner asks that a portion of a reservoir be retained after CBNG operations are complete, the requirements of this policy shall apply only to the portions of the reservoir the landowner does not ask to be retained.

Section 8 - Bond Release and Forfeiture Procedures

(a) When a permittee has determined that a reservoir has been successfully reclaimed, he shall send a written request to the Administrator that an inspection of the site be made.

(b) Except as provided under the Waiver section of this guidance, no security shall be released until the reclamation requirements have been completed. The security will be retained until successful reclamation has been confirmed by an on-site investigation by the Administrator or his representative.

(c) If the Director determines that the permittee has failed to do the construction work necessary to reclaim the reservoir within one year after cessation of CBNG discharge to the reservoir, the Director may request that the Attorney General begin bond forfeiture proceedings. For good cause, the permittee may request an extension for not more than one additional year.

(d) If, after three growing seasons, the Director determines that re-vegetation of the site has failed and that the permittee is no longer making a good faith effort to re-vegetate the site, the Director may request that the Attorney General begin bond forfeiture proceedings.

(e) The Director may request that the Attorney General begin bond forfeiture proceedings without delay if the permittee declares bankruptcy or abandons the project.

(f) The Attorney General shall institute forfeiture proceedings by providing written notice to the surety and the permittee that the bond will be forfeited. The permittee will have 30 days from receipt of the Attorney General's notice to demand a hearing before the Environmental Quality Council. If no demand for hearing is made, the Attorney General shall proceed with the forfeiture.

Appendix A

I. Soil Quality Limits

Parameter	Limits
pH	5.5 – 8.5
Conductivity (umhos/cm)	8,000
SAR	15
Selenium	.1 ppm
Boron	5 ppm
Molybdenum	1 ppm
Arsenic	2 ppm

II. Sampling Locations

Each reservoir shall be sampled at two locations. One location shall be at the lowest elevation within the reservoir. The second location shall be at a point approximately halfway between the lowest elevation and the high water mark.

III. Sampling Methodology

At each location described above, two samples shall be collected for analysis. The first sample shall be a soil increment of 0-6 inches from the surface. The second sample shall be a soil increment of 6-48 inches from the surface.

IV. Analytical Methods

Analytical methods shall be as described in Wyoming Department of Environmental Quality, Land Quality Division, Guideline No. 1 available at the following website: http://deq.state.wy.us/lqd/guidelns/guide1.pdf

Appendix B

Requirements for Well Plugging and Abandonment

Wells that are not properly plugged can act as a preferential pathway for surface contamination to reach and impair groundwater quality, and could cause injury to livestock, wildlife, or humans. Permittees, consultants, and others who construct and install monitor wells, test wells, injection wells, artificial recharge wells, public drinking water supply wells, and geothermal wells are reminded that wells that are no longer useful must be plugged in order to ensure that groundwater is protected and preserved for future use, and to eliminate the potential for physical injury. Wells need to be properly plugged and abandoned when they "…have not been used for a period of one year, unless the owner demonstrates his intention to use the well again by properly maintaining it".

Properly maintaining a well means: 1) the well has no defects which will allow the impairment of the quality of water in the well or in the water bearing formation penetrated; 2) the well is covered and the cover is water tight; 3) the well is marked so that it can be clearly seen; and 4) the area surrounding the well is kept clear of brush or debris. (Water Quality Rules and Regulations, Chapter 11, Part G, Section 70 "Plugging and Abandonment").

Plugging and Abandonment requirements (Water Quality Rules and Regulations, Chapter 11, Part G, Section 70) include: filling and sealing part or all of the well with impervious material; marking the location of the well; and filing a plugging and abandonment report. Abandoned public water supply wells must be plugged by filling the well with cement grout (Water Quality Rules and Regulations, Chapter 12, Section 9).

Further information on the requirements for well plugging and abandonment, including a form to report the plugging and abandonment of wells can be downloaded from the Groundwater Section's webpage:

Plugging and Abandonment Requirements:
http://deq.state.wy.us/wqd/groundwater/downloads/Rules%20and%20Regs/CHAPXI%20-%20Part%20G.pdf

Plugging and Abandonment Form:
http://deq.state.wy.us/wqd/groundwater/downloads/P&A%20Form.pdf

Plugging requirements for solid mineral exploration boreholes are regulated by the Department's Land Quality Division (307-777-7756).

Appendix C

Reservoir Closure Application

BOND INFORMATION

Bond Number: _____
WYPDES Permit Number: _____
Permittee: _____
Reservoir Name: _____
Legal Description: _____STATE LANDS?_____

SOIL SAMPLING RESULTS

Lowest elevation in reservoir results:

0-6 inch increment.

pH	_____
Conductivity (umhos/cm)	_____
SAR	_____
Selenium (ppm)	_____
Boron (ppm)	_____
Molybdenum (ppm)	_____
Arsenic (ppm)	_____

6-48 inch increment.

pH	_____
Conductivity (umhos/cm)	_____
SAR	_____
Selenium (ppm)	_____
Boron (ppm)	_____
Molybdenum (ppm)	_____
Arsenic (ppm)	_____

Mid-level in reservoir results:

0-6 inch increment.

pH	_____
Conductivity (umhos/cm)	_____
SAR	_____
Selenium (ppm)	_____
Boron (ppm)	_____
Molybdenum (ppm)	_____
Arsenic (ppm)	_____

6-48 inch increment.

pH	_____
Conductivity (umhos/cm)	_____
SAR	_____
Selenium (ppm)	_____
Boron (ppm)	_____
Molybdenum (ppm)	_____

Arsenic (ppm) _____

Please attach supporting laboratory analysis reports

If any soil analysis results are in exceedence of limits defined in Appendix A provide a detailed plan for mitigation of the residue.

JFW/10-0229

Feds reject plan to pump Moneta oilfield waste into potential drinking water

At Moneta Divide field in Fremont County, EPA says plan by driller Aethon doesn't meet standards to exempt Madison underground aquifer from protection.

by **Angus M. Thuermer Jr.**15 hours ago

On the Wind River Indian Reservation, Fort Washakie is home to nearly 1,800 people. (Matthew Copeland/WyoFile)

Federal environmental officials have rejected a request by Aethon Energy to pump Moneta Divide oilfield wastewater into the Madison aquifer, saying the deep reservoir could be used for drinking water, especially by tribal nations on the Wind River Indian Reservation.

The Wyoming Oil and Gas Conservation Commission in November 2020 approved wastewater disposal into the 15,000-foot deep well, but the U.S.

Environmental Protection Agency said last week the state's decision did not align with federal rules.

Aethon's plan does not support a finding "that the aquifer cannot now and will not in the future serve as a source of drinking water," the EPA wrote in a 20-page record of decision. Aethon argued, and the Wyoming commission agreed 4-1, that the underground Madison formation was too deep and remote to be used for drinking water.

The EPA relied on the Safe Drinking Water Act as the authority under which to protect the aquifer. It also cited climate, environmental justice and tribal interests in its decision, pointing to the nearby Wind River Indian Reservation as a community that could use the water.

"We have to make sure our future generations have a reliable source of clean water."

WES MARTEL

"The significance of that is the EPA finally didn't wimp out on us," said Wes Martel, a member of the Wind River Water Resources Control Board. "We're just glad they now have some people in place following up on their Indian policy."

The Eastern Shoshone and Northern Arapaho Tribes "foresee increased reliance on groundwater for drinking water purposes and anticipate needing to access deeper aquifers, such as the Madison aquifer, as the climate changes and water resources grow scarcer," the EPA wrote in a 94-page analysis of tribal interests. The agency cited historic cultural and spiritual ties to the land and water and tribes' status as sovereign nations in its decision.

"We have to make sure our future generations have a reliable source of clean water," Martel said. "Our reservation, this is all we have left. We've got to do our best to protect it."

The Powder River Basin Resource Council, along with the Wyoming Outdoor Council and others, has spent years monitoring discharge reports and industry

The EPA understood that science, and the law did not support Aethon's request, said Shannon Anderson, organizing director and staff attorney with the resource council. "They recognized the value of our groundwater resources and the need to protect those into the future," she said, hailing the decision.

Vast quantities of water

Aethon must find a way to dispose of produced water — a brine pumped from energy wells to release gas and oil — as it expands the Moneta Divide field by 4,500 wells. The U.S. Bureau of Land Management authorized that expansion in 2020, leaving the question of water disposal to Wyoming, which has authority over surface and underground water quality under overarching federal standards.

Aethon must find a way to dispose of the equivalent of 120 Olympic-sized swimming pools full of produced water a day to expand the field. Aethon and Burlington Resources, a co-producer at Moneta, could generate $182 million a year in federal royalties, $87.5 million a year in Wyoming severance taxes and $106 million annually in County Ad Valorem taxes from the expansion.

An elk skull adorns a fencepost near the Eastern Shoshone's buffalo management land on the Wind River Indian Reservation. (Katie Klingsporn/WyoFile)

But Aethon has violated state permits that allow it to pump some produced water into Alkali and Badwater creeks that flow into Boysen Reservoir, a drinking water source for the town of Thermopolis. Wyoming's Department of Environmental Quality has notified the Dallas-based investment company of its infraction and has required Aethon to reduce the salinity of surface discharges this year.

The DEQ this year listed the two creeks as "impaired" and unable to sustain aquatic life. Underground injection of wastewater into the Madison was to be a new component of the disposal program.

The EPA cited climate change, drought, increasing temperatures and use of reservation surface water by others as some of the reasons to preserve the Madison aquifer.

"Removing the existing statutory and regulatory protections for a potential source of high-quality drinking water for the rural and overburdened communities in Fremont County and on the WRIR would further exacerbate existing inequities particularly with respect to historic and ongoing adverse and cumulative impacts to water resources and community health," the EPA wrote.

"Thus, equity and environmental justice considerations, which include Tribal interest considerations, support maintaining the existing [Safe Drinking Water Act] protections that apply to the aquifers consistent with Congressional intent to protect both current and potential future sources of drinking water," EPA documents state.

Neither Aethon nor a representative of the Oil and Gas Conservation Commission responded immediately to a request for comment Wednesday. But WyoFile received this response from Tom Kropatsch, oil and gas supervisor for the Wyoming Oil and Gas Conservation Commission, shortly after publication:

"We do not agree with EPA's decision on this application. We are still reviewing their decision and the information utilized by EPA in support of their decision. Much of this information was not part of the original application or a part of the record. EPA did not follow the standard procedure of allowing the WOGCC and the applicant to review and respond to the additional information they had available prior to making their final decision. EPA evaluated data that differs in its

geographic, geologic, engineering, and other technical information. EPA also inappropriately related the proposed injection location to other areas of the state. Since the data EPA reviewed does not accurately reflect the conditions at the location of the proposed disposal well it is not appropriate to rely on it for a decision on this application. The WOGCC is reviewing EPA's decision and weighing its options for further action."

FEATURED TOP STORY

State gives Aethon OK to inject Moneta pollutants into aquifer

by **Angus M. Thuermer Jr.**November 12, 2020

An Aethon pump jack in the Moneta Divide oil and gas field east of Shoshoni. (Angus M. Thuermer Jr./WyoFile)

Wyoming regulators voted 4-1 Tuesday to permit Aethon Energy to pump millions of gallons of pollutants into an underground aquifer near Shoshoni that critics say is too valuable to pollute.

The Dallas investment firm argued through attorney Tom Throne that it would be uneconomic and impractical to use the 15,000-foot-deep Madison aquifer for

nearby towns' or cities' domestic supplies. That's one reason to grant the company an exemption to federal Clean Water Act rules and regulations, he said.

"We clearly fall into that category," Throne said, of the "uneconomic and impractical" standard. Nearby municipalities, an Aethon consultant told the five-member Wyoming Oil and Gas Conservation Commission, have ample water sources for at least another 190 years.

Aethon's request, heard during a day-long Zoom meeting, included science that was "thorough and compelling," Commissioner Ken Hendricks, a petroleum engineer who supported the exemption, said. Although it was the fourth attempt to secure an underground injection permit for the existing but unused Marlin well, "the drawbacks of the past shouldn't be drawbacks now," Commissioner Jimmy Goolsby, a geologist, said.

Gov. Mark Gordon and Commissioner and Director of the Office of State Lands and Investments Jenifer Scoggin joined the majority vote.

But State Geologist and Commissioner Erin Campbell called the venture "a gamble I don't feel comfortable taking." Before casting the lone dissenting vote, she asked fellow commission members, "do we want to risk contaminating a viable aquifer?

"What's impractical now may not be impractical in 50 years," she said of domestic development of the deep, potential water source. "I'm reluctant to jeopardize our future water needs."

Battle not over

Wyoming administers the underground injection program under federal laws, rules and regulations. The state's pending order will go to the federal Environmental Protection Agency "to confirm the commission decision," OGCC Deputy Supervisor Tom Kropatsch said. If the EPA has significant problems or questions, Aethon could be called back before the commission for answers, he said.

Conservationists who challenged the Aethon proposal “are not giving up,” said Jill Morrison, executive director of the Powder River Basin Resource Council. “This is not over,” she said after the commission’s decision.


A worker takes a water sample from an outfall at the Moneta Divide Field. (DEQ)

Her group has contested using the Marlin well for disposal since 2013 and, along with the Wyoming Outdoor Council, challenged the Aethon application again Tuesday. Wyoming’s own Department of Environmental Quality, she said, concluded the aquifer near the Marlin injection well could be developed as a domestic supply for $169 million.

That’s less than the $200-million-plus spent recently by Wyoming for water for the city of Gillette, she said. Contrary to Aethon’s position, it is practical to develop the aquifer for domestic use, she told the commission.

More than 100 letters of public comment emphasize support for clean water, PRBC attorney Shannon Anderson told the commission. She warned the

commission against setting a precedent “that water like that is available to pollute.”

Conservation consultant Sue Spencer said the depth of the Madison at the Marlin Well — one reason Aethon claimed the aquifer would be impractical to develop for domestic use — is essentially immaterial. The Aethon request must be considered in the face of drought and climate change, plus technical advances in drilling and pumps that make deep development easier, she said.

Neighboring communities today also use shallower aquifers that have “kind of unreliable water quality,” she said. In one of those — Pavilion, about 60 miles from the Marlin Well — some residents have seen their shallow domestic wells polluted from oil and gas activity and now get domestic water trucked to their homes.

On the Wind River Indian Reservation, which is scant miles from the Moneta Divide field, “about a third of wells are polluted by uranium tailings,” said Rev. Sally Palmer of the Wyoming Association of Churches.

Many towns in Wyoming “would kill” for a Madison source of drinking water, Spencer told the commission. “I think we can all agree water and groundwater are the lifeblood of our state,” she said.

Water disposal vs. pace of development

Aethon’s predecessor, Encana, had built and operated the Neptune water treatment plant at the Moneta Divide Field, Aethon executive Tom Nelson told the commission. But that facility has become “uneconomical to operate” and has been shut down, he said.

Aethon and Burlington Resources won permission from the U.S. Bureau of Land Management to expand the small Moneta Divide Field by 4,250 wells. But Aethon has not resolved how to dispose of 59 million gallons of tainted water a day that would be produced during peak field development.

 A DEQ photograph of Aethon discharges below a Moneta Divide gas- and oilfield discharge facility. (Department of Environmental Quality via Wyoming Outdoor Council and Powder River Basin Resource Council)

Aethon has “very limited” opportunities to dispose of the water, attorney Throne told the commission. Water pumped out of energy wells releases hydrocarbons but laws and regulations limit what can then be done with the briny flow.

Aethon could build treatment plants or evaporation and settling ponds or it could limit the pace of production, the BLM has said.

Wyoming DEQ cut back Aethon’s request to dump millions of gallons of produced water from Moneta Divide into creeks and waterways that would flow into Boysen Reservoir, a state park and a source of drinking water for the Town of Thermopolis. Aethon can also inject some tainted water into 160 disposal wells that are shallower than the 15,364-foot-deep Marlin Well.

All that accounts for only about 26% of the polluted water pumped from Moneta energy wells at full production, according to WyoFile calculations made from BLM and state documents.

On average, the Madison under the Marlin Well would only accommodate a fraction — as little as 0.5% — of the water produced daily during full production, according to WyoFile calculations. Even if the company used the Marlin Well, it would still lack a place to dispose some two-thirds of the contaminated water it hopes to produce.

Geologic structures would contain the injected water within a 3.2-mile-diameter zone around the Marlin Well during the disposal well's 50-year life, Keith Thompson, hydrologist with Aethon's Tetra Tech consultants, told the commission. The water in the Madison Aquifer at the well bottom flows only about three feet a year, he said.

Another Aethon consultant, Bonnie Percy, appeared to discount company claims that the Madison is polluted with benzene at the Marlin Well site. Aethon's application said samples from the well showed concentrations of the carcinogen well above the EPA's maximum contaminant level for consumption.

Disagreement continues over whether the detected benzene was naturally occurring, as Aethon contends, or introduced during the drilling of the Marlin Well. Naturally occurring benzene would buttress Aethon's case.

But Percy produced a table that showed how benzene concentrations fell dramatically over a five-week testing period. The decline suggested to critics that the carcinogen resulted from the drilling.

The initial benzene reading registered 110 micrograms per liter, far above the federal 5 ug/l standard, according to Percy's table. But that reading declined in about a month to near, at or below the federal maximum contaminant level, according to an exhibit she presented.

Subsidizing profits in Dallas

During public comment Converse County resident Maria Katherman told the commission that clean-water rules "are not meant to accommodate a lack of economic water treatment by the company.

“If they cannot treat this water at the present gas prices, don’t produce it.” she told the commission. “If they can’t treat it economically, that meant the State of Wyoming is subsidizing them, allowing them to pollute our water.

Albert Huddleston founded the Dallas-based private energy investment firm Aethon Energy, whose website includes the image above, in 1990. Since then it has managed over $1.6 billion in oil and gas assets, the website says. (Aethon)

“I don’t think Wyoming should bear that cost,” she said.

Morrison agreed the commission approval would allow Aethon to pocket more money at Wyoming residents’ expense. “They are externalizing the cost of producing that gas onto our future generations and our future need for water,” she said after the hearing.

Aethon did not respond to an email seeking reaction to the state approval. The company says it’s a responsible operator, even though Wyoming’s DEQ found the Aethon water discharges from existing Moneta Divide energy wells violated standards.

Albert Huddleston, a veteran industry executive, established the private Texas equity company in 1990, attorney Throne said, “with highest regard for health safety and the environment.”

Aethon is exploring all methods to dispose of the produced water, he said. The Marlin well, located “in the middle of nowhere,” could be used “with no significant environmental impact,” and is entitled to an aquifer exemption, he said

Radioactivity from Oil and Gas Wastewater Persists in Pennsylvania Stream Sediments

January 19, 2018

Treated oil and gas wastewater flows into a western Pennsylvania stream. A new study find stream sediments at disposal sites such as this one have radioactivity levels 650 times higher than at upstream sites. (Credit: Avner Vengosh, Duke Univ.)

Note: Avner Vengosh is available for additional comments at (919) 681-8050 or vengosh@duke.edu. Nancy Lauer is available at nancy.lauer@duke.edu.

DURHAM, N.C. – More than seven years after Pennsylvania officials requested that the disposal of radium-laden fracking wastewater into surface waters be restricted, a new Duke University study finds that high levels of radioactivity persist in stream sediments at three disposal sites.

The contamination is coming from the disposal of conventional, or non-fracked, oil and gas wastewater, which, under current state regulations, can still be treated and discharged to local streams.

“It’s not only fracking fluids that pose a risk; produced water from conventional, or non-fracked, oil and gas wells also contains high levels of radium, which is a radioactive element. Disposal of this wastewater causes an accumulation of radium on the stream sediments that decays over time and converts into other radioactive elements,” said Avner Vengosh, professor of geochemistry and water quality at Duke’s Nicholas School of the Environment.

The level of radiation found in stream sediments at the disposal sites was about 650 times higher than radiation in upstream sediments. In some cases, it even exceeded the radioactivity level that requires disposal only at federally designated radioactive waste disposal sites.

“Our analysis confirms that this accumulation of radioactivity is derived from the disposal of conventional

oil and gas wastewater after 2011, when authorities limited the disposal of unconventional oil and gas wastewater," said Nancy Lauer, a Nicholas School PhD student who led the study.

"The radionuclide ratios we measured in the sediments and the rates of decay and growth of radioactive elements in the impacted sediments allowed us to essentially age-date the contamination to after 2011," she explained.

The researchers published their findings in a peer-reviewed policy paper Jan. 4 in Environmental Science and Technology.

To conduct the study, they collected stream sediments from three wastewater disposal sites in western Pennsylvania, as well as three upstream sites, and analyzed the radioactive elements in the sediments. Samples were collected annually from 2014 to 2017 at disposal sites on Blacklick Creek in Josephine, on the Allegheny River in Franklin, and on McKee Run in Creekside.

In 2011, in response to growing public concern about the possible environmental and human health effects of fracking wastewater, Pennsylvania's Department of Environmental Protection requested that the discharge of fracking fluids and other unconventional oil and gas wastewater into surface waters be prohibited from central water-treatment facilities that release high salinity effluents. However, the disposal of treated wastewater from conventional oil and gas operations was allowed to continue.

"Despite the fact that conventional oil and gas wastewater is treated to reduce its radium content, we still found high levels of radioactive build-up in the stream sediments we sampled," Vengosh said. "Radium is attached to these sediments, and over time even a small amount of radium being discharged into a stream accumulates to generate high radioactivity in the stream sediments."

"While restricting the disposal of fracking fluids to the environment was important, it's not enough," he said. "Conventional oil and gas wastewaters also contain radioactivity, and their disposal to the environment must be stopped, too."

Nathaniel Warner, a former PhD student in Vengosh's lab at Duke who is now an assistant professor of civil and environmental engineering at Penn State University, coauthored the new study.

Funding came from the National Science Foundation (#EAR-1441497) and the Park Foundation.

CITATION: "Sources of Radium Accumulation in Stream Sediments Near Disposal Sites in Pennsylvania: Implications for Disposal of Conventional Oil and Gas Wastewater," Nancy Lauer, Nathaniel Warner, Avner Vengosh, *Environmental Science and Technology*, DATE Jan, 4, 2018, DOI: 10.1021/acs.est.7b04952

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GUIDANCE ON TREATED AND UNTREATED PRODUCED WATER SAMPLING PROCEDURE

NEW MEXICO PRODUCED WATER RESEARCH CONSORTIUM

MAY 15, 2023

PREFACE

This guidance report was prepared by the New Mexico Produced Water Research Consortium (NMPWRC or the Consortium) in support of the New Mexico Environment Department and the United States Environmental Protection Agency's National Water Reuse Action Plan.

The report presents a general water sampling protocol for produced water quality analysis, pilot demonstration of produced water treatment, and use for fit-for-purpose applications. The guidance is based on the standard methods SW-846 by the United States Environmental Protection Agency, and methods used by commercial laboratories for produced water analysis[1]. The sampling protocol provides the standard operating protocol for collecting untreated and treated produced water samples during field measurements and for laboratory analyses of inorganic, wet chemistry, metals, organics, radioactive materials, microbes, and Whole Effluent Toxicity tests. For sampling of soil, plants, and groundwater during treatment and fit-for-purpose uses, the case-specific protocols should be followed and approved by the Technical Steering Committee of the Consortium.

The protocol provides step-by-step guidance and information on sample collection and preservation of produced water samples in the oil and gas field. It aims to serve as a guide to the field sampling crew. This document is general guidance, from which study-specific or laboratory-specific standard operating procedures are developed for strict adherence. The technology and use developer will provide more specific sampling plans, and the Consortium will approve on a case-by-case basis.

[1] https://www.eurofinsus.com/media/447768/appendix-d-section-5-attachment-holdtime-container-list_2016-july.pdf

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Acronyms

bbl	Barrels (42 gallons)
BOD_5	Biochemical Oxygen Demand, 5-day
COD	Chemical Oxygen Demand
EPA	Environmental Protection Agency
HASP	Health and Safety Plan
HEM/SGT-HEM	n-Hexane Extractable Material/ Silica Gel Treated n-Hexane Extractable Material
HPLC	High Performance Liquid Chromatography
GC	Gas Chromatography
ITTD	Innovative Technology Treatment Demonstration
NMED	New Mexico Environment Department
NMPWRC	New Mexico Produced Water Research Consortium
ORP	Oxidation-Reduction Potential
OSHA	Occupational Safety and Health Administration
PFAS	Perfluoroalkyl and Polyfluoroalkyl Substances
PPE	Personal Protection Equipment
QA/QC	Quality Assurance and Quality Control
SOP	Standard Operating Procedure
TDS	Total Dissolved Solids
TOC	Total Organic Carbon
TSS	Total Suspended Solids
TSC	Technical Steering Committee
VOA	Volatile Organic Analysis

SAMPLING PROCEDURE

OBJECTIVE: provide general information and guidance regarding sample collection and preservation through the life cycle of produced water from production (well head), preliminary treatment, storage (tanks), to pretreatment, treatment and desalination, post-treatment, applications, and residual management in the oil and gas field. This document serves as a guide from which a standard operating procedure (SOP) should be developed to be adhered to by the field sampling crew. A specific field sampling and analysis plan will be prepared for each site and pilot test based on this general guidance and other relevant information.

SAFETY: Samplers must wear personal protection equipment, such as safety goggles, gloves, and other personal protection equipment (PPE) required by the facility. Always work in a team of two or more. If no facility requirements exist, then follow PPE includes safety glasses or goggles, appropriate gloves for the process at hand (e.g., nitrile gloves for sample handling), coveralls or a protective apron, and face shields if necessary, for handling materials that can splash and are hazardous. Gloves should be chosen to match the properties of liquids or solids handled. Training should be provided for sampling personnel so that they can choose the correct PPE while following the sampling procedures. Figure 1 shows proper PPE based on Occupational Safety and Health Administration (OSAH) requirements. Table 1 provides PPE instructions for samplers to follow. For detailed information, check 29 CRF 1910 subpart I.

Figure 1. Proper personal protective equipment. (Source: www.futuremanagers.com)

Table 1. Examples of personal protection equipment.

	Examples of equipment		Examples of equipment
Head Protection	Helmets have a full brim; helmets are brimless with a peak extending forward from the crown.	Hand Protection	Disposable safety gloves.
Foot Protection	Metatarsal guards; toe guards; safety shoes or boots; combination foot and shin guards.	Respiratory Protection	Filtering face pieces (dust masks) and other air-purifying respirators; atmosphere-supplying respirators.
Eye and Face Protection	Safety spectacles or glasses; goggles; face shields; welding shields.	Body Protection	Coveralls; fire retardant clothing; reflective clothing.
Hearing Protection	Single use earplugs; earmuffs; pre-formed or molded earplugs.		

General Guidelines

Samplers and analytical laboratories must maintain close coordination to ensure that adequate sampling procedures and sampling quality control objectives are met.

To ensure sample representability, comparability, and reproducibility of the performance of the treatment facility, sampling personnel must verify with the facility operators that the facility had not shown any upset, alteration, or disruption of their normal operations; this can be done based on the overall data repository and routine measurements of the facility. If the facility has shown any alteration of their normal operation during the days of sampling procedures or five (5) days before, the sampling procedures must be re-scheduled when the facility retrieves normal operations.

In the event that sampling personnel considers that any of the procedures described in this manual are inappropriate, inadequate, or impractical and that another procedure must be used to obtain the sample, the variant procedure must be documented and provided to the analytical laboratory with the field notes.

1. SAMPLING POINTS

Sampling points and locations have to be chosen to be representative of the water samples in the treatment facility. Typical sampling points include well head, surge tanks, oil-water separator tanks, storage tanks, points before and after treatment units, and locations identified during

applications (Figure 2). Sampling locations will vary depending on the purpose of the proposed study. Sampling points should be chosen so that sampling events will be consistent over the timeframe of the test plan, to assure sample representability, comparability, and reproducibility.

Samplers need to work in teams of two or more to ensure each team member's safety, that proper sampling techniques are followed, and that adequate notes are taken at each sampling location. Take pictures of each sample location and record any observations specific to the sample location in the field notes. To prevent sample cross-contamination, samplers should wear a new pair of nitrile disposable gloves at each sampling point and use new disposable equipment or properly cleaned reusable equipment for sampling.

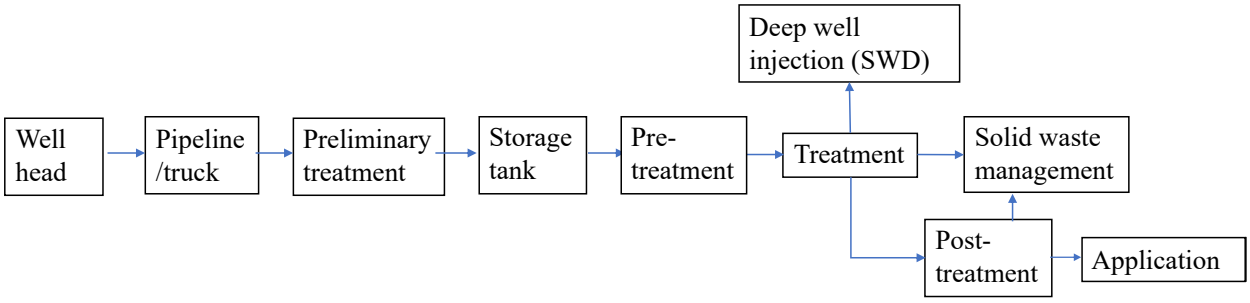


Figure 2. Common sampling points for produced water analysis.

2. ANALYTE SELECTION, CONTAINERS, AND LABELS

Sampling personnel must only use the container indicated by the analytical laboratory. Laboratory members should carefully choose the appropriate container for the target analyte(s) and coordinate with sampling personnel on the type and volume of the container to use. Table 2 lists the containers for different analytes. Container size can be different, but sample volume and characteristics for analysis should be collected strictly following the requirements of the analytical laboratory, e.g. samples collected in zero-headspace containers for volatile organic analysis (VOA). Certified clean containers, available from many scientific product vendors, are recommended for all samples.

It must be ensured that the sample container material is compatible with the analysis and "strictly follows" lab and/or Standard Methods requirements (Table 2). The most conservative container type should be selected based on the proposed analytical/testing request (e.g. if a tests program recommends two different containers, glass, and plastic, the primary sample should be taken in glass, and at no time should the sample touch a plastic container until separated for analyses that allow for plastic sampling containers). The same is true for analysis. If the sample received is in a plastic container, but the analysis requires a sample from a glass container, the desired analytical test may not be conducted if a sample is taken or received in the incorrect container.

Sampling personnel should code each sample with a unique sample ID and label it prior to sample collection to maintain identity and integrity. A sample identification protocol should be

established, which assigns completely unique sample numbers that cannot be mistaken for other containers. Sample numbers should also be unique to the date and time of sampling. It is recommended to prepare the sample labels and label the sample containers prior to sampling, and to log each sample number into a log sheet or spreadsheet prior to field collection. The log sheet can be printed for field use, or samples can be logged electronically in the field.

Sample labels should be made of material that is waterproof and will adhere to the sample containers even if wet. Label printing should also be waterproof. If there is a change in sample collection procedures that are made at the site that necessitates a label change, samplers should complete labels as they collect each sample and add them to the spreadsheet. Each self-adhesive label should be completed in indelible ink and contains the following information: sampling episode, sample ID, additives, sampling point, sample analysis, date and time of sample collection, bottle type, preservation, and samplers' initials. It is a good practice to prepare a bottle sample summary sheet that lists bottle type, size, preservative and intended analysis. This can serve as a checklist for both the sampler and the laboratory to ensure all containers are properly accounted for. If there is not enough space on the label, the sample ID and generic description should be recorded on the container and the remaining information should be recorded on the log sheet.

If any of the pre-printed information is incorrect, samplers should revise it using indelible ink. In particular, if a required preservation is not used, samplers should mark it out and document the deviation in the sample log sheet (Refer to an example in Appendix B).

Samplers will follow the following general protocols to maintain proper sample custody and to ensure that bottles do not get mixed up:

- Once the bottle label is applied to the sample container, cover labels with clear tape to prevent tampering, abrasion, smearing, peeling off, or loss during transit, sample preservation, or handling.
- Assemble the required sample containers for each sampling location and store them in boxes or ice chests labeled for each sampling location;
- Sample bottles have to be numbered on the lids using a permanent marker to ensure that none are missing;
- Sample bottles have to be filled in numerical order and double checked to ensure that none are skipped; and
- Samplers must keep samples in visual sight or in locked areas at all times. A chain of custody (Refer to an example in Appendix C) has to be filled to trace each sample container from the sampling point through shipping, analysis, and subsequent disposal.

3. SAMPLING AND PRESERVATION

3.1 Field measurement

During the sampling process, several parameters should be measured onsite when each sample is collected to estimate the sample variation, verify normal operations of the facility, and guide sample preservation methods. Samplers first need to perform the purge process as in Section 3.2 when sampling from a sample tap. Then samplers need to fill a 1-L glass jar during the collection of each sample or use a flow cell for some sampling points for field measurements.

- Temperature (SM 2550, a thermometer)
- pH [a pH meter or SM 4500-H B (Four color indicator strip)]
- Total sulfides (to include H_2S, EPA method 9030B)
- Conductivity (2520 B, a conductivity meter)
- Oxidation-Reduction Potential (ORP) (e.g., SESDPROC-113-R2, an ORP probe, or HQ11D Portable ORP/RedOx Meter)
- CO_2 (ASTM D 513-88, a gas sensing electrode or a titrator)
- Alkalinity (SM 2320 B-1997, a pH meter and a titrator)
- Ammonia
- If chlorine is used in the operation process, free residual chlorine in chlorinated water should be measured (SM 4500-Cl G). If a suitable disposal method/location is not available in the field for method SM 4500-Cl G, the EPA DPD method can be used by using a Hach test kit.

Temperature, pH, and total sulfides should be measured immediately after sample collection. All the meters should be calibrated before measurement based on procedures specified by the manufacturer. If a pH paper is used to measure the pH, measure the pH of the sample by transferring a drop of a sample using a disposable lab-certified-clean plastic pipette onto a pH paper. **The pH paper should not be inserted into the sample bottle**. Free chlorine measurements will be used to guide the sample preservation. Gross density and conductivity do not require immediate analysis and may be analyzed at the sampling point or later at the sampling staging area. If more field tests are required, such as chemical oxygen demand (COD), cyanide, and dissolved oxygen, a Hach DR900 Portable colorimeter with test kits could be a good candidate for these tests. Field measurement data should be included alongside samples for the duration of their life. If samples are taken and shipped to another facility, field measurement data should accompany all samples.

3.2 Sampling

Samplers will collect all samples as one-time grab samples unless other instructions are given by the analytical laboratory. Depending on the sampling points, an appropriate sample collection methodology should be chosen.

Sampling from a sample tap: the first step is to sufficiently purge the sample line by opening the tap and flushing the sample line, allowing water to flow into a slop bucket. The slop bucket should have a volume large enough to ensure that all non-sampled water can be accommodated in the bucket without any overflow. The sample tap should be allowed to flush for a minimum of 30 seconds, or 2 to 3 gallons (whichever results in a smaller flush volume) prior to collecting samples. After finishing this step, the water should be allowed to flow slowly and continuously into the slop bucket (that is, do not close the sample tap). The sampler will start filling sample bottles as follows:

- Retrieve a sample bottle, confirm that the label already affixed to the bottle matches the location being sampled, and remove the cap. Do not touch the inside of the sample bottle or the underside of the cap.
- Introduce the sample bottle into the water stream and fill to the required level. Then replace the cap. Samplers should be careful to prevent contact with the sample tap with the inside of the sample bottle. Sample bottles should be filled carefully, with minimal agitation or aeration allowed.
- Retrieve the next sample bottle and repeat the above steps until all bottles have been filled.
- Once all bottles have been filled, close the tap and dispose of the contents of the slop bucket via the facility's drain system, or bring to the lab for safe disposal.

Sampling from a water tank: Samplers will use a pole dipper to sample. Sample containers will be filled directly and sequentially by attaching them to the pole dipper using a zip tie. For 40-ml volatile organic analysis (VOA) vials and any other sample bottles that cannot be attached to the pole dipper, a 1-L glass transfer jar will be filled directly by attaching it to the pole dipper using zip-ties and lowering it directly into the open tank. The 1-L sample jar will also be used for field measurements as described above, taking care not to use the field sample "dip" for the analytical samples but rather discarding into the slop bucket for disposal in the sewer. Samplers will fill sample containers by pouring the contents slowly, avoiding aeration that may oxidize sensitive metals, from the sample transfer jar directly by tipping the pole dipper. Samplers have to minimize direct contact with the sample transfer jar and any part of the pole dipper that is lowered into the open tank. One approach may be to have one sampler manage the pole and outside of the jar while one or more others are careful to avoid all contact with it while taking samples and field measurements and recording information. It might be worthwhile to consider three-person sample teams if sample access will be via dipping or other approaches than sample taps.

When sampling from any tank, samplers must observe the presence/absence of an oil sheen. If the water tank is stratified, using a dipper will not produce a representative sample. Sludge judge can determine the presence/absence of multiphasic layers and provide information on the relative abundance of each layer. Tanks have guided wave radar level sensors that can also provide

information on phase presence. Representative samples must be collected based on the target analytes of the study and the instructions of the analytical laboratory.

Sampling from solid residual: The sampler can collect the sample by scooping a sample directly into the sample bottle and/or using a clean spatula to move solids into the sample container. The scoop and spatula must be cleaned between samples using reagent grade (or better quality) water. Samplers will be careful to keep the outside of the bottle clean by using gloves and minimizing contact of the outside of the bottle and the trough contents. It is important to ensure that the solid sample is representative of the residual being analyzed. The lab handling the solid sample should homogenize the solid sample and perform disaggregation if necessary.

Sample collection in VOA vials: For samples collected in 40-mL VOA vials, the VOA vials will be pre-preserved with HCl if needed. If free chlorine exists in a sample (Section 3.1), sodium thiosulfate will need to be added to the VOC method 624 VOA vials (Table 1). If sodium thiosulfate is needed a few crystals (10 mg/40 mL is sufficient for up to 5 part-per-million (ppm) Cl_2) must be added immediately after sample collection and prior to capping the vial.
For all VOA vials, samplers should eliminate any headspace in the vials by first reducing water flow and collecting the sample at an angle so that the water flows gently into the vial along the inner sidewall to reduce agitation and avoid introducing air bubbles, then filling the vial to form a convex meniscus of water (forms a "dome" just above the vial top) at the mouth of the vial. Cap the vial to ensure no bubbles are present once the lid has been placed. Check to make sure that the vial does not contain bubbles by inverting the bottle several times.

After the sample is collected, check vial threads to ensure they are clean and free of debris that would inhibit complete closure. Tighten the lid on each filled sample bottle, being careful not to over-tighten. If bottle threads are dirty such that the lid is impeded from closing, clear the threads on the bottle, being careful not to introduce contamination into the sample. Clean the sample bottle with a clean, dry cloth or paper towel. Samples should be stored properly as practically possible, as discussed below. Samplers need to put sampling point description, sample information, and sample representativeness and concerns in the field sampling log sheets (Refer to an example in Appendix A) at each sampling point. Take sampling point pictures with any observations.

Sampling for Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS): Sampling equipment used for PFAS sampling must be made from acceptable materials, which include high-density polyethylene (HDPE), polypropylene, silicone, stainless steel, nylon, polyvinyl chloride (PVC), acetate, and cotton. Sampling equipment that contain PFAS-based (fluoropolymers) parts that would be in direct contact with the sample or sampling environment are prohibited. These fluoropolymers include, but are not limited to polytetrafluoroethylene (PTFE, including the trademark Teflon® and Hostaflon®), polyvinylidene fluoride (PVDF, including the trademark

Kynar®), polychlorotrifluoroethylene (PCTFE, including the trademark Neoflon®), ethylene-tetrafluoro-ethylene (ETFE, including the trademark Tefzel®), fluorinated ethylene propylene (FEP, including the trademarks Teflon® FEP, Hostaflon® FEP, and Neoflon®).

All sample containers used for PFAS sampling should come from the laboratory that is performing the PFAS analysis. High-density polyethylene (HDPE) or polypropylene sample bottles with Teflon®-free caps are the preferred sampling containers for PFAS sampling. PFAS may adsorb to glass containers and therefore should not be used for water, leachate, or other aqueous samples.

3.3 Quality assurance of samples

For quality assurance, samplers need to collect duplicate samples. The number of duplicate samples with sampling locations should be given before sampling; duplicate sample jars should be numbered and identified prior to field sampling, in the same manner as the regular samples. Samplers should collect duplicate samples as sequential grab samples. To minimize duplicate sample variability resulting from temporal variability in wastewater characteristics, the duplicate sample bottle for each analyte will be filled immediately after the original sample bottle for that analyte is filled (as opposed to filling all sample bottles for the original sample and then filling all the samples bottles for the duplicate sample). Duplicate sampling should follow the same procedure as the original samples. It may be advisable to label all samples with an alphanumeric code instead of an identification that describes the location to minimize the 'bias' when laboratory testing the samples.

Field blanks must be collected to evaluate potential sample contamination from exposure to the sampling site conditions, field handling, storage, and preservation procedures. Field blanks will be collected in the same type of bottles for each analytical type and be analyzed for the same list of analytes. To collect field blanks, samplers will pour the laboratory prepared water (deionized water has been analyzed for the parameters of interest) into sampling bottles and follow the sample procedures for other samples. Equipment blanks are collected to determine if the sampling equipment is a source of sample contamination. They are collected by rinsing sampling equipment with an analyte-free matrix (typically HPLC grade water), and in the case of tubing and similar disposable (single use) collection equipment, one equipment blank will be prepared for each lot of equipment purchased. Equipment blanks will be analyzed for the same parameters as those analyzed on the samples collected using the sampling equipment.

3.4 Sample Preservation

Table 2 provides the sample container and preservation information for various target analytes. The type and amount of preservative used have to be recorded on sample preservation log sheets (Appendix B). The preservatives must be analyzed for the parameters of interest in the research lab to certify that the concentrations are below the reporting limit of concentration of concern. During the sampling process, the sampling team has to confirm that the pH of the samples meets

the preservation requirement. If not, then the sampling team will add additional preservatives to each sample to adjust the pH to meet the requirement.

Preservatives can be added in the lab before field sampling to minimize the field work. For example, 1 mL of concentrated nitric acid can be added into 1-L glass bottle for total metal sampling before the field sampling trip. However, the preservative should never exceed 10 percent of the total volume.

pH adjustment for plastic bottles:

1. For samples collected in plastic bottles that require pH adjustment, samplers will measure the pH of the sample by transferring a drop of the sample using a disposable lab-certified-clean plastic pipette onto a pH paper. Record value as initial pH on sample preservation log sheet (Appendix B). If the sample does not meet the pH preservation requirement, complete step 2.
2. Add 20 drops (1 mL) of the specified preservation chemical to every 1-liter sample using a plastic pipette (e.g., graduated disposable pipettes, 3 mL) dedicated to that preservation chemical. Close and tighten the sample container lid and then mix the sample. Record the quantity of preservative addition on the sample preservation log sheet.
3. Repeat steps 1 and 2 as needed until the target preservation is reached without exceeding 10% of the sample volume.

pH adjustment for glass bottles:

Some analytical methods may require glass containers (e.g., non-borosilicate glass that does not leach Na, clear or amber borosilicate glass VOA vials) and chemical preservation. For example, the measurement of n-Hexane extractable material/silica gel treated n-Hexane extractable material (HEM/SGT-HEM) requires the samples collected in VOA vials (Table 2). VOA vials will be pre-preserved with acid and then screened for the presence of free chlorine.

HEM/SGT-HEM samples will be preserved as follows:

1. An additional 1-L glass field jar will be used to collect an extra sample that will be used to determine the amount of chemical preservation needed for a 1-L sample. This extra sample will be used only for the purpose of determining HEM/SGT-HEM preservation, and then the contents will be disposed of.
2. Samplers will measure the pH of the extra sample by transferring a drop of sample using a disposable lab-certified-clean plastic pipette onto a pH paper. Record value as initial pH on sample preservation log sheet. If the sample does not meet the pH preservation requirement, continue to step 3.
3. Add 20 drops (1 mL) of preservation chemical to every 1-liter sample using a plastic pipette (e.g., graduated disposable pipettes, 3 mL) dedicated to the preservation chemical. Close and tighten the extra sample container lid and then mix the sample. Record quantity of preservation addition on the sample preservation log sheet.

4. Repeat step 2 and 3 as needed until the target preservation is reached without exceeding 10% of the sample volume.
5. Once the target preservation pH is met and the total volume of required preservative is known, samplers will add the same volume of acid to the HEM/SGT-HEM samples that will be sent to the lab for that sampling point. These sample jars will not be pH tested using pipettes to minimize loss of oil and grease onto the pipette.

After sampling, field sampling log sheets will be filled to record the sampling method, sampling equipment, names of the samplers, sample collection times, field measurements, and any notes and observations.

4. SAMPLE PACKING, SHIPPING, AND TRAFFIC REPORT

If the collected samples need to be stored in cool conditions (Table 2), the samples will be quickly chilled by immersion in ice water, packed in ice chests with sufficient wet ice to maintain a temperature below 6 °C, and then sent to analytical laboratories as soon as possible. For samples with a holding time of less than 48 hours, it is more practical to perform onsite analysis if possible, or the sample should be sent out on the sampling day or the next day after collection. Each shipment to the laboratory will contain a temperature blank, and the temperature will be taken and noted on the traffic report at the time of shipping. The temperature of the temperature blank will also be recorded by the laboratory upon receipt of samples. Exceptions include metals samples and radiological solids samples which have no temperature preservation requirements. The details about sample holding time are summarized in Table 2.

To maintain a record of sample collection, transfer between personnel, shipment carrier, and the laboratory, samplers will complete Chain of Custody reports for all samples sent to all laboratories. These forms are used to document sample custody transfer and preservation maintenance from the field to the laboratory.

Table 2. Analytes, containers, preservations, and holding times

Analyte	Method (Technique)	Sample Container[1]	On-Site Preservation	Holding Time
Inorganic and Wet Chemistry				
Alkalinity, Carbonate, Bicarbonate	SM 2320 B-1997 (Titration)	250 mL - Plastic	Cool to ≤ 6°C	14 Days[2]
Ammonia	EPA 350.1 (Colorimetric)	250 mL - Plastic	H_2SO_4 until pH < 2, Cool to ≤ 6°C	28 Days
Asbestos	EPA 100.1/100.2	1 L- Plastic	None. Contact with acid should be avoided	Not specified
Biochemical Oxygen Demand (BOD_5)	SM 5210 B-2001 (Titrimetric)	1000 mL - Plastic	Cool to ≤ 6°C	48 Hours
Chemical Oxygen Demand (COD)	EPA 410.4 (Spectrophotometric)	500 mL - Plastic	H_2SO_4 until pH < 2, Cool to ≤ 6°C	28 Days
Chlorine, Total Residual	SM 4500 Cl- G	250 mL - Plastic	Not required	15 Minutes
Dissolved Oxygen	SM 4500–O G–2011 (Probe method)	500 mL - Glass	Not required	15 Minutes
Dissolved Organic Carbon	EPA 415.1 SM 5310 B-2000 (Combustion)	250 mL – Amber Glass	H_2SO_4 or H_3PO_4 until pH < 2, Cool to ≤ 6°C	28 Days
Fluoride, Chloride, Nitrite, Ortho-Phosphate-p, Bromide, Nitrate, Sulfate, Bromate, Chlorite, Chlorate	EPA 300.0 (Ion Chromatography)	500 mL - Plastic	Cool to ≤ 6°C	28 Days except NO_2, NO_3, Ortho-P 48 Hours
Fluoride, Chloride, Nitrite, Ortho-Phosphate, Bromide, Nitrate, Sulfate	ASTM D4327 (Suppressed Ion Chromatography)	500 mL - Plastic	Cool to ≤ 6°C	28 Days except NO_2, NO_3, Ortho-P 48 Hours
Hardness	SM 2340B	250 mL - Plastic	HNO3 until pH is < 2, Cool to ≤ 6°C	6 Months
Iodide	EPA 345.1	250 mL - Plastic	Cool to ≤ 6°C	24 Hours
Methylene Blue Active Substances (Surfactants, anionic)	EPA 425.1 or SM 5540 C	250 mL - Plastic	Cool to ≤ 6°C	48 Hours

N-Hexane Extractable Material (HEM) and Silica Gel Treated N-Hexane Extractable Material (SGT-HEM)	EPA 1664A (Gravimetric)	1 L - Wide-Mouth Glass	HCl or H_2SO_4 until pH < 2, Cool to ≤ 6°C	28 Days
Nitrogen, Ammonia	SM 4500 NH3-B,C	500 mL - Plastic	H_2SO_4 until pH < 2, Cool to ≤ 6°C	28 Days
Nitrogen, Total Kjeldahl	SM 4500Norg B,C SM 4500 NH3-C	500 mL - Plastic	H_2SO_4 until pH < 2, Cool to ≤ 6°C	28 Days
Oxidation Reduction Potential (ORP)	SM 2580 B-1997	100 mL - Plastic	Not specified	15 minutes
Perchlorate	SW-846 6860	125 mL - Plastic	0.2 µm filtration through PTFE membrane within 15 mintes	28 Days
pH	SM 4500–H+ B–2011	100 mL – Plastic	Not required	15 mintues
Phenolics	EPA 420.4	1 L - Glass	H_2SO_4 until pH < 2, Cool to ≤ 6°C	28 Days
Phosphorous, Total	ASTM D515	500 mL - Plastic	H_2SO_4 until pH < 2, Cool to ≤ 6°C	28 Days
Salinity	SM 2520	250 mL - Plastic	Cool to ≤ 6°C	28 Days
Silica	EPA 200.7/6010 D	250 mL - Plastic	Cool to ≤ 6°C	28 Days
Specific Conductance	2510 B–2011 (Conductivity Meter)	100 mL – Plastic	Cool to ≤ 6°C	28 Days
Sulfate	300.0/375.4	500 mL - Plastic	Cool to ≤ 6°C	28 Days
Sulfide	SM 4500-S^{2-} D-2011	500 mL - Plastic	Cool to ≤ 6°C Zn Acetate & NaOH to pH > 9	7 Days
Sulfite	SM 4500 SO3-B	100 mL - Plastic	Not required	15 Minutes
Temperature	SM 2550 B–2010	100 mL – Plastic	Not required	15 Minutes

Total Dissolved Solids (TDS)	SM 2540 C-1997 (Gravimetric)	250 mL - Plastic	Cool to ≤ 6°C	7 Days
Total Hardness	SM 2340 C-1997 (Titrimetric)	250 mL - Plastic	HNO_3 or H_2SO_4 until pH is < 2, Cool to ≤ 6°C	6 Months
Total Organic Carbon (TOC)	EPA 415.1 SM 5310 B-2000 (Combustion)	250 mL – Amber Glass	H_2SO_4 or H_3PO_4 until pH < 2, Cool to ≤ 6°C	28 Days
Total Suspended Solids (TSS)	SM 2540 D-1997 (Gravimetric)	1000 mL - Plastic	Cool to ≤ 6°C	7 Days
Turbidity	EPA 180.1	100 mL - Plastic	Cool to ≤ 6°C	48 Hours
Metals				
Trace elements [Al, Sb, As, Ba, Be, B, Cd, Ca, Cr, Co, Cu, Au, Fe, Pb, Li, Mg, Mn, Mo, Ni,P, K, Se, Ag, Na, Sr, Tl, Sn, Ti, U, V, Zn] (Total)	EPA 200.7 (ICP), EPA 200.8/EPA 6020B(ICPMS)	500 mL - Plastic	HNO_3 until pH is < 2	6 Months
Trace elements [Al, Sb, As, Ba, Be, B, Cd, Ca, Cr, Co, Cu, Au, Fe, Pb, Li, Mg, Mn, Mo, Ni,P, K, Se, Ag, Na, Sr, Tl, Sn, Ti, U, V, Zn] (Dissolved)	EPA 200.7 (ICP), EPA 200.8/EPA 6020B(ICPMS)	500 mL - Plastic	0.45 µm filtration in 15 minutes, HNO_3 until pH is < 2	6 Months
Mercury	EPA 245.1 or 245.2 (Cold Vapor Atomic Absorption)	500 mL - Plastic	HNO_3 until pH is < 2	28 Days
Silica	EPA 200.7/6010 D	250 mL - Plastic	Cool to ≤ 6°C	28 Days
Hexavalent Chromium	SM 3500 -Cr B-2009 (Colorimetric)/ EPA 7199	250 mL - Plastic	Cool to ≤ 6°C	24 Hours
Organics				
2,4-dichlorophenoxyacetic acid	EPA 615	1-L - Glass	Cool to ≤ 6°C	7 Days

Agent Breakdown Products	EPA Method 538	40-mL VOA vials (Amber)	1.5 g/L Ammonium acetate and 64 mg/L Sodium Omadine, Cool to ≤ 6°C	14 Days
Alcohols	EPA 8260C, 8270D, and 8015C (GC/MS)	40-mL VOA vials	HCl until pH < 2, Cool to ≤ 6°C	14 Days
Aldehydes	EPA 8315(HPLC)	250 mL - Amber Glass	Cool to ≤ 6°C	3 Days
Carbaryl	EPA 632	1-L - Glass	Cool to ≤ 6°C	7 Days
Chlorpyrifos	EPA 622	1 L - Glass	Cool to ≤ 6°C	7 Days
Diazinon	EPA 614	1 L - Glass	Cool to ≤ 6°C	7 Days
Demeton	EPA 614	1 L - Glass	Cool to ≤ 6°C	7 Days
Dioxins	EPA 1613B; SW846 (2,3,7,8 TCDD)	1-L - Amber Glass	Cool to ≤ 6°C	7 Days
Diesel Range [C10 - C28]	EPA 3520C (sample preparation) EPA 8015D (analysis) (GC)	1-L - Amber Glass	Cool to ≤ 6°C	7 Days
Explosives	SW 846 – 8330B (HPLC)	1-L - Amber Glass	Cool to ≤ 6°C	7 Days
Gasoline Range [C6 - C10]	EPA 5030B (sample preparation) EPA 8015D (analysis) (GC)	40-mL VOA vials (Amber)	Cool to ≤ 6°C	7 Days
GCMS Purgeables	EPA 524.2	40-mL VOA vials (Amber)	Ascorbic acid and HCl until pH < 2, Cool to ≤ 6°C	14 Days
GCMS Purgeables	EPA 624/8260C	40-mL VOA vials (Amber)	HCl until pH < 2, Cool to ≤ 6°C	14 Days
Guthion (Azinphos-methyl)	EPA 614	1 L - Glass	Cool to ≤ 6°C	7 Days
Haloacetic Acids	EPA 552.2	250 mL - Amber Glass	Cool to ≤ 6°C, NH4Cl	14 Days
Herbicides	EPA 8151A (GC)	1-L - Amber Glass	Cool to ≤ 6°C	7 Days

Malathion	EPA 614	1 L - Glass	Cool to ≤ 6°C	7 Days
Mirex	EPA 617	1 L - Glass	Cool to ≤ 6°C, pH adjusted to 6-8 with NaOH or H_2SO_4	7 Days
Oil & Grease	EPA 1664B (Extraction and Gravimetry)	1-L Amber Glass	HCl or H_2SO_4 until pH < 2, Cool to ≤ 6°C	28 Days
Oil Range [C28-40]	EPA 5030B (sample preparation) EPA 8015D (analysis) (GC)	1-L - Amber Glass	Cool to ≤ 6°C	7 Days
Organic Acids	SM 5560 C	1-L - Amber Glass	Cool to ≤ 6°C	7 Days
Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS)	SW-846 Method 8327	1-L HDPE, no contact with Teflon	5 ml HNO_3	28 Days
Pesticides	EPA 608/8081B /8115 (GC)	1-L Amber Glass	Cool to ≤ 6°C	7 Days
Polyaromatic hydrocarbons (PAHs)	SW 8270 C	1-L Amber Glass	Cool to ≤ 6°C	7 Days
Polychlorinated biphenyls (PCBs)	SW 8082 A	1-L Amber Glass	Cool to ≤ 6°C	Not specified
Semivolatile Organic Compounds + Tentative Identified compounds	EPA 3520C/8270C (GC /MS)	1-L - Amber Glass	Cool to ≤ 6°C	7 Days
Semivolatile Organic Compounds + Tentative Identified compounds	EPA 625/8270D (GC)	1-L - Glass	Cool to ≤ 6°C, Add $Na_2S_2O_3$in the presence of residual chlorine	7 Days
Total Organic Halides (TOX)	SW 846 9020	250 mL Amber Glass	H_2SO_4 until pH < 2, Cool to ≤ 6°C	28 Days
Total Petroleum Hydrocarbons	EPA 1664B (Extraction and Gravimetry) EPA 8015D (GC)	1-L Amber Glass	HCl or H_2SO_4 until pH < 2, Cool to ≤ 6°C	28 Days
Tributyltin	EPA 6020: Metals-Total Subbed	1 L - Glass	Cool to ≤ 6°C	Not specified

Tributyltin (Tributyltin chloride)	EPA 8323	1 L - Glass	Cool to ≤ 6°C	24 Hours
Volatile Organic Compounds + Tentative Identified compounds	EPA 5030 or EPA 5035/8260B (GC/MS)	40-mL VOA vials (Amber)	HCl until pH < 2, Cool to ≤ 6°C	14 Days
Volatile Organic Compounds + Tentative Identified compounds	EPA 624.1 (GC /MS)	40-mL VOA vials (Amber)	HCl until pH < 2, Cool to ≤ 6°C, Add $Na_2S_2O_3$ (a few crystals) in the presence of residual chlorine	14 Days
Radioactive				
Total Radium 226 (Liquid Samples)	EPA 903.1 (Radon Emanation)	1-L - Plastic	HNO_3 until pH is < 2	6 Months
Total Radium 228 (Liquid Samples)	EPA 904.0 (Radiochemical/Precipitation)	1-L - Plastic	HNO_3 until pH is < 2	6 Months
Total Radium 226 and 228 (Solid Samples)	EPA 901.1 (Gamma Spectroscopy)	215 grams - Wide-Mouth Plastic	None	6 Months
Gross Alpha/Beta (Liquid Samples)	EPA 900.0 (Evaporation)	500 mL –Wide-Mouth Plastic	HNO_3 until pH is < 2	6 Months
Gross Alpha/Beta (Solid Samples)	EPA 900.0 (Evaporation)	30 grams - Wide-Mouth Plastic	None	6 Months
Strontium 90	EPA 905.0	1-L - Plastic	HNO_3 until pH is < 2	6 Months
Microbiological				
Coliform, Fecal	SM 9222D	250 mL - Sterile Plastic	Cool to ≤ 6°C	8 Hours
Coliform, Fecal Strep	SM 9230A/B	250 mL - Sterile Plastic	Cool to ≤ 6°C	6 Hours
Coliform, Total	EPA 1603	250 mL - Sterile Plastic	Cool to ≤ 6°C	8 Hours
Coliform, E.Coli	EPA 1603	250 mL - Sterile Plastic	Cool to ≤ 6°C	8 Hours
Enterococci	EPA 1600	250 mL - Sterile Plastic	Cool to ≤ 6°C	8 Hours
Heterotrophic Plate Count	SM 9215B	250 mL - Sterile Plastic	Cool to ≤ 6°C	8 Hours

Whole Effluent Toxicity (WET)				
Acute Nonvertebrate	*Ceriodaphnia dubia* EPA 2002.0	4-L –Plastic Cubitainer	Cool to ≤ 6°C	36 Hours
Acute Vertebrate	*Pimephales promelas* EPA 2000.0	4-L –Plastic Cubitainer	Cool to ≤ 6°C	36 Hours
Chronic algae	*Selenastrum capricornutum* EPA 1003.0	4-L –Plastic Cubitainer	Cool to ≤ 6°C	36 Hours
Chronic Nonvertebrate	*Ceriodaphnia dubia* EPA 1002.0	4-L –Plastic Cubitainer	Cool to ≤ 6°C	36 Hours
Chronic Vertebrate	*Pimephales promelas* EPA 1000.0	4-L - Plastic Cubitainer	Cool to ≤ 6°C	36 Hours

1. The sample container material must be chemically inert and compatible with the analytes and "strictly follows" lab and/or Standard Methods requirements
2. Alkalinity: 14 days holding time for treated samples, and should be analyzed as soon as possible for untreated samples.

Appendix A. Field Sampling Log Sheet

Samplers' Names: _____

Sampling Episode: _____

Sampling Method and Sampling Equipment Used:

_____

_____

_____

Sample ID	Date and Time	Temp (ºC)	pH	Conductivity	Weight of 100 mL of Sample	Free Chlorine

Notes: (include observations of odor and color of each aliquot, take photographs, and note any deviations from the plan):

_____

_____

_____

_____

Appendix B. Sample Preservation Log Sheet

Preservation Chemicals - List Strength of Solution from Bottle								
HCl _____ HNO_3 _____ H_2SO_4 _____ $Na_2S_2O_3$ _____NaOH _____ Other_____								
Sample Number	Analysis	Bottle type	Date	Name of Sampler	Chemical	Initial pH	Final pH	Number of Drops

Appendix C. Sample Chain of Custody

CHAIN OF CUSTODY

Address:

WEATHER	Fog	Rain	Snow	Wind	Clear
LEVEL None					
LEVEL Light					
LEVEL Moderate					
LEVEL Heavy					

REQUESTED SERVICES

CONTACT INFORMATION			
Company:		Address:	
Contact:		Special instructions:	
Phone:			

PROJECT INFORMATION				TRUN AROUND TIME CODES - (TAT)	
Project ID:				STD - Standard (Defualt)	Rushes received after 2pm or on weekends, will be considered received the next business day. Please alert us in advance of weekend analysis needs.
Project Description:				ND - Next Business Day	
Project Zip Code		Sampling Date/Time:		SD - Same Business Day	
PO number		Sampled By:		WH - Weekend/Holiday/ASAP	

SAMPLE ID	DESCRIPTION	Sample Type (Below)	TAT (Above)	Total Volume/Area (as applicable)		NOTES (Time of the day, Temp, RH, etc.)		

SAMPLE TYPE CODES				RELINQUISHED BY	DATA & TIME

RECEIVED BY	DATA & TIME

Kanalis Greenhouse Pilot (HPOC, LLC)

OCD Permitting—Searches—Wells—District 3 – Aztec- Status: Active:
Total active wells in the state: 55,802
Active Wells: District 1: 17,332
District 2: 15,830
District 3 Aztec—21,098
District 4 1,542
District 3
Total active oil: 1,874
Total active gas: 19,104

OCD Permitting—Searches—Wells—District 3 – Aztec- Status- Active-Pool Contains "entrada", well type= All
Search on Entrada pool wells:
2024 01 19

https://wwwapps.emnrd.nm.gov/OCD/OCDPermitting/Data/Wells.aspx

70 records

1 acid gas injection well
1 misc well (carbon safe strat well)
6 oil wells (3 active, 2 shut in, 1 expired temp abandonment)
1 injection well
62 salt water disposal wells

API	Well Name	Current Operator	Well Number	Type	Work Type	Mineral Owner	Surface Owner	Status
30-045-35172	PATHFINDER AGI	[307625] CCI SAN JUAN LLC	#001	Acid Gas Injection	New	Federal	Private	Active
30-031-20124	SOUTH HOSPAH UNIT	[291567] DOMINION PRODUCTION COMPANY, LLC	#033	Injection	New	Federal	Federal	Active
30-045-38272	SJB CARBON SAFE STRAT TEST	[15847] NEW MEXICO INSTITUTE OF MINING & TECHNOLOGY	#001	Miscellaneous	New	Private	Federal	New
30-043-20949	EAGLE SPRINGS 8 FEDERAL	[246238] HPOC, LLC	#001H	Oil	Plugback	Federal	Federal	Active
30-043-20950	EAGLE SPRINGS 8 FEDERAL	[246238] HPOC, LLC	#002M	Oil	Re-entry	Federal	Federal	Active
30-031-21107	OJO ENCINO 21 FEDERAL	[246238] HPOC, LLC	#001H	Oil	New	Federal	Indian	Active
30-031-21111	OJO ENCINO 21 FEDERAL DWS	[246238] HPOC, LLC	#002	Oil	New	Federal	Federal	Shut In
30-031-21006	TORREON WASH 36 STATE	[246238] HPOC, LLC	#001	Oil	Re-entry	State	Federal	Shut In
30-043-20926	HERRERA BIG GAME	[140786] SAN JUAN GAS CORPORATION	#001	Oil	New	Private	Private	Expired Temporary Abandonment
30-045-38304	NAGEEZI UNIT SWD	[371838] DJR OPERATING, LLC	#001	Salt Water Disposal	New	Federal	Federal	New
		[291567] DOMINION PRODUCTION						

5 HPOC wells= 3 active oil, 2 SWD (included in the SWD count)

Conclusions:
Entrada is a disposal formation, not a routine producing formation in the SJ Basin= 56 SWDs out of 60 in the SJB are SWD.
Only 3 active oil wells in the Entrada formation in the entire District 3- Aztec---- the 3 HPOC wells
Of the 1874 oil wells in the basin, 3 are producing from the Entrada
Of the 21,098 active wells in the basin, 3 are producing from the Entrada.

Oil:Water Ratio for the 3 oil wells

Data from OCD Permitting: https://www.emnrd.nm.gov/ocd/ocd-e-permitting/
(NM OCD ArcGis hub- oil and gas map, 2023 10 20, 2023-11-09), also OCD Permitting- Searches- Wells- search by API
Data obtained from production data for each well looked up using its API well number

(Oil Well) 30-043-20949 Eagle Springs 8 Fed 1H

2021: 8629 bbls oil, 670,919 bls PW, 316 days	Oil:27.3 bbl/day	PW: 2123 bbl/day	Oil- Water Cut 1: 78
2022: 9006 Bbls oil, 900,227 bbl PW, 340 days	Oil: 26.4 bbl/day	PW: 2647 bbl/day	Oil-Water Cut 1: 101

(Oil Well) 30-043-20950 Eagle Springs 8 Fed 2M

2021: 293 bbls oil, 33,771 bls PW, 97 days	Oil: 3 bls/day	PW: 348 bbl/day	Oil-Water Cut: 1: 116
2022: 93 bls oil, 10,720 bls PW, 31days	Oil: 3 bls/day	PW: 345 bbl/day	Oil-Water Cut: 1: 115

The 2 Eagle Springs oil wells are on the same well pad, and the Eagle Springs SWD is 2644 feet to the east

(SWD) 30-043-21065 Eagle Springs 9 Fed #1
2021: 704,690, unknown # of days Example: assume 365 days- 1930 bls/day
2022: 910,947, unknown # of days Example: assume 365 days- 2495 bls/day
Nearest well – 2644 feet to west- 2 HPOC wells- Entrada oil wells

Assume the Kanalis produced water analyzed was from the SWD well at Eagle Springs.
Kanalis TPW was analyzed by the PWRC. The results should have been submitted to the NM WaterStar PW Data Portal and made available

(Oil Well) 30-031-21107 Ojo Encino 21 Federal 001H

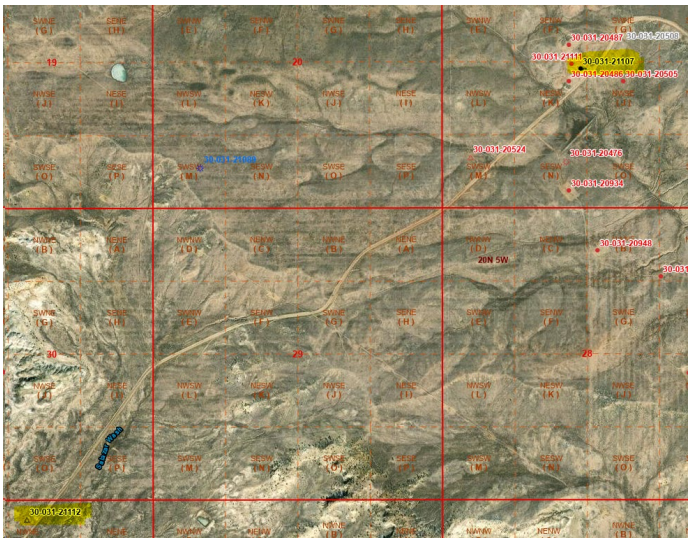
2021: 6379 bbl oil, 1,594,886 bbl PW, 273 days	Oil: 23 bbl/day	PW: 5,842 bbl/day	Oil-Water Cut: 1: 254
2022: 7,110 bbl oil, 2,278,693 bbl PW, 145 days	Oil: 49 bbl/day	PW: 15,715 bbl/day	Oil-Water Cut: 1: 320

⊞ 2021	6,379	0	1,594,886	273
⊞ 2022	7,110	0	2,278,693	328
⊞ 2023	3,028	0	1,024,248	145

(SWD) 30-031-21112 Ojo Encino 31 Federal SWD
2021: 2,176,145, unknown # of days Example: assume 365 days- 5,962 bls/day disposal rate
2022: 2,930,044, unknown # of days Example: assume 365 days- 8,027 2495 bls/day
Nearest well- 7200 feet north—active fruitland coal—30-031-21089

⊞ 2020	0	0	0	0	1,005,101
⊞ 2021	0	0	0	0	2,176,145
⊞ 2022	0	0	0	0	2,930,044
⊞ 2023	0	0	0	0	1,280,295
Grand Total:	0	0	0	0	12,423,449

NMED Exhibit 200



NMED Exhibit 200

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Non-targeted analysis and toxicity prediction for evaluation of photocatalytic membrane distillation removing organic contaminants from hypersaline oil and gas field-produced water

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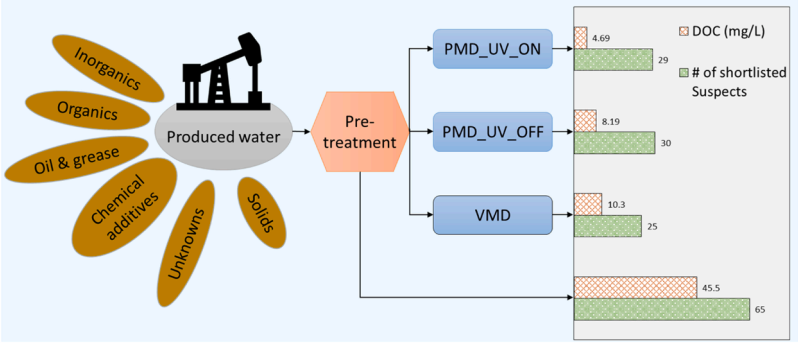
HIGHLIGHTS

- Non-targeted chemical screening tools were used to evaluate treated produced water.
- Fates of different suspect compounds were studied.
- Photocatalytic membrane distillation resulted in better removal of dissolved organics.
- Human health and environment-based concerns of suspect compounds were discussed.
- Non-targeted chemical screening is helpful in identifying critical target analytes.

GRAPHICAL ABSTRACT



ARTICLE INFO

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Vacuum membrane distillation
Produced water treatment
Physicochemical properties
Liquid chromatography-mass spectrometry
Cheminformatics

ABSTRACT

Membrane distillation (MD) has received ample recognition for treating complex wastewater, including hypersaline oil and gas (O&G) produced water (PW). Rigorous water quality assessment is critical in evaluating PW treatment because PW consists of numerous contaminants beyond the targets listed in general discharge and reuse standards. This study evaluated a novel photocatalytic membrane distillation (PMD) process, with and without a UV light source, against a standard vacuum membrane distillation (VMD) process for treating PW, utilizing targeted analyses and a non-targeted chemical identification workflow coupled with toxicity predictions. PMD with UV light resulted in better removals of dissolved organic carbon, ammoniacal nitrogen, and conductivity. Targeted organic analyses identified only trace amounts of acetone and 2-butanone in distillates. According to non-targeted analysis, the number of suspects reduced from 65 in feed to 25–30 across all distillate

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samples. Certain physicochemical properties of compounds influenced contaminant rejection in different MD configurations. According to preliminary toxicity predictions, VMD, PMD with and without UV distillate samples, respectively contained 21, 22, and 23 suspects associated with critical toxicity concerns. Overall, non-targeted analysis together with toxicity prediction provides a competent supportive tool to assess treatment efficiency and potential impacts on public health and the environment during PW reuse.

1. Introduction

Advanced horizontal drilling technologies with hydraulic fracturing expanded oil and natural gas (O&G) extraction and development in the United States (U.S.), positioning the country among the top producers of O&G in the world [1]. During the O&G extraction, a substantial amount of liquid waste stream called produced water (PW) is generated. For instance, over 25 billion bbl/year (3.97×10^9 m^3/year) of PW was generated from onshore production in the U.S. alone in 2021 [2–4]. PW encompasses dissolved and dispersed oil residues, organics, anions, cations, heavy metals, solids, gaseous constituents, naturally occurring radioactive materials (NORMs) distinct to geochemical properties of the basin/formation, and diverse synthetic chemical additives used for O&G extraction and production [2,5,6]. Safe PW management and disposal is crucial as certain constituents in the PW can potentially cause acute and chronic toxicity effects, endangering humans and the environment [7,8]. PW management is challenging due to high salinity and variation of PW quality spatially and temporally as well as the diversity of potential contaminants present [2,9]. Currently, over 96% of the PW generated in the U.S. from onshore production is managed via injection into enhanced oil recovery wells and/or disposal in Class II saltwater disposal wells, after traditional treatment using gravity-based phase separation and coarse filtration [4,5]. Growing freshwater scarcity and the possibility of increased seismic incidents associated with PW injection into deep wells have encouraged recycling of PW within O&G fields and/or reuse outside O&G fields with adequate treatment [10].

The complex composition of PW necessitates a combination of meticulous treatment processes including physical, chemical, biological, electrochemical, and thermal processes, lined up stage-wise (e.g., primary, secondary, tertiary, advanced/desalination, and/or zero liquid discharge) to attain certain treatment goals depending on the raw PW quality and the intended PW management options [3,5,11–15]. In current practice, strainers, API separators, or hydrocyclones are utilized upstream to separate large solids, oil, and gas [11,12,15]. Flotation, aeration, oxidation, flocculant-coagulant aided precipitation, chemical precipitation, and skimming are also considered to remove residual oil droplets, grease, suspended solids, colloidal matter, organics, bacteria, heavy metals, anions, cations, and hardness from PW stream prior to disposal [12,13,16–18]. With advanced treatment such as ion exchange, distillation, evaporation, crystallization, and membrane filtration processes [e.g.: ceramic microfiltration (MF)/ultrafiltration (UF), polymeric MF/UF, nanofiltration (NF), reverse osmosis (RO), membrane distillation (MD)] further removal of dissolved solids (TDS), metals, heavy metals, NORMs, inorganic scaling agents, and organics can be achieved for certain recycling/reuse purposes [12,13,18,19]. The valuable minerals in PW such as NaCl, $CaCl_2$, LiOH & Li_2CO_3 could be recovered from PW brine while achieving zero liquid discharge goals [20]. A "fit-for--purpose treatment" concept is currently emerging at laboratory and pilot as well as commercial scales to identify effective and efficient PW management pathways [5,16,17].

MD has been recognized as a promising technology for fit-for-purpose PW treatment due to its ability to withstand hypersaline waters, less sensitivity to feed water concentrations, high selectivity, and ability to utilize waste heat [21–27]. MD is driven by the vapor pressure gradient across a hydrophobic membrane which incorporates water vaporization and condensation. MD is operated at lower pressures compared to traditional pressure-driven membranes and at lower temperatures compared to other thermal desalination technologies [22,23]. Theoretically, MD can achieve nearly 100% rejection of salts, heavy metals, and non-volatile organics [21,22]. Challenges of MD include the necessity of high-performance membranes with good thermal stability, chemical stability, and wetting resistance; high energy requirements for water heating (~628 kWh/ton of treated water); and the tendency for membrane fouling/scaling [21]. To overcome some of these challenges, MD processes have been developed considering different membrane types/materials (e.g., ceramic and polymeric) and MD configurations [e.g., direct contact MD (DCMD), air-gap MD (AGMD), sweep gas MD (SGMD), vacuum MD (VMD)] [21,22,24].

Among different MD configurations, DCMD is widely employed in treating a variety of water types including O&G PW, considering the simplicity of design and operation as well as higher salts and organic removal [26,28]. Its thermal efficiency is relatively low (22–44%) as it suffers from significant conductive heat loss [29]. VMD configuration is recently getting attention for hypersaline O&G water treatment due to its ability to achieve relatively high permeate flux (15–20 kg/m^2·hr for 150 g/L NaCl) and thermal efficiency (~100%) [26,29,30]. However, VMD has greater susceptibility to membrane fouling and wetting due to the applied vacuum pressure, affecting long-term stable operation [31]. Moreover, most of the previous MD studies have utilized polymeric membranes (e.g., polytetrafluoroethylene, polypropylene, polyethylene, and polyvinylidene fluoride) owing to the high porosity and hydrophobicity. These polymeric membranes show less thermal and chemical stability towards long-term MD operations which undergo high temperatures and pH environments [32]. Recently, ceramic membranes have gained recognition for MD operations because of their high thermal and chemical stability [32]. As ceramic membranes are hydrophilic in nature, the membrane surface must be hydrophobized before its application in MD processes.

Previous studies have evaluated various surface modifications of membranes and innovative MD designs to control membrane wetting and fouling [22,33,34]. Several studies have reported surface-modified membranes in MD treatment processes [e.g., titanium dioxide (TiO_2), silver (Ag), carbon nanotubes] coupled with solar irradiation or UV irradiation, or in combination with photocatalysis, that enable the photochemical degradation of diverse complex organics in PW thereby enhancing anti-fouling characteristics and contributing to energy-efficient contaminant separation [22,33–38]. As the energy requirement for water heating is another critical concern, previous studies have developed innovative MD configurations to utilize solar irradiation and waste heat as low-cost energy sources to improve energy sustainability. Likewise, certain configurations can recover conductive heat from the permeate side to enhance energy efficiency [39–41].

PW characterization is as equally challenging as PW treatment due to its complex composition which varies both temporally and spatially [42–45]. High total dissolved solids (TDS) concentrations of ~ 3000 – 300,000 mg/L in PW restrict the application of existing standard analytical methods that were originally developed for freshwaters and municipal wastewaters [45]. A previous study reported that only 24% of the unique constituents identified (~1198) in PW could be quantified by the analytical procedures approved by the United States Environmental Protection Agency (USEPA) [6]. Many of the existing targeted analytical methods are focused on constituents that are included in the National Pollutant Discharge Elimination System (NPDES) program and the Underground Injection Control (UIC) program. However, there are many PW constituents beyond the targets specified in these regulations. Non-targeted chemical constituent identification has gained traction

recently because of its ability to identify new contaminants and well-known constituents (i.e., suspects) without prior understanding of their presence in the sampled PW, and its ability to identify thousands of constituents in a single analysis with molecular formula and structure information which later could be used for toxicity prediction [46]. Therefore, non-targeted analytical methods are ideal for initial characterization of PW and for shortlisting possible targets for future targeted analyses.

Research on MD treatment for hypersaline O&G PW is rapidly evolving, given its ability to minimize fouling- and scaling-related maintenance and provide reliable treatment efficacy during long-term, stable operation. Most previous studies are focused on increasing water flux and salt rejection while minimizing fouling. However, if the end goal of O&G PW treatment is beneficial reuse, more emphasis should be given to detailed water quality of the permeate when evaluating treatment technologies due to the numerous inorganic and organic contaminants potentially in PW that can present human and ecological health risks.

The objective of the current study is to evaluate the suitability of a novel photocatalytic membrane distillation (PMD) system equipped with hydrophobically modified tubular ceramic membranes coated with TiO_2 nanoparticles for PW treatment at bench scale. Previously, this MD system has shown improved resistance to fouling and scaling and resulted in over 80% removal of total organic carbon from hypersaline, pre-treated unconventional PW with a TDS concentration of 175 g/L collected from the Permian Basin in the U.S. [47]. The goal of the current study is to evaluate the organic contaminant removal capabilities of this emerging technology using state-of-the-art non-targeted screening tools. Specifically, this study intends to 1) compare the performance of an emergent PMD system against a traditional vacuum membrane distillation (VMD) system using general water quality data, targeted analysis, and non-targeted suspect screening tools; 2) understand the fates of different organic contaminant groups during PMD and VMD treatment; and 3) identify putative toxicity characteristics of residual organic contaminants in the distillates using the Cheminformatics Modules software applications developed by the USEPA.

2. Methodology

2.1. Membrane distillation treatment

Design and operation of the vacuum membrane distillation (VMD) and photocatalytic membrane distillation (PMD) treatments have been reported in detail previously by Chen et al. [47]. Briefly, VMD treatment utilizes a ceramic tubular membrane (substrate: alumina, membrane thickness; 2 mm, outer diameter: 12 mm, inner diameter: 8 mm) hydrophobically modified (both sides) using 0.1 M hexadecyltrimethoxysilane mixed in ethanol [47,48]. VMD was operated at a feed water temperature of 68.5 °C, a feed flow rate of 2 liters per minute (LPM), and a vacuum pressure of 11 kPa (absolute) [47]. For the PMD treatment, the hydrophobically modified ceramic membranes used in VMD treatment were further improved with a TiO_2 coating using 0.5 wt % TiO_2 solution [47]. Operating conditions (feed temperature, feed flow rate, and vacuum pressure) for the PMD treatment were the same as in the VMD treatment. To stimulate photocatalytic reactions, the tubular membrane module was surrounded by eight 70 mW UV-LED lamps [47]. For this study PMD was operated under two modes: 1) UV-LED lamps on and 2) UV-LED lamps off. The left side of Fig. 1 shows a schematic arrangement of the VMD and PMD treatments. Both VMD and PMD treatment studies were carried out for 55 h under feed-and-bleed mode where concentrate was continuously recycled to the feed tank while distillate was simultaneously withdrawn to the clean water tank. Distillate flux varied between 3.62 and 2.14 kg per square meter of membrane area per hour (KMH) in PMD treatment with and without UV whereas in VMD treatment flux rapidly declined from 4.22 to 1.88 KMH.

2.2. Feed water characteristics

PW pre-treated using two-stage cartridge filters (5 μm filter followed by 0.15 μm filter) was collected from the Permian Basin, New Mexico, and used as the feed water for MD experiments in this study. Pre-treated PW had a TDS concentration of 175 g/L. pH varied between 5.20 to 5.30 and the turbidity was less than 0.2 NTU. Average concentrations of dissolved organic carbon (DOC) and ammoniacal nitrogen (NH_3-N), in

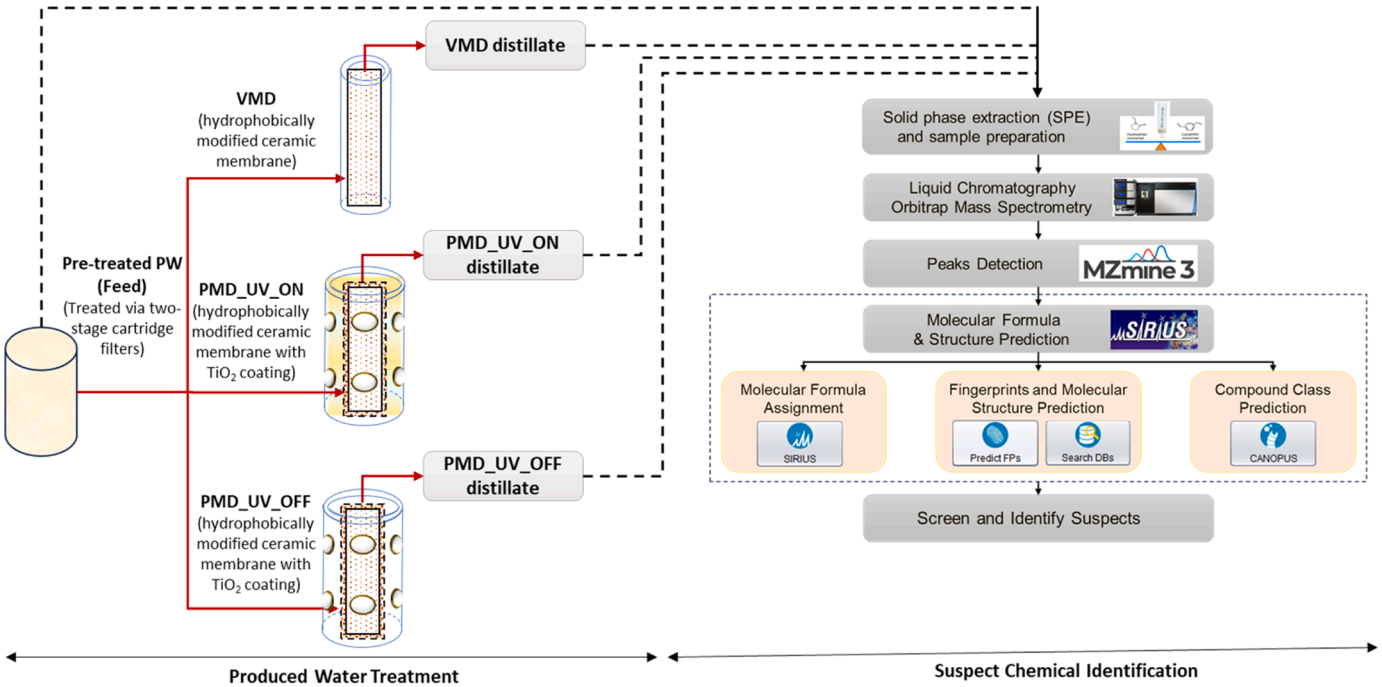

Fig. 1. Schematic of produced water (PW) treatment via vacuum membrane distillation (VMD) and photocatalytic membrane distillation (PMD) and subsequent suspect chemical identification.

the pre-treated PW water were 45.5 ± 0.47 mg/L and 613 ± 1 mg/L, respectively. Concentrations of metals and anions are reported elsewhere [47].

2.3. General water quality assessment and targeted analysis

Basic water quality parameters were measured using in-house handheld/benchtop meters: pH by Accumet AB 315 pH/mV meter (Fisherbrand, USA), electrical conductivity by Sension5 conductivity meter (Hach, USA), and turbidity via AQUAfast AQ3010 Turbidity Meter (Thermo Scientific, USA). Dissolved organic carbon concentration was measured using a Shimadzu TOC-V carbon analyzer (Kyoto, Japan) after filtering samples through 0.45 μm cellulose acetate filters. Dissolved NH_3-N was measured via Dionex ICS-2100 ion chromatography system (Thermo Scientific, USA). Feed and distillate samples were sent to a commercial laboratory (Cardinal Laboratories, NM, USA) to analyze hydrocarbons, volatiles, and semi-volatiles. A detailed list of organics analyzed in this laboratory is provided in Appendix A.

2.4. Liquid chromatography-based non-targeted screening

2.4.1. Sample preparation

Composite samples (500 mL) were initially filtered via 0.45 μm nylon filters to remove solid matter. For sample concentration and the elimination of nonvolatile salts, solid phase extraction was performed using Oasis hydrophilic-lipophilic balanced (HLB) cartridges (6 cc Vac Cartridge, 200 mg Sorbent per cartridge). Cartridges were assembled on Resprep 24-Port Vacuum Manifolds connected to a vacuum pump (Restek Corporation, Bellefonte, USA). Following the manufacturer's specification, cartridges were conditioned with 5 mL of methanol and then equilibrated with 5 mL of deionized (DI) water before loading samples. Thereafter, samples were loaded into the cartridges using tubing connected to filtered sample bottles. Cartridges were washed with 5 mL DI water after the entire sample volume was passed through the cartridge and allowed to dry at room temperature for 5 min. Then, the extracted organic content was eluted using 5 mL methanol, collected into glass vials, and evaporated to a final volume of ~200 μl using a pure nitrogen gas flow. Prior to analysis, the resulting sample was diluted 10 times to 2 mL using DI water, sonicated for 10 min, and filtered through 0.45 μm Nylon chromatographic filters. DI water blanks were included for extraction and analysis to identify any background features that stemmed from sample preparation and/or analytical instrumentation.

2.4.2. Liquid chromatography Orbitrap mass spectrometry analysis

The samples were analyzed using an Acquity M-class UPLC (Waters) coupled to an Orbitrap Fusion Tribrid mass spectrometer (Thermo Fisher Scientific). The chromatographic separation was completed using a C18 column (Waters nanoEase M/Z HSS, 0.3 × 150 mm, 1.8 μm). Mobile phases were comprised of 0.1% formic acid in water (A) and 0.1% formic acid in acetonitrile (B). The initial gradient started at 1% B for 1 min and then ramped up to 95% B over 60 min, held at 95% B for 6 min, followed by re-equilibration at 5% A for 15 min. The total run time was 82 min. The column oven was set to 35 °C, and the sample injection volume was 2 μL. The samples were ionized in positive mode with a heated electrospray ionization (HESI-II) probe (Thermo Scientific).

The mass spectrometer was operated in full scan mode for MS1 measurements and data-dependent acquisition (DDA) mode for MS2 measurements. For MS1 measurements, the mass spectrometer was operated with a scan range of 150–1000 m/z at 60,000 resolution using an intensity threshold of 2.5×10^5. EASY-IC™ was used for internal calibration, and the automatic gain control (AGC) was set to 4×10^5 ions with a maximum injection time of 500 ms. For MS2 measurements, the mass spectrometer was operated at a resolution of 15,000 with an isolation window of 1.5 m/z. The AGC was set to 5×10^4 ions with a maximum injection time of 35 ms, and the normalized higher energy collisional dissociation (HCD) was set to 20%, 30%, and 40%. Apex detection was used with a desired apex window of 25% and an expected peak width (FWHM) of 10 s. To avoid repetitive MS2 acquisitions of the same precursor ion, dynamic exclusion was triggered to exclude precursor ions for 5 s after detection 1 time using a mass tolerance of 10 ppm. Nitrogen was used as a drying, nebulizing, and collision gas.

2.4.3. Mass spectral data processing workflow

The resulting raw data files were centroided and converted to mzML files using MSConvert prior to mass and feature detection and alignment using MZmine 3. The noise level for mass detection was 1×10^4 for MS1 and 5×10^3 for MS2. Ion chromatograms were extracted using the ADAP chromatogram builder, a minimum feature height of 1.5×10^5, and an m/z tolerance of 5 ppm or 0.002. Then features were detected using the ADAP peak resolver with a minimum feature height of 1.5×10^5, a coefficient to area threshold of 120, a 0.2 to 1 min peak width, and an RT wavelet range of 0.2 to 1 min. After deisotoping, detected features were aligned with the Join aligner using an m/z tolerance of 5 ppm or 0.001 and a retention time tolerance of 0.2 min. After gap-filling using inbuilt tools in MZmine, the detected features were searched against the MassBank database using a precursor mass tolerance of 10 ppm or 0.01, a spectral m/z tolerance of 100 ppm or 0.1, a minimum of 3 matched signals, and a cosine similarity score of 0.6 using the MassBank weights.

Once the precursor peaks were identified and aligned across samples using MZmine 3 software, identified peaks were processed in SIRIUS (version 5.8.1) to assign molecular formulas, structures, and compound classes (right side of Fig. 1). SIRIUS has gained substantial attention recently for high-resolution mass spectrometry data processing on account of its demonstrated ability to identify compounds with high accuracy [49–51]. For the molecular formula annotation process, SIRIUS analyzes MS/MS spectra as well as isotope patterns while considering all theoretically viable formulas for a given monoisotopic mass and generating corresponding fragmentation trees [49–51]. SIRIUS offers several scores/indices to rank predicted molecular formulas for a given mass such as Sirius score, Zodiac score, number of peaks explained, total explained intensity, and mass error. Then, CSI: FingerID uses the mass spectrum and fragmentation tree of a detected compound to predict a molecular fingerprint, which can then be used to search for molecular structures in a chemical (not mass spectral) database [49,52,53]. The SIRIUS software interface provides the opportunity to visualize matching substructures and annotated spectra and enables exploring structure information in corresponding structural databases. Finally, CANOPUS is a machine learning-based tool used to predict ClassyFire compound classifications directly from MS2 spectra, together with a probability value [54,55].

Previous studies have considered different filtering criteria for the resulting formula annotations and structure predictions depending on the purpose of the chemical analysis [50,51,56–59]. In the current study, formula annotations with a number of explained intensity ≥ 3 and a total explained intensity $\geq 70\%$ were considered reliable molecular formulas. Reliable molecular formulas with accompanying molecular structure predictions were shortlisted and individually evaluated for their fragmentation trees, explained peaks, structure predictions, CSI: FingerID scores, and matching substructure annotations to determine the most confident candidate structures in the samples of interest [60]. Background features/compounds identified via DI water blanks were excluded from follow-up treatment performance assessments. The non-targeted chemical analysis herein did not include any chemical standards in the analysis to minimize interferences and quantification bias on unknown compounds. Therefore, this study provides qualitative or semi-quantitative outcomes. Mass spectral peak area was considered as an indicator of signal strength and used to calculate relative abundance (Relative abundance = mass spectral peak area of a particular monoisotopic mass/peak area of all monoisotopic masses detected in a sample).

2.4.4. Non-targeted screening data validation

Confidence of compound identifications was determined in accordance with the 5-level classification system widely followed for non-targeted analysis using high-resolution mass spectrometry [60–62]. In general, Level 1 describes a confirmed structure, which can only be achieved with a reference standard. Level 2 describes a probable structure, which requires clear evidence from mass spectral database matching or other diagnostic evidence. Level 3 describes a tentative candidate, including suspect screening matches, most mass spectral database matches, and most candidate structures generated in the absence of spectral matching (i.e., CSI: FingerID candidate structures). Finally, Level 4 represents unequivocal molecular formulas (possibly including those generated by SIRIUS), and Level 5 represents an exact mass of interest, the common starting point for further identification efforts.

Spectral database matching was performed using the MassBank database and spectral library matching tools built into MZmine 3. In addition, the accurate masses of features detected by MZmine 3 were screened against aggregate compound lists hosted on the USEPA's CompTox Chemicals Dashboard: PRODWATER, a list of compounds found to be present in PW by Danforth et al. (n = 1197 compounds) [6] and EPAHFR, a list of chemicals associated with hydraulic fracturing (n = 1693 compounds) [63] using a 1 ppm mass error window. Finally, the molecular formulas and candidate structures generated by SIRIUS and CSI: FingerID were compared to the candidates generated by MassBank spectral database searching and USEPA suspect list screening. Similar to many non-targeted analyses, most of the detected features were Level 3, tentative candidates, subject to confirmation with reference standards.

3. Results and discussions

3.1. General water quality and targeted analysis

The general treatment performance of the VMD system and PMD system (with and without UV) was assessed via DOC, NH_3-N, and conductivity indices as presented in Fig. 2. Organic content measured as dissolved organic carbon was the highest in the VMD distillate accounting for a 77.4% reduction from feed water. Modification of the ceramic membrane with a TiO_2 coating layer (PMD_UV_OFF) resulted in an 82% reduction in DOC concentration. TiO_2 modification with a UV light source to facilitate photocatalytic reactions (PMD_UV_ON) resulted in the highest organic removal of 89.7%. All MD configurations were capable of producing distillates with a conductivity as low as < 20 μS/cm. Advanced volatile organics and petroleum hydrocarbon analyses were conducted only for feed water, VMD distillate, and PMD_UV_ON distillate. A list of organic contaminants and their concentration in each sample is provided in Appendix A. Hydrocarbons in the gasoline range (C6 – C10), diesel range (C10 – C28), and extended diesel range (C28 – C36) were below detection levels (< 1 mg/L) in all samples including feedwater samples owing to the pre-treatment via two-stage cartridge filtration. Even though samples were analyzed for ~72 volatile organics, only six compounds were detected in the feed water (Fig. 2). Among the six compounds, methylene chloride, benzene, toluene, and total xylene were below detection levels (< 0.0005 mg/L) in both VMD and PMD distillates. Trace concentrations of acetone and 2-butanone were detected in both distillate samples.

Comparing the current performance to that of previous VMD studies is challenging because the majority of MD applications are centered on polymeric membranes and utilize synthetic water [26,28]. Available studies on VMD utilizing ceramic membranes for treating real O&G PW

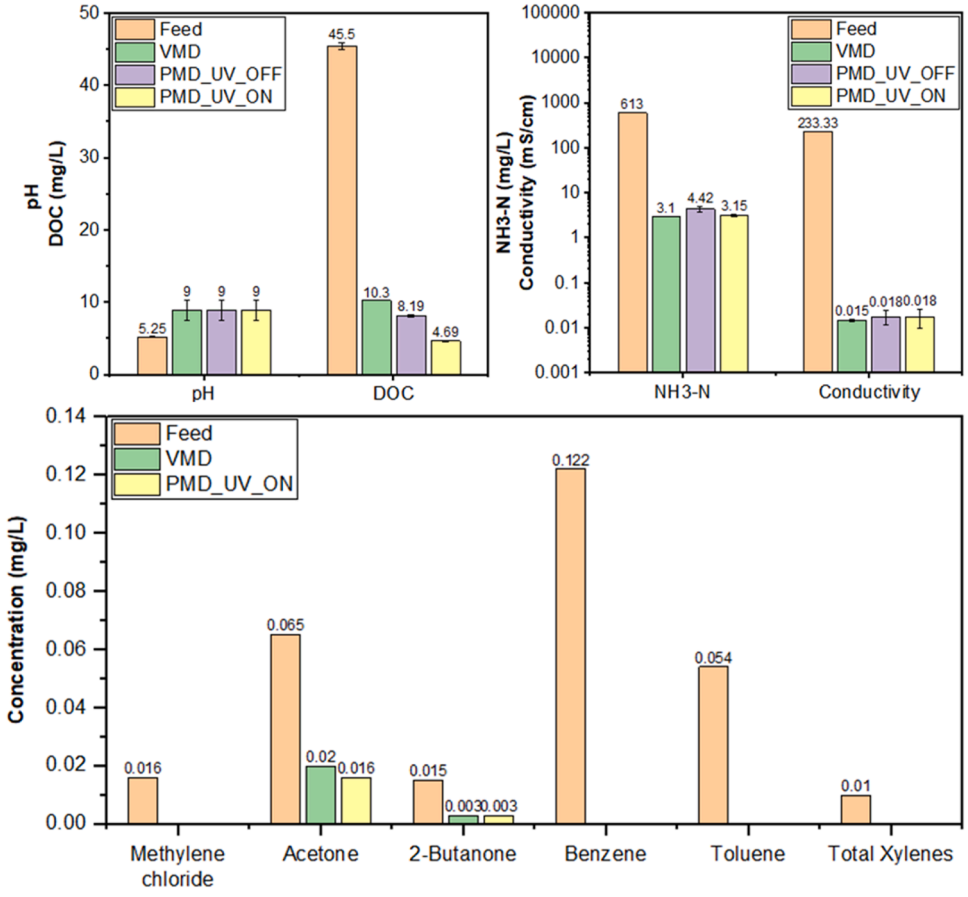

Fig. 2. Water quality characterization of feed water and distillate samples (Note: Error bars represent the standard deviation).

are limited and based on diverse membrane modifications, pre-treatment technologies, and operating conditions [64]. Instead, many previous studies focused on salt rejection and flux enhancement performance of modified ceramic membranes utilizing synthetic salt solutions [48,65,66]. For instance, Dong et al. evaluated an alumina hollow ceramic membrane modified with 1H,1H,2H,2H-Perfluorodecyl-silane-triethoxy, and TiO_2 nanorods for application in VMD systems using 100 g/L NaCl solution at 65 °C, under 0.085 kPa vacuum pressure [67]. Surface modifications exhibited anti-fouling and self-cleaning properties and resulted in ~99.9% salt rejections [67]. Another study by Ko et al. demonstrated the applicability of polymethylsilsesquioxane-coated and fluoroalkylsilane-coated alumina ceramic membranes for VMD systems [64]. This study was also limited to synthetic salt solutions and flux-related performance concerns. Several studies have tested modified ceramic membranes on organic solutions as well using VMD configuration [68,69]. For example, Kujawa et al. reported the effectiveness of modified ceramic membranes in removing volatile organics from aqueous solutions (e.g., methyl-tert-butyl ether and ethyl acetate) in a VMD design [69]. A handful of studies have demonstrated photocatalysis-enabled membrane modifications to minimize fouling while degrading organics and oils in O&G wastewater. A study by Alias et al. demonstrated over 97% reduction of oil from O&G PW utilizing a photocatalytic nanofiber-(polyacrylonitrile and graphitic carbon nitride) incorporated alumina hollow fiber membrane under cross-flow filtration [70]. The current study holds substantial novelty due to the application of hydrophobically modified ceramic tubular membranes coupled with different MD configurations and the detailed assessment of organic contaminant removal from hypersaline, real O&G PW.

3.2. Non-targeted chemical screening

3.2.1. Non-targeted data analysis summary

Fig. 3 illustrates a summary of non-targeted chemical analysis results (under positive ion mode) across the feed water and effluent samples resulting from different treatments. A total of 792 features were detected across the different samples considered in this study. Pre-treated PW, which was the feed water for VMD and PMD systems, consisted of 654 peaks whereas distillates from VMD, PMD_UV_OFF, and PMD_UV_ON contained a three-times lower number of peaks, indicating removal by the treatments. Among the total 792 features, 133 features matched with the MassBank spectral database via MZmine 3 with a cosine score greater than 0.6, and SIRIUS was able to predict molecular formulas for ~34% of the peaks and structures for ~17% of the peaks. As detailed in Section 2.4.3, the predicted molecular formulas and structures were further filtered to shortlist the best tentative candidates. Yellow bars in Fig. 3 indicate the number of shortlisted candidates excluding background features detected through DI blanks. The number of unique suspect compounds is shown in light blue bars excluding any duplicate predictions. Overall, 75 tentative candidates were shortlisted as suspect compounds across the four samples (Table 1). VMD distillate consisted of the least number of suspects (25) while PMD_UV_OFF and PMD_UV_ON contained 30 and 29, respectively. The number of compounds alone does not provide robust information on the organic contaminant removal performance of the tested treatment technologies, and hence DOC concentration is plotted on the same figure for preliminary quantitative comparison. Agreeing with the qualitative findings, DOC concentration drops after treatment via distillation processes, resulting in the lowest concentration in PMD_UV_ON distillate. This emphasizes the ability of the PMD_UV_ON process to achieve better organic removal than others. A detailed list of suspect chemicals is provided in Appendix A.

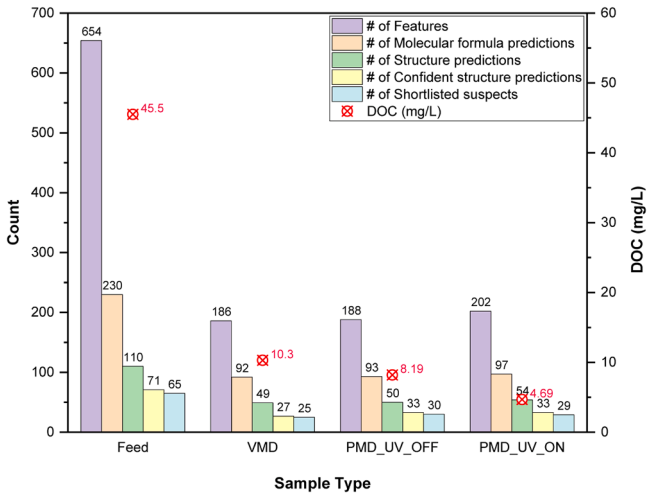

Fig. 3. Summary of non-targeted chemical screening via NTA workflow.

3.2.2. Data validation

Approximately 50 features with accompanying structure information were tentatively identified by MassBank spectral database matching. Among these identifications, 10 compounds were matched with the formula and structure predictions obtained from SIRIUS [triethanolamine, 4-hydroxy-1-(2-hydroxyethyl)-2,2,6,6-tetramethylpiperidine, pentaethylene glycol, hexaethylene glycol, nonaethylene glycol, 3,6,9,12,15,18,21,24,27-nonaoxanonacosane-1,29-diol, lumichrome, diethyltoluamide, 3,6,9,12,15,18,21,24,27,30-decaoxadotriacontane-1,32-diol, 1-octylpyrrolidin-2-one]. Similarly, comparison with existing PW databases resulted in four compound matches from the EPAHFR database (triethanolamine, N,N-diethyl-meta-toluamide (DEET), 2,6,10-trimethyl-9-undecenoic acid, triethyl citrate) and five from the PROD-WATER database (3-methoxyacetanilide, 5,6,7,8-tetrahydro-2-naphthoic acid, 1-methyl-2,3-dihydro[1,1′-biphenyl]-4(1H)-one, N,N-diethyl-meta-toluamide (DEET), and 3,6,9,12,15,18,21,24,27-nonaoxanonacosane-1,29-diol). Additional details of the matched compounds are provided in Appendix A.

PW composition varies substantially both spatially and temporally and consists of numerous organics (natural and synthetic), inorganics, metals, and radioactive materials [2]. PW composition is not fully identified or understood, and many unknown constituents are likely yet to be discovered. Indeed, the majority of the compounds identified in the current study (~94% of the compounds identified in total along with predicted molecular formula and structures) are not listed in existing PW databases, emphasizing the necessity of non-targeted chemical screening to unveil such unknowns.

3.3. Treatment performance evaluation based on non-targeted chemical screening

3.3.1. Fate of suspect compounds across treatments

Fig. 4 illustrates the fate of 75 shortlisted suspects across the feed (pre-treated PW), VMD distillate, PMD_UV_OFF distillate, and PMD_UV_ON distillate. Compound IDs denoted in the x-axis correspond to the compound IDs listed in Table 1 and additional details are provided in Appendix A. Relative abundance is provided in Fig. 4 as a semi-quantitative measure of the suspected compounds in the sample. Out of the 65 suspects detected in the feed water sample, 46 suspects were not detected in VMD distillate, while 39 and 44 suspects were not detected in PMD_UV_OFF and PMD_UV_ON distillates, respectively, indicating contaminant removal.

However, certain compounds that were not detected in feed water were later detected in treated effluents (Table 2). In the VMD and PMD_UV_OFF treatments, the organic removal mechanism is predominantly a physical separation and the likelihood of forming new compounds is rare. Therefore, the unique compounds detected in distillates from VMD and PMD_UV_OFF treatment appear to result from matrix

Table 1
Shortlisted organic suspects.

ID	mz	Molecular Formula	PubChem ID
1	841.8	C18H20I3N3O10	102182157
2	365.1	C10H24N2O8S2	20107
3	166.1	C9H11NO2	12092
4	160.1	C8H17NO2	13283520
5	302.2	C15H27NO5	5317361
6	239.1	C10H22O6	62551
7	252.1	C13H17NO4	1770752
8	283.2	C12H26O7	17472
9	327.2	C14H30O8	79718
10	316.2	C16H29NO5	77405
11	311.2	C15H28O5	131751198
12	415.3	C18H38O10	4867
13	459.3	C20H42O11	79689
14	460.3	C23H42NO6P	20261095
15	503.3	C22H46O12	81260
16	521.3	C27H50N2O5	28962604
17	547.3	C24H50O13	81248
18	453.3	C24H44N4O4	10961409
19	373.2	C18H32N2O6	21899582
20	264.2	C15H21NO3	44557025
21	181.1	C14H12	11502
22	217.1	C10H16O5	81576
23	173.1	C6H12N4S	2393252
24	173.1	C8H12O4	10702328
25	218.2	C12H27NO2	84963
26	243.1	C12H10N4O2	5326566
27	239.2	C14H22O3	45783232
28	246.2	C14H31NO2	119970
29	262.2	C14H31NO3	86289970
30	337.2	C15H24N6O3	85361
31	260.3	C15H33NO2	102496
32	313.3	C18H36N2O2	3067797
33	329.3	C18H36N2O3	3024596
34	306.3	C16H35NO4	14415758
35	318.3	C17H35NO4	44145805
36	345.3	C18H36N2O4	22621443
37	350.3	C17H35NO6	128703
38	361.3	C18H36N2O5	10571106
39	274.3	C16H35NO2	352309
40	190.1	C9H19NO3	5305380
41	258.2	C15H31NO2	103990
42	334.3	C17H35NO5	56965943
43	357.3	C20H40N2O3	6454263
44	318.3	C18H39NO3	74429
45	362.3	C19H39NO5	138858240
46	334.3	C18H39NO4	102492
47	322.3	C16H35NO5	25210470
48	329.3	C18H36N2O3	137333762
49	290.3	C16H35NO3	108487
50	362.3	C20H43NO4	110350
51	284.2	C15H25NO4	114962
52	244.3	C15H33NO	65596
57	288.3	C17H37NO2	109646
58	213.1	C9H16N4S	3044804
59	304.3	C17H37NO3	86740
60	158.2	C9H19NO	208725
61	268.1	C10H19N3O4	129439
62	267.1	C14H18O5	575881
63	387.2	C22H26O6	6850837
64	389.2	C24H24N2O3	3816325
65	403.2	C22H26O7	24796591
66	489.2	C30H32O6	25231263
67	281.1	C14H16O6	318242
68	405.2	C19H32O9	132934653
69	433.2	C21H36O9	10694035
70	177.1	C11H12O2	96611
71	329.0	C5H14O12P2	3400853
72	251.0	C6H13Cl2O4P	101640759
73	327.0	C9H18Cl3O4P	14034
74	187.1	C13H14O	98926
75	198.2	C12H23NO	3033871

Note 1:mz -Mass to charge ratio
Note 2: These compounds are suspected to be present in the samples of interest and not yet confirmed via *target analyses. Hence, represents confidence level 3.*
Note 3: additional details of the suspects are provided in Appendix A

effects caused by the highly complex nature of PW consisting of chemical additives (e.g., surfactants, biocides, and corrosion inhibitors), geogenic contaminants, salts, and transformation products [71–74]. Matrix effects can suppress or enhance the ionization of targeted chemicals and interfere with sample processing and analysis. For instance, surfactants are capable of dominating and enhancing their detection while suppressing the detection of other analytes in the sample [71,72]. Therefore, certain contaminants of interest may not be detected in highly complex mixtures such as raw and minimally treated PW due to interference caused by other dominating compounds. However, they tend to appear in further treated samples with the removal of interferences by advanced treatments [73]. Nell and Helbling reported such behavior caused by surfactants in hydraulic fracturing fluid analysis by liquid chromatography-electrospray ionization mass spectrometry techniques [72]. In contrast, lycurim, 1-(5-Ethyl-1,3,4-thiadiazol-2-yl)-4-methylpiperazine, N-{2-[(2-Amino-1-hydroxyethylidene)amino]-1-hydroxypropylidene}valine, and N-Octyl pyrrolidone were only detected in distillates from the PMD_UV_ON treatment. This suggests that they could be transformation products resulting from photochemical reactions.

3.3.2. *Impact of physicochemical properties on fate and rejection*

Certain physiochemical properties of contaminants influence the fate and rejection of contaminants through MD-based treatment processes [75,76]. Hence, relevant experimental or predicted properties (based on mathematical or computer models) of suspect contaminants available in the USEPA CompTox Chemicals Dashboard were extracted (Fig. 5 and Appendix A). Most of the suspect compounds retained in distillates (VMD, PMD_UV_OFF, PMD_UV_ON) pertained to higher Henry's law constant (Fig. 5-a) and vapor pressure (Fig. 5-b) compared to the pre-treated PW (feed water). However, the mean value of Henry's law constant and the vapor pressure of the compounds in distillate samples were not significantly different from that of pre-treated PW samples according to the statistical t-tests at a 95% confidence level (Appendix A). In general, the majority of the compounds in distillates had lower boiling points than the feed water (Fig. 5-d). The average boiling point of the compounds in VMD and PMD_UV_ON was statistically low compared to compounds in pre-treated PW at a 95% confidence level (Appendix A). Higher Henry's law constant and vapor pressure and lower boiling point indicate higher vaporability/volatility of the compounds and the possibility of escaping with water vapor in the VMD process [75,76]. Indirectly, this highlights that VMD and PMD (with and without UV) are less effective on highly volatile compounds and more selective towards low volatile compounds despite their ability to achieve 100% theoretical salt rejections. As per Henry's law, when the vapor pressure of a compound is higher, the solubility of the compound is lower. Accordingly, the water solubility of the suspect compounds detected in distillates was relatively low in the range of ~0.22 – 0.28 mol/L (mean values) while feed water had an average value of 0.80 mol/L (Fig. 5-c).

In the case of viscosity, suspect compounds detected in distillate samples pertained to an average value of ~20 mPa.s, which was less than half (46.04 mPa.s) of those in the feed water (Fig. 5-e), suggesting relatively higher selectivity towards high viscous compound rejection via MD processes in the current study. This implies that viscosity is another chemical property influencing contaminant rejection/separation in MD technologies. Octanol-water partition coefficients ($LogK_{ow}$) of compounds detected in each sample (Fig. 5-f) demonstrate compound selectivity of the MD treatments based on hydrophobicity. The higher the $LogK_{ow}$, the greater the hydrophobicity and thus the possibility of partitioning into the octanol phase (non-polar) over the water phase (polar). Compounds detected in distillate samples were associated with slightly lower $LogK_{ow}$ than the compounds detected in the feed water, suggesting poor rejection of hydrophilic compounds by the MD processes. However, the mean $LogK_{ow}$ value of the compounds in the distillate samples was not significantly different than that of the compounds in the pre-treated PW at a 95% confidence level (Appendix A).

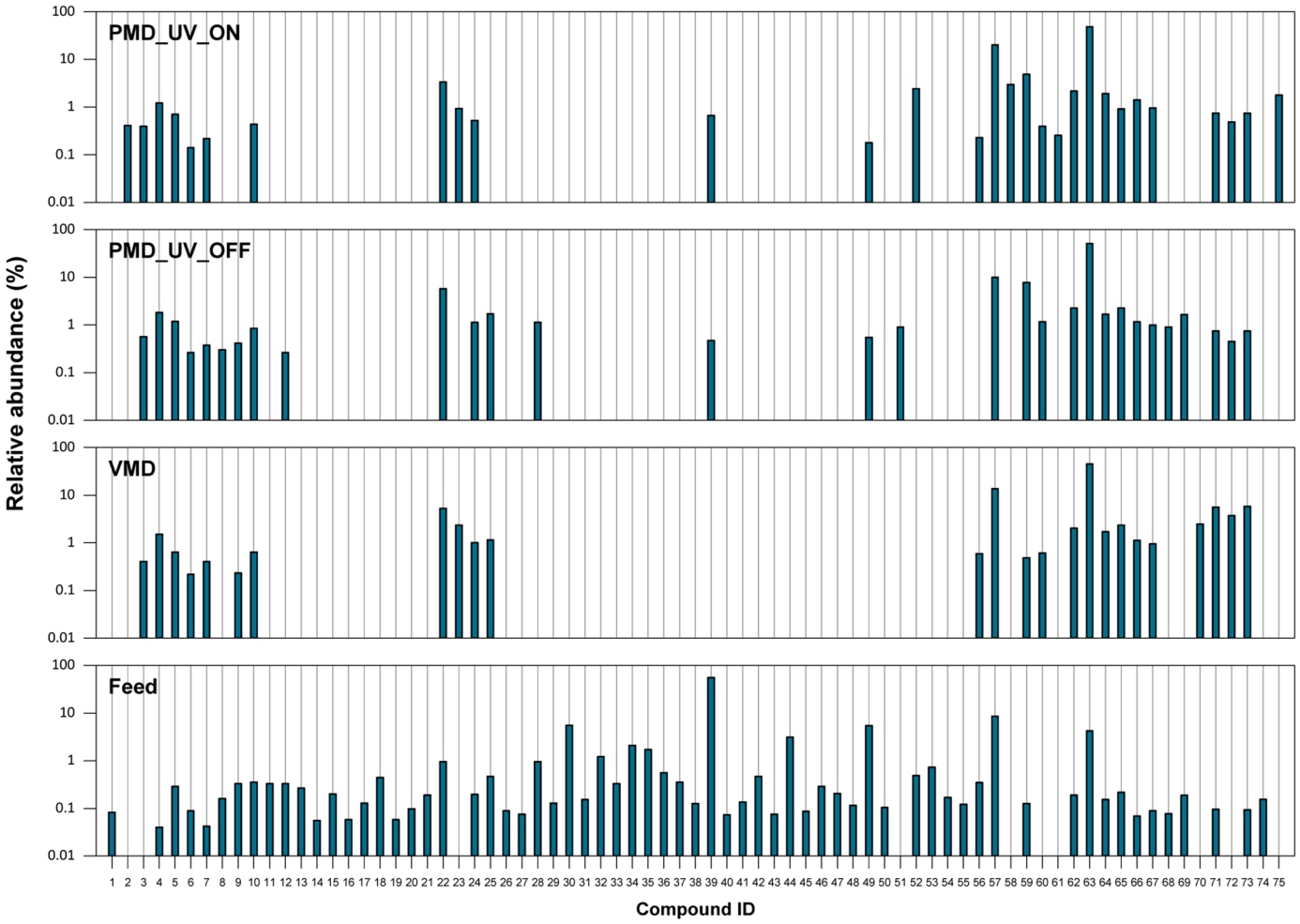

Fig. 4. Fate of shortlisted suspect chemicals across different samples.

Table 2
List of new organic suspects detected only in distillate samples.

Compound ID as per Fig. 4	Molecular Formula	Name	CASRN	Detection Status		
				VMD	PMD_UV_OFF	PMD_UV_ON
2	C10H24N2O8S2	Lycurim	-			DETECTED
3	C9H11NO2	4-(dimethylamino)benzoate	619-84-1	DETECTED	DETECTED	DETECTED
23	C6H12N4S	4-amino-5-tert-butyl-1,2,4-triazole-3-thiol	73396-58-4	DETECTED		DETECTED
51	C15H25NO4	4-(2-Hydroxy-3-((1-methylethyl)amino)propoxy)-alpha-(methoxymethyl)benzenemethanol	56392-16-6		DETECTED	
58	C9H16N4S	1-(5-Ethyl-1,3,4-thiadiazol-2-yl)-4-methylpiperazine	57709-33-8			DETECTED
60	C9H19NO	2,2,4,4-Tetramethylvaleramide	32905-64-9	DETECTED	DETECTED	DETECTED
61	C10H19N3O4	N-{2-[(2-Amino-1-hydroxyethylidene)amino]-1-hydroxypropylidene}valine	121428-48-6			DETECTED
70	C11H12O2	Mesityl glyoxal	22185-97-3	DETECTED		
72	C6H13Cl2O4P	bis(1-Chloropropan-2-yl) hydrogen phosphate	789440-10-4	DETECTED	DETECTED	DETECTED
75	C12H23NO	N-Octyl pyrrolidone	2687-94-7			DETECTED

No substantial influence was observed in the density or surface tension of the compounds on the contaminant separation (Appendix A). Additionally, the average number of heavy atoms in the compounds detected in the VMD and PMD_UV_ON samples was statistically lower (at 95% confidence level) than that of in feed sample, indicating better separation of compounds with a higher number of heavy atoms via MD processes (Appendix A). In addition, physicochemical properties of the suspect compounds detected in the feed water sample were statistically compared to those of the new compounds detected only in distillate samples (Appendix A) to identify underlying factors influencing detectability. The average boiling point of the new compounds was statistically lower than that of the compounds detected in feed water at a 95% confidence level. This suggests weaker intermolecular forces between the undetected molecules, allowing them to be more easily volatilized. Additionally, these new compounds had a lower carbon number and heavy atom count, indicating lower molecular weight. This suggests they may be newly formed products during treatment or influenced by the matrix effect. Detailed analyses are recommended for

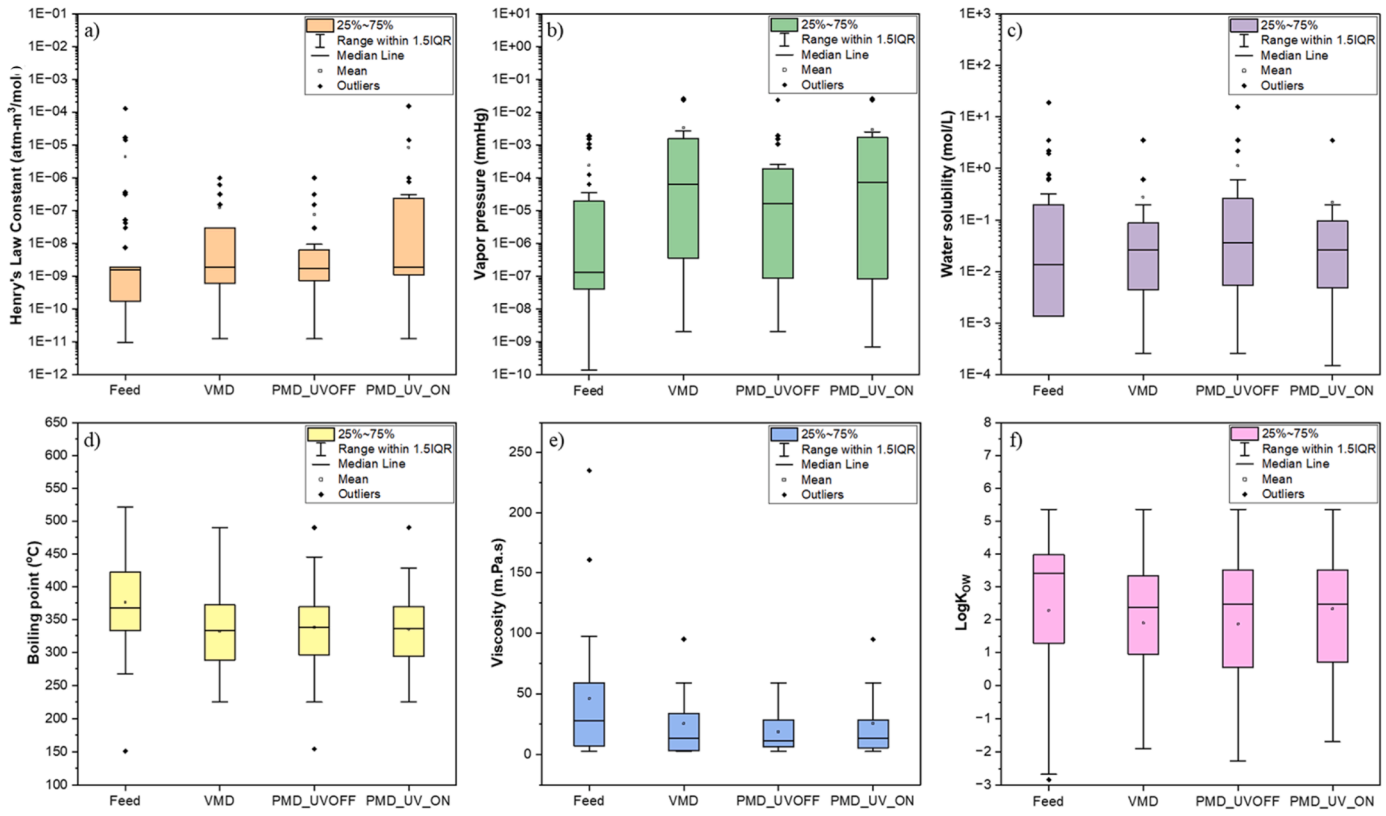

Fig. 5. Variation of certain properties of shortlisted suspect contaminants in feed water, VMD distillate, PMD_UV_OFF distillate, and PMD_UV_ON distillate: a) Henry's Law Constant, b) Vapor pressure, c) Water solubility, d) Boiling point, e) Viscosity, and f) $LogK_{ow}$.

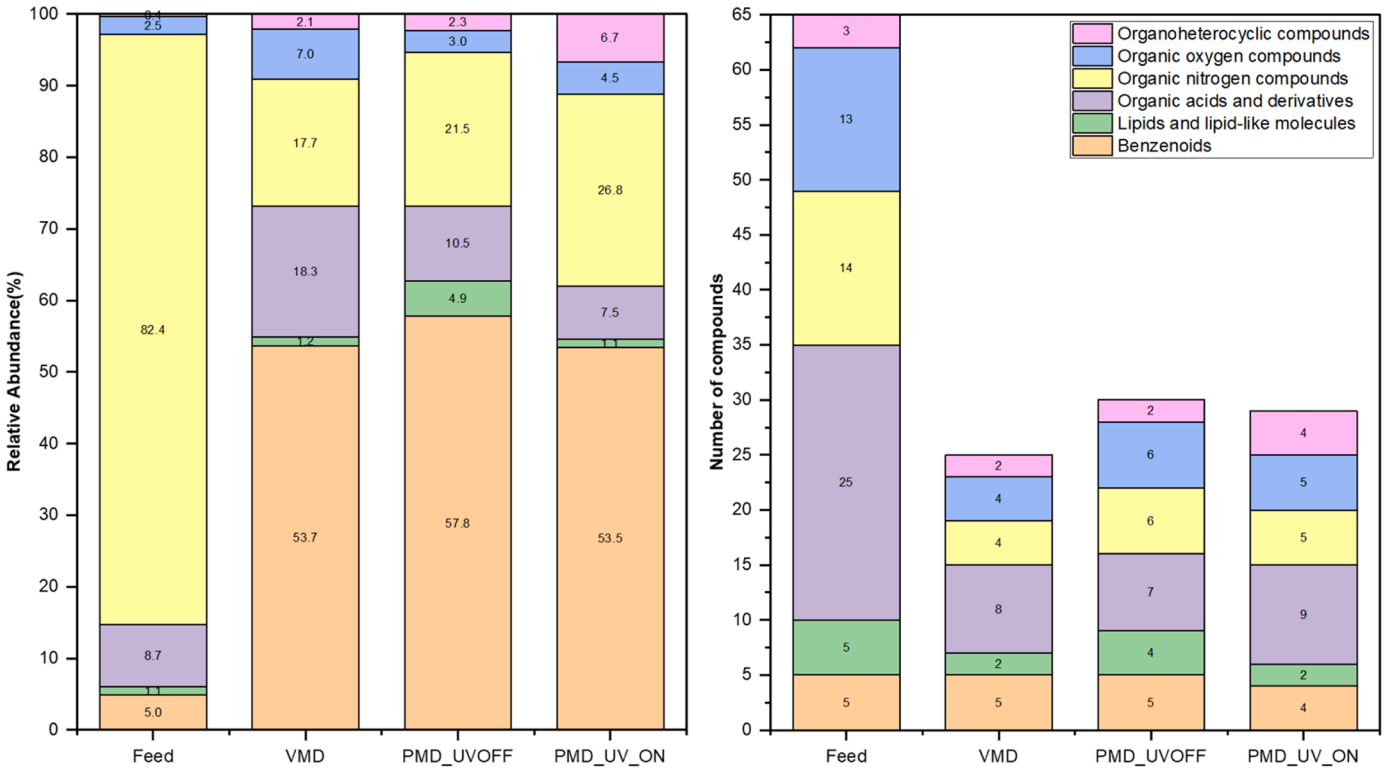

Fig. 6. Classification of shortlisted suspect compounds based on their ClassyFire superclass in different water samples.

a more conclusive interpretation of these observations.

3.3.3. Impact of chemical classification on fate and rejection

The classification of shortlisted suspect compounds based on their superclass is illustrated in Fig. 6 to assess the selectivity of compound rejection via treatment processes of interest in this study. The CANOPUS tool was capable of classifying most of the compounds up to six classification levels (Kingdom, superclass, class, subclass, level 5, and most specific level). In Fig. 6, the 75 shortlisted suspect compounds were classified into six major superclasses (benzenoids, organic acids, and derivatives, organic oxygen compounds, lipids and lipid-like molecules, organic nitrogen compounds, and organoheterocyclic compounds) using ClassyFire-integrated taxonomy. Pre-treated PW contained a high relative abundance of organic nitrogen compounds (~82%) constituted from 14 different suspect compounds. Even though the feed water contained 25 different organic acids and derivative compounds, their abundance was limited to ~9%. In addition, feed water contained 13 organic oxygen compounds constituting 2.5% relative abundance, 5 benzenoid compounds constituting 5% relative abundance, 5 lipids and lipid-like molecules constituting ~1.1% relative abundance, and 3 organoheterocyclic compounds constituting ~0.4% relative abundance. Benzenoids dominated (> 53%) in all distillate samples with over 50% relative abundance. VMD sample contained a comparable abundance of organic acids and derivatives (18.3%) and organic nitrogen compounds (17.7%). Organic nitrogen compounds were the second most abundant compound class in both PMD_UV_OFF (21.5%) and PMD_UV_ON (26.8%).

Overall, MD treatments were capable of reducing the number of compounds from all categories detected in the feed water. On the contrary, a slight increment was observed in relative abundance and number of compounds of the organoheterocyclic category following PMD_UV_ON which could be due to transformation products resulting from photocatalytic reaction enabled by the UV light source. Unfortunately, relative abundance does not necessarily and accurately represent the environmental concentration of individual suspect compounds. Moreover, matrix interference could substantially impact results, particularly in the feed water. Hence, follow-up targeted analysis of the shortlisted suspects is warranted to obtain quantitative measurements and confirm the presence of identified suspects. Based on the DOC concentration, which is a widely used indicator for organic contaminants, PMD_UV_ON outranked PMD_UV_OFF and VMD resulting in the highest organic removal of 89.7%.

Even though feed and distillate samples were analyzed for ~72 targeted VOCs and petroleum hydrocarbons, the majority of them were below detection levels in all the samples. A handful of six targeted compounds (methylene chloride, acetone, 2-butanone, benzene, toluene, and xylene) were detected in trace levels in the feed water while only acetone and 2-butanone were detected in distillate samples. This indicates the analytical limitation of targeted analyses and the necessity of advanced technologies to identify a broader diversity of contaminants at trace concentrations. However, tentatively identified benzene and derivative compounds, certain fatty acids, and amino acids at the most specific classification level in this non-targeted screening pathway agree with the initial targeted analyses, indirectly validating the findings of the non-targeted analysis. A previous study by Emmons et al. unraveled the presence of ketones, alcohols, and branched alky chained molecules in PW samples collected from the Permian and Eagle Ford basins in Texas using gas chromatography techniques which likewise support the sub-classification level identifications of the current study [77].

3.3.4. Environmental fate and putative toxicity of the suspect compounds

Even though ~75 suspect compounds were tentatively identified across the samples, not all of the compounds may be of significant interest to consider for follow-up targeted analyses, which are costly and time-intensive. Hence, hazard reports were generated for shortlisted suspect compounds using the Cheminformatics Modules (version: DEV, build: 2023–03-09 06:08:29 UTC) developed and facilitated by USEPA [78,79]. This web-based tool is a derivative of a desktop software application, the Alternatives Assessment Dashboard [80], and it combines a large database of experimental toxicity data with integrated QSAR prediction algorithms. This tool assembles data corresponding to human health effects (e.g., acute mammalian toxicity [oral and dermal], carcinogenicity, genotoxicity, mutagenicity, endocrine disruption, reproductive health, developmental health, neurotoxicity, systemic toxicity, skin sensitization, skin irritation, eye irritation), ecotoxicity (e.g., acute and chronic aquatic toxicity) as well as environmental fate (e.g., persistence, bioaccumulation, and exposure) of chemicals on a qualitative scale. A limited number of toxicity and fate endpoints are supported as QSAR predictions and can act as gap-filling data when no experimental data are available. Chemicals can be searched based on CAS RNs, chemical names, or structural inputs (such as SMILES or InChI Keys) and hazard reports can be generated. Depending on the complexity of the chemicals, hundreds of chemicals can be passed through the module to produce a hazard report in minutes. Such hazard reports were generated for shortlisted suspect compounds to prioritize compounds for thorough targeted follow-up analysis. Among the toxicity data provided in the hazard report, four human health-based, two ecotoxicity-based, and three environmental fate-based criteria are illustrated in Fig. 7, and the full report including toxicity details of each shortlisted suspect is provided in Appendix A.

Fig. 7 illustrates the number of suspect compounds associated with very high (VH), high (H), medium (M), low (L), inconclusive (I), and unknown toxicities (empty cells) under a given toxicity or fate category. Each individual cell displayed in the original hazard report is an active link to display the underlying data whether from authoritative sources (e.g., US-EPA IRIS risk assessments) or screening sources (e.g., the University of Maryland (UMD) list of acute toxins, teratogens, carcinogens, or mutagens). The call displayed on an individual cell associated with a specific endpoint is the most conservative call based on the underlying data (which can be observed by clicking on the individual cell). The font on each individual cell depicts whether the call is based on authoritative data (bold font), screening data (normal font), or predicted data (italic font). A detailed hazard report is provided in Appendix A.

Out of the 65 shortlisted compounds tentatively identified in the feed water, number of compounds linked with high to medium toxicity was 20 for acute mammalian oral toxicity. None of the water samples contained shortlisted suspects with very high acute mammalian oral toxicity. Two suspects linked with high acute mammalian oral toxicity and 10–13 suspects with medium toxicity were tentatively identified in both VMD and PMD (with and without UV) treatment effluents. Even though the feed water contained 18 tentatively identified compounds linked with very high to medium genotoxicity mutagenicity, that was reduced to 11 in the VMD, 13 in the PMD_UV_OFF, and 9 in the PMD_UV_ON distillates. None of the samples were linked with very high levels of endocrine disruption and developmental health-based toxicity. Feed water samples contained 15 and 23 shortlisted suspects linked to high levels of endocrine disruption and developmental health-based toxicity, respectively. Among the shortlisted suspect compounds tentatively identified in distillate samples, 7–8 of them had high endocrine disruption, and 13–16 of them with high developmental health-based toxicity. None of the suspect compounds tentatively identified in distillate samples were associated with carcinogenicity, dermal toxicity, or reproductive health toxicity (Appendix A). Certain suspect compounds identified in distillate samples were also associated with skin and eye irritations (Appendix A). In the case of ecotoxicity, ~20 suspects isolated from VMD and PMD distillates were related to very high to medium acute aquatic toxicity whereas, ~3 suspects were related to chronic aquatic toxicity. In the case of environmental fate, none of the compounds was linked with very high criticality for persistence, bioaccumulation, or exposure. The potential for bioaccumulation was negligible except for one compound [3-(Dodecyloxy)propylamine] observed in the PMD_UV_ON distillate. Several suspect compounds

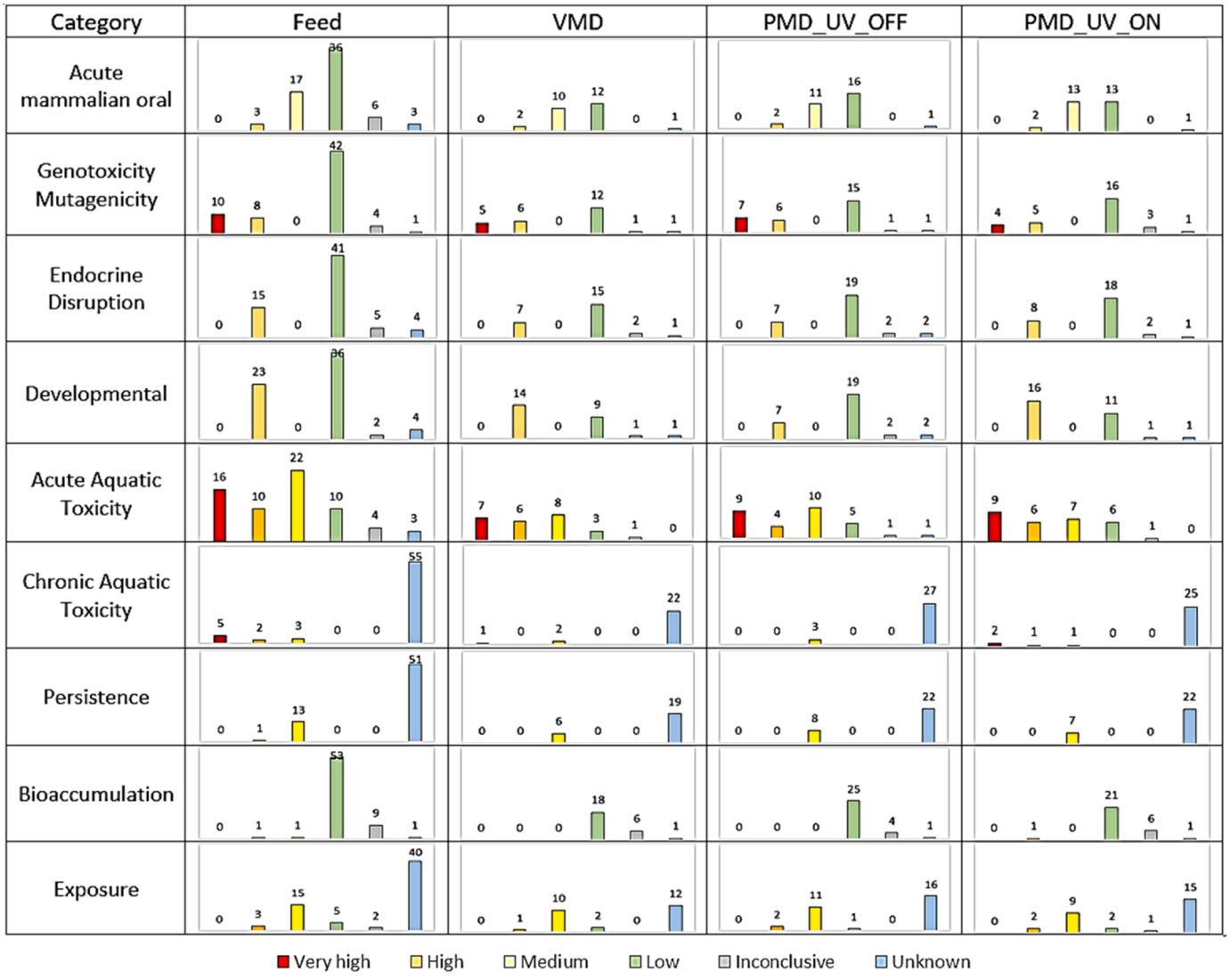

Fig. 7. Number of suspect compounds associated with human health, ecotoxicity, and environmental fate-related toxicity concerns in different water samples.

observed in distillate samples were associated with environmental persistence and risk of exposure. Additionally, the majority of the compounds initially undetected in feed water and later observed in distillate samples exhibited levels of toxicity ranging from very high to high in one or more toxicity categories (mostly developmental toxicity and acute ecotoxicity) while three compounds [4-(2-Hydroxy-3-((1-methylethyl)amino)propoxy)-alpha-(methoxymethyl)benzenemethanol, 1-(5-Ethyl-1,3,4-thiadiazol-2-yl)-4-methylpiperazine, and N-{2-[(2-Amino-1-hydroxyethylidene)amino]-1-hydroxypropylidene}valine] were associated with medium to unknown toxicity levels in all considered toxicity categories.

Therefore, utilizing these treated PW samples for different reuse activities outside O&G fields that have high possibilities for direct or indirect human and environmental contact remains questionable because the majority of the shortlisted suspects are associated with some form of human health, ecotoxicity, or environmental fate-based concerns. However, qualitative findings obtained from this non-targeted suspect screening coupled with toxicity prediction tools alone are insufficient to fully characterize potential risks during the reuse of treated PW. Therefore, it is recommended to confirm the presence and concentrations of these likely toxic compounds in treated water with targeted analyses in order to perform quantitative risk assessments. In addition, post-treatment is required such as using granular activated carbon to further remove the organic contaminants in distillate and polish the product water quality to reduce the risks during fit-for-purpose applications.

3.4. Outlook

Propositions are rising to consider PW as an alternative source of water for diverse reuse applications in arid regions, provided that treated PW is of sufficient quality for the specific reuse scenario [9]. In the meantime, significant opposition also exists due to the complex nature and unknown composition of the PW matrix. High salinity together with complex composition makes it challenging to perform targeted chemical analyses using standard methods, necessitating modifications of standard methods or new methods exclusively for the PW matrix [81]. In addition, identifying unknowns using solely targeted techniques is nearly impossible due to the complex composition of PW, the lack of appropriate internal standards, and unreasonably high analytical costs for the multitude of potential constituents. Most of the existing literature on PW treatment technology evaluations is based on limited targeted analyte removals and therefore does not demonstrate human health and ecological safety in long-term reuse applications.

Recently, non-targeted chemical screening analytical workflows have gained substantial attention as cost-effective tools for unraveling

the composition of obscure samples containing thousands of contaminants, such as PW [77,79,81]. Nevertheless, non-targeted chemical analysis also has its limitations, including tentative non-quantitative identifications; sensitivity to matrix effects, interfering compounds, and sample preparation methods; and sensitivity limits of the instrumentation [77]. Therefore, non-targeted chemical screening techniques should be utilized as a preliminary step to capture the presence of a wide spectrum of compounds as either qualitative or semi-quantitative measures. Identified compounds can be prioritized based on compound classifications, their associated human health and ecological toxicity, and environmental fate considerations [79]. Compounds with substantial health, ecological, and/or environmental fate concerns can then be quantitatively confirmed using targeted analytical techniques. The application of non-targeted chemical screening coupled with a toxicity prediction workflow prior to rigorous targeted analysis will help to narrow down and prioritize contaminants of interest and thereby enable resource-efficient and cost-effective characterization.

4. Conclusions

A novel PMD process utilizing hydrophobically modified ceramic membranes was evaluated for treating real oil and gas field PW using general water quality measures, targeted analysis, non-targeted chemical screening tools, and toxicity prediction tools. PMD with TiO_2 coating and UV light (PMD_UV_ON) resulted in better removal of DOC, NH_4-N, and conductivity than PMD without UV (PMD_UV_OFF) and VMD. According to the targeted analysis of ~72 volatile organics, only six compounds were in pre-treated PW while trace concentrations of acetone and 2-butanone were in distillates. Non-targeted chemical analysis using high-resolution LC-Orbitrap-MS followed by MZmine 3, SIRIUS, and CANOPUS identified 75, 65, 25, 30, and 29 suspect organic compounds in all PW samples (pretreated and distillates), pre-treated PW sample, VMD distillate, PMD_UV_OFF distillate, and PMD_UV_ON distillate, respectively, belonging to six different compound classifications. It was found that certain physicochemical properties of compounds, for instance, vapor pressure, Henry's Law constant, and boiling point, influenced contaminant rejection in the different MD configurations. According to preliminary toxicity predictions, VMD, PMD_UV_OFF, and PMD_UV_ON distillate samples, respectively contained 21, 23, and 22 suspect contaminants associated with critical toxicity concerns. These findings warrant follow-up targeted analyses on the suspected critical contaminants and the requirement of post-treatment to further polish the water quality of distillates prior to potential disposal or reuse of PW. Non-targeted chemical screening together with toxicity prediction tools was found to be a promising pathway for efficient and effective preliminary technology evaluations.

CRediT authorship contribution statement

Lin Chen: Writing – review & editing, Methodology, Investigation, Formal analysis, Conceptualization. **Huiyao Wang:** Writing – review & editing, Validation, Supervision, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization. **Robert B. Young:** Writing – review & editing, Writing – original draft, Validation, Supervision, Software, Methodology, Investigation, Formal analysis, Conceptualization. **Maha T. Abutokaikah:** Writing – review & editing, Writing – original draft, Software, Methodology, Investigation, Formal analysis. **Michael A. Jahne:** Writing – review & editing, Validation, Software, Methodology, Investigation, Formal analysis. **Antony J. Williams:** Writing – review & editing, Validation, Software, Methodology, Investigation, Formal analysis. **Kanchana A. B. I. Imihamillage:** Writing – review & editing, Software, Methodology, Investigation, Formal analysis. **Sean Thimons:** Writing – review & editing, Software, Methodology, Investigation, Formal analysis. **Himali M. K. Delanka-Pedige:** Writing – review & editing, Writing – original draft, Visualization, Software, Methodology, Investigation, Formal analysis, Conceptualization. **Yanyan Zhang:** Writing – review & editing, Validation, Investigation, Formal analysis. **Pei Xu:** Writing – review & editing, Writing – original draft, Validation, Supervision, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data used for this manuscript is provided in the Supplementary Information Section.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jhazmat.2024.134436.

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Title 40 —Protection of Environment
Chapter I —Environmental Protection Agency
Subchapter N —Effluent Guidelines and Standards

PART 435—OIL AND GAS EXTRACTION POINT SOURCE CATEGORY

Authority: 33 U.S.C. 1251, 1311, 1314, 1316, 1317, 1318, 1342 and 1361.

Source: 44 FR 22075, Apr. 13, 1979, unless otherwise noted.

Subpart A—Offshore Subcategory

Source: 58 FR 12504, Mar. 4, 1993, unless otherwise noted.

§ 435.10 Applicability; description of the offshore subcategory.

The provisions of this subpart are applicable to those facilities engaged in field exploration, drilling, well production, and well treatment in the oil and gas industry which are located in waters that are seaward of the inner boundary of the territorial seas ("offshore") as defined in section 502(g) of the Clean Water Act.

[61 FR 66123, Dec. 16, 1996]

§ 435.11 Specialized definitions.

For the purpose of this subpart:

(a) Except as provided below, the general definitions, abbreviations and methods of analysis set forth in 40 CFR part 401 shall apply to this subpart.

(b) ***Average of daily values for 30 consecutive days*** means the average of the daily values obtained during any 30 consecutive day period.

(c) ***Base fluid*** means the continuous phase or suspending medium of a drilling fluid formulation.

(d) ***Base fluid retained on cuttings*** as applied to BAT effluent limitations and NSPS refers to the "Determination of the Amount of Non-Aqueous Drilling Fluid (NAF) Base Fluid from Drill Cuttings by a Retort Chamber (Derived from API Recommended Practice 13B-2)", EPA Method 1674, which is published as an appendix to subpart A of this part and in "Analytic Methods for the Oil and Gas Extraction Point Source Category," EPA-821-R-11-004. See paragraph (uu) of this section.

(e) ***Biodegradation rate*** as applied to BAT effluent limitations and NSPS for drilling fluids and drill cuttings refers to the "Protocol for the Determination of Degradation of Non Aqueous Base Fluids in a Marine Closed Bottle Biodegradation Test System: Modified ISO 11734:1995," EPA Method 1647, supplemented with "Procedure for Mixing Base Fluids With Sediments," EPA Method 1646. Both EPA Method 1646 and 1647 are published as appendices to subpart A of this part and in "Analytic Methods for the Oil and Gas Extraction Point Source Category," EPA-821-R-11-004. See paragraph (uu) of this section.

(f) ***Daily values*** as applied to produced water effluent limitations and NSPS means the daily measurements used to assess compliance with the maximum for any one day.

(g) ***Deck drainage*** means any waste resulting from deck washings, spillage, rainwater, and runoff from gutters and drains including drip pans and work areas within facilities subject to this subpart.

(h) ***Development facility*** means any fixed or mobile structure subject to this subpart that is engaged in the drilling of productive wells.

(i) ***Diesel oil*** refers to the grade of distillate fuel oil, as specified in the American Society for Testing and Materials Standard Specification for Diesel Fuel Oils D975-91, that is typically used as the continuous phase in conventional oil-based drilling fluids. This incorporation by reference was approved by the Director of the Federal Register in accordance with 5 U.S.C. 552(a) and 1 CFR part 51. Copies may be obtained from the American Society for Testing and Materials, 100 Barr Harbor Drive, West Conshohocken, PA, 19428. Copies may be inspected at the National Archives and Records Administration (NARA). For information on the availability of this material at NARA, call 202-741-6030, or go to: *http://www.archives.gov/federal_register/code_of_federal_regulations/ibr_locations.html.* A copy may also be inspected at EPA's Water Docket, 1200 Pennsylvania Ave., NW., Washington, DC 20460.

(j) ***Domestic waste*** means materials discharged from sinks, showers, laundries, safety showers, eye-wash stations, hand-wash stations, fish cleaning stations, and galleys located within facilities subject to this subpart.

(k) ***Drill cuttings*** means the particles generated by drilling into subsurface geologic formations and carried out from the wellbore with the drilling fluid. Examples of drill cuttings include small pieces of rock varying in size and texture from fine silt to gravel. Drill cuttings are generally generated from solids control equipment and settle out and accumulate in quiescent areas in the solids control equipment or other equipment processing drilling fluid (*i.e.,* accumulated solids).

(1) ***Wet drill cuttings*** means the unaltered drill cuttings and adhering drilling fluid and formation oil carried out from the wellbore with the drilling fluid.

(2) ***Dry drill cuttings*** means the residue remaining in the retort vessel after completing the retort procedure specified in EPA Method 1674, which is published as an appendix to subpart A of this part and in "Analytic Methods for the Oil and Gas Extraction Point Source Category," EPA-821-R-11-004. See paragraph (uu) of this section.

(l) ***Drilling fluid*** means the circulating fluid (mud) used in the rotary drilling of wells to clean and condition the hole and to counterbalance formation pressure. Classes of drilling fluids are:

(1) ***Water-based drilling fluid*** means the continuous phase and suspending medium for solids is a water-miscible fluid, regardless of the presence of oil.

(2) ***Non-aqueous drilling fluid*** means the continuous phase and suspending medium for solids is a water-immiscible fluid, such as oleaginous materials (e.g., mineral oil, enhanced mineral oil, paraffinic oil, C_{16}-C_{18} internal olefins, and C_8-C_{16} fatty acid/2-ethylhexyl esters).

(i) ***Oil-based*** means the continuous phase of the drilling fluid consists of diesel oil, mineral oil, or some other oil, but contains no synthetic material or enhanced mineral oil.

(ii) ***Enhanced mineral oil-based*** means the continuous phase of the drilling fluid is enhanced mineral oil.

(iii) ***Synthetic-based*** means the continuous phase of the drilling fluid is a synthetic material or a combination of synthetic materials.

(m) ***Enhanced mineral oil*** as applied to enhanced mineral oil-based drilling fluid means a petroleum distillate which has been highly purified and is distinguished from diesel oil and conventional mineral oil in having a lower polycyclic aromatic hydrocarbon (PAH) content. Typically, conventional mineral oils have a PAH content on the order of 0.35 weight percent expressed as phenanthrene, whereas enhanced mineral oils typically have a PAH content of 0.001 or lower weight percent PAH expressed as phenanthrene.

(n) ***Exploratory facility*** means any fixed or mobile structure subject to this subpart that is engaged in the drilling of wells to determine the nature of potential hydrocarbon reservoirs.

(o) ***Formation oil*** means the oil from a producing formation which is detected in the drilling fluid, as determined by the GC/MS compliance assurance method, EPA Method 1655, when the drilling fluid is analyzed before being shipped offshore, and as determined by the RPE method, EPA Method 1670, when the drilling fluid is analyzed at the offshore point of discharge. The GC/MS compliance assurance method and the RPE method approved for use with this part are published as appendices to subpart A of this part and in "Analytic Methods for the Oil and Gas Extraction Point Source Category," EPA-821-R-11-004. See paragraph (uu) of this section. Detection of formation oil by the RPE method may be confirmed by the GC/MS compliance assurance method, and the results of the GC/MS compliance assurance method shall apply instead of those of the RPE method.

(p) ***M9IM*** means those offshore facilities continuously manned by nine (9) or fewer persons or only intermittently manned by any number of persons.

(q) ***M10*** means those offshore facilities continuously manned by ten (10) or more persons.

(r) ***Maximum*** as applied to BAT effluent limitations and NSPS for drilling fluids and drill cuttings means the maximum concentration allowed as measured in any single sample of the barite for determination of cadmium and mercury content.

(s) ***Maximum for any one day*** as applied to BPT, BCT and BAT effluent limitations and NSPS for oil and grease in produced water means the maximum concentration allowed as measured by the average of four grab samples collected over a 24-hour period that are analyzed separately. Alternatively, for BAT and NSPS the maximum concentration allowed may be determined on the basis of physical composition of the four grab samples prior to a single analysis.

(t) ***Maximum weighted mass ratio averaged over all NAF well sections*** for BAT effluent limitations and NSPS for base fluid retained on cuttings means the weighted average base fluid retention for all NAF well sections as determined by EPA Method 1674, which is published as an appendix to subpart A of this part and in "Analytic Methods for the Oil and Gas Extraction Point Source Category," EPA-821-R-11-004. See paragraph (uu) of this section.

(u) ***Method 1654A*** refers to EPA Method 1654, Revision A, entitled "PAH Content of Oil by HPLC/UV," December 1992, which is published as an appendix to subpart A of this part and in "Analytic Methods for the Oil and Gas Extraction Point Source Category," EPA-821-R-11-004. See paragraph (uu) of this section.

(v) ***Minimum*** as applied to BAT effluent limitations and NSPS for drilling fluids and drill cuttings means the minimum 96-hour LC_5. value allowed as measured in any single sample of the discharged waste stream. *Minimum* as applied to BPT and BCT effluent limitations and NSPS for sanitary wastes means the minimum concentration value allowed as measured in any single sample of the discharged waste stream.

(w)

(1) ***New source*** means any facility or activity of this subcategory that meets the definition of "new source" under 40 CFR 122.2 and meets the criteria for determination of new sources under 40 CFR 122.29(b) applied consistently with all of the following definitions:

(i) ***Water area*** as used in "site" in 40 CFR 122.29 and 122.2 means the water area and water body floor beneath any exploratory, development, or production facility where such facility is conducting its exploratory, development or production activities.

(ii) ***Significant site preparation work*** as used in 40 CFR 122.29 means the process of surveying, clearing or preparing an area of the water body floor for the purpose of constructing or placing a development or production facility on or over the site.

(2) "New Source" does not include facilities covered by an existing NPDES permit immediately prior to the effective date of these guidelines pending EPA issuance of a new source NPDES permit.

(x) ***No discharge of free oil*** means that waste streams may not be discharged that contain free oil as evidenced by the monitoring method specified for that particular stream, e.g., deck drainage or miscellaneous discharges cannot be discharged when they would cause a film or sheen upon or discoloration of the surface of the receiving water; drilling fluids or cuttings may not be discharged when they fail EPA Method 1617 (Static Sheen Test), which is published as an appendix to subpart A of this part and in "Analytic Methods for the Oil and Gas Extraction Point Source Category," EPA-821-R-11-004. See paragraph (uu) of this section.

(y) Parameters that are regulated in this subpart and listed with approved methods of analysis in Table 1B at 40 CFR 136.3 are defined as follows:

(1) ***Cadmium*** means total cadmium.

(2) ***Chlorine*** means total residual chlorine.

(3) ***Mercury*** means total mercury.

(4) ***Oil and Grease*** means total recoverable oil and grease.

(z) ***PAH (as phenanthrene)*** means polynuclear aromatic hydrocarbons reported as phenanthrene.

(aa) ***Produced sand*** means the slurried particles used in hydraulic fracturing, the accumulated formation sands and scales particles generated during production. Produced sand also includes desander discharge from the produced water waste stream, and blowdown of the water phase from the produced water treating system.

(bb) ***Produced water*** means the water (brine) brought up from the hydrocarbon-bearing strata during the extraction of oil and gas, and can include formation water, injection water, and any chemicals added downhole or during the oil/water separation process.

(cc) ***Production facility*** means any fixed or mobile structure subject to this subpart that is either engaged in well completion or used for active recovery of hydrocarbons from producing formations.

(dd) ***Sanitary waste*** means the human body waste discharged from toilets and urinals located within facilities subject to this subpart.

(ee) ***Sediment toxicity*** as applied to BAT effluent limitations and NSPS for drilling fluids and drill cuttings refers to EPA Method 1644: "Method for Conducting a Sediment Toxicity Test with *Leptocheirus plumulosus* and Non-Aqueous Drilling Fluids or Synthetic-Based Drilling Muds" and sediment preparation procedures

specified in EPA Method 1646. EPA Method 1644 is published in "Analytic Methods for the Oil and Gas Extraction Point Source Category," (see paragraph (uu) of this section) and EPA Method 1646 is published as an appendix to subpart A of this part.

(ff) ***Solids control equipment*** means shale shakers, centrifuges, mud cleaners, and other equipment used to separate drill cuttings and/or stock barite solids from drilling fluid recovered from the wellbore.

(gg) ***SPP toxicity*** as applied to BAT effluent limitations and NSPS for drilling fluids and drill cuttings refers to the bioassay test procedure, "Suspended Particulate Phase (SPP) Toxicity Test," presented in EPA Method 1619, which is published as an appendix to subpart A of this part and in "Analytic Methods for the Oil and Gas Extraction Point Source Category," EPA-821-R-11-004. See paragraph (uu) of this section.

(hh) ***Static sheen test*** means the standard test procedure that has been developed for this industrial subcategory for the purpose of demonstrating compliance with the requirement of no discharge of free oil. The methodology for performing the static sheen test is presented in EPA Method 1617, which is published as an appendix to subpart A of this part and in "Analytic Methods for the Oil and Gas Extraction Point Source Category," EPA-821-R-11-004. See paragraph (uu) of this section.

(ii) ***Stock barite*** means the barite that was used to formulate a drilling fluid.

(jj) ***Stock base fluid*** means the base fluid that was used to formulate a drilling fluid.

(kk) ***Synthetic material*** as applied to synthetic-based drilling fluid means material produced by the reaction of specific purified chemical feedstock, as opposed to the traditional base fluids such as diesel and mineral oil which are derived from crude oil solely through physical separation processes. Physical separation processes include fractionation and distillation and/or minor chemical reactions such as cracking and hydro processing. Since they are synthesized by the reaction of purified compounds, synthetic materials suitable for use in drilling fluids are typically free of polycyclic aromatic hydrocarbons (PAH's) but are sometimes found to contain levels of PAH up to 0.001 weight percent PAH expressed as phenanthrene. Internal olefins and vegetable esters are two examples of synthetic materials suitable for use by the oil and gas extraction industry in formulating drilling fluids. Internal olefins are synthesized from the isomerization of purified straight-chain (linear) hydrocarbons such as C_{16}-C_{18} linear alpha olefins. C_{16}-C_{18} linear alpha olefins are unsaturated hydrocarbons with the carbon to carbon double bond in the terminal position. Internal olefins are typically formed from heating linear alpha olefins with a catalyst. The feed material for synthetic linear alpha olefins is typically purified ethylene. Vegetable esters are synthesized from the acid-catalyzed esterification of vegetable fatty acids with various alcohols. EPA listed these two branches of synthetic fluid base materials to provide examples, and EPA does not mean to exclude other synthetic materials that are either in current use or may be used in the future. A synthetic-based drilling fluid may include a combination of synthetic materials.

(ll) ***Well completion fluids*** means salt solutions, weighted brines, polymers, and various additives used to prevent damage to the well bore during operations which prepare the drilled well for hydrocarbon production.

(mm) ***Well treatment fluids*** means any fluid used to restore or improve productivity by chemically or physically altering hydrocarbon-bearing strata after a well has been drilled.

(nn) ***Workover fluids*** means salt solutions, weighted brines, polymers, or other specialty additives used in a producing well to allow for maintenance, repair or abandonment procedures.

(oo) ***4-day LC_5.*** as applied to the sediment toxicity BAT effluent limitations and NSPS means the concentration (milligrams/kilogram dry sediment) of the drilling fluid in sediment that is lethal to 50 percent of the Leptocheirus plumulosus test organisms exposed to that concentration of the drilling fluids after four days of constant exposure.

(pp) ***10-day LC_5.*** as applied to the sediment toxicity BAT effluent limitations and NSPS means the concentration (milligrams/kilogram dry sediment) of the base fluid in sediment that is lethal to 50 percent of the Leptocheirus plumulosus test organisms exposed to that concentration of the base fluids after ten days of constant exposure.

(qq) ***96-hour LC_5.*** means the concentration (parts per million) or percent of the suspended particulate phase (SPP) from a sample that is lethal to 50 percent of the test organisms exposed to that concentration of the SPP after 96 hours of constant exposure.

(rr) ***C_{16} -C_{18} internal olefin*** means a 65/35 blend, proportioned by mass, of hexadecene and octadecene, respectively. Hexadecene is an unsaturated hydrocarbon with a carbon chain length of 16, an internal double carbon bond, and is represented by the Chemical Abstracts Service (CAS) No. 26952-14-7. Octadecene is an unsaturated hydrocarbon with a carbon chain length of 18, an internal double carbon bond, and is represented by the Chemical Abstracts Service (CAS) No. 27070-58-2. (Properties available from the Chemical Abstracts Service, 2540 Olentangy River Road, PO Box 3012, Columbus, OH, 43210).

(ss) ***C_{16} -C_{18} internal olefin drilling fluid*** means a C_{16}-C_{18} internal olefin drilling fluid formulated as specified in appendix 1 of subpart A of this part.

(tt) ***C_{12} -C_{14} ester*** and ***C_8 ester*** means the fatty acid/2-ethylhexyl esters with carbon chain lengths ranging from 8 to 16 and represented by the Chemical Abstracts Service (CAS) No. 135800-37-2. (Properties available from the Chemical Abstracts Service, 2540 Olentangy River Road, PO Box 3012, Columbus, OH, 43210)

(uu) ***Analytic Methods for the Oil and Gas Extraction Point Source Category*** is the EPA document, "Analytic Methods for the Oil and Gas Point Source Category," December 2011, EPA-821-R-11-004, that compiles analytic methods for this category. This incorporation by reference was approved by the Director of the Federal Register in accordance with 5 U.S.C. 552(a) and 1 CFR part 51. Copies may be inspected at the National Archives and Records Administration (NARA). For information on the availability of this material at NARA, call 202-741-6030, or go to: *http://www.archives.gov/federal_register/code_of_federal_regulations/ibr_locations.html.* A copy may also be inspected at EPA's Water Docket, 1200 Pennsylvania Ave. NW., Washington, DC 20460. This method may be obtained at *http://water.epa.gov/scitech/methods/cwa/index.cfm*.

[61 FR 66124, Dec. 16, 1996, as amended at 66 FR 6895, Jan. 22, 2001; 69 FR 18803, Apr. 9, 2004; 77 FR 29834, May 18, 2012]

§ 435.12 Effluent limitations guidelines representing the degree of effluent reduction attainable by the application of the best practicable control technology currently available (BPT).

Except as provided in 40 CFR 125.30-32, any existing point source subject to this subpart must achieve the following effluent limitations representing the degree of effluent reduction attainable by the application of the best practicable control technology currently available:

BPT Effluent Limitations—Oil and Grease

[In milligrams per liter]

Pollutant parameter waste source	Maximum for any 1 day	Average of values for 30 consecutive days shall not exceed	Residual chlorine minimum for any 1 day
Produced water	72	48	NA
Deck drainage	(1)	(1)	NA
Water-based:			
Drilling fluids	(1)	(1)	NA
Drill Cuttings	(1)	(1)	NA
Non-aqueous:			
Drilling fluids	No discharge	No discharge	NA
Drill Cuttings	(1)	(1)	NA
Well treatment fluids	(1)	(1)	NA
Sanitary:			
M10	NA	NA	[2] 1
M9IM[3]	NA	NA	NA
Domestic	NA	NA	NA

[1] No discharge of free oil. See § 435.11(x).

[2] Minimum of 1 mg/l and maintained as close to this concentration as possible.

[3] There shall be no floating solids as a result of the discharge of these wastes.

[58 FR 12504, Apr. 13, 1979, as amended at 66 FR 6897, Jan. 22, 2001; 77 FR 29836, May 18, 2012]

§ 435.13 Effluent limitations guidelines representing the degree of effluent reduction attainable by the application of the best available technology economically achievable (BAT).

Except as provided in 40 CFR 125.30-32, any existing point source subject to this subpart must achieve the following effluent limitations representing the degree of effluent reduction attainable by the application of the best available technology economically achievable (BAT):

BAT Effluent Limitations

Waste source	Pollutant parameter	BAT effluent limitation
Produced water	Oil & grease	The maximum for any one day shall not exceed 42 mg/l; the average of daily values for 30 consecutive days shall not exceed 29 mg/l.
Drilling fluids and drill cuttings:		
(A) For facilities located within 3 miles from shore		No discharge.[1]

Waste source	Pollutant parameter	BAT effluent limitation
(B) For facilities located beyond 3 miles from shore:		
Water-based drilling fluids and associated drill cuttings	SPP Toxicity	Minimum 96-hour LC_{50}. of the SPP Toxicity Test[2] shall be 3% by volume.
	Free oil	No discharge.[3]
	Diesel oil	No discharge.
	Mercury	1 mg/kg dry weight maximum in the stock barite.
	Cadmium	3 mg/kg dry weight maximum in the stock barite.
Non-aqueous drilling fluids (NAFs)		No discharge.
Drill cuttings associated with non-aqueous drilling fluids:		
Stock Limitations (C_{16}-C_{18} internal olefin)	Mercury	1 mg/kg dry weight maximum in the stock barite.
	Cadmium	3 mg/kg dry weight maximum in the stock barite.
	Polynuclear Aromatic Hydrocarbons (PAH)	PAH mass ratio[5] shall not exceed $1 \times 10^{-5.}$
	Sediment toxicity	Base fluid sediment toxicity ratio[6] shall not exceed 1.0.
	Biodegradation rate	Biodegradation rate ratio[7] shall not exceed 1.0.
Discharge Limitations	Diesel oil	No discharge.
	SPP Toxicity	Minimum 96-hour LC_{50}. of the SPP Toxicity Test[2] shall be 3% by volume.
	Sediment toxicity	Drilling fluid sediment toxicity ratio[8] shall not exceed 1.0.
	Formation Oil	No discharge.[9]
	Base fluid retained on cuttings	For NAFs that meet the stock limitations (C_{16}-C_{18} internal olefin) in this table, the maximum weighted mass ratio averaged over all NAF well sections shall be 6.9 g-NAF base fluid/100 g-wet drill cuttings.[10] For NAFs that meet the C_{12}-C_{14} ester or C_8 ester stock limitations in

Waste source	Pollutant parameter	BAT effluent limitation
		footnote 11 of this table, the maximum weighted mass ratio averaged over all NAF well sections shall be 9.4 g-NAF base fluid/100 g-wet drill cuttings.
Well treatment, completion, and workover fluids	Oil and grease	The maximum for any one day shall not exceed 42 mg/l; the average of daily values for 30 consecutive days shall not exceed 29 mg/l.
Deck drainage	Free oil	No discharge.[4]
Produced sand		No discharge.
Domestic Waste	Foam	No discharge.

[1] All Alaskan facilities are subject to the drilling fluids and drill cuttings discharge limitations for facilities located beyond 3 miles offshore.

[2] As determined by the suspended particulate phase (SPP) toxicity test. See § 435.11(gg).

[3] As determined by the static sheen test. See § 435.11(hh).

[4] As determined by the presence of a film or sheen upon or a discoloration of the surface of the receiving water (visual sheen).

[5] PAH mass ratio = Mass (g) of PAH (as phenanthrene)/Mass (g) of stock base fluid as determined by EPA Method 1654, Revision A, [specified at § 435.11(u)] entitled "PAH Content of Oil by HPLC/UV," December 1992, which is published as an appendix to subpart A of this part and in "Analytic Methods for the Oil and Gas Extraction Point Source Category," EPA-821-R-11-004. See § 435.11(uu).

[6] Base fluid sediment toxicity ratio = 10-day LC_5. of C_{16}-C_{18} internal olefin/10-day LC_5. of stock base fluid as determined by EPA Method 1644: "Method for Conducting a Sediment Toxicity Test with *Leptocheirus plumulosus* and Non-Aqueous Drilling Fluids or Synthetic-Based Drilling Muds" after preparing the sediment according to the procedure specified in EPA Method 1646, which are published as appendices to subpart A of this part and in "Analytic Methods for the Oil and Gas Extraction Point Source Category," EPA-821-R-11-004. See § 435.11(ee) and (uu).

[7] Biodegradation rate ratio = Cumulative headspace gas production (ml) of C_{16}-C_{18} internal olefin/Cumulative headspace gas production (ml) of stock base fluid, both at 275 days as determined by EPA Method 1647, which is published as an appendix to subpart A of this part and in "Analytic Methods for the Oil and Gas Extraction Point Source Category," EPA-821-R-11-004. See § 435.11(e) and (uu).

[8] Drilling fluid sediment toxicity ratio = 4-day LC_5. of C_{16}-C_{18} internal olefin drilling fluid/4-day LC_5. of drilling fluid removed from drill cuttings at the solids control equipment as determined by EPA Method 1644: "Method for Conducting a Sediment Toxicity Test with *Leptocheirus plumulosus* and Non-Aqueous Drilling Fluids or Synthetic-Based Drilling Muds" after sediment preparation

procedures specified in EPA Method 1646, which are published as appendices to subpart A of this part and in "Analytic Methods for the Oil and Gas Extraction Point Source Category," EPA-821-R-11-004. See § 435.11(ee) and (uu).

[9] As determined before drilling fluids are shipped offshore by the GC/MS compliance assurance method (EPA Method 1655), and as determined prior to discharge by the RPE method (EPA Method 1670) applied to drilling fluid removed from drill cuttings. If the operator wishes to confirm the results of the RPE method (EPA Method 1670), the operator may use the GC/MS compliance assurance method (EPA Method 1655). Results from the GC/MS compliance assurance method (EPA Method 1655) shall supersede the results of the RPE method (EPA Method 1670). EPA Method 1655 and 1670 are published as appendices to subpart A of this part and in "Analytic Methods for the Oil and Gas Extraction Point Source Category," EPA-821-R-11-004. See § 435.11(uu).

[10] Maximum permissible retention of non-aqueous drilling fluid (NAF) base fluid on wet drill cuttings averaged over drilling intervals using NAFs as determined by EPA Method 1674, which is published as an appendix to subpart A of this part and in "Analytic Methods for the Oil and Gas Extraction Point Source Category," EPA-821-R-11-004. See § 435.11(uu). This limitation is applicable for NAF base fluids that meet the base fluid sediment toxicity ratio (Footnote 6), biodegradation rate ratio (Footnote 7), PAH, mercury, and cadmium stock limitations (C_{16}-C_{18} internal olefin) defined above in this table.

[11] Maximum permissible retention of non-aqueous drilling fluid (NAF) base fluid on wet drill cuttings average over drilling intervals using NAFs as determined by EPA Method 1674, which is published as an appendix to subpart A of this part and in "Analytic Methods for the Oil and Gas Extraction Point Source Category," EPA-821-R-11-004. See § 435.11(uu). This limitation is applicable for NAF base fluids that meet the ester base fluid sediment toxicity ratio and ester biodegradation rate ratio stock limitations defined as:

(a) ester base fluid sediment toxicity ratio = 10-day LC_5. of C_{12}-C_{14} ester or C_8 ester/10-day LC_5. of stock base fluid as determined by EPA Method 1644: "Method for Conducting a Sediment Toxicity Test with *Leptocheirus plumulosus* and Non-Aqueous Drilling Fluids or Synthetic-Based Drilling Muds" after sediment preparation procedures specified in EPA Method 1646, which are published as appendices to subpart A of this part and in "Analytic Methods for the Oil and Gas Extraction Point Source Category," EPA-821-R-11-004. See § 435.11(ee) and (uu);

(b) ester biodegradation rate ratio = Cumulative headspace gas production (ml) of C_{12}-C_{14} ester or C_8 ester/Cumulative headspace gas production (ml) of stock base fluid, both at 275 days as determined by EPA Method 1647, which is published as an appendix to subpart A of this part and in "Analytic Methods for the Oil and Gas Extraction Point Source Category," EPA-821-R-11-004. See § 435.11(e) and (uu); and

(c) PAH mass ratio (Footnote 5), mercury, and cadmium stock limitations (C_{16}-C_{18} internal olefin) defined above in this table.

[58 FR 12504, Apr. 13, 1979, as amended at 66 FR 6898, Jan. 22, 2001; 69 FR 18803, Apr. 9, 2004; 77 FR 29836, May 18, 2012]

§ 435.14 Effluent limitations guidelines representing the degree of effluent reduction attainable by the application of the best conventional pollutant control technology (BCT).

Except as provided in 40 CFR 125.30-32, any existing point source subject to this subpart must achieve the following effluent limitations representing the degree of effluent reduction attainable by the application of the best conventional pollutant control technology (BCT):

BCT Effluent Limitations

Waste source	Pollutant parameter	BCT effluent limitation
Produced water	Oil & grease	The maximum for any one day shall not exceed 72 mg/l; the average of values for 30 consecutive days shall not exceed 48 mg/l.
Drilling fluids and drill cuttings:		
(A) For facilities located within 3 miles from shore		No discharge.[1]
(B) For facilities located beyond 3 miles from shore:		
Water-based drilling fluids and associated drill cuttings	Free Oil	No discharge.[2]
Non-aqueous drilling fluids		No discharge.
Drill cuttings associated with non-aqueous drilling fluids	Free Oil	No discharge.[2]
Well treatment, completion and workover fluids	Free oil	No discharge.[2]
Deck drainage	Free oil	No discharge.[3]
Produced sand		No discharge.
Sanitary M10	Residual chlorine	Minimum of 1 mg/l and maintained as close to this concentration as possible.
Sanitary M91M	Floating solids	No discharge.
Domestic Waste	Floating solids	No discharge.
	All other domestic waste	See 33 CFR part 151.

[1] All Alaskan facilities are subject to the drilling fluids and drill cuttings discharge limitations for facilities located more than 3 miles offshore.

[2] As determined by the static sheen test. See § 435.11(hh).

[3] As determined by the presence of a film or sheen upon or a discoloration of the surface of the receiving water (visual sheen).

[58 FR 12504, Apr. 13, 1979, as amended at 66 FR 6899, Jan. 22, 2001; 77 FR 29836, May 18, 2012]

§ 435.15 Standards of performance for new sources (NSPS).

Any new source subject to this subpart must achieve the following new source performance standards (NSPS):

New Source Performance Standards

Waste source	Pollutant parameter	NSPS
Produced water	Oil and grease	The maximum for any one day shall not exceed 42 mg/l; the average of daily values for 30 consecutive days shall not exceed 29 mg/l.
Drilling fluids and drill cuttings:		
(A) For facilities located within 3 miles from shore		No discharge.[1]
(B) For facilities located beyond 3 miles from shore:		
Water-based drilling fluids and associated drill cuttings	SPP Toxicity	Minimum 96-hour LC_{50}. of the SPP Toxicity Test[2] shall be 3% by volume.
	Free oil	No discharge.[3]
	Diesel oil	No discharge.
	Mercury	1mg/kg dry weight maximum in the stock barite.
	Cadmium	3 mg/kg dry weight maximum in the stock barite.
Non-aqueous drilling fluids		No charge.
Drill cuttings associated with non-aqueous drilling fluids:		
Stock Limitations (C_{16}-C_{18} internal olefin	Mercury	1mg/kg dry weight maximum in the stock barite.
	Cadmium	3 mg/kg dry weight maximum in the stock barite.
	Polynuclear Aromatic Hydrocarbons	PAH mass ratio[5] shall not exceed $1 \times 10^{-5.}$

Waste source	Pollutant parameter	NSPS
	(PAH)	
	Sediment toxicity	Base fluid sediment toxicity ratio[6] shall not exceed 1.0.
	Biodegradation rate	Biodegradation rate ratio[7] shall not exceed 1.0.
Discharge Limitations	Diesel oil	No discharge.
	SPP Toxicity	Minimum 96-hour LC_{50}. of the SPP Toxicity Test[2] shall be 3% by volume.
	Sediment toxicity	Drilling fluid sediment toxicity ratio[8] shall not exceed 1.0.
	Formation Oil	No discharge.[9]
	Base fluid retained on cuttings	For NAFs that meet the stock limitations (C_{16}-C_{18} internal olefin) in this table, the maximum weighted mass ratio averaged over all NAF well sections shall be 6.9 g-NAF base fluid/100 g-wet drill cuttings.[10] For NAFs that meet the C_{12}-C_{14} ester or C_8 ester stock limitations in footnote 11 of this table, the maximum weighted mass ratio averaged over all NAF well sections shall be 9.4 g-NAF base fluid/100 g-wet drill cuttings.
Well treatment, completion, and workover fluids	Oil and grease	The maximum for any one day shall not exceed 42 mg/l; the average of daily values for 30 consecutive days shall not exceed 29 mg/l.
Deck drainage	Free oil	No discharge.[4]
Produced sand		No discharge.
Sanitary M10	Residual chlorine	Minimum of 1 mg/l and maintained as close to this as possible.
Sanitary M9IM	Floating solids	No discharge.
Domestic Waste	Floating solids	No discharge.
	Foam	No discharge.
	All other domestic wastes	See 33 CFR part 151.

[1] All Alaskan facilities are subject to the drilling fluids and drill cuttings discharge standards for facilities located more than three miles offshore.

[2] As determined by the suspended particulate phase (SPP) toxicity test. See § 435.11(gg).

[3] As determined by the static sheen test. See § 435.11(hh).

[4] As determined by the presence of a film or sheen upon or a discoloration of the surface of the receiving water (visual sheen).

[5] PAH mass ratio = Mass (g) of PAH (as phenanthrene)/Mass (g) of stock base fluid as determined by EPA Method 1654, Revision A, [specified at § 435.11(u)] entitled "PAH Content of Oil by HPLC/UV," December 1992, which is published as an appendix to subpart A of this part and in "Analytic Methods for the Oil and Gas Extraction Point Source Category," EPA-821-R-11-004. See § 435.11(uu).

[6] Base fluid sediment toxicity ratio = 10-day LC_5. of C_{16}-C_{18} internal olefin/10-day LC_5. of stock base fluid as determined by EPA Method 1644: "Method for Conducting a Sediment Toxicity Test with *Leptocheirus plumulosus* and Non-Aqueous Drilling Fluids or Synthetic-Based Drilling Muds" after preparing the sediment according to the procedure specified in EPA Method 1646, which are published as appendices to subpart A of this part and in "Analytic Methods for the Oil and Gas Extraction Point Source Category," EPA-821-R-11-004. See § 435.11(ee) and (uu).

[7] Biodegradation rate ratio = Cumulative headspace gas production (ml) of C_{16}-C_{18} internal olefin/Cumulative headspace gas production (ml) of stock base fluid, both at 275 days as determined by EPA Method 1647, which is published as an appendix to subpart A of this part and in "Analytic Methods for the Oil and Gas Extraction Point Source Category," EPA-821-R-11-004. See § 435.11(e) and (uu).

[8] Drilling fluid sediment toxicity ratio = 4-day LC_5. of C_{16}-C_{18} internal olefin drilling fluid/4-day LC_5. of drilling fluid removed from drill cuttings at the solids control equipment as determined by EPA Method 1644: "Method for Conducting a Sediment Toxicity Test with *Leptocheirus plumulosus* and Non-Aqueous Drilling Fluids or Synthetic-Based Drilling Muds" after sediment preparation procedures specified in EPA Method 1646, which are published as appendices to subpart A of this part and in "Analytic Methods for the Oil and Gas Extraction Point Source Category," EPA-821-R-11-004. See § 435.11(ee) and (uu).

[9] As determined before drilling fluids are shipped offshore by the GC/MS compliance assurance method (EPA Method 1655), and as determined prior to discharge by the RPE method (EPA Method 1670) applied to drilling fluid removed from drill cuttings. If the operator wishes to confirm the results of the RPE method (EPA Method 1670), the operator may use the GC/MS compliance assurance method (EPA Method 1655). Results from the GC/MS compliance assurance method (EPA Method 1655) shall supersede the results of the RPE method (EPA Method 1670). EPA Method 1655 and 1670 are published as appendices to subpart A of this part and in "Analytic Methods for the Oil and Gas Extraction Point Source Category," EPA-821-R-11-004. See § 435.11(uu).

[10] Maximum permissible retention of non-aqueous drilling fluid (NAF) base fluid on wet drill cuttings averaged over drilling intervals using NAFs as determined by EPA Method 1674, which is published as an appendix to subpart A of this part and in "Analytic Methods for the Oil and Gas Extraction Point Source Category," EPA-821-R-11-004. See § 435.11(uu). This limitation is applicable for NAF base fluids that meet the base fluid sediment toxicity ratio (Footnote 6), biodegradation rate ratio (Footnote 7), PAH, mercury, and cadmium stock limitations (C_{16}-C_{18} internal olefin) defined above in this table.

[11] Maximum permissible retention of non-aqueous drilling fluid (NAF) base fluid on wet drill cuttings average over drilling intervals using NAFs as determined by EPA Method 1674, which is published as an appendix to subpart A of this part and in "Analytic Methods for the Oil and Gas Extraction Point Source Category," EPA-821-R-11-004. See § 435.11(uu). This limitation is applicable for NAF base fluids that meet the ester base fluid sediment toxicity ratio and ester biodegradation rate ratio stock limitations defined as:

(a) ester base fluid sediment toxicity ratio = 10-day LC_5. of C_{12}-C_{14} ester or C_8 ester/10-day LC_5. of stock base fluid as determined by EPA Method 1644: "Method for Conducting a Sediment Toxicity Test with *Leptocheirus plumulosus* and Non-Aqueous Drilling Fluids or Synthetic-Based Drilling Muds" after sediment preparation procedures specified in EPA Method 1646, which are published as appendices to subpart A of this part and in "Analytic Methods for the Oil and Gas Extraction Point Source Category," EPA-821-R-11-004. See § 435.11(ee) and (uu);

(b) ester biodegradation rate ratio = Cumulative headspace gas production (ml) of C_{12}-C_{14} ester or C_8 ester/Cumulative headspace gas production (ml) of stock base fluid, both at 275 days as determined by EPA Method 1647, which is published as an appendix to subpart A of this part and in "Analytic Methods for the Oil and Gas Extraction Point Source Category," EPA-821-R-11-004. See § 435.11(e) and (uu); and (c) PAH mass ratio (Footnote 5), mercury, and cadmium stock limitations (C_{16}-C_{18} internal olefin) defined above in this table.

[58 FR 12504, Apr. 13, 1979, as amended at 66 FR 6900, Jan. 22, 2001; 66 FR 33134, June 20, 2001; 69 FR 18803, Apr. 9, 2004; 77 FR 29836, May 16, 2012]

Appendix 1 to Subpart A of Part 435—Static Sheen Test (EPA Method 1617)

1. Scope and Application

This method is to be used as a compliance test for the "no discharge of free oil" requirement for discharges of drilling fluids, drill cuttings, produced sand, and well treatment, completion and workover fluids. "Free oil" refers to any oil contained in a waste stream that when discharged will cause a film or sheen upon or a discoloration of the surface of the receiving water.

2. Summary of Method

15 -mL samples of drilling fluids or well treatment, completion, and workover fluids, and 15-g samples (wet weight basis) of drill cuttings or produced sand are introduced into ambient seawater in a container having an air-to-liquid interface area of 1000 cm^2 (155.5 in^2). Samples are dispersed within the container and observations made no more than one hour later to ascertain if these materials cause a sheen, iridescence, gloss, or increased reflectance on the surface of the test seawater. The occurrence of any of these visual observations will constitute a demonstration that the tested material contains "free oil," and therefore results in a prohibition of its discharge into receiving waters.

3. Interferences

Residual “free oil” adhering to sampling containers, the magnetic stirring bar used to mix the sample, and the stainless steel spatula used to mix the sample will be the principal sources of contamination problems. These problems should only occur if improperly washed and cleaned equipment are used for the test. The use of disposable equipment minimizes the potential for similar contamination from pipettes and the test container.

4. Apparatus, Materials, and Reagents

4.1 Apparatus

4.1.1 Sampling Containers: 1-liter polyethylene beakers and 1-liter glass beakers.

4.1.2 Graduated cylinder: 100-mL graduated cylinder required only for operations where predilution of mud discharges is required.

4.1.3 Plastic disposable weighing boats.

4.1.4 Triple-beam scale.

4.1.5 Disposable pipettes: 25-mL disposable pipettes.

4.1.6 Magnetic stirrer and stirring bar.

4.1.7 Stainless steel spatula.

4.1.8 Test container: Open plastic container whose internal cross-section parallel to its opening has an area of 1000 cm^2±50 cm^2 (155.5 ±7.75 in^2), and a depth of at least 13 cm (5 inches) and no more than 30 cm (11.8 inches).

4.2 Materials and Reagents.

4.2.1 Plastic liners for the test container: Oil-free, heavy-duty plastic trash can liners that do not inhibit the spreading of an oil film. Liners must be of sufficient size to completely cover the interior surface of the test container. Permittees must determine an appropriate local source of liners that do not inhibit the spreading of 0.05 mL of diesel fuel added to the lined test container under the test conditions and protocol described below.

4.2.2 Ambient receiving water.

5. Calibration

None currently specified.

6. Quality Control Procedures

None currently specified.

7. Sample Collection and Handling

7.1 Sampling containers must be thoroughly washed with detergent, rinsed a minimum of three times with fresh water, and allowed to air dry before samples are collected.

7.2 Samples of drilling fluid to be tested shall be taken at the shale shaker after cuttings have been removed. The sample volume should range between 200 mL and 500 mL.

7.3 Samples of drill cuttings will be taken from the shale shaker screens with a clean spatula or similar instrument and placed in a glass beaker. Cuttings samples shall be collected prior to the addition of any washdown water and should range between 200 g and 500 g.

7.4 Samples of produced sand must be obtained from the solids control equipment from which the discharge occurs on any given day and shall be collected prior to the addition of any washdown water; samples should range between 200 g and 500 g.

7.5 Samples of well treatment, completion, and workover fluids must be obtained from the holding facility prior to discharge; the sample volume should range between 200 mL and 500 mL.

7.6 Samples must be tested no later than 1 hour after collection.

7.7 Drilling fluid samples must be mixed in their sampling containers for 5 minutes prior to the test using a magnetic bar stirrer. If predilution is imposed as a permit condition, the sample must be mixed at the same ratio with the same prediluting water as the discharged muds and stirred for 5 minutes.

7.8 Drill cuttings must be stirred and well mixed by hand in their sampling containers prior to testing, using a stainless steel spatula.

8. Procedure

8.1 Ambient receiving water must be used as the “receiving water” in the test. The temperature of the test water shall be as close as practicable to the ambient conditions in the receiving water, not the room temperature of the observation facility. The test container must have an air-to-liquid interface area of 1000 ±50 cm^2. The surface of the water should be no more than 1.27 cm (.5 inch) below the top of the test container.

8.2 Plastic liners shall be used, one per test container, and discarded afterwards. Some liners may inhibit spreading of added oil; operators shall determine an appropriate local source of liners that do not inhibit the spreading of the oil film.

8.3 A 15-mL sample of drilling fluid or well treatment, completion, and workover fluids must be introduced by pipette into the test container 1 cm below the water surface. Pipettes must be filled and discharged with test material prior to the transfer of test material and its introduction into test containers. The test water/test material mixture must be stirred using the pipette to distribute the test material homogeneously throughout the test water. The pipette must be used only once for a test and then discarded.

8.4 Drill cuttings or produced sand should be weighed on plastic weighing boats; 15-g samples must be transferred by scraping test material into the test water with a stainless steel spatula. Drill cuttings shall not be prediluted prior to testing. Also, drilling fluids and cuttings will be tested separately. The weighing boat must be immersed in the test water and scraped with the spatula to transfer any residual material to the test container. The drill cuttings or produced sand must be stirred with the spatula to an even distribution of solids on the bottom of the test container.

8.5 Observations must be made no later than 1 hour after the test material is transferred to the test container. Viewing points above the test container should be made from at least three sides of the test container, at viewing angles of approximately 60° and 30° from the horizontal. Illumination of the test container must be representative of adequate lighting for a working environment to conduct

routine laboratory procedures. It is recommended that the water surface of the test container be observed under a fluorescent light source such as a dissecting microscope light. The light source shall be positioned above and directed over the entire surface of the pan.

8.6 Detection of a “silvery” or “metallic” sheen or gloss, increased reflectivity, visual color, iridescence, or an oil slick on the water surface of the test container surface shall constitute a demonstration of “free oil.” These visual observations include patches, streaks, or sheets of such altered surface characteristics. If the free oil content of the sample approaches or exceeds 10%, the water surface of the test container may lack color, a sheen, or iridescence, due to the increased thickness of the film; thus, the observation for an oil slick is required. The surface of the test container shall not be disturbed in any manner that reduces the size of any sheen or slick that may be present.

If an oil sheen or slick occurs on less than one-half of the surface area after the sample is introduced to the test container, observations will continue for up to 1 hour. If the sheen or slick increases in size and covers greater than one-half of the surface area of the test container during the observation period, the discharge of the material shall cease. If the sheen or slick does not increase in size to cover greater than one-half of the test container surface area after one hour of observation, discharge may continue and additional sampling is not required.

If a sheen or slick occurs on greater than one-half of the surface area of the test container after the test material is introduced, discharge of the tested material shall cease. The permittee may retest the material causing the sheen or slick. If subsequent tests do not result in a sheen or slick covering greater than one-half of the surface area of the test container, discharge may continue.

Appendix 2 to Subpart A of Part 435—Drilling Fluids Toxicity Test (EPA Method 1619)

I. Sample Collection

The collection and preservation methods for drilling fluids (muds) and water samples presented here are designed to minimize sample contamination and alteration of the physical or chemical properties of the samples due to freezing, air oxidation, or drying.

I-A. Apparatus

(1) The following items are required for water and drilling mud sampling and storage:

a. Acid-rinsed linear-polyethylene bottles or other appropriate noncontaminating drilling mud sampler.

b. Acid-rinsed linear-polyethylene bottles or other appropriate noncontaminating water sampler.

c. Acid-rinsed linear-polyethylene bottles or other appropriate noncontaminated vessels for water and mud samples.

d. Ice chests for preservation and shipping of mud and water samples.

I-B. Water Sampling

(1) Collection of water samples shall be made with appropriate acid-rinsed linear-polyethylene bottles or other appropriate non-contaminating water sampling devices. Special care shall be taken to avoid the introduction of contaminants from the sampling devices and containers. Prior to use, the sampling devices and containers should be thoroughly cleaned with a detergent solution, rinsed with tap water, soaked in 10 percent hydrochloric acid (HCl) for 4 hours, and then thoroughly rinsed with glass-distilled water.

I-C. Drilling Mud Sampling

(1) Drilling mud formulations to be tested shall be collected from active field systems. Obtain a well-mixed sample from beneath the shale shaker after the mud has passed through the screens. Samples shall be stored in polyethylene containers or in other appropriate uncontaminated vessels. Prior to sealing the sample containers on the platform, flush as much air out of the container by filling it with drilling fluid sample, leaving a one inch space at the top.

(2) Mud samples shall be immediately shipped to the testing facility on blue or wet ice (do not use dry ice) and continuously maintained at 0-4 °C until the time of testing.

(3) Bulk mud samples shall be thoroughly mixed in the laboratory using a 1000 rpm high shear mixer and then subdivided into individual, small wide-mouthed (e.g., one or two liter) non-contaminating containers for storage.

(4) The drilling muds stored in the laboratory shall have any excess air removed by flushing the storage containers with nitrogen under pressure anytime the containers are opened. Moreover, the sample in any container opened for testing must be thoroughly stirred using a 1000 rpm high shear mixer prior to use.

(5) Most drilling mud samples may be stored for periods of time longer than 2 weeks prior to toxicity testing provided that proper containers are used and proper condition are maintained.

II. Suspended Particulate Phase Sample Preparation

(1) Mud samples that have been stored under specified conditions in this protocol shall be prepared for tests within three months after collection. The SPP shall be prepared as detailed below.

II-A. Apparatus

(1) The following items are required:

a. Magnetic stir plates and bars.

b. Several graduated cylinders, ranging in volume from 10 mL to 1 L

c. Large (15 cm) powder funnels.

d. Several 2-liter graduated cylinders.

e. Several 2-liter large mouth graduated Erlenmeyer flasks.

(2) Prior to use, all glassware shall be thoroughly cleaned. Wash all glassware with detergent, rinse five times with tap water, rinse once with acetone, rinse several times with distilled or deionized water, place in a clean 10-percent (or stronger) HCl acid bath for a minimum of 4 hours, rinse five times with tap water, and then rinse five times with distilled or deionized water. For test samples containing mineral oil or diesel oil, glassware should be washed with petroleum ether to assure removal of all residual oil.

Note: If the glassware with nytex cups soaks in the acid solution longer than 24 hours, then an equally long deionized water soak should be performed.

II-B. Test Seawater Sample Preparation

(1) Diluent seawater and exposure seawater samples are prepared by filtration through a 1.0 micrometer filter prior to analysis.

(2) Artificial seawater may be used as long as the seawater has been prepared by standard methods or ASTM methods, has been properly “seasoned,” filtered, and has been diluted with distilled water to the same specified 20±2 ppt salinity and 20±2 °C temperature as the “natural” seawater.

II-C. Sample Preparation

(1) The pH of the mud shall be tested prior to its use. If the pH is less than 9, if black spots have appeared on the walls of the sample container, or if the mud sample has a foul odor, that sample shall be discarded. Subsample a manageable aliquot of mud from the well-mixed original sample. Mix the mud and filtered test seawater in a volumetric mud-to-water ratio of 1 to 9. This is best done by the method of volumetric displacement in a 2-L, large mouth, graduated Erlenmeyer flask. Place 1000 mL of seawater into the graduated Erlenmeyer flask. The mud subsample is then carefully added via a powder funnel to obtain a total volume of 1200 mL. (A 200 mL volume of the mud will now be in the flask).

The 2-L, large mouth, graduated Erlenmeyer flask is then filled to the 2000 mL mark with 800 mL of seawater, which produces a slurry with a final ratio of one volume drilling mud to nine volumes water. If the volume of SPP required for testing or analysis exceeds 1500 to 1600 mL, the initial volumes should be proportionately increased. Alternatively, several 2-L drill mud/water slurries may be prepared as outlined above and combined to provide sufficient SPP.

(2) Mix this mud/water slurry with magnetic stirrers for 5 minutes. Measure the pH and, if necessary, adjust (decrease) the pH of the slurry to within 0.2 units of the seawater by adding 6N HCl while stirring the slurry. Then, allow the slurry to settle for 1 hour. Record the amount of HCl added.

(3) At the end of the settling period, carefully decant (do not siphon) the Suspended Particulate Phase (SPP) into an appropriate container. Decanting the SPP is one continuous action. In some cases no clear interface will be present; that is, there will be no solid phase that has settled to the bottom. For those samples the entire SPP solution should be used when preparing test concentrations. However, in those cases when no clear interface is present, the sample must be remixed for five minutes. This insures the homogeneity of the mixture prior to the preparation of the test concentrations. In other

cases, there will be samples with two or more phases, including a solid phase. For those samples, carefully and continuously decant the supernatant until the solid phase on the bottom of the flask is reached. The decanted solution is defined to be 100 percent SPP. Any other concentration of SPP refers to a percentage of SPP that is obtained by volumetrically mixing 100 percent SPP with seawater.

(4) SPP samples to be used in toxicity tests shall be mixed for 5 minutes and must not be preserved or stored.

(5) Measure the filterable and unfilterable residue of each SPP prepared for testing. Measure the dissolved oxygen (DO) and pH of the SPP. If the DO is less than 4.9 ppm, aerate the SPP to at least 4.9 ppm which is 65 percent of saturation. Maximum allowable aeration time is 5 minutes using a generic commercial air pump and air stone. Neutralize the pH of the SPP to a pH 7.8 ±.1 using a dilute HCl solution. If too much acid is added to lower the pH saturated NaOH may be used to raise the pH to 7.8 ±.1 units. Record the amount of acid or NaOH needed to lower/raise to the appropriate pH. Three repeated DO and pH measurements are needed to insure homogeneity and stability of the SPP. Preparation of test concentrations may begin after this step is complete.

(6) Add the appropriate volume of 100 percent SPP to the appropriate volume of seawater to obtain the desired SPP concentration. The control is seawater only. Mix all concentrations and the control for 5 minutes by using magnetic stirrers. Then, the animals shall be randomly selected and placed in the dishes in order to begin the 96-hour toxicity test.

III. Guidance for Performing Suspended Particulate Phase Toxicity Tests Using Mysidopsis bahia

III-A. Apparatus

(1) Each definitive test consists of 18 test containers: 3 replicates of a control and 5 SPP dilutions. Test containers should be Pyrex or equivalent glass. For definitive tests, 5 SPP dilutions with 3 replicates of at least 500 ml each are required. Twenty mysids per replicate, 360 per definitive test are required.

III-B. Sample Collection Preservation

(1) Drilling muds and water samples are collected and stored, and the suspended particulate phase prepared as described in section 1-C.

III-C. Species Selection

(1) The Suspended Particulate Phase (SPP) tests on drilling muds shall utilize the test species *Mysidopsis bahia.* Test animals shall be 3 to 6 days old on the first day of exposure. Whatever the source of the animals, collection and handling should be as gentle as possible. Transportation to the laboratory should be in well-aerated water from the animal culture site at the temperature and

salinity from which they were cultured. Methods for handling, acclimating, and sizing bioassay organisms given by Borthwick [1] and Nimmo [2] shall be followed in matters for which no guidance is given here.

III-D. Experimental Conditions

(1) Suspended particulate phase (SPP) tests should be conducted at a salinity of 20 ±2 ppt. Experimental temperature should be 20 ±2 °C. Dissolved oxygen in the SPP shall be raised to or maintained above 65 percent of saturation prior to preparation of the test concentrations. Under these conditions of temperature and salinity, 65 percent saturation is a DO of 5.3 ppm. Beginning at Day 0-before the animals are placed in the test containers DO, temperature, salinity, and pH shall be measured every 24 hours. DO should be reported in milligrams per liter.

(2) Aeration of test media is required during the entire test with a rate estimated to be 50-140 cubic centimeters/minute. This air flow to each test dish may be achieved through polyethylene tubing (0.045-inch inner diameter and 0.062-inch outer diameter) by a small generic aquarium pump. The delivery method, surface area of the aeration stone, and flow characteristics shall be documented. All treatments, including control, shall be the same.

(3) Light intensity shall be 1200 microwatts/cm^2 using cool white fluorescent bulbs with a 14-hr light and 10-hr dark cycle. This light/dark cycle shall also be maintained during the acclimation period and the test.

III-E. Experimental Procedure

(1) Wash all glassware with detergent, rinse five times with tap water, rinse once with acetone, rinse several times with distilled or deionized water, place in a clean 10 percent HCl acid bath for a minimum of 4 hours, rinse five times with tap water, and then rinse five times with distilled water.

(2) Establish the definitive test concentrations based on results of a range finding test or based on prior experience and knowledge of the mud system.

(3) Twenty organisms are exposed in each test dish. Nytex ® cups shall be inserted into every test dish prior to adding the animals. These “nylon mesh screen” nytex holding cups are fabricated by gluing a collar of 363-micrometer mesh nylon screen to a 15-centimeter wide Petri dish with silicone sealant. The nylon screen collar is approximately 5 centimeters high. The animals are then placed into the test concentration within the confines of the Nytex cups.

(4) Individual organisms shall be randomly assigned to treatment. A randomization procedure is presented in section V of this protocol. Make every attempt to expose animals of approximately equal size. The technique described by Borthwick [1], or other suitable substitutes, should be used for transferring specimens. Throughout the test period, mysids shall be fed daily with approximately 50 *Artemia* (brine shrimp) nauplii per mysid. This will reduce stress and decrease cannibalism.

(5) Cover the dishes, aerate, and incubate the test containers in an appropriate test chamber. Positioning of the test containers holding various concentrations of test solution should be randomized if incubator arrangement indicates potential position difference. The test medium is not replaced during the 96-hour test.

(6) Observations may be attempted at 4, 6 and 8 hours; they must be attempted at 0, 24, 48, and 72 hours and must be made at 96 hours. Attempts at observations refers to placing a test dish on a light table and visually counting the animals. Do not lift the “nylon mesh screen” cup out of the test dish to make the observation. No unnecessary handling of the animals should occur during the 96 hour test period. DO and pH measurements must also be made at 0, 24, 48, 72, and 96 hours. Take and replace the test medium necessary for the DO and pH measurements outside of the nytex cups to minimize stresses on the animals.

(7) At the end of 96 hours, all live animals must be counted. Death is the end point, so the number of living organisms is recorded. Death is determined by lack of spontaneous movement. All crustaceans molt at regular intervals, shedding a complete exoskeleton. Care should be taken not to count an exoskeleton. Dead animals might decompose or be eaten between observations. Therefore, always count living, not dead animals. If daily observations are made, remove dead organisms and molted exoskeletons with a pipette or forceps. Care must be taken not to disturb living organisms and to minimize the amount of liquid withdrawn.

IV. Methods for Positive Control Tests (Reference Toxicant)

(1) Sodium lauryl sulfate (dodecyl sodium sulfate) is used as a reference toxicant for the positive control. The chemical used should be approximately 95 percent pure. The source, lot number, and percent purity shall be reported.

(2) Test methods are those used for the drilling fluid tests, except that the test material was prepared by weighing one gram sodium lauryl sulfate on an analytical balance, adding the chemical to a 100-milliliter volumetric flask, and bringing the flask to volume with deionized water. After mixing this stock solution, the test mixtures are prepared by adding 0.1 milliliter of the stock solution for each part per million desired to one liter of seawater.

(3) The mixtures are stirred briefly, water quality is measured, animals are added to holding cups, and the test begins. Incubation and monitoring procedures are the same as those for the drilling fluids.

V. Randomization Procedure

V-A. Purpose and Procedure

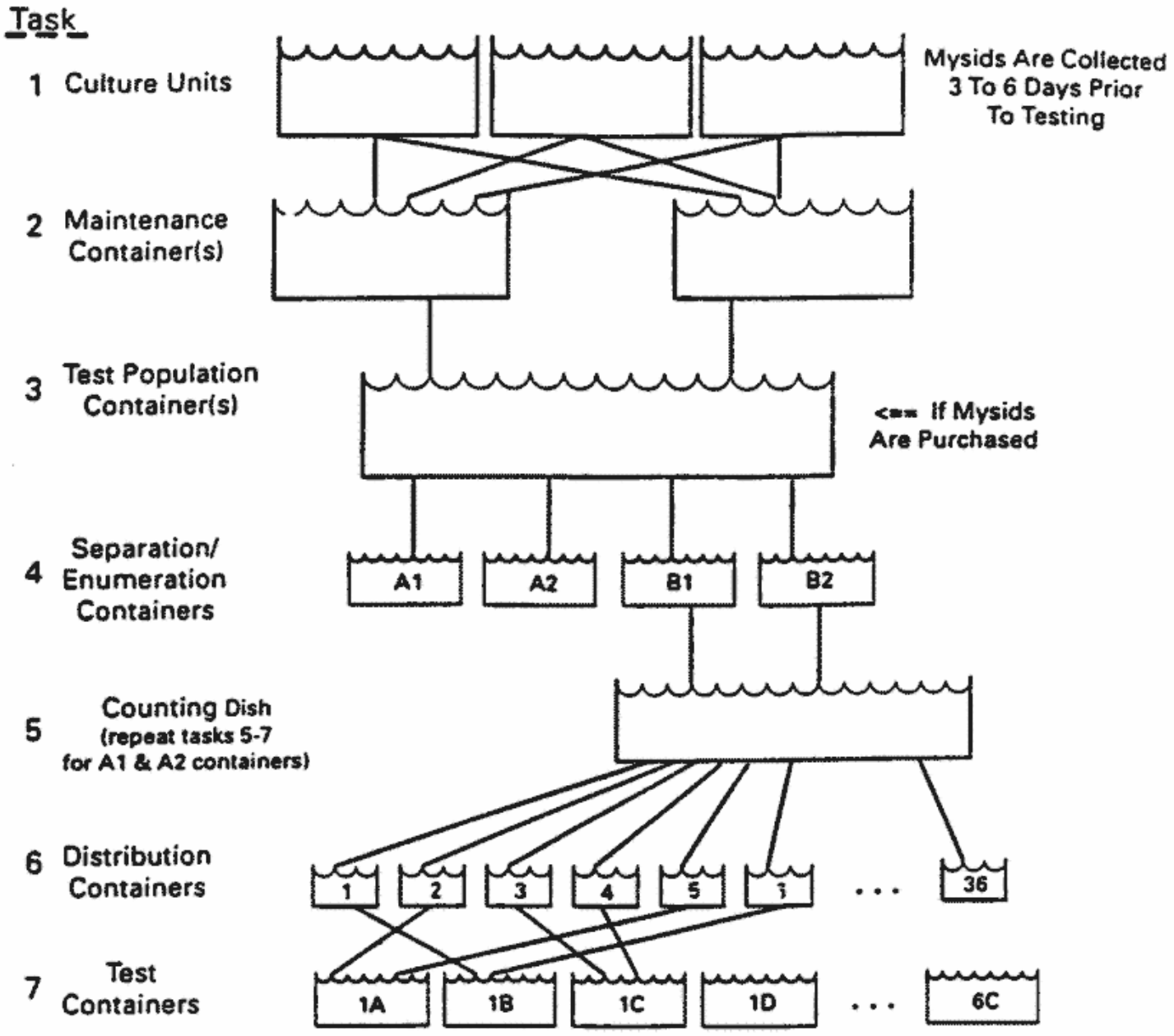
(1) The purpose of this procedure is to assure that mysids are impartially selected and randomly assigned to six test treatments (five drilling fluid or reference toxicant concentrations and a control) and impartially counted at the end of the 96-hour test. Thus, each test setup, as specified in the randomization procedure, consists of 3 replicates of 20 animals for each of the six treatments, *i.e.*, 360 animals per test. Figure 1 is a flow diagram that depicts the procedure schematically and should be reviewed to understand the over-all operation. The following tasks shall be performed in the order listed.

(2) Mysids are cultured in the laboratory in appropriate units. If mysids are purchased, go to Task 3.

(3) Remove mysids from culture tanks (6, 5, 4, and 3 days before the test will begin, *i.e.*, Tuesday, Wednesday, Thursday, and Friday if the test will begin on Monday) and place them in suitably large maintenance containers so that they can swim about freely and be fed.

Note: Not every detail (the definition of suitably large containers, for example) is provided here. Training and experience in aquatic animal culture and testing will be required to successfully complete these tests.

Figure 1
Mysid Randomization Procedure



(4) Remove mysids from maintenance containers and place all animals in a single container. The intent is to have homogeneous test population of mysids of a known age (3-6 days old).

(5) For each toxicity test, assign two suitable containers (500-milliliter (mL) beakers are recommended) for mysid separation/enumeration. Label each container (A1, A2, B1, B2, and C1, C2, for example, if two drilling fluid tests and a reference toxicant test are to be set up on one day). The purpose of this task is to allow the investigator to obtain a close estimate of the number of animals available for testing and to prevent unnecessary crowding of the mysids while they are being counted and assigned to test containers. Transfer the mysids from the large test population container to the labeled separation and enumeration containers but do not place more than 200 mysids in a 500-mL beaker. Be impartial in transferring the mysids; place approximately equal numbers of animals (10-15 mysids is convenient) in each container in a cyclic manner rather than placing the maximum number each container at one time.

Note: It is important that the animals not be unduly stressed during this selection and assignment procedure. Therefore, it will probably be necessary to place all animals (except the batch immediately being assigned to test containers) in mesh cups with flowing seawater or in large volume containers with aeration. The idea is to provide the animals with near optimal conditions to avoid additional stress.

(6) Place the mysids from the two labeled enumeration containers assigned to a specific test into one or more suitable containers to be used as counting dishes (2-liter Carolina dishes are suggested). Because of the time required to separate, count, and assign mysids, two or more people may be involved in completing this task. If this is done, two or more counting dishes may be used, but the investigator must make sure that approximately equal numbers of mysids from each labeled container are placed in each counting dish.

(7) By using a large-bore, smooth-tip glass pipette, select mysids from the counting dish(es) and place them in the 36 individually numbered distribution containers (10-ml beakers are suggested). The mysids are assigned two at a time to the 36 containers by using a randomization schedule similar to the one presented below. At the end of selection/assignment round 1, each container will contain two mysids; at the end of round 2, they will contain four mysids; and so on until each contains ten mysids.

Example of a Randomization Schedule

Selection/assignment round (2 mysids each)	Place mysid in the numbered distribution containers in the random order shown
1	8, 21, 6, 28, 33, 32, 1, 3, 10, 9, 4, 14, 23, 2, 34, 22, 36, 27, 5, 30, 35, 24, 12, 25, 11, 17, 19, 26, 31, 7, 20, 15, 18, 13, 16, 29.
2	35, 18, 5, 12, 32, 34, 22, 3, 9, 16, 26, 13, 20, 28, 6, 21, 24, 30, 8, 31, 7, 23, 2, 15, 25, 17, 1, 11, 27, 4, 19, 36, 10, 33, 14, 29.
3	7, 19, 14, 11, 34, 21, 25, 27, 17, 18, 6, 16, 29, 2, 32, 10, 4, 20, 3, 9, 1, 5, 28, 24, 31, 15, 22, 13, 33, 26, 36, 12, 8, 30, 35, 23.
4	30, 2, 18, 5, 8, 27, 10, 25, 4, 20, 26, 15, 31, 36, 35, 23, 11, 29, 16, 17, 28, 1, 33, 14, 9, 34, 7, 3, 12, 22, 21, 6, 19, 24, 32, 13.

Selection/assignment round (2 mysids each)	Place mysid in the numbered distribution containers in the random order shown
5	34, 28, 16, 17, 10, 12, 1, 36, 20, 18, 15, 22, 2, 4, 19, 23, 27, 29, 25, 21, 30, 3, 9, 33, 32, 6, 14, 11, 35, 24, 26, 7, 31, 5, 13, 8.

(8) Transfer mysids from the 36 distribution containers to 18 labeled test containers in random order. A label is assigned to each of the three replicates (A, B, C) of the six test concentrations. Count and record the 96 hour response in an impartial order.

(9) Repeat tasks 5-7 for each toxicity test. A new random schedule should be followed in Tasks 6 and 7 for each test.

Note: If a partial toxicity test is conducted, the procedures described above are appropriate and should be used to prepare the single test concentration and control, along with the reference toxicant test.

V-B. Data Analysis and Interpretation

(1) Complete survival data in all test containers at each observation time shall be presented in tabular form. If greater than 10 percent mortality occurs in the controls, all data shall be discarded and the experiment repeated. Unacceptably high control mortality indicates the presence of important stresses on the organisms other than the material being tested, such as injury or disease, stressful physical or chemical conditions in the containers, or improper handling, acclimation, or feeding. If 10 percent mortality or less occurs in the controls, the data may be evaluated and reported.

(2) A definitive, full bioassay conducted according to the EPA protocol is used to estimate the concentration that is lethal to 50 percent of the test organisms that do not die naturally. This toxicity measure is known as the median lethal concentration, or LC-50. The LC-50 is adjusted for natural mortality or natural responsiveness. The maximum likelihood estimation procedure with the adjustments for natural responsiveness as given by D.J. Finney, in *Probit Analysis* 3rd edition, 1971, Cambridge University Press, chapter 7, can be used to obtain the probit model estimate of the LC-50 and the 95 percent fiducial (confidence) limits for the LC-50. These estimates are obtained using the logarithmic transform of the concentration. The heterogeneity factor (Finney 1971, pages 70-72) is not used. For a test material to pass the toxicity test, according to the requirements stated in the offshore oil and gas extraction industry BAT effluent limitations and NSPS, the LC-50, adjusted for natural responsiveness, must be greater than 3 percent suspended particulate phase (SPP) concentration by volume unadjusted for the 1 to 9 dilution. Other toxicity test models may be used to obtain toxicity estimates provided the modeled mathematical expression for the lethality rate must increase continuously with concentration. The lethality rate is modeled to increase with concentration to reflect an assumed increase in toxicity with concentration even though the observed lethality may not increase uniformly because of the unpredictable animal response fluctuations.

(3) The range finding test is used to establish a reasonable set of test concentrations in order to run the definitive test. However, if the lethality rate changes rapidly over a narrow range of concentrations, the range finding assay may be too coarse to establish an adequate set of test concentrations for a definitive test.

(4) The EPA Environmental Research Laboratory in Gulf Breeze, Florida prepared a Research and Development Report entitled Acute Toxicity of Eight Drilling Fluids to Mysid Shrimp (*Mysidopsis bahia*), May 1984 EPA-600/3-84-067. The Gulf Breeze data for drilling fluid number 1 are displayed in Table 1 for purposes of an example of the probit analysis described above. The SAS Probit Procedure (SAS Institute, Statistical Analysis System, Cary, North Carolina, 1982) was used to analyze these data. The 96-hour LC50 adjusted for the estimated spontaneous mortality rate is 3.3 percent SPP with 95 percent limits of 3.0 and 3.5 percent SPP with the 1 to 9 dilution. The estimated spontaneous mortality rate based on all of the data is 9.6 percent.

Table 1—Listing of Acute Toxicity Test Data (August 1983 to September 1983) with Eight Generic Drilling Fluids and Mysid Shrimp

[fluid N2 = 1]

Percent concentration	Number exposed	Number dead (96 hours)	Number alive (96 hours)
0	60	3	57
1	60	11	49
2	60	11	49
3	60	25	35
4	60	48	12
5	60	60	0

V-C. The Partial Toxicity Test for Evaluation of Test Material

(1) A partial test conducted according to EPA protocol can be used economically to demonstrate that a test material passes the toxicity test. The partial test cannot be used to estimate the LC-50 adjusted for natural response.

(2) To conduct a partial test follow the test protocol for preparation of the test material and organisms. Prepare the control (zero concentration), one test concentration (3 percent suspended particulate phase) and the reference toxicant according to the methods of the full test. A range finding test is not used for the partial test.

(3) Sixty test organisms are used for each test concentration. Find the number of test organisms killed in the control (zero percent SPP) concentration in the column labeled X_0 of Table 2. If the number of organisms in the control (zero percent SPP) exceeds the table values, then the test is unacceptable and must be repeated. If the number of organisms killed in the 3 percent test concentration is less than or equal to corresponding number in the column labeled X_1 then the test material passes the partial toxicity test. Otherwise the test material fails the toxicity test.

(4) Data shall be reported as percent suspended particulate phase.

Table 2

X_0	X_1
0	22

X_0	X_1
1	22
2	23
3	23
4	24
5	24
6	25

VI. References

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[58 FR 12504, Mar. 4, 1993, as amended at 77 FR 29837, May 18, 2012]

Appendix 3 to Subpart A of Part 435—Procedure for Mixing Base Fluids With Sediments (EPA Method 1646)

This procedure describes a method for amending uncontaminated and nontoxic (control) sediments with the base fluids that are used to formulate synthetic-based drilling fluids and other non-aqueous drilling fluids. Initially, control sediments shall be press-sieved through a 2000 micron mesh sieve to remove large debris. Then press-sieve the sediment through a 500 micron sieve to remove indigenous organisms that may prey on the test species or otherwise confound test results. Homogenize control sediment to limit the effects of settling that may have occurred during storage. Sediments should be homogenized before density determinations and addition of base fluid to control sediment. Because base fluids are strongly hydrophobic and do not readily mix with sediment, care must be taken to ensure base fluids are thoroughly homogenized within the sediment. All concentrations are weight-to-weight (mg of base fluid to kg of dry control sediment). Sediment and base fluid mixing shall be accomplished by using the following method.

1. Determine the wet to dry ratio for the control sediment by weighing approximately 10 g subsamples of the screened and homogenized wet sediment into tared aluminum weigh pans. Dry sediment at 105 °C for 18-24 h. Remove sediment and cool in a desiccator until a constant weight is achieved. Re-weigh the samples to determine the dry weight. Determine the wet/dry ratio by dividing the net wet weight by the net dry weight:

   [Wet Sediment Weight (g)]/[Dry Sediment Weight (g)] = Wet to Dry Ratio [1]

2. Determine the density (g/mL) of the wet control or dilution sediment. This shall be used to determine total volume of wet sediment needed for the various test treatments.

   [Mean Wet Sediment Weight (g)]/[Mean Wet Sediment Volume (mL)] = Wet Sediment Density (g/mL) [2]

3. To determine the amount of base fluid needed to obtain a test concentration of 500 mg base fluid per kg dry sediment use the following formulas:

   Determine the amount of wet sediment required:

   [Wet Sediment Density (g/mL)] × [Volume of Sediment Required per Concentration (mL)] = Weight Wet Sediment Required per Conc. (g) [3]

   Determine the amount of dry sediment in kilograms (kg) required for each concentration:

   {[Wet Sediment per Concentration (g)]/[Mean Wet to Dry Ratio]} × (1kg/1000g) = Dry Weight Sediment (kg) [4]

   Finally, determine the amount of base fluid required to spike the control sediment at each concentration:

   [Conc. Desired (mg/kg)] × [Dry Weight Sediment (kg)] = Base Fluid Required (mg) [5]

   For spiking test substances other than pure base fluids (e.g., whole mud formulations), determine the spike amount as follows:

   [Conc. Desired (mL/kg)] × [Dry Weight Sediment (kg)] × [Test Substance Density (g/mL)] = Test Substance Required (g) [6]

4. For primary mixing, place appropriate amounts of weighed base fluid into stainless mixing bowls, tare the vessel weight, then add sediment and mix with a high-shear dispersing impeller for 9 minutes. The concentration of base fluid in sediment from this mix, rather than the nominal concentration, shall be used in calculating LC_5. values.

5. Tests for homogeneity of base fluid in sediment are to be performed during the procedure development phase. Because of difficulty of homogeneously mixing base fluid with sediment, it is important to demonstrate that the base fluid is evenly mixed with sediment. The sediment shall be analyzed for total petroleum hydrocarbons (TPH) using EPA Methods 3550A and 8015M, with samples taken both prior to and after distribution to replicate test containers. Base-fluid content is measured as TPH. After mixing the sediment, a minimum of three replicate sediment samples shall be taken prior to distribution into test containers. After the test sediment is distributed to test containers, an additional three sediment samples shall be taken from three test containers to ensure proper distribution of base fluid within test containers. Base-fluid content results shall be reported within 48 hours of mixing. The coefficient of variation (CV) for the replicate samples must be less than 20%. If base-fluid content results are not within the 20% CV limit, the test sediment shall be remixed. Tests shall not begin until the CV is determined to be below the maximum limit of 20%. During the test, a minimum of three replicate containers shall be sampled to determine base-fluid content during each sampling period.

6. Mix enough sediment in this way to allow for its use in the preparation of all test concentrations and as a negative control. When commencing the sediment toxicity test, range-finding tests may be required to determine the concentrations that produce a toxic effect if these data are otherwise unavailable. The definitive test shall bracket the LC_{5}., which is the desired endpoint. The results for the base fluids shall be reported in mg of base fluid per kg of dry sediment.

References

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[66 FR 6901, Jan. 22, 2001]

Appendix 4 to Subpart A of Part 435—Protocol for the Determination of Degradation of Non-Aqueous Base Fluids in a Marine Closed Bottle Biodegradation Test System: Modified ISO 11734:1995 (EPA Method 1647)

1.0. Summary of EPA Method 1647

a. This method determines the anaerobic degradation potential of mineral oils, paraffin oils and non-aqueous fluids (NAF) in sediments. These substrates are base fluids for formulating offshore drilling fluids. The test evaluates base fluid biodegradation rates by monitoring gas production due to microbial degradation of the test fluid in natural marine sediment.

b. The test procedure places a mixture of marine/estuarine sediment, test substrate (hydrocarbon or controls) and seawater into clean 120 mL (150 mL actual volume) Wheaton serum bottles. The test is run using four replicate serum bottles containing 2,000 mg carbon/kg dry weight concentration of test substrate in sediment. The use of resazurin dye solution (1 ppm) evaluates the anaerobic (redox) condition of the bottles (dye is blue when oxygen is present, reddish in low oxygen conditions and colorless if oxygen free). After capping the bottles, a nitrogen sparge removes air in the headspace before incubation begins. During the incubation period, the sample should be kept at a constant temperature of 29 ±1 °C. Gas production and composition is measured approximately every two weeks. The samples need to be brought to ambient temperature before making the measurements. Measure gas production using a pressure gauge. Barometric pressure is measured at the time of testing to make necessary volume adjustments.

c. ISO 11734:1995 specifies that total gas is the standard measure of biodegradation. While modifying this test for evaluating biodegradation of NAFs, methane was also monitored and found to be an acceptable method of evaluating biodegradation. Section 7 contains the procedures used to follow biodegradation by methane production. Measurement of either total gas or methane production is permitted. If methane is followed, determine the composition of the gas by using gas chromatography (GC) analysis at each sampling. At the end of the test when gas production stops, or at around 275 days, an analysis of sediment for substrate content is possible. Common methods which have been successfully used for analyzing NAFs from sediments are listed in Section 8.

2.0 System Requirements

This environmental test system has three phases, spiked sediment, overlying seawater, and a gas headspace. The sediment/test compound mixture is combined with synthetic sea water and transferred into 120-mL serum bottles. The total volume of sediment/sea water mixture in the bottles is 75 mL. The volume of the sediment layer will be approximately 50 mL, but the exact volume of the sediment will depend on sediment characteristics (wet:dry ratio and density). The amount of synthetic sea water will be calculated to bring the total volume in the bottles to 75 mL. The test systems are maintained at a temperature of 29 ±1 °C during incubation. The test systems are brought to ambient temperatures prior to measuring pressure or gas volume.

2.1 Sample Requirements

a. The concentration of base fluids are at least 2,000 mg carbon test material/kg dry sediment. Carbon concentration is determined by theoretical composition based on the chemical formula or by chemical analysis by ASTM D5291-96. Sediments with positive, intermediate and negative control substances as well as a C_{16}-C_{18} internal olefin type base fluid will be run in conjunction with test materials under the same conditions. The positive control is ethyl oleate (CAS 111-62-6), the intermediate control is 1-hexadecene (CAS 629-73-2), and the negative control is squalane (CAS 111-01-3). Controls must be of analytical grade or the highest grade available. Each test control concentration should be prepared according to the mixing procedure described in Section 3.1.

b. Product names will be used for examples or clarification in the following text. Any use of trade or product names in this publication is for descriptive use only, and does not constitute endorsement by EPA or the authors.

2.2. Seawater Requirements

Synthetic seawater at a salinity of 25 ±1 ppt should be used for the test. The synthetic seawater should be prepared by mixing a commercially available artificial seawater mix, into high purity distilled or de-ionized water. The seawater should be aerated and allowed to age for approximately one month prior to use.

2.3. Sediment Requirements

a. The dilution sediment must be from a natural estuarine or marine environment and be free of the compounds of interest. The collection location, date and time will be documented and reported. The sediment is prepared by press-sieving through a 2,000-micron mesh sieve to

remove large debris, then press-sieving through a 500-micron sieve to remove indigenous organisms that may confound test results. The water content of the sediment should be less than 60% (w/w) or a wet to dry ratio of 2.5. The sediment should have a minimum organic matter content of 3% (w/w) as determined by ASTM D2974-07a (Method A and D and calculate organic matter as in Section 8.3 of method ASTM D2974-07a).

b. To reduce the osmotic shock to the microorganisms in the sediment the salinity of the sediment's pore water should be between 20-30 ppt. Sediment should be used for testing as soon as possible after field collection. If required, sediment can be stored in the dark at 4 °C with 3-6 inches of overlying water in a sealed container for a maximum period of 2 months prior to use.

3.0 Test Set Up

The test is set up by first mixing the test or control substrates into the sediment inoculum, then mixing in seawater to make a pourable slurry. The slurry is then poured into serum bottles, which are then flushed with nitrogen and sealed.

3.1. Mixing Procedure

Because base fluids are strongly hydrophobic and do not readily mix with sediments, care must be taken to ensure base fluids are thoroughly homogenized within the sediment. All concentrations are weight-to-weight comparisons (mg of base fluid to kg of dry control sediment). Sediment and base fluid mixing will be accomplished by using the following method.

3.1.1. Determine the wet to dry weight ratio for the control sediment by weighing approximately 10 sub-samples of approximately 1 g each of the screened and homogenized wet sediment into tared aluminum weigh pans. Dry sediment at 105 °C for 18-24 h. Remove the dried sediments and cool in a desiccator. Repeat the drying, cooling, and weighing cycle until a constant weight is achieved (within 4% of previous weight). Re-weigh the samples to determine the dry weight. Calculate the mean wet and dry weights of the 10 sub samples and determine the wet/dry ratio by dividing the mean wet weight by the mean dry weight using Equation 5-1. This is required to determine the weight of wet sediment needed to prepare the test samples.

$$\frac{\text{Mean Wet Sediment Weight (g)}}{\text{Mean Dry Sediment Weight (g)}} = \text{Wet to Dry Ratio} \qquad \text{[Eq.1]}$$

3.1.2. Determine the density (g/ml) of the wet sediment. This will be used to determine total volume of wet sediment needed for the various test treatments. One method is to tare a 5 ml graduated cylinder and add about 5 ml of homogenized sediment. Carefully record the volume then weigh this volume of sediment. Repeat this a total of three times. To determine the wet sediment density, divide the weight by volume per the following formula:

$$\frac{\text{Mean Wet Sediment Weight (g)}}{\text{Mean Wet Sediment Volume (mL)}} = \text{Wet Sediment Density (g/mL)} \qquad \text{[Eq. 2]}$$

3.1.3. Determine the amount of base fluid to be spiked into wet sediment in order to obtain the desired initial base fluid concentration of 2,000 mg carbon/kg dry weight. An amount of wet sediment that is the equivalent of 30 g of dry sediment will be added to each bottle. A typical procedure is to prepare enough sediment for 8 serum bottles (3 bottles to be sacrificed at the

start of the test, 4 bottles incubated for headspace analysis, and enough extra sediment for 2 extra bottles). Extra sediment is needed because some of the sediment will remain coated onto the mixing bowl and utensils. Experience with this test may indicate that preparing larger volumes of spiked sediment is a useful practice, then the following calculations should be adjusted accordingly.

a. Determine the total weight of dry sediment needed to add 30 g dry sediment to 8 bottles. If more bottles are used then the calculations should be modified accordingly. For example:

$$30\text{ g dry sediment per bottle} \times 8 = 240\text{ g dry sediment} \quad \text{[Eq.3]}$$

b. Determine the weight of base fluid, in terms of carbon, needed to obtain a final base fluid concentration of 2,000 mg carbon/kg dry weight. For example:

$$\frac{2{,}000\text{ mg carbon}}{\text{Per kg dry sediment}} \times \frac{240\text{ g}}{1{,}000} = 480\text{ mg carbon} \quad \text{[Eq. 4]}$$

c.

i. Convert from mg of carbon to mg of base fluid. This calculation will depend on the % fraction of carbon present in the molecular structure of each base fluid. For the control fluids, ethyl oleate is composed of 77.3% carbon, hexadecene is composed of 85.7% carbon, and squalane is composed of 85.3% carbon. The carbon fraction of each base fluid should be supplied by the manufacturer or determined before use. ASTM D5291-96 or equivalent will be used to determine composition of fluid.

ii. To calculate the amount of base fluid to add to the sediment, divide the amount of carbon (480 mg) by the percent fraction of carbon in the fluid.

iii. For example, the amount of ethyl oleate added to 240 g dry weight sediment can be calculated from the following equation:

$$\frac{480\text{ mg carbon}}{(77.3 \div 100)} = 621\text{ mg ethyl oleate} \quad \text{[Eq. 5]}$$

iv. Therefore, add 621 mg of ethyl oleate to 240 g dry weight sediment for a final concentration of 2,000 mg carbon/kg sediment dry weight.

3.1.4. Mix the calculated amount of base fluid with the appropriate weight of wet sediment.

a. Use the wet:dry ratio to convert from g sediment dry weight to g sediment wet weight, as follows:

$$240\text{ g dry sediment} \times \text{wet:dry ratio} = \text{g wet sediment needed} \quad \text{[Eq. 6]}$$

b.

i. Weigh the appropriate amount of base fluid (calculated in Section 3.1.3.c) into stainless mixing bowls, tare the vessel weight, then add the wet sediment calculated in Equation 5, and mix with a high shear dispersing impeller for 9 minutes.

ii. The sediment is now mixed with synthetic sea water to form a slurry that will be transferred into the bottles.

3.2. Creating Seawater/Sediment Slurry

Given that the total volume of sediment/sea water slurry in each bottle is to be 75 mL, determine the volume of sea water to add to the wet sediment.

3.2.1. If each bottle is to contain 30 g dry sediment, calculate the weight, and then the volume, of wet sediment to be added to each bottle.

$$30\text{ g dry sediment} \times \text{wet:dry ratio} = \text{g wet sediment added to each bottle} \quad \text{[Eq. 7]}$$

$$\frac{\text{g wet sediment}}{\text{Density (g/mL) of wet sediment}} = \text{mL wet sediment} \quad \text{[Eq. 8]}$$

3.2.2. Calculate volume of sea water to be added to each bottle.

$$75\text{ mL total volume} - \text{mL wet sediment (from Eq. 8)} = \text{mL of sea water} \quad \text{[Eq. 9]}$$

3.2.3. Determine the ratio of sea water to wet sediment (volume:volume) in each bottle.

$$\frac{\text{Volume sea water per bottle (Eq. 9)}}{\text{Volume sediment water per bottle (Eq. 8)}} = \text{Ratio of sea water:wet sediment} \quad \text{[Eq. 10]}$$

3.2.4. Convert the wet sediment weight from Equation 6 into a volume using the sediment density.

$$\text{g wet sediment (Eq. 6) density} = \text{volume (mL) of sediment} \quad \text{[Eq. 11]}$$

3.2.5. Determine the amount of sea water to mix with the wet sediment.

$$\underset{\text{(Eq. 11)}}{\text{mL wet sediment}} \times \underset{\text{(Eq. 10)}}{\text{Sea water:sediment ratio}} = \text{mL sea water to add to wet sediment} \quad \text{[Eq. 12]}$$

Mix sea water thoroughly with wet sediment to form a sediment/sea water slurry.

3.3. Bottling the Sediment Seawater Slurry

The total volume of sediment/sea water slurry in each bottle is to be 75 mL. Convert the volume (mL) of sediment/sea water slurry into a weight (g) using the density of the sediment and the seawater.

3.3.1. Determine the weight of sediment to be added to each bottle.

$$\text{mL sediment (Eq. 8)} \times \text{density of wet sediment (g/mL)} = \text{g wet sediment} \quad \text{[Eq. 13]}$$

3.3.2. Determine the weight of sea water to be added to each bottle.

$$\text{mL sea water (Eq. 9)} \times \text{density of sea water (1.01 g/mL)} = \text{g sea water} \quad \text{[Eq. 14]}$$

3.3.3. Determine weight of sediment/sea water slurry to be added to each bottle.

$$\text{g wet sediment (Eq. 13)} + \text{g sea water (Eq. 14)} = \text{g sediment/sea water slurry} \quad \text{[Eq. 15]}$$

This should provide each bottle with 30 g dry sediment in a total volume of 75 mL.

3.3.4. Putting the sediment:seawater slurry in the serum bottles.

a. NOTE: The slurry will need to be constantly stirred to keep the sediment suspended.

b. Place a tared serum bottle on a balance and add the appropriate amount of slurry to the bottle using a funnel. Once the required slurry is in the bottle remove the funnel, add 2-3 drops (25 µL) of a 1 gram/L resazurin dye stock solution. Cap the bottle with a butyl rubber stopper (Bellco Glass, Part #2048-11800) and crimp with an aluminum seal (Bellco Glass Part #2048-11020).

c. Using a plastic tube with a (23-gauge, 1-inch long) needle attached to one side and a nitrogen source to the other, puncture the serum cap with the needle. Puncture the serum cap again with a second needle to sparge the bottle's headspace of residual air for two minutes. The nitrogen should be flowing at no more than 100 mL/min to encourage gentle displacement of oxygenated air with nitrogen. Faster nitrogen flow rates would cause mixing and complete oxygen removal would take much longer. Remove the nitrogen needle first to avoid any initial pressure problems. The second (vent) needle should be removed within 30 seconds of removing the nitrogen needle.

d. Triplicate blank test systems are prepared, with similar quantities of sediment and seawater without any base fluid. Incubate in the dark at a constant temperature of 29 ±1 °C.

e. Record the test temperature. The test duration is dependent on base fluid performance, but at a maximum should be no more than 275 days. Stop the test after all base fluids have achieved a plateau of gas production. At termination, base fluid concentrations can be verified in the terminated samples by extraction and GC analysis according to Section 8.

4.0. Concentration Verification Chemical Analyses

a. Because of the difficulty of homogeneously mixing base fluid with sediment, it is important to demonstrate that the base fluid is evenly mixed within the sediment sea water slurry that was added to each bottle. Of the seven serum bottles set up for each test or control condition, three are randomly selected for concentration verification analyses. These should be immediately placed at 4 °C and a sample of sediment from each bottle should be analyzed for base fluid content as soon as possible. The coefficient of variation (CV) for the replicate samples must be less than 20%. The results should show recovery of at least 70% of the spiked base fluid. Use an appropriate analytical procedure described in Section 8 to perform the extractions and analyses. If any set of sediments fail the criteria for concentration verification, then the corrective action for that set of sediments is also outlined in Section 8.

b. The nominal concentrations and the measured concentrations from the three bottles selected for concentration verification should be reported for the initial test concentrations. The coefficient of variation (CV) for the replicate samples must be less than 20%. If base fluid content results are not within the 20% CV limit, the test must be stopped and restarted with adequately mixed sediment.

5.0. Gas Monitoring Procedures

Biodegradation is measured by total gas as specified in ISO 11734:1995. Methane production can also be tracked and is described in Section 7.

5.1. Total Gas Monitoring Procedures

Bottles should be brought to room temperature before readings are taken. a. The bottles are observed to confirm that the resazurin has not oxidized to pink or blue. Total gas production in the culture bottles should be measured using a pressure transducer (one source is Biotech International). The pressure readings from test and control cultures are evaluated against a calibration curve created by analyzing the pressure created by known additions of gas to bottles established identically to the culture bottles. Bottles used for the standard curve contain 75 mL of water, and are sealed with the same rubber septa and crimp cap seals used for the bottles containing sediment. After the bottles used in the standard curve have been sealed, a syringe needle inserted through the septa is used to equilibrate the pressure inside the bottles to the outside atmosphere. The syringe needle is removed and known volumes of air are injected into the headspace of the bottles. Pressure readings provide a standard curve relating the volume of gas injected into the bottles and headspace pressure. No less than three points may be used to generate the standard curve. A typical standard curve may use 0, 1, 5, 10, 20 and 40 mL of gas added to the standard curve bottles.

b. The room temperature and barometric pressure (to two digits) should be recorded at the time of sampling. One option for the barometer is Fisher Part #02-400 or 02-401. Gas production by the sediment is expressed in terms of the volume (mL) of gas at standard temperature (0 °C = 273 °K) and pressure (1 atm = 30 inches of Hg) using Eq. 16.

$$V_2 = \frac{P_1 \times V_1 \times T_2}{T_1 \times P_2} \quad \text{[Eq.16]}$$

Where:

V_2 = Volume of gas production at standard temperature and pressure

P_1 = Barometric pressure on day of sampling (inches of Hg)

V_1 = Volume of gas measured on day of sampling (mL)

T_2 = Standard temperature = 273 °K

T_1 = Temperature on day of sampling (°C + 273 = °K)

P_2 = Standard pressure = 30 inches Hg

c. An estimate can be made of the total volume of anaerobic gas that will be produced in the bottles. The gas production measured for each base fluid can be expressed as a percent of predicted total anaerobic gas production.

5.1.1. Calculate the total amount of carbon in the form of the base fluid present in each bottle.

a. Each bottle is to contain 30 g dry weight sediment. The base fluid concentration is 2,000 mg carbon/kg dry weight sediment. Therefore:

$$2{,}000 \text{ mg carbon/kg sediment} \times (30 \text{ g} \div 1{,}000) = 60 \text{ mg carbon per bottle} \quad \text{[Eq. 17]}$$

5.1.2. Theory states that anaerobic microorganisms will convert 1 mole of carbon substrate into 1 mole of total anaerobic gas production.

a. Calculate the number of moles of carbon in each bottle.

b. The molecular weight of carbon is 12 (*i.e.*, 1 mole of carbon = 12 g). Therefore, the number of moles of carbon in each bottle can be calculated.

$$\frac{60 \text{ mg carbon per bottle}/1{,}000}{12 \text{ g/mole}} = 0.005 \text{ moles carbon} \qquad \text{[Eq. 18]}$$

5.1.3. Calculate the predicted volume of anaerobic gas.

One mole of gas equals 22.4 L (at standard temperature and pressure), therefore,

$$0.005 \text{ moles} \times 22.4 \text{ L} = 0.112\text{L (or 112 mL total gas production)} \qquad \text{[Eq. 19]}$$

5.2. Gas Venting

a. If the pressure in the serum bottle is too great for the pressure transducer or syringe, some of the excess gas must be wasted. The best method to do this is to vent the excess gas right after measurement. To do this, remove the barrel from a 10-mL syringe and fill it $^1/_3$ full with water. This is then inserted into the bottle through the stopper using a small diameter (high gauge) needle. The excess pressure is allowed to vent through the water until the bubbles stop. This allows equalization of the pressure inside the bottle to atmospheric without introducing oxygen. The amount of gas vented (which is equal to the volume determined that day) must be kept track of each time the bottles are vented. A simple way to do this in a spreadsheet format is to have a separate column in which cumulative vented gas is tabulated. Each time the volume of gas in the cultures is analyzed, the total gas produced is equal to the gas in the culture at that time plus the total of the vented gas.

b. To keep track of the methane lost in the venting procedure, multiply the amount of gas vented each time by the corrected % methane determined on that day. The answer gives the volume of methane wasted. This must be added into the cumulative totals similarly to the total gas additions.

6.0. Test Acceptability and Interpretation

6.1. Test Acceptability

At day 275 or when gas production has plateaued, whichever is first, the controls are evaluated to confirm that the test has been performed appropriately. In order for this modification of the closed bottle biodegradation test to be considered acceptable, all the controls must meet the biodegradation levels indicated in Table 1. The intermediate control hexadecene must produce at least 30% of the theoretical gas production. This level may be reexamined after two years and more data has been generated.

Table 1—Test Acceptability Criteria

Concentration	Percent biodegradability as a function of gas measurement		
	Positive control	Squalane negative control	Hexadecene intermediate control
2,000 mg carbon/kg	≥60% theoretical	≤5% theoretical	≥30% theoretical.

6.2 Interpretation

a. In order for a fluid to pass the closed bottle test, the biodegradation of the base fluid as indicated by the total amount of total gas (or methane) generated once gas production has plateaued (or at the end of 275 days, which ever is first) must be greater than or equal to the volume of gas (or methane) produced by the reference standard (internal elefin or ester).

b. The method for evaluating the data to determine whether a fluid has passed the biodegradation test must use the equations:

$$\frac{\%\ \text{Theoretical gas production of reference fluid}}{\%\ \text{Theoretical gas production of NAF}} \leq 1.0 \qquad \text{[Eq. 20]}$$

Where:

NAF = Stock base fluid being tested for compliance

Reference fluid = C_{16}-C_{18} internal olefin or C_{12} -C_{14} or C_8 ester reference fluid

7.0. Methane Measurement

7.1. Methane Monitoring Procedures

a. The use of total gas production alone may result in an underestimation of the actual metabolism occurring since CO_2 is slightly soluble in water. An acceptable alternative method is to monitor methane production and total gas production. This is easily done using GC analysis. A direct injection of headspace gases can be made into a GC using almost any packed or capillary column with an FID detector. Unless volatile fuels or solvents are present in the test material or the inocula, the only component of the headspace gas that can be detected using an FID detector is methane. The percent methane in the headspace gas is determined by comparing the response of the sample injections to the response from injections of known percent methane standards. The percent methane is corrected for water vapor saturation using Eq. 21 and then converted to a volume of dry methane using Eq. 22.

$$\text{Corrected \% } CH_4 = \frac{\text{\% } CH_4}{1 - \frac{D \times 22.4 \text{ L/mol}}{18 \text{ g/mol} \times 1{,}000}} \quad \text{[Eq. 21]}$$

Where:

D = The density of water vapor at saturation (g/m^3, can be found in CRC Handbook of Chemistry and Physics) for the temperature of sampling.

$$V_{CH4}\,(ml) = (S + V) \times \frac{P - P_w}{T + 273} \times \frac{CH_4}{100} \times \frac{273}{760} \quad \text{[Eq. 22]}$$

Where:

V_{CH4} = Volume of methane in the bottle

S = Volume of excess gas production (measured with a pressure transducer)

V = Volume of the headspace in the culture bottle (total volume—liquid phase)

P = Barometric pressure (mm Hg, measured with barometer)

T = Temperature (°C)

P_w = Vapor pressure of water at T (mm Hg, can be found in CRC Handbook of Chemistry and Physics)

CH_4 = % methane in headspace gas (after correction for water vapor)

b. The total volume of serum bottles sold as 125 mL bottles (Wheaton) is 154.8 mL.

c. The volumes of methane produced are then compared to the volumes of methane in the controls to determine if a significant inhibition of methane production or a significant increase of methane production has been observed. Effective statistical analyses are important, as variability in the results is common due to the heterogeneity of the inoculum's source. It is also common to observe that the timing of the initiation of culture activity is not equal in all of the cultures. Expect a great variability over the period when the cultures are active, some replicates will start sooner than others, but all of the replicates should eventually reach similar levels of base fluid degradation and methane production.

7.2. Expected Methane Production Calculations

a. The amount of methane expected can be calculated using the equation of Symons and Buswell (Eq. 23). In the case of complete mineralization, all of the carbon will appear as wither CO_2 or CH_4, thus the total moles of gas produced will be equal to the total moles of carbon in the parent molecule. The use of the Buswell equation allows you to calculate the effects the redox potential will have on the distribution of the products in methanogenic cultures. More reduced electron donors will allow the production of more methane, while more oxidized electron donors will cause a production of more carbon dioxide.

$$\frac{12 \text{ mole } CH_4}{\text{mole hexadecene}} \times \frac{22.4 \text{ L}}{\text{mole } CH_4} \times \frac{1{,}000 \text{ ml}}{\text{L}} \times \frac{1 \text{ mole hexadecene}}{224.4 \text{ g hexadecene}} \times \frac{23 \text{ g hexadecene}}{\text{kg dry soil}} \times \frac{0.03 \text{ kg}}{\text{culture}} = 84 \text{ (ml)} \quad \text{[Eq. 24]}$$

b. An example calculation of the expected methane volume in a culture fed 2,000 mg/kg hexadecene is as follows. The application of Symons and Buswell's equation reveals that hexadecene ($C_{16}H_{32}$) will yield 4 moles of CO_2 and 12 moles of CH_4. Assuming 30 g of dry sediment are added to the bottles with 2,334 mg hexadecene/kg dry sediment (*i.e.,* equivalent to 2,000 mg carbon/kg dry sediment) the calculation is as follows.

$$\frac{12 \text{ mole } CH_4}{\text{mole hexadecene}} \times \frac{22.4 \text{ L}}{\text{mole } CH_4} \times \frac{1{,}000 \text{ ml}}{\text{L}} \times \frac{1 \text{ mole hexadecene}}{224.4 \text{ g hexadecene}} \times \frac{23 \text{ g hexadecene}}{\text{kg dry soil}} \times \frac{0.03 \text{ kg}}{\text{culture}} = 84 \text{ (ml)} \quad \text{[Eq. 24]}$$

c. By subtracting the average amount of methane in control bottles from the test bottles and then dividing by the expected volume an evaluation of the completion of the process may be conducted.

8.0. Concentration Verification Analysis

The Concentration Verification analysis is required at the beginning of the test to ensure homogeneity and confirm that the required amount of fluid was delivered to the sediments at the start of the test.

8.1. Three samples per fluid need to be analyzed and achieve ≤20% Coefficient of Variability and an average of ≥70% to ≤120% of fluid delivered to sediment.

8.2. If a third party performs the analysis, then the laboratory should be capable of delivering the homogeneity data within seven days, in order to identify any samples that do not meet the homogeneity requirement as quickly as possible.

8.3. If one sediment/fluid set, out a multiple set batch of samples, fails these criteria, then that one set of samples must be discarded and a fresh set of spiked sediment prepared, started, and analyzed to ensure homogeneity. The same stock sediment is used to prepare the replacement set(s). The remaining sets do not need to be re-mixed or restarted.

8.4. The re-mixed set(s) will need to be run the additional days as appropriate to ensure that the total number of days is the same for all sets of bottles, even though the specific days are not aligned.

8.5. Re-mixing of bottle sets can be performed multiple times as a result of a failure of the analytical criteria, until the holding time for the stock sediment has expired (60 days). If the problem set(s) has not fallen within the acceptable analytical criteria by then, it must not be part of the batch of bottles run. If the problem batch is one of the controls, and those controls were not successfully prepared when the sediment holding time expired, then the entire test must be restarted.

9.0 Program Quality Assurance and Quality Control

9.1 Calibration

9.1.1. All equipment/instrumentation will be calibrated in accordance with the test method or the manufacturer's instructions and may be scheduled or triggered.

9.1.2. Where possible, standards used in calibration will be traceable to a nationally recognized standard (e.g., certified standard by NIST).

9.1.3. All calibration activities will be documented and the records retained.

9.1.4. The source, lot, batch number, and expiration date of all reagents used with be documented and retained.

9.2. Maintenance

9.2.1. All equipment/instrumentation will be maintained in accordance with the test method or the manufacturer's instructions and may be scheduled or triggered.

9.2.2. All maintenance activities will be documented and the records retained.

9.3. Data Management and Handling

9.3.1. All primary (raw) data will be correct, complete, without selective reporting, and will be maintained.

9.3.2. Hand-written data will be recorded in lab notebooks or electronically at the time of observation.

9.3.3. All hand-written records will be legible and amenable to reproduction by electrostatic copiers.

9.3.4. All changes to data or other records will be made by:

a. Using a single line to mark-through the erroneous entry (maintaining original data legibility).

b. Write the revision.

c. Initial, date, and provide revision code (*see* attached or laboratory's equivalent).

9.3.5. All data entry, transcriptions, and calculations will be verified by a qualified person.

a. Verification will be documented by initials of verifier and date.

9.3.6. Procedures will be in place to address data management procedures used (at minimum):

a. Significant figures.

b. Rounding practices.

c. Identification of outliers in data series.

d. Required statistics.

9.4. Document Control

9.4.1. All technical procedures, methods, work instructions, standard operating procedures must be documented and approved by laboratory management prior to the implementation.

9.4.2. All primary data will be maintained by the contractor for a minimum of five (5) years.

9.5. Personnel and Training

9.5.1. Only qualified personnel shall perform laboratory activities.

9.5.2. Records of staff training and experience will be available. This will include initial and refresher training (as appropriate).

9.6. Test Performance

9.6.1. All testing will done in accordance with the specified test methods.

9.6.2. Receipt, arrival condition, storage conditions, dispersal, and accountability of the test article will be documented and maintained.

9.6.3. Receipt or production, arrival or initial condition, storage conditions, dispersal, and accountability of the test matrix (e.g., sediment or artificial seawater) will be documented and maintained.

9.6.4. Source, receipt, arrival condition, storage conditions, dispersal, and accountability of the test organisms (including inoculum) will be documented and maintained.

9.6.5. Actual concentrations administered at each treatment level will be verified by appropriate methodologies.

9.6.6. Any data originating at a different laboratory will be identified and the laboratory fully referenced in the final report.

9.7. The following references identify analytical methods that have historically been successful for achieving the analytical quality criteria.

9.7.1. Continental Shelf Associates Report 1998. Joint EPA/Industry Screening Survey to Assess the Deposition of Drill Cuttings and Associated Synthetic Based Mud on the Seabed of the Louisiana Continental Shelf, Gulf of Mexico. Analysis by Charlie Henry Report Number IES/RCAT97-36 GC-FID and GC/MS.

9.7.2. EPA Method 3550 for extraction with EPA Method 8015 for GC-FID. EPA Method 3550C, Revision 3. February 2007. Ultrasonic Extraction. EPA Method 8015C, Revision 3. February 2007. Nonhalogenated Organics by Gas Chromatography.

9.7.3. Chandler, J.E., S.P. Rabke, and A.J.J. Leuterman. 1999. Predicting the Potential Impact of Synthetic-Based Muds With the Use of Biodegradation Studies. Society of Petroleum Engineers SPE 52742.

9.7.4. Chandler, J.E., B. Lee, S.P. Rabke, J.M. Geliff, R. Stauffer, and J. Hein. 2000. Modification of a Standardized Anaerobic Biodegradation Test to Discriminate Performance of Various Non-Aqueous Base Fluids. Society of Petroleum Engineers SPE 61203.

9.7.5. Munro, P.D., B Croce, C.F. Moffet, N.A Brown, A.D. McIntosh, S.J. Hird, and R.M. Stagg. 1998. Solid-Phase Test for Comparison for Degradation Rates of Synthetic Mud Base Fluids Used in the Off-shore Drilling Industry. *Environ. Toxicol. Chem.* 17:1951-1959.

9.7.6. Webster, L., P.R. Mackie, S.J. Hird, P.D. Munro, N.A. Brown, and C.F. Moffat. 1997. Development of Analytical Methods for the Determination of Synthetic Mud Base Fluids in Marine Sediments. *The Analyst* 122:1485-1490.

9.8 The following standards are approved for incorporation by reference by the Director of the Federal Register in accordance with 5 U.S.C. 552(a) and 1 CFR part 51. Copies may also be inspected at EPA's Water Docket, 1200 Pennsylvania Ave. NW., Washington, DC 20460 and at at the National Archives and Records Administration (NARA). For information on the availability of this material at NARA, call 202-741-6030, or go to: *http://www.archives.gov/federal_register/code_of_federal_regulations/ibr_locations.html*.

9.8.1 ASTM International. Available from ASTM International, 100 Barr Harbor Drive, P.O. Box C700, West Conshohocken, PA 19428-2959, or online at *http://www.astm.org*.

9.8.1.1 ASTM D5291-96, Standard Test Methods for Instrumental Determination of Carbon, Hydrogen, and Nitrogen in Petroleum Products and Lubricants, approved April 10, 1996.

9.8.1.2 ASTM D2974-07a, Standard Test Methods for Moisture, Ash, and Organic Matter of Peat and Other Organic Soils, approved March 15, 2007.

[77 FR 29837, May 18, 2012]

Appendix 5 to Subpart A of Part 435—Determination of Crude Oil Contamination in Non-Aqueous Drilling Fluids by Gas Chromatography/Mass Spectrometry (GC/MS) (EPA Method 1655)

1.0 Scope and Application

1.1 This method determines crude (formation) oil contamination, or other petroleum oil contamination, in non-aqueous drilling fluids (NAFs) by comparing the gas chromatography/mass spectrometry (GC/MS) fingerprint scan and extracted ion scans of the test sample to that of an uncontaminated sample.

1.2 This method can be used for monitoring oil contamination of NAFs or monitoring oil contamination of the base fluid used in the NAF formulations.

1.3 Any modification of this method beyond those expressly permitted shall be considered as a major modification subject to application and approval of alternative test procedures under 40 CFR 136.4 and 136.5.

1.4 The gas chromatography/mass spectrometry portions of this method are restricted to use by, or under the supervision of analysts experienced in the use of GC/MS and in the interpretation of gas chromatograms and extracted ion scans. Each laboratory that uses this method must generate acceptable results using the procedures described in Sections 7, 9.2, and 12 of this appendix.

2.0 Summary of Method

2.1 Analysis of NAF for crude oil contamination is a step-wise process. The analyst first performs a qualitative assessment of the presence or absence of crude oil in the sample. If crude oil is detected during this qualitative assessment, the analyst must perform a quantitative analysis of the crude oil concentration.

2.2 A sample of NAF is centrifuged to obtain a solids free supernate.

2.3 The test sample is prepared by removing an aliquot of the solids free supernate, spiking it with internal standard, and analyzing it using GC/MS techniques. The components are separated by the gas chromatograph and detected by the mass spectrometer.

2.4 Qualitative identification of crude oil contamination is performed by comparing the Total Ion Chromatograph (TIC) scans and Extracted Ion Profile (EIP) scans of test sample to that of uncontaminated base fluids, and examining the profiles for chromatographic signatures diagnostic of oil contamination.

2.5 The presence or absence of crude oil contamination observed in the full scan profiles and selected extracted ion profiles determines further sample quantitation and reporting requirements.

2.6 If crude oil is detected in the qualitative analysis, quantitative analysis must be performed by calibrating the GC/MS using a designated NAF spiked with known concentrations of a designated oil.

2.7 Quality is assured through reproducible calibration and testing of GC/MS system and through analysis of quality control samples.

3.0 Definitions

3.1 A NAF is one in which the continuous—phase is a water immiscible fluid such as an oleaginous material (e.g., mineral oil, enhance mineral oil, paraffinic oil, or synthetic material such as olefins and vegetable esters).

3.2 TIC—Total Ion Chromatograph.

3.3 EIP—Extracted Ion Profile.

3.4 TCB—1,3,5-trichlorobenzene is used as the internal standard in this method.

3.5 SPTM—System Performance Test Mix standards are used to establish retention times and monitor detection levels.

4.0 Interferences and Limitations

4.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or elevated baselines causing misinterpretation of chromatograms.

4.2 All Materials used in the analysis shall be demonstrated to be free from interferences by running method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

4.3 Glassware shall be cleaned by rinsing with solvent and baking at 400 °C for a minimum of 1 hour.

4.4 Interferences may vary from source to source, depending on the diversity of the samples being tested.

4.5 Variations in and additions of base fluids and/or drilling fluid additives (emulsifiers, dispersants, fluid loss control agents, etc.) might also cause interferences and misinterpretation of chromatograms.

4.6 Difference in light crude oils, medium crude oils, and heavy crude oils will result in different responses and thus different interpretation of scans and calculated percentages.

5.0 Safety

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however each chemical shall be treated as a potential health hazard. Exposure to these chemicals should be reduced to the lowest possible level.

5.2 Unknown samples may contain high concentration of volatile toxic compounds. Sample containers should be opened in a hood and handled with gloves to prevent exposure. In addition, all sample preparation should be conducted in a fume hood to limit the potential exposure to harmful contaminates.

5.3 This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (MSDSs) shall be available to all personnel involved in these analyses. Additional references to laboratory safety can be found in References 16.1 through 16.3.

5.4 NAF base fluids may cause skin irritation, protective gloves are recommended while handling these samples.

6.0 Apparatus and Materials

Note: Brand names, suppliers, and part numbers are for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using apparatus and materials other than those specified here, but demonstration of equivalent performance meeting the requirements of this method is the responsibility of the laboratory.

6.1 Equipment for glassware cleaning.

6.1.1 Laboratory sink with overhead fume hood.

6.1.2 Kiln—Capable of reaching 450 °C within 2 hours and holding 450 °C within ±10 °C, with temperature controller and safety switch (Cress Manufacturing Co., Santa Fe Springs, CA B31H or X31TS or equivalent).

6.2 Equipment for sample preparation.

6.2.1 Laboratory fume hood.

6.2.2 Analytical balance—Capable of weighing 0.1 mg.

6.2.3 Glassware.

6.2.3.1 Disposable pipettes—Pasteur, 150 mm long by 5 mm ID (Fisher Scientific 13-678-6A, or equivalent) baked at 400 °C for a minimum of 1 hour.

6.2.3.2 Glass volumetric pipettes or gas tight syringes—1.0-mL ±1% and 0.5-mL ±1%.

6.2.3.3 Volumetric flasks—Glass, class A, 10-mL, 50-mL and 100-mL.

6.2.3.4 —Sample vials—Glass, 1- to 3-mL (baked at 400 °C for a minimum of 1 hour) with PTFE-lined screw or crimp cap.

6.2.3.5 Centrifuge and centrifuge tubes—Centrifuge capable of 10,000 rpm, or better, (International Equipment Co., IEC Centra MP4 or equivalent) and 50-mL centrifuge tubes (Nalgene, Ultratube, Thin Wall 25 × 89 mm, #3410-2539).

6.3 Gas Chromatograph/Mass Spectrometer (GC/MS):

6.3.1 Gas Chromatograph—An analytical system complete with a temperature-programmable gas chromatograph suitable for split/splitless injection and all required accessories, including syringes, analytical columns, and gases.

6.3.1.1 Column—30 m (or 60 m) × 0.32 mm ID (or 0.25 mm ID) 1 µm film thickness (or 0.25 µm film thickness) silicone-coated fused-silica capillary column (J&W Scientific DB-5 or equivalent).

6.3.2 Mass Spectrometer—Capable of scanning from 35 to 600 amu every 1 sec or less, using 70 volts (nominal) electron energy in the electron impact ionization mode (Hewlett Packard 5970MS or comparable).

6.3.3 GC/MS interface—the interface is a capillary-direct interface from the GC to the MS.

6.3.4 —Data system—A computer system must be interfaced to the mass spectrometer. The system must allow the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that can search any GC/MS data file for ions of a specific mass and that can plot such ion abundance versus retention time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EIP). Software must also be available that allows integrating the abundance in any total ion chromatogram (TIC) or EIP between specified retention time or scan-number limits. It is advisable that the most recent version of the EPA/NIST Mass Spectral Library be available.

7.0 Reagents and Standards

7.1 Methylene chloride—Pesticide grade or equivalent. Use when necessary for sample dilution.

7.2 Standards—Prepare from pure individual standard materials or purchase as certified solutions. If compound purity is 96% or greater, the weight may be used without correction to compute the concentration of the standard.

7.2.1 Crude Oil Reference—Obtain a sample of a crude oil with a known API gravity. This oil shall be used in the calibration procedures.

7.2.2 Synthetic Base Fluid—Obtain a sample of clean internal olefin (IO) Lab drilling fluid (as sent from the supplier—has not been circulated downhole). This drilling fluid shall be used in the calibration procedures.

7.2.3 Internal standard—Prepare a 0.01 g/mL solution of 1,3,5-trichlorobenzene (TCB). Dissolve 1.0 g of TCB in methylene chloride and dilute to volume in a 100-mL volumetric flask. Stopper, vortex, and transfer the solution to a 150-mL bottle with PTFE-lined cap. Label appropriately, and store at −5 °C to 20 °C. Mark the level of the meniscus on the bottle to detect solvent loss.

7.2.4 GC/MS system performance test mix (SPTM) standards—The SPTM standards shall contain octane, decane, dodecane, tetradecane, tetradecene, toluene, ethylbenzene, 1,2,4-trimethylbenzene, 1-methylnaphthalene and 1,3-dimethylnaphthalene. These compounds

can be purchased individually or obtained as a mixture (*i.e.*, Supelco, Catalog No. 4-7300). Prepare a high concentration of the SPTM standard at 62.5 mg/mL in methylene chloride. Prepare a medium concentration SPTM standard at 1.25 mg/mL by transferring 1.0 mL of the 62.5 mg/mL solution into a 50 mL volumetric flask and diluting to the mark with methylene chloride. Finally, prepare a low concentration SPTM standard at 0.125 mg/mL by transferring 1.0 mL of the 1.25 mg/mL solution into a 10-mL volumetric flask and diluting to the mark with methylene chloride.

7.2.5 Crude oil/drilling fluid calibration standards—Prepare a 4-point crude oil/drilling fluid calibration at concentrations of 0% (no spike—clean drilling fluid), 0.5%, 1.0%, and 2.0% by weight according to the procedures outlined in this appendix using the Reference Crude Oil:

7.2.5.1 Label 4 jars with the following identification: Jar 1—0%Ref-IOLab, Jar 2—0.5%Ref-IOLab, Jar 3—1%Ref-IOLab, and Jar 4—2%Ref-IOLab.

7.2.5.2 Weigh 4, 50-g aliquots of well mixed IO Lab drilling fluid into each of the 4 jars.

7.2.5.3 Add Reference Oil at 0.5%, 1.0%, and 2.0% by weight to jars 2, 3, and 4 respectively. Jar 1 shall not be spiked with Reference Oil in order to retain a “0%” oil concentration.

7.2.5.4 Thoroughly mix the contents of each of the 4 jars, using clean glass stirring rods.

7.2.5.5 Transfer (weigh) a 30-g aliquot from Jar 1 to a labeled centrifuge tube. Centrifuge the aliquot for a minimum of 15 min at approximately 15,000 rpm, in order to obtain a solids free supernate. Weigh 0.5 g of the supernate directly into a tared and appropriately labeled GC straight vial. Spike the 0.5-g supernate with 500 µL of the 0.01g/mL 1,3,5-trichlorobenzene internal standard solution (*see* Section 7.2.3 of this appendix), cap with a Teflon lined crimp cap, and vortex for ca. 10 sec.

7.2.5.6 Repeat step 7.2.5.5 except use an aliquot from Jar 2.

7.2.5.7 Repeat step 7.2.5.5 except use an aliquot from Jar 3.

7.2.5.8 Repeat step 7.2.5.5 except use an aliquot from Jar 4.

7.2.5.9 These 4 crude/oil drilling fluid calibration standards are now used for qualitative and quantitative GC/MS analysis.

7.2.6 Precision and recovery standard (mid level crude oil/drilling fluid calibration standard)—Prepare a mid point crude oil/ drilling fluid calibration using IO Lab drilling fluid and Reference Oil at a concentration of 1.0% by weight. Prepare this standard according to the procedures outlined in Section 7.2.5.1 through 7.2.5.5 of this appendix, with the exception that only “Jar 3” needs to be prepared. Remove and spike with internal standard, as many 0.5-g aliquots as needed to complete the GC/MS analysis (*see* Section 11.6 of this appendix—bracketing authentic samples every 12 hours with precision and recovery standard) and the initial demonstration exercise described in Section 9.2 of this appendix.

7.2.7 Stability of standards

7.2.7.1 When not used, standards shall be stored in the dark, at −5 to −20 °C in screw-capped vials with PTFE-lined lids. Place a mark on the vial at the level of the solution so that solvent loss by evaporation can be detected. Bring the vial to room temperature prior to use.

7.2.7.2 Solutions used for quantitative purposes shall be analyzed within 48 hours of preparation and on a monthly basis thereafter for signs of degradation. A standard shall remain acceptable if the peak area remains within ±15% of the area obtained in the initial analysis of the standard.

8.0 Sample Collection Preservation and Storage

8.1 Collect NAF and base fluid samples in 100- to 200-mL glass bottles with PTFE- or aluminum foil lined caps.

8.2 Samples collected in the field shall be stored refrigerated until time of preparation.

8.3 Sample and extract holding times for this method have not yet been established. However, based on initial experience with the method, samples should be analyzed within seven to ten days of collection and extracts should be analyzed within seven days of preparation.

8.4 After completion of GC/MS analysis, extracts shall be refrigerated at 4 °C until further notification of sample disposal.

9.0 Quality Control

9.1 Each laboratory that uses this method is required to operate a formal quality assurance program (Reference 16.4). The minimum requirements of this program shall consist of an initial demonstration of laboratory capability, and ongoing analysis of standards, and blanks as a test of continued performance, analyses of spiked samples to assess accuracy and analysis of duplicates to assess precision. Laboratory performance shall be compared to established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

9.1.1 The analyst shall make an initial demonstration of the ability to generate acceptable accuracy and precision with this method. This ability shall be established as described in Section 9.2 of this appendix.

9.1.2 The analyst is permitted to modify this method to improve separations or lower the cost of measurements, provided all performance requirements are met. Each time a modification is made to the method, the analyst is required to repeat the calibration (Section 10.4 of this appendix) and to repeat the initial demonstration procedure described in Section 9.2 of this appendix.

9.1.3 Analyses of blanks are required to demonstrate freedom from contamination. The procedures and criteria for analysis of a blank are described in Section 9.3 of this appendix.

9.1.4 Analysis of a matrix spike sample is required to demonstrate method accuracy. The procedure and QC criteria for spiking are described in Section 9.4 of this appendix.

9.1.5 Analysis of a duplicate field sample is required to demonstrate method precision. The procedure and QC criteria for duplicates are described in Section 9.5 of this appendix.

9.1.6 Analysis of a sample of the clean NAF(s) (as sent from the supplier—*i.e.*, has not been circulated downhole) used in the drilling operations is required.

9.1.7 The laboratory shall, on an ongoing basis, demonstrate through calibration verification and the analysis of the precision and recovery standard (Section 7.2.6 of this appendix) that the analysis system is in control. These procedures are described in Section 11.6 of this appendix.

9.1.8 The laboratory shall maintain records to define the quality of data that is generated.

9.2 Initial precision and accuracy—The initial precision and recovery test shall be performed using the precision and recovery standard (1% by weight Reference Oil in IO Lab drilling fluid). The laboratory shall generate acceptable precision and recovery by performing the following operations.

9.2.1 Prepare four separate aliquots of the precision and recovery standard using the procedure outlined in Section 7.2.6 of this appendix. Analyze these aliquots using the procedures outlined in Section 11 of this appendix.

9.2.2 Using the results of the set of four analyses, compute the average recovery (X) in weight percent and the standard deviation of the recovery(s) for each sample.

9.2.3 If s and X meet the acceptance criteria of 80% to 110%, system performance is acceptable and analysis of samples may begin. If, however, s exceeds the precision limit or X falls outside the range for accuracy, system performance is unacceptable. In this event, review this method, correct the problem, and repeat the test.

9.2.4 Accuracy and precision—The average percent recovery (P) and the standard deviation of the percent recovery (Sp) Express the accuracy assessment as a percent recovery interval from P-2S_p to P + 2S_p. For example, if P = 90% and S_p = 10% for four analyses of crude oil in NAF, the accuracy interval is expressed as 70% to 110%. Update the accuracy assessment on a regular basis.

9.3 Blanks—Rinse glassware and centrifuge tubes used in the method with 30 mL of methylene chloride, remove a 0.5-g aliquot of the solvent, spike it with the 500 µL of the internal standard solution (Section 7.2.3 of this appendix) and analyze a 1-µL aliquot of the blank sample using the procedure in Section 11 of this appendix. Compute results per Section 12 of this appendix.

9.4 Matrix spike sample—Prepare a matrix spike sample according to procedure outlined in Section 7.2.6 of this appendix. Analyze the sample and calculate the concentration (% oil) in the drilling fluid and % recovery of oil from the spiked drilling fluid using the methods described in Sections 11 and 12 of this appendix.

9.5 Duplicates—A duplicate field sample shall be prepared and analyzed according to Section 11. The relative percent difference (RPD) of the calculated concentrations shall be less than 15%.

9.5.1 Analyze each of the duplicates per the procedure in Section 11 of this appendix and compute the results per Section 12 of this appendix.

9.5.2 Calculate the relative percent difference (RPD) between the two results per the following equation:

$$RPD = \frac{|D_1 - D_2|}{[(D_1 + D_2)/2]} \times 100$$

where:

D_1 = Concentration of crude oil in the sample; and

D_2 = Concentration of crude oil in the duplicate sample.

9.5.3 If the RPD criteria are not met, the analytical system shall be judged to be out of control, and the problem must be immediately identified and corrected, and the sample batch re-analyzed.

9.6 A clean NAF sample shall be prepared and analyzed according to Section 11. Ultimately the oil-equivalent concentration from the TIC or EIP signal measured in the clean NAF sample shall be subtracted from the corresponding authentic field samples in order to calculate the true contaminant concentration (% oil) in the field samples (*see* Section 12).

9.7 The specifications contained in this method can be met if the apparatus used is calibrated properly, and maintained in a calibrated state. The standards used for initial precision and recovery (Section 9.2 of this appendix) and ongoing precision and recovery (Section 11.6 of this appendix) shall be identical, so that the most precise results will be obtained. The GC/MS instrument will provide the most reproducible results if dedicated to the setting and conditions required for the analyses given in this method.

9.8 Depending on specific program requirements, field replicates and field spikes of crude oil into samples may be required when this method is used to assess the precision and accuracy of the sampling and sample transporting techniques.

10.0 Calibration

10.1 Establish gas chromatographic/mass spectrometer operating conditions given in Table 1 of this appendix. Perform the GC/MS system hardware-tune as outlined by the manufacture. The gas chromatograph shall be calibrated using the internal standard technique.

Note: Because each GC is slightly different, it may be necessary to adjust the operating conditions (carrier gas flow rate and column temperature and temperature program) slightly until the retention times in Table 2 of this appendix are met.

Table 1—Gas Chromatograph/Mass Spectrometer (GC/MS) Operation Conditions

Parameter	Setting
Injection pot	280 °C
Transfer line	280 °C
Detector	280 °C
Initial Temperature	50 °C
Initial Time	5 minutes
Ramp	50 to 300 °C @ 5 °C per minute
Final Temperature	300 °C
Final Hold	20 minutes or until all peaks have eluted
Carrier Gas	Helium
Flow rate	As required for standard operation
Split ratio	As required to meet performance criteria (~1:100)
Mass range	35 to 600 amu

Table 2—Approximate Retention Time for Compounds

Compound	Approximate retention time (minutes)
Toluene	5.6
Octane, n–C_8	7.2
Ethylbenzene	10.3
1,2,4-Trimethylbenzene	16.0
Decane, –C_{10}	16.1
TCB (Internal Standard)	21.3
Dodecane, –C_{12}	22.9
1-Methylnaphthalene	26.7
1-Tetradecene	28.4
Tetradecane, –C_{14}	28.7
1,3-Dimethylnaphthalene	29.7

10.2 Internal standard calibration procedure—1,3,5-trichlorobenzene (TCB) has been shown to be free of interferences from diesel and crude oils and is a suitable internal standard.

10.3 The system performance test mix standards prepared in Section 7.2.4 of this appendix shall be used to establish retention times and establish qualitative detection limits.

10.3.1 Spike a 500-mL aliquot of the 1.25 mg/mL SPTM standard with 500 µL of the TCB internal standard solution.

10.3.2 Inject 1.0 µL of this spiked SPTM standard onto the GC/MS in order to demonstrate proper retention times. For the GC/MS used in the development of this method, the ten compounds in the mixture had typical retention times shown in Table 2 of this appendix. Extracted ion scans for m/z 91 and 105 showed a maximum abundance of 400,000.

10.3.3 Spike a 500-mL aliquot of the 0.125 mg/mL SPTM standard with 500 µL of the TCB internal standard solution.

10.3.4 Inject 1.0 µL of this spiked SPTM standard onto the GC/MS to monitor detectable levels. For the GC/MS used in the development of this test, all ten compounds showed a minimum peak height of three times signal to noise. Extracted ion scans for m/z 91 and 105 showed a maximum abundance of 40,000.

10.4 GC/MS crude oil/drilling fluid calibration—There are two methods of quantification: Total Area Integration (C_8-C_{13}) and EIP Area Integration using m/z's 91 and 105. The Total Area Integration method should be used as the primary technique for quantifying crude oil in NAFs. The EIP Area Integration method should be used as a confirmatory technique for NAFs. However, the EIP Area Integration method shall be used as the primary method for quantifying oil in enhanced mineral oil (EMO) based drilling fluid. Inject 1.0 µL of each of the four crude oil/drilling fluid calibration standards prepared in Section 7.2.5 of this appendix into the GC/MS. The internal standard should elute approximately 21-22 minutes after injection. For the GC/MS used in the development of this method, the internal standard peak was (35 to 40)% of full scale at an abundance of about 3.5e + 07.

10.4.1 Total Area Integration Method—For each of the four calibration standards obtain the following: Using a straight baseline integration technique, obtain the total ion chromatogram (TIC) area from C_8 to C_{13}. Obtain the TIC area of the internal standard (TCB). Subtract the TCB area from the C_8-C_{13} area to obtain the true C_8-C_{13} area. Using the C_8-C_{13} and TCB areas, and known internal standard concentration, generate a linear regression calibration using the internal standard method. The r^2 value for the linear regression curve shall be greater than or equal to 0.998. Some synthetic fluids might have peaks that elute in the window and would interfere with the analysis. In this case the integration window can be shifted to other areas of scan where there are no interfering peaks from the synthetic base fluid.

10.4.2 EIP Area Integration—For each of the four calibration standards generate Extracted Ion Profiles (EIPs) for m/z 91 and 105. Using straight baseline integration techniques, obtain the following EIP areas:

10.4.2.1 For m/z 91 integrate the area under the curve from approximately 9 minutes to 21-22 minutes, just prior to but not including the internal standard.

10.4.2.2 For m/z 105 integrate the area under the curve from approximately 10.5 minutes to 26.5 minutes.

10.4.2.3 Obtain the internal standard area from the TCB in each of the four calibration standards, using m/z 180.

10.4.2.4 Using the EIP areas for TCB, m/z 91 and m/z105, and the known concentration of internal standard, generate linear regression calibration curves for the target ions 91 and 105 using the internal standard method. The r^2 value for each of the EIP linear regression curves shall be greater than or equal to 0.998.

10.4.2.5 Some base fluids might produce a background level that would show up on the extracted ion profiles, but there should not be any real peaks (signal to noise ratio of 1:3) from the clean base fluids.

11.0 Procedure

11.1 Sample Preparation—

11.1.1 Mix the authentic field sample (drilling fluid) well. Transfer (weigh) a 30-g aliquot of the sample to a labeled centrifuge tube.

11.1.2 Centrifuge the aliquot for a minimum of 15 min at approximately 15,000 rpm, in order to obtain a solids free supernate.

11.1.3 Weigh 0.5 g of the supernate directly into a tared and appropriately labeled GC straight vial.

11.1.4 Spike the 0.5-g supernate with 500 µL of the 0.01g/mL 1,3,5-trichlorobenzene internal standard solution (*see* Section 7.2.3 of this appendix), cap with a Teflon lined crimp cap, and vortex for ca. 10 sec.

11.1.5 The sample is ready for GC/MS analysis.

11.2 Gas Chromatography.

Table 1 of this appendix summarizes the recommended operating conditions for the GC/MS. Retention times for the n-alkanes obtained under these conditions are given in Table 2 of this appendix. Other columns, chromatographic conditions, or detectors may be used if initial precision and accuracy requirements (Section 9.2 of this appendix) are met. The system shall be calibrated according to the procedures outlined in Section 10 of this appendix, and verified every 12 hours according to Section 11.6 of this appendix.

11.2.1 Samples shall be prepared (extracted) in a batch of no more than 20 samples. The batch shall consist of 20 authentic samples, 1 blank (Section 9.3 of this appendix), 1 matrix spike sample (9.4), and 1 duplicate field sample (9.5), and a prepared sample of the corresponding clean NAF used in the drilling process.

11.2.2 An analytical sequence shall be analyzed on the GC/MS where the 3 SPTM standards (Section 7.2.4 of this appendix) containing internal standard are analyzed first, followed by analysis of the four GC/MS crude oil/drilling fluid calibration standards (Section 7.2.5 of this appendix), analysis of the blank, matrix spike sample, the duplicate sample, the clean NAF sample, followed by the authentic samples.

11.2.3 Samples requiring dilution due to excessive signal shall be diluted using methylene chloride.

11.2.4 Inject 1.0 µL of the test sample or standard into the GC, using the conditions in Table 1 of this appendix.

11.2.5 Begin data collection and the temperature program at the time of injection.

11.2.6 Obtain a TIC and EIP fingerprint scans of the sample (Table 3 of this appendix).

11.2.7 If the area of the C_8 to C_{13} peaks exceeds the calibration range of the system, dilute a fresh aliquot of the test sample weighing 0.50-g and re-analyze.

11.2.8 Determine the C_8 to C_{13} TIC area, the TCB internal standard area, and the areas for the m/z 91 and 105 EIPs. These shall be used in the calculation of oil concentration in the samples (see Section 12 of this appendix).

Table 3—Recommended Ion Mass Numbers

Selected ion mass numbers	Corresponding aromatic compounds	Typical rentention time (minutes)
91	Methylbenzene	6.0
	Ethylbenzene	10.3
	1,4-Dimethylbenzene	10.9
	1,3-Dimethylbenzene	10.9
	1,2-Dimethylbenzene	11.9
105	1,3,5-Trimethylbenzene	15.1
	1,2,4-Trimethylbenzene	16.0
	1,2,3-Trimethylbenzene	17.4
156	2,6-Dimethylnaphthalene	28.9
	1,2-Dimethylnaphthalene	29.4
	1,3-Dimethylnaphthalene	29.7

11.2.9 Observe the presence of peaks in the EIPs that would confirm the presence of any target aromatic compounds. Using the EIP areas and EIP linear regression calibrations compare the abundance of the aromatic peaks, and if appropriate, determine approximate crude oil contamination in the sample for each of the target ions.

11.3 Qualitative Identification—See Section 17 of this method for schematic flowchart.

11.3.1 Qualitative identification shall be accomplished by comparison of the TIC and EIP area data from an authentic sample to the TIC and EIP area data from the calibration standards (*see* Section 10.4). Crude oil shall be identified by the presence of C_{10} to C_{13} n-alkanes and corresponding target aromatics.

11.3.2 Using the calibration data, establish the identity of the C_8 to C_{13} peaks in the chromatogram of the sample. Using the calibration data, establish the identity of any target aromatics present on the extracted ion scans.

11.3.3 Crude oil is not present in a detectable amount in the sample if there are no target aromatics seen on the extracted ion scans. The experience of the analyst shall weigh heavily in the determination of the presence of peaks at a signal-to-noise ratio of 3 or greater.

11.3.4 If the chromatogram shows n-alkanes from C_8 to C_{13} and target aromatics to be present, contamination by crude oil or diesel shall be suspected and quantitative analysis shall be determined. If there are no n-alkanes present that are not seen on the blank, and no target aromatics are seen, the sample can be considered to be free of contamination.

11.4 Quantitative Identification—

11.4.1 Determine the area of the peaks from C_8 to C_{13} as outlined in the calibration section (10.4.1 of this appendix). If the area of the peaks for the sample is greater than that for the clean NAF (base fluid) use the crude oil/drilling fluid calibration TIC linear regression curve to determine approximate crude oil contamination.

11.4.2 Using the EIPs outlined in Section 10.4.2 of this appendix, determine the presence of any target aromatics. Using the integration techniques outlined in Section 10.4.2 of this appendix, obtain the EIP areas for m/z 91 and 105. Use the crude oil/drilling fluid calibration EIP linear regression curves to determine approximate crude oil contamination.

11.5 Complex Samples—

11.5.1 The most common interferences in the determination of crude oil can be from mineral oil, diesel oil, and proprietary additives in drilling fluids.

11.5.2 Mineral oil can typically be identified by its lower target aromatic content, and narrow range of strong peaks.

11.5.3 Diesel oil can typically be identified by low amounts of n-alkanes from C_7 to C_9, and the absence of n-alkanes greater than C_{25}.

11.5.4 Crude oils can usually be distinguished by the presence of high aromatics, increased intensities of C_8 to C_{13} peaks, and/ or the presence of higher hydrocarbons of C_{25} and greater (which may be difficult to see in some synthetic fluids at low contamination levels).

11.5.4.1 Oil condensates from gas wells are low in molecular weight and will normally produce strong chromatographic peaks in the C_8-C_{13} range. If a sample of the gas condensate crude oil from the formation is available, the oil can be distinguished from other potential sources of contamination by using it to prepare a calibration standard.

11.5.4.2 Asphaltene crude oils with API gravity <20 may not produce chromatographic peaks strong enough to show contamination at levels of the calibration. Extracted ion peaks should be easier to see than increased intensities for the C8 to C13 peaks. If a sample of asphaltene crude from the formation is available, a calibration standard shall be prepared.

11.6 System and Laboratory Performance—

11.6.1 At the beginning of each 8-hour shift during which analyses are performed, GC crude oil/ drilling fluid calibration and system performance test mixes shall be verified. For these tests, analysis of the medium-level calibration standard (1-% Reference Oil in IO Lab drilling fluid, and 1.25 mg/mL SPTM with internal standard) shall be used to verify all performance criteria. Adjustments and/or re-calibration (per Section 10 of this appendix) shall be performed until all performance criteria are met. Only after all performance criteria are met may samples and blanks be analyzed.

11.6.2 Inject 1.0 µL of the medium-level GC/MS crude oil/drilling fluid calibration standard into the GC instrument according to the procedures in Section 11.2 of this appendix. Verify that the linear regression curves for both TIC area and EIP areas are still valid using this continuing calibration standard.

11.6.3 After this analysis is complete, inject 1.0 µL of the 1.25 mg/mL SPTM (containing internal standard) into the GC instrument and verify the proper retention times are met (*see* Table 2 of this appendix).

11.6.4 Retention times—Retention time of the internal standard. The absolute retention time of the TCB internal standard shall be within the range 21.0 ±0.5 minutes. Relative retention times of the n-alkanes: The retention times of the n-alkanes relative to the TCB internal standard shall be similar to those given in Table 2 of this appendix.

11.6.17 Schematic Flowchart for Qualitative Identification

6.17 Schematic Flowchart for Qualitative Identification

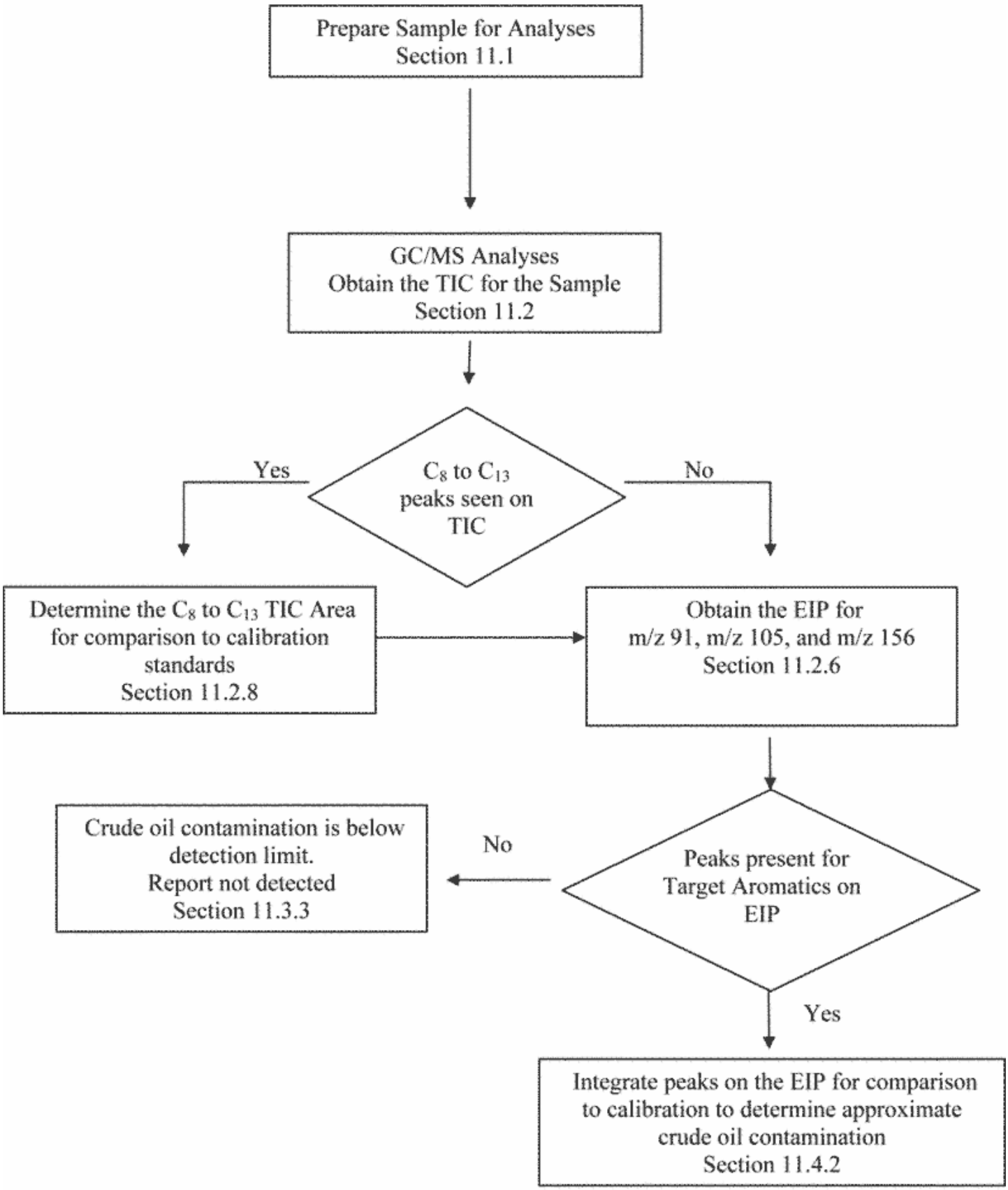

Figure 1. Schematic Flowchart for Qualitative Identification

12.0 Calculations

The concentration of oil in NAFs drilling fluids shall be computed relative to peak areas between C_8 and C_{13} (using the Total Area Integration method) or total peak areas from extracted ion profiles (using the Extracted Ion Profile Method). In either case, there is a measurable amount of peak area, even in clean drilling fluid samples, due to spurious peaks and electrometer “noise” that contributes to the total signal measured using either of the quantification methods. In this procedure, a correction for this signal is applied, using the blank or clean sample correction technique described in American Society for Testing Materials (ASTM) Method D-3328-90, Comparison of Waterborne Oil by Gas Chromatography. In this method, the “oil equivalents” measured in a blank sample by total area gas chromatography are subtracted from that determined for a field sample to arrive at the most accurate measure of oil residue in the authentic sample.

12.1 Total Area Integration Method

12.1.1 Using C_8 to C_{13} TIC area, the TCB area in the clean NAF sample and the TIC linear regression curve, compute the oil equivalent concentration of the C_8 to C_{13} retention time range in the clean NAF.

> Note: The actual TIC area of the C_8 to C_{13} is equal to the C_8 to C_{13} area minus the area of the TCB.

12.1.2 Using the corresponding information for the authentic sample, compute the oil equivalent concentration of the C_8 to C_{13} retention time range in the authentic sample.

12.1.3 Calculate the concentration (% oil) of oil in the sample by subtracting the oil equivalent concentration (% oil) found in the clean NAF from the oil equivalent concentration (% oil) found in the authentic sample.

12.2 EIP Area Integration Method

12.2.1 Using either m/z 91 or 105 EIP areas, the TCB area in the clean NAF sample, and the appropriate EIP linear regression curve, compute the oil equivalent concentration of the in the clean NAF.

12.2.2 Using the corresponding information for the authentic sample, compute its oil equivalent concentration.

12.2.3 Calculate the concentration (% oil) of oil in the sample by subtracting the oil equivalent concentration (% oil) found in the clean NAF from the oil equivalent concentration (% oil) found in the authentic sample.

13.0 Method Performance

13.1 Specification in this method are adopted from EPA Method 1663, Differentiation of Diesel and Crude Oil by GC/FID (Reference 16.5).

13.2 Single laboratory method performance using an Internal Olefin (IO) drilling fluid fortified at 0.5% oil using a 35 API gravity oil was:

Precision and accuracy 94 ±4%

Accuracy interval—86.3% to 102%

Relative percent difference in duplicate analysis—6.2%

14.0 Pollution Prevention

14.1 The solvent used in this method poses little threat to the environment when recycled and managed properly.

15.0 Waste Management

15.1 It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restriction, and to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is also required.

15.2 All authentic samples (drilling fluids) failing the RPE (fluorescence) test (indicated by the presence of fluorescence) shall be retained and classified as contaminated samples. Treatment and ultimate fate of these samples is not outlined in this SOP.

15.3 For further information on waste management, consult "The Waste Management Manual for Laboratory Personnel", and "Less is Better: Laboratory Chemical Management for Waste Reduction", both available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street NW, Washington, DC 20036.

16.0 References

16.1 Carcinogens—"Working With Carcinogens." Department of Health, Education, and Welfare, Public Health Service, Centers for Disease Control (available through National Technical Information Systems, 5285 Port Royal Road, Springfield, VA 22161, document no. PB-277256): August 1977.

16.2 ***"OSHA Safety and Health Standards, General Industry [29 CFR 1910], Revised."*** Occupational Safety and Health Administration, OSHA 2206. Washington, DC: January 1976.

16.3 ***"Handbook of Analytical Quality Control in Water and Wastewater Laboratories."*** USEPA, EMSSL-CI, EPA-600/4-79-019. Cincinnati, OH: March 1979.

16.4 "Method 1663, Differentiation of Diesel and Crude Oil by GC/FID, Methods for the Determination of Diesel, Mineral, and Crude Oils in Offshore Oil and Gas Industry Discharges, EPA 821-R-92-008, Office of Water Engineering and Analysis Division, Washington, DC: December 1992.

[66 FR 6901, Jan. 22, 2001, as amended at 77 FR 29843, May 18, 2012]

Appendix 6 to Subpart A of Part 435—Reverse Phase Extraction (RPE) Method for Detection of Oil Contamination in Non-Aqueous Drilling Fluids (NAF) (GC/MS) (EPA Method 1670)

1.0 Scope and Application

1.1 This method is used for determination of crude or formation oil, or other petroleum oil contamination, in non-aqueous drilling fluids (NAFs).

1.2 This method is intended as a positive/negative test to determine a presence of crude oil in NAF prior to discharging drill cuttings from offshore production platforms.

1.3 This method is for use in the Environmental Protection Agency's (EPA's) survey and monitoring programs under the Clean Water Act, including monitoring of compliance with the Gulf of Mexico NPDES General Permit for monitoring of oil contamination in drilling fluids.

1.4 This method has been designed to show positive contamination for 5% of representative crude oils at a concentration of 0.1% in drilling fluid (vol/vol), 50% of representative crude oils at a concentration of 0.5%, and 95% of representative crude oils at a concentration of 1%.

1.5 Any modification of this method, beyond those expressly permitted, shall be considered a major modification subject to application and approval of alternate test procedures under 40 CFR parts 136.4 and 136.5.

1.6 Each laboratory that uses this method must demonstrate the ability to generate acceptable results using the procedure in Section 9.2 of this appendix.

2.0 Summary of Method

2.1 An aliquot of drilling fluid is extracted using isopropyl alcohol.

2.2 The mixture is allowed to settle and then filtered to separate out residual solids.

2.3 An aliquot of the filtered extract is charged onto a reverse phase extraction (RPE) cartridge.

2.4 The cartridge is eluted with isopropyl alcohol.

2.5 Crude oil contaminates are retained on the cartridge and their presence (or absence) is detected based on observed fluorescence using a black light.

3.0 Definitions

3.1 A NAF is one in which the continuous phase is a water immiscible fluid such as an oleaginous material (e.g., mineral oil, enhance mineral oil, paraffinic oil, or synthetic material such as olefins and vegetable esters).

4.0 Interferences

4.1 Solvents, reagents, glassware, and other sample-processing hardware may yield artifacts that affect results. Specific selection of reagents and purification of solvents may be required.

4.2 All materials used in the analysis shall be demonstrated to be free from interferences under the conditions of analysis by running laboratory reagent blanks as described in Section 9.5 of this appendix.

5.0 Safety

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical shall be treated as a potential health hazard. Exposure to these chemicals should be reduced to the lowest possible level. Material Safety Data Sheets (MSDSs) shall be available for all reagents.

5.2 Isopropyl alcohol is flammable and should be used in a well-ventilated area.

5.3 Unknown samples may contain high concentration of volatile toxic compounds. Sample containers should be opened in a hood and handled with gloves to prevent exposure. In addition, all sample preparation should be conducted in a well-ventilated area to limit the potential exposure to harmful contaminants. Drilling fluid samples should be handled with the same precautions used in the drilling fluid handling areas of the drilling rig.

5.4 This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (MSDSs) shall be available to all personnel involved in these analyses. Additional information on laboratory safety can be found in References 16.1-16.2.

6.0 Equipment and Supplies

Note: Brand names, suppliers, and part numbers are for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using apparatus and materials other than those specified here, but demonstration of equivalent performance that meets the requirements of this method is the responsibility of the laboratory.

6.1 Sampling equipment.

6.1.1 Sample collection bottles/jars—New, pre-cleaned bottles/jars, lot-certified to be free of artifacts. Glass preferable, plastic acceptable, wide mouth approximately 1-L, with Teflon-lined screw cap.

6.2 Equipment for glassware cleaning.

6.2.1 Laboratory sink.

6.2.2 Oven—Capable of maintaining a temperature within ±5 °C in the range of 100-250 °C.

6.3 Equipment for sample extraction.

6.3.1 Vials—Glass, 25 mL and 4 mL, with Teflon-lined screw caps, baked at 200-250 °C for 1-h minimum prior to use.

6.3.2 Gas-tight syringes—Glass, various sizes, 0.5 mL to 2.5 mL (if spiking of drilling fluids with oils is to occur).

6.3.3 Auto pipetters—various sizes, 0.1 mL, 0.5 mL, 1 to 5 mL delivery, and 10 mL delivery, with appropriate size disposable pipette tips, calibrated to within ±0.5%.

6.3.4 Glass stirring rod.

6.3.5 Vortex mixer.

6.3.6 Disposable syringes—Plastic, 5 mL.

6.3.7 Teflon syringe filter, 25-mm, 0.45 µm pore size—Acrodisc ® CR Teflon (or equivalent).

6.3.8 Reverse Phase Extraction C_{18} Cartridge—Waters Sep-Pak ®Plus, C_{18} Cartridge, 360 mg of sorbent (or equivalent).

6.3.9 SPE vacuum manifold—Supelco Brand, 12 unit (or equivalent). Used as support for cartridge/syringe assembly only. Vacuum apparatus not required.

6.4 Equipment for fluorescence detection.

6.4.1 Black light—UV Lamp, Model UVG 11, Mineral Light Lamp, Shortwave 254 nm, or Longwave 365 nm, 15 volts, 60 Hz, 0.16 amps (or equivalent).

6.4.2 Black box—cartridge viewing area. A commercially available ultraviolet viewing cabinet with viewing lamp, or alternatively, a cardboard box or equivalent, approximately 14" × 7.5" × 7.5" in size and painted flat black inside. Lamp positioned in fitted and sealed slot in center on top of box. Sample cartridges sit in a tray, ca. 6" from lamp. Cardboard flaps cut on top panel and side of front panel for sample viewing and sample cartridge introduction, respectively.

6.4.3 Viewing platform for cartridges. Simple support (hand made vial tray—black in color) for cartridges so that they do not move during the fluorescence testing.

7.0 Reagents and Standards

7.1 Isopropyl alcohol—99% purity.

7.2 NAF—Appropriate NAF as sent from the supplier (has not been circulated downhole). Use the clean NAF corresponding to the NAF being used in the current drilling operation.

7.3 Standard crude oil—NIST SRM 1582 petroleum crude oil.

8.0 Sample Collection, Preservation, and Storage

8.1 Collect approximately one liter of representative sample (NAF, which has been circulated downhole) in a glass bottle or jar. Cover with a Teflon lined cap. To allow for a potential need to re-analyze and/or re-process the sample, it is recommended that a second sample aliquot be collected.

8.2 Label the sample appropriately.

8.3 All samples must be refrigerated at 0-4 °C from the time of collection until extraction (40 CFR part 136, Table II).

8.4 All samples must be analyzed within 28 days of the date and time of collection (40 CFR part 136, Table II).

9.0 Quality Control

9.1 Each laboratory that uses this method is required to operate a formal quality assurance program (Reference 16.3). The minimum requirements of this program consist of an initial demonstration of laboratory capability, and ongoing analyses of blanks and spiked duplicates to assess accuracy and precision and to demonstrate continued performance. Each field sample is analyzed in duplicate to demonstrate representativeness.

9.1.1 The analyst shall make an initial demonstration of the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 9.2 of this appendix.

9.1.2 Preparation and analysis of a set of spiked duplicate samples to document accuracy and precision. The procedure for the preparation and analysis of these samples is described in Section 9.4 of this appendix.

9.1.3 Analyses of laboratory reagent blanks are required to demonstrate freedom from contamination. The procedure and criteria for preparation and analysis of a reagent blank are described in Section 9.5 of this appendix.

9.1.4 The laboratory shall maintain records to define the quality of the data that is generated.

9.1.5 Accompanying QC for the determination of oil in NAF is required per analytical batch. An analytical batch is a set of samples extracted at the same time, to a maximum of 10 samples. Each analytical batch of 10 or fewer samples must be accompanied by a laboratory reagent blank (Section 9.5 of this appendix), corresponding NAF reference blanks (Section 9.6 of this appendix), a set of spiked duplicate samples blank (Section 9.4 of this appendix), and duplicate analysis of each field sample. If greater than 10 samples are to be extracted at one time, the samples must be separated into analytical batches of 10 or fewer samples.

9.2 Initial demonstration of laboratory capability. To demonstrate the capability to perform the test, the analyst shall analyze two representative unused drilling fluids (e.g., internal olefin-based drilling fluid, vegetable ester-based drilling fluid), each prepared separately containing 0.1%, 1%, and 2% or a representative oil. Each drilling fluid/concentration combination shall be analyzed 10 times, and successful demonstration will yield the following average results for the data set:

0.1% oil—Detected in <20% of samples

1 % oil—Detected in >75% of samples

2 % oil—Detected in >90% of samples

9.3 Sample duplicates.

9.3.1 The laboratory shall prepare and analyze (Section 11.2 and 11.4 of this appendix) each authentic sample in duplicate, from a given sampling site or, if for compliance monitoring, from a given discharge.

9.3.2 The duplicate samples must be compared versus the prepared corresponding NAF blank.

9.3.3 Prepare and analyze the duplicate samples according to procedures outlined in Section 11 of this appendix.

9.3.4 The results of the duplicate analyses are acceptable if each of the results give the same response (fluorescence or no fluorescence). If the results are different, sample non-homogenicity issues may be a concern. Prepare the samples again, ensuring a well-mixed sample prior to extraction. Analyze the samples once again.

9.3.5 If different results are obtained for the duplicate a second time, the analytical system is judged to be out of control and the problem shall be identified and corrected, and the samples re-analyzed.

9.4 Spiked duplicates—Laboratory prepared spiked duplicates are analyzed to demonstrate acceptable accuracy and precision.

9.4.1 Preparation and analysis of a set of spiked duplicate samples with each set of no more than 10 field samples is required to demonstrate method accuracy and precision and to monitor matrix interferences (interferences caused by the sample matrix). A field NAF sample expected to contain less than 0.5% crude oil (and documented to not fluoresce as part of the sample batch analysis) shall be spiked with 1% (by volume) of suitable reference crude oil and analyzed as field samples, as described in Section 11 of this appendix. If no low-level drilling fluid is available, then the unused NAF can be used as the drilling fluid sample.

9.5 Laboratory reagent blanks—Laboratory reagent blanks are analyzed to demonstrate freedom from contamination.

9.5.1 A reagent blank is prepared by passing 4 mL of the isopropyl alcohol through a Teflon syringe filter and collecting the filtrate in a 4-mL glass vial. A Sep Pak ® C_{18} cartridge is then preconditioned with 3 mL of isopropyl alcohol. A 0.5-mL aliquot of the filtered isopropyl alcohol is added to the syringe barrel along with 3.0 mL of isopropyl alcohol. The solvent is passed through the preconditioned Sep Pak ® cartridge. An additional 2-mL of isopropyl alcohol is eluted through the cartridge. The cartridge is now considered the “reagent blank” cartridge and is ready for viewing (analysis). Check the reagent blank cartridge under the black light for fluorescence. If the isopropyl alcohol and filter are clean, no fluorescence will be observed.

9.5.2 If fluorescence is detected in the reagent blank cartridge, analysis of the samples is halted until the source of contamination is eliminated and a prepared reagent blank shows no fluorescence under a black light. All samples shall be associated with an uncontaminated method blank before the results may be reported for regulatory compliance purposes.

9.6 NAF reference blanks—NAF reference blanks are prepared from the NAFs sent from the supplier (NAF that has not been circulated downhole) and used as the reference when viewing the fluorescence of the test samples.

9.6.1 A NAF reference blank is prepared identically to the authentic samples. Place a 0.1 mL aliquot of the “clean” NAF into a 25-mL glass vial. Add 10 mL of isopropyl alcohol to the vial. Cap the vial. Vortex the vial for approximately 10 sec. Allow the solids to settle for approximately 15 minutes. Using a 5-mL syringe, draw up 4 mL of the extract and filter it through a PTFE syringe filter, collecting the filtrate in a 4-mL glass vial. Precondition a Sep Pak ® C_{18} cartridge with 3 mL of isopropyl alcohol. Add a 0.5-mL aliquot of the filtered extract to the syringe barrel along with 3.0 mL of isopropyl alcohol. Pass the extract and solvent through the preconditioned Sep Pak ® cartridge. Pass an additional 2-mL of isopropyl alcohol through the cartridge. The cartridge is now considered the NAF blank cartridge and is ready for viewing (analysis). This cartridge is used as the reference cartridge for determining the absence or presence of fluorescence in all authentic drilling fluid samples that originate from the same NAF. That is, the specific NAF reference blank cartridge is put under the black light along with a prepared cartridge of an authentic sample originating from the same NAF material. The fluorescence or absence of fluorescence in the authentic sample cartridge is determined relative to the NAF reference cartridge.

9.6.2 Positive control solution, equivalent to 1% crude oil contaminated mud extract, is prepared by dissolving 87 mg of standard crude oil into 10.00 mL of methylene chloride. Then mix 40 µL of this solution into 10.00 mL of IPA. Transfer 0.5 mL of this solution into a preconditioned C18 cartridge, followed by 2 ml of IPA.

10.0 Calibration and Standardization

10.1 Calibration and standardization methods are not employed for this procedure.

11.0 Procedure

This method is a screening-level test. Precise and accurate results can be obtained only by strict adherence to all details.

11.1 Preparation of the analytical batch.

11.1.1 Bring the analytical batch of samples to room temperature.

11.1.2 Using a large glass stirring rod, mix the authentic sample thoroughly.

11.1.3 Using a large glass stirring rod, mix the clean NAF (sent from the supplier) thoroughly.

11.2 Extraction.

11.2.1 Using an automatic positive displacement pipetter and a disposable pipette tip transfer 0.1-mL of the authentic sample into a 25-mL vial.

11.2.2 Using an automatic pipetter and a disposable pipette tip dispense a 10-mL aliquot of solvent grade isopropyl alcohol (IPA) into the 25 mL vial.

11.2.3 Cap the vial and vortex the vial for ca. 10-15 seconds.

11.2.4 Let the sample extract stand for approximately 5 minutes, allowing the solids to separate.

11.2.5 Using a 5-mL disposable plastic syringe remove 4 mL of the extract from the 25-mL vial.

11.2.6 Filter 4 mL of extract through a Teflon syringe filter (25-mm diameter, 0.45 µm pore size), collecting the filtrate in a labeled 4-mL vial.

11.2.7 Dispose of the PFTE syringe filter.

11.2.8 Using a black permanent marker, label a Sep Pak ® C_{18} cartridge with the sample identification.

11.2.9 Place the labeled Sep Pak ® C_{18} cartridge onto the head of a SPE vacuum manifold.

11.2.10 Using a 5-mL disposable plastic syringe, draw up exactly 3-mL (air free) of isopropyl alcohol.

11.2.11 Attach the syringe tip to the top of the C_{18} cartridge.

11.2.12 Condition the C_{18} cartridge with the 3-mL of isopropyl alcohol by depressing the plunger slowly.

> Note: Depress the plunger just to the point when no liquid remains in the syringe barrel. Do not force air through the cartridge. Collect the eluate in a waste vial.

11.2.13 Remove the syringe temporarily from the top of the cartridge, then remove the plunger, and finally reattach the syringe barrel to the top of the C_{18} cartridge.

11.2.14 Using automatic pipetters and disposable pipette tips, transfer 0.5 mL of the filtered extract into the syringe barrel, followed by a 3.0-mL transfer of isopropyl alcohol to the syringe barrel.

11.2.15 Insert the plunger and slowly depress it to pass only the extract and solvent through the preconditioned C_{18} cartridge.

> Note: Depress the plunger just to the point when no liquid remains in the syringe barrel. Do not force air through the cartridge. Collect the eluate in a waste vial.

11.2.16 Remove the syringe temporarily from the top of the cartridge, then remove the plunger, and finally reattach the syringe barrel to the top of the C_{18} cartridge.

11.2.17 Using an automatic pipetter and disposable pipette tip, transfer 2.0 mL of isopropyl alcohol to the syringe barrel.

11.2.18 Insert the plunger and slowly depress it to pass the solvent through the C_{18} cartridge.

> Note: Depress the plunger just to the point when no liquid remains in the syringe barrel. Do not force air through the cartridge. Collect the eluate in a waste vial.

11.2.19 Remove the syringe and labeled C_{18} cartridge from the top of the SPE vacuum manifold.

11.2.20 Prepare a reagent blank according to the procedures outlined in Section 9.5 of this appendix.

11.2.21 Prepare the necessary NAF reference blanks for each type of NAF encountered in the field samples according to the procedures outlined in Section 9.6 of this appendix.

11.2.22 Prepare the positive control (1% crude oil equivalent) according to Section 9.6.2 of this appendix.

11.3 Reagent blank fluorescence testing.

11.3.1 Place the reagent blank cartridge in a black box, under a black light.

11.3.2 Determine the presence or absence of fluorescence for the reagent blank cartridge. If fluorescence is detected in the blank, analysis of the samples is halted until the source of contamination is eliminated and a prepared reagent blank shows no fluorescence under a black light. All samples must be associated with an uncontaminated method blank before the results may be reported for regulatory compliance purposes.

11.4 Sample fluorescence testing.

11.4.1 Place the respective NAF reference blank (Section 9.6 of this appendix) onto the tray inside the black box.

11.4.2 Place the authentic field sample cartridge (derived from the same NAF as the NAF reference blank) onto the tray, adjacent and to the right of the NAF reference blank.

11.4.3 Turn on the black light.

11.4.4 Compare the fluorescence of the sample cartridge with that of the negative control cartridge (NAF blank, Section 9.6.1 of this appendix) and positive control cartridge (1% crude oil equivalent, Section 9.6.2 of this appendix).

11.4.5 If the fluorescence of the sample cartridge is equal to or brighter than the positive control cartridge (1% crude oil equivalent, Section 9.6.2 of this appendix), the sample is considered contaminated. Otherwise, the sample is clean.

12.0 Data Analysis and Calculations

Specific data analysis techniques and calculations are not performed in this SOP.

13.0 Method Performance

This method was validated through a single laboratory study, conducted with rigorous statistical experimental design and interpretation (Reference 16.4).

14.0 Pollution Prevention

14.1 The solvent used in this method poses little threat to the environment when recycled and managed properly.

15.0 Waste Management

15.1 It is the laboratory's responsibility to comply with all Federal, State, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restriction, and to protect the air, water, and land by minimizing and controlling all releases from bench operations. Compliance with all sewage discharge permits and regulations is also required.

15.2 All authentic samples (drilling fluids) failing the fluorescence test (indicated by the presence of fluorescence) shall be retained and classified as contaminated samples. Treatment and ultimate fate of these samples is not outlined in this SOP.

15.3 For further information on waste management, consult “The Waste Management Manual for Laboratory Personnel,” and “Less is Better: Laboratory Chemical Management for Waste Reduction,” both available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street, NW, Washington, DC 20036.

16.0 References

16.1 ***“Carcinogen—Working with Carcinogens,”*** Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Publication No. 77-206, August 1977.

16.2 ***“OSHA Safety and Health Standards, General Industry,”*** (29 CFR 1910), Occupational Safety and Health Administration, OSHA 2206 (Revised, January 1976).

16.3 ***“Handbook of Analytical Quality Control in Water and Wastewater Laboratories,”*** USEPA, EMSL-Ci, Cincinnati, OH 45268, EPA-600/4-79-019, March 1979.

16.4 Report of the Laboratory Evaluation of Static Sheen Test Replacements—Reverse Phase Extraction (RPE) Method for Detecting Oil Contamination in Synthetic Based Mud (SBM). October 1998. Available from API, 1220 L Street, NW, Washington, DC 20005-4070, 202-682-8000.

[66 FR 6901, Jan. 22, 2001; 66 FR 30811, June 8, 2001]

Appendix 7 to Subpart A of Part 435—Determination of the Amount of Non-Aqueous Drilling Fluid (NAF) Base Fluid From Drill Cuttings by a Retort Chamber (Derived From API Recommended Practice 13B-2) (EPA Method 1674)

1. Description

a. This procedure is specifically intended to measure the amount of non-aqueous drilling fluid (NAF) base fluid from cuttings generated during a drilling operation. This procedure is a retort test which measures all oily material (NAF base fluid) and water released from a cuttings sample when heated in a calibrated and properly operating "Retort" instrument.

b. In this retort test a known mass of cuttings is heated in the retort chamber to vaporize the liquids associated with the sample. The NAF base fluid and water vapors are then condensed, collected, and measured in a precision graduated receiver.

> Note: Obtaining a representative sample requires special attention to the details of sample handling (e.g., location, method, frequency). See Addendum A and B for minimum requirements for collecting representative samples. Additional sampling procedures in a given area may be specified by the NPDES permit controlling authority.

2. Equipment

a. Retort instrument—The recommended retort instrument has a 50-cm^3 volume with an external heating jacket.

Retort Specifications:

1. Retort assembly—retort body, cup and lid.

(a) Material: 303 stainless steel or equivalent.

(b) Volume: Retort cup with lid.

Cup Volume: 50-cm^3.

Precision: ±0.25-cm^3.

2. Condenser—capable of cooling the oil and water vapors below their liquification temperature.

3. Heating jacket—nominal 350 watts.

4. Temperature control—capable of limiting temperature of retort to at least 930 °F (500 °C) and enough to boil off all NAFs.

b. Liquid receiver (10-cm^3, 20-cm^3)—the 10-cm^3 and 20-cm^3 receivers are specially designed cylindrical glassware with rounded bottom to facilitate cleaning and funnel-shaped top to catch falling drops. For compliance monitoring under the NPDES program, the analyst shall use the 10-cm^3 liquid receiver with 0.1 ml graduations to achieve greater accuracy.

1. Receiver specifications:

Total volume: 10-cm^3, 20-cm^3.

Precision (0 to 100%): ±0.05 cm^3, ±0.05 cm^3.

Outside diameter: 10-mm, 13-mm.

Wall thickness: 1.5 ±0.1mm, 1.2 ±0.1mm.

Frequency of graduation marks (0 to 100%): 0.10-cm^3, 0.10-cm^3.

Calibration: To contain "TC" @ 20 °C.

Scale: cm^3, cm^3

2. Material—Pyrex ® or equivalent glass.

c. Toploading balance—capable of weighing 2000 g and precision of at least 0.1 g. Unless motion is a problem, the analyst shall use an electronic balance. Where motion is a problem, the analyst may use a triple beam balance.

d. Fine steel wool (No. 000)—for packing retort body.

e. Thread sealant lubricant: high temperature lubricant, e.g. Never-Seez ® or equivalent.

f. Pipe cleaners—to clean condenser and retort stem.

g. Brush—to clean receivers.

h. Retort spatula—to clean retort cup.

i. Corkscrew—to remove spent steel wool.

3. Procedure

a. Clean and dry the retort assembly and condenser.

b. Pack the retort body with steel wool.

c. Apply lubricant/sealant to threads of retort cup and retort stem.

d. Weigh and record the total mass of the retort cup, lid, and retort body with steel wool. This is mass (A), grams.

e. Collect a representative cuttings sample (*see* note in section 1 of this appendix).

f. Partially fill the retort cup with cuttings and place the lid on the cup.

g. Screw the retort cup (with lid) onto the retort body, weigh and record the total mass. This is mass (B), grams.

h. Attach the condenser. Place the retort assembly into the heating jacket.

i. Weigh and record the mass of the clean and dry liquid receiver. This is mass (C), grams. Place the receiver below condenser outlet.

j. Turn on the retort. Allow it to run a minimum of 1 hour.

Note: If solids boil over into receiver, the test shall be rerun. Pack the retort body with a greater

amount of steel wool and repeat the test.

k. Remove the liquid receiver. Allow it to cool. Record the volume of water recovered. This is (V), cm^3.

Note: If an emulsion interface is present between the oil and water phases, heating the interface may break the emulsion. As a suggestion, remove the retort assembly from the heating jacket by grasping the condenser. Carefully heat the receiver along the emulsion band by gently touching the receiver for short intervals with the hot retort assembly. Avoid boiling the liquids. After the emulsion interface is broken, allow the liquid receiver to cool. Read the water volume at the lowest point of the meniscus.

l. Weigh and record the mass of the receiver and its liquid contents (oil plus water). This is mass (D), grams.

m. Turn off the retort. Remove the retort assembly and condenser from the heating jacket and allow them to cool. Remove the condenser.

n. Weigh and record the mass of the cooled retort assembly without the condenser. This is mass (E), grams.

o. Clean the retort assembly and condenser.

4. Calculations

a. Calculate the mass of oil (NAF base fluid) from the cuttings as follows:

1. Mass of the wet cuttings sample (M_w) equals the mass of the retort assembly with the wet cuttings sample (B) minus the mass of the empty retort assembly (A).

   $M_w = B - A$ [1]

2. Mass of the dry retorted cuttings (M_D) equals the mass of the cooled retort assembly (E) minus the mass of the empty retort assembly (A).

   $M_D = E - A$ [2]

3. Mass of the NAF base fluid (M_{BF}) equals the mass of the liquid receiver with its contents (D) minus the sum of the mass of the dry receiver (C) and the mass of the water (V).

   $M_{BF} = D - (C + V)$ [3]

   Note: Assuming the density of water is 1 g/cm^3, the volume of water is equivalent to the mass of the water.

b. Mass balance requirement:

The sum of M_D, M_{BF}, and V shall be within 5% of the mass of the wet sample.

$(M_D + M_{BF} + V)/M_w = 0.95$ to 1.05 [4]

The procedure shall be repeated if this requirement is not met.

c. Reporting oil from cuttings:

1. Assume that all oil recovered is NAF base fluid.

2. The mass percent NAF base fluid retained on the cuttings ($\%BF_i$) for the sampled discharge "i" is equal to 100 times the mass of the NAF base fluid (M_{BF}) divided by the mass of the wet cuttings sample (M_w).

   $\%BF_i = (M_{BF}/M_w) \times 100$ [5]

   Operators discharging small volume NAF-cuttings discharges which do not occur during a NAF-cuttings discharge sampling interval (*i.e.*, displaced interfaces, accumulated solids in sand traps, pit clean-out solids, or centrifuge discharges while cutting mud weight) shall either: (a) Measure the mass percent NAF base fluid retained on the cuttings ($\%BF_{SVD}$) for each small volume NAF-cuttings discharges; or (b) use a default value of 25% NAF base fluid retained on the cuttings.

3. The mass percent NAF base fluid retained on the cuttings is determined for all cuttings wastestreams and includes fines discharges and any accumulated solids discharged [*see* Section 4.c.6 of this appendix for procedures on measuring or estimating the mass percent NAF base fluid retained on the cuttings (%BF) for dual gradient drilling seafloor discharges performed to ensure proper operation of subsea pumps].

4. A mass NAF-cuttings discharge fraction (X, unitless) is calculated for all NAF-cuttings, fines, or accumulated solids discharges every time a set of retorts is performed (*see* Section 4.c.6 of this appendix for procedures on measuring or estimating the mass NAF-cuttings discharge fraction (X) for dual gradient drilling seafloor discharges performed to ensure proper operation of subsea pumps). The mass NAF-cuttings discharge fraction (X) combines the mass of NAF-cuttings, fines, or accumulated solids discharged from a particular discharge over a set period of time with the total mass of NAF-cuttings, fines, or accumulated solids discharged into the ocean during the same period of time (*see* Addendum A and B of this appendix). The mass NAF-cuttings discharge fraction (X) for each discharge is calculated by direct measurement as:

   $X_i = (F_i)/(G)$ [6]

where:

X_i = Mass NAF-cuttings discharge fraction for NAF-cuttings, fines, or accumulated solids discharge "i", (unitless)

F_i = Mass of NAF-cuttings discharged from NAF-cuttings, fines, or accumulated solids discharge "i" over a specified period of time (*see* Addendum A and B of this appendix), (kg)

G = Mass of all NAF-cuttings discharges into the ocean during the same period of time as used to calculate F_i, (kg)

If an operator has more than one point of NAF-cuttings discharge, the mass faction (X_i) must be determined by: (a) Direct measurement (*see* Equation 6 of this appendix); (b) using the following default values of 0.85 and 0.15 for the cuttings dryer (e.g., horizontal centrifuge, vertical centrifuge, squeeze press, High-G linear shakers) and fines removal unit (e.g., decanting centrifuges, mud cleaners), respectively, when the operator is only discharging from the cuttings dryer and the fines removal unit; or (c) using direct measurement of "F_i" (*see* Equation 6 of this appendix) for fines and accumulated solids, using Equation 6A of this appendix to calculate "G_{EST}" for use as "G" in Equation

6 of this Appendix, and calculating the mass (kg) of NAF-cuttings discharged from the cuttings dryer (F_i) as the difference between the mass of "G_{EST}" calculated in Equation 6A of this appendix (kg) and the sum of all fines and accumulated solids mass directly measured (kg) (*see* Equation 6 of this appendix).

G_{EST} = Estimated mass of all NAF-cuttings discharges into the ocean during the same period of time as used to calculate F_i (*see* Equation 6 of this appendix), (kg) [6A]

where:

G_{EST} = Hole Volume (bbl) × (396.9 kg/bbl) × (1 + Z/100)

Z = The base fluid retained on cuttings limitation or standard (%) which apply to the NAF being discharge (*see* §§ 435.13. and 435.15).

Hole Volume (bbl) = [Cross-Section Area of NAF interval (in^2)] × Average Rate of Penetration (feet/hr) × period of time (min) used to calculate F_i (*see* Equation 6 of this appendix) × (1 hr/60 min) × (1 bbl/ 5.61 ft^3) × (1 ft/12 in)^2

Cross-Section Area of NAF interval (in^2) = (3.14 × [Bit Diameter (in)]^2)/4

Bit Diameter (in) = Diameter of drilling bit for the NAF interval producing drilling cuttings during the same period of time as used to calculate F_i (*see* Equation 6 of this appendix)

Average Rate of Penetration (feet/hr) = Arithmetic average of rate of penetration into the formation during the same period of time as used to calculate F_i (*see* Equation 6 of this appendix)

Note: Operators with one NAF-cuttings discharge may set the mass NAF-cuttings discharge fraction (X_i) equal to 1.0.

5. Each NAF-cuttings, fines, or accumulated solids discharge has an associated mass percent NAF base fluid retained on cuttings value (%BF) and mass NAF-cuttings discharge fraction (X) each time a set of retorts is performed. A single total mass percent NAF base fluid retained on cuttings value ($\%BF_T$) is calculated every time a set of retorts is performed. The single total mass percent NAF base fluid retained on cuttings value ($\%BF_T$) is calculated as:

$\%BF_{T,j} = \Sigma(X_i) \times (\%BF_i)$ [7]

where:

$\%BF_{T,j}$ = Total mass percent NAF base fluid retained on cuttings value for retort set "j" (unitless as percentage, %)

X_i = Mass NAF-cuttings discharge fraction for NAF-cuttings, fines, or accumulated solids discharge "i", (unitless)

$\%BF_i$ = Mass percent NAF base fluid retained on the cuttings for NAF-cuttings, fines, or accumulated solids discharge "i" , (unitless as percentage, %)

Note: $\Sigma X_i = 1$.

Operators with one NAF-cuttings discharge may set $\%BF_{T,j}$ equal to $\%BF_i$.

6. Operators performing dual gradient drilling operations may require seafloor discharges of large cuttings (> 1/4') to ensure the proper operation of subsea pumps (e.g., electrical submersible pumps). Operators performing dual gradient drilling operations which lead to seafloor discharges of large cuttings for the proper operation of subsea pumps shall either: (a) Measure the mass percent NAF base fluid retained on cuttings value (%BF) and mass NAF-cuttings discharge fraction (X) for seafloor discharges each time a set of retorts is performed; (b) use the following set of default values, (%BF = 14%; X = 0.15); or (c) use a combination of (a) and (b) (e.g., use a default value for %BF and measure X).

   Additionally, operators performing dual gradient drilling operations which lead to seafloor discharges of large cuttings for the proper operation of subsea pumps shall also perform the following tasks:

   (a) Use side scan sonar or shallow seismic to determine the presence of high density chemosynthetic communities. Chemosynthetic communities are assemblages of tube worms, clams, mussels, and bacterial mats that occur at natural hydrocarbon seeps or vents, generally in water depths of 500 meters or deeper. Seafloor discharges of large cuttings for the proper operation of subsea pumps shall not be permitted within 1000 feet of a high density chemosynthetic community.

   (b) Seafloor discharges of large cuttings for the proper operation of subsea pumps shall be visually monitored and documented by a Remotely Operated Vehicle (ROV) within the tether limit (approximately 300 feet). The visual monitoring shall be conducted prior to each time the discharge point is relocated (cuttings discharge hose) and conducted along the same direction as the discharge hose position. Near-seabed currents shall be obtained at the time of the visual monitoring.

   (c) Seafloor discharges of large cuttings for the proper operation of subsea pumps shall be directed within a 150 foot radius of the wellbore.

7. The weighted mass ratio averaged over all NAF well sections ($\%BF_{well}$) is the compliance value that is compared with the "maximum weighted mass ratio averaged over all NAF well sections" BAT discharge limitations (*see* the table in § 435.13 and footnote 5 of the table in § 435.43) or the "maximum weighted mass ratio averaged over all NAF well sections" NSPS discharge limitations (*see* the table in § 435.15 and footnote 5 of the table in § 435.45). The weighted mass ratio averaged over all NAF well sections ($\%BF_{well}$) is calculated as the arithmetic average of all total mass percent NAF base fluid retained on cuttings values ($\%BF_T$) and is given by the following expression:

$$\%BF_{well} = [j = 1 \text{ to } j = n\ \Sigma\ (\%BF_{T,j})]/n \quad [8]$$

where:

$\%BF_{well}$ = Weighted mass ratio averaged over all NAF well sections (unitless as percentage, %)

$\%BF_{T,j}$ = Total mass percent NAF base fluid retained on cuttings value for retort set "j" (unitless as percentage, %)

n = Total number of retort sets performed over all NAF well sections (unitless)

Small volume NAF-cuttings discharges which do not occur during a NAF-cuttings discharge sampling interval (*i.e.*, displaced interfaces, accumulated solids in sand traps, pit clean-out solids, or centrifuge discharges while cutting mud weight) shall be mass averaged with the arithmetic average of all total mass percent NAF base fluid retained on cuttings values (see Equation 8 of this appendix). An additional sampling interval shall be added to the calculation of the weighted mass ratio averaged over all NAF well sections ($\%BF_{well}$). The mass fraction of the small volume NAF-cuttings discharges (X_{SVD}) will be determined by dividing the mass of the small volume NAF-cuttings discharges (F_{SVD}) by the total mass of NAF-cuttings discharges for the well drilling operation ($G_{WELL} + F_{SVD}$).

$X_{SVD} = F_{SVD} / (G_{WELL} + F_{SVD})$ [9]

where:

X_{SVD} = mass fraction of the small volume NAF-cuttings discharges (unitless)

F_{SVD} = mass of the small volume NAF-cuttings discharges (kg)

G_{WELL} = mass of total NAF-cuttings from the well (kg)

The mass of small volume NAF-cuttings discharges (F_{SVD}) shall be determined by multiplying the density of the small volume NAF-cuttings discharges (ρ_{svd}) times the volume of the small volume NAF-cuttings discharges (V_{SVD}).

$F_{SVD} = \rho_{svd} \times V_{SVD}$ [10]

where:

F_{SVD} = mass of small volume NAF-cuttings discharges (kg)

ρ_{svd} = density of the small volume NAF-cuttings discharges (kg/bbl)

V_{SVD} = volume of the small volume NAF-cuttings discharges (bbl)

The density of the small volume NAF-cuttings discharges shall be measured. The volume of small volume discharges (V_{SVD}) shall be either: (a) Be measured or (b) use default values of 10 bbl of SBF for each interface loss and 75 bbl of SBM for pit cleanout per well.

The total mass of NAF-cuttings discharges for the well (G_{WELL}) shall be either: (a) Measured; or (b) calculated by multiplying 1.0 plus the arithmetic average of all total mass percent NAF base fluid retained on cuttings values [see Equation 8 of this appendix] times the total hole volume (V_{WELL}) for all NAF well sections times a default value for the density the formation of 2.5 g/cm^3 (396.9 kg/bbl).

$$G_{WELL} = (1 + (\left[i = 1 \text{ to } j = n \sum (\%BF_{T,j})\right] / n)) \times V_{WELL}(bbl) \times 396.9(kg/bbl) \quad [11]$$

where:

G_{WELL} = total mass of NAF-cuttings discharges for the well (kg)

[j = 1 to j = n $\Sigma(\%BF_{T,j})$]/n = see Equation 8 of this appendix (unitless as a percentage)

V_{WELL} = total hole volume (V_{WELL}) for all NAF well sections (bbl)

The total hole volume of NAF well sections (V_{WELL}) will be calculated as:

$$V_{WELL}\,(\text{barrels}) = \sum \frac{\text{Bit diameter (in)}^2}{1029} \times \text{change in measured depth (ft)} \qquad [12]$$

For wells where small volume discharges associated with cuttings are made, $\%BF_{WELL}$ becomes:

$$\%BF_{WELL} = ((1 - X_{SVD}) \times \left[i = 1 \text{ to } j = n \sum \left(\%BF_{T,j} \right) \right] / n \ ]) + X_{SVD} \times \%BF_{SVD} \qquad [13]$$

Note: See Addendum A and B to determine the sampling frequency to determine the total number of retort sets required for all NAF well sections.

8. The total number of retort sets (n) is increased by 1 for each sampling interval (*see* Section 2.4, Addendum A of this appendix) when all NAF cuttings, fines, or accumulated solids for that sampling interval are retained for no discharge. A zero discharge interval shall be at least 500 feet up to a maximum of three per day. This action has the effect of setting the total mass percent NAF base fluid retained on cuttings value ($\%BF_T$) at zero for that NAF sampling interval when all NAF cuttings, fines, or accumulated solids are retained for no discharge.

9. Operators that elect to use the Best Management Practices (BMPs) for NAF-cuttings shall use the procedures outlined in Addendum B.

Addendum A to Appendix 7 to Subpart A of Part 435—Sampling of Cuttings Discharge Streams for use with API Recommended Practice 13B-2

1.0 Sampling Locations

1.1 Each NAF-cuttings waste stream that discharges into the ocean shall be sampled and analyzed as detailed in appendix 7. NAF-cuttings discharges to the ocean may include discharges from primary shakers, secondary shakers, cuttings dryer, fines removal unit, accumulated solids, and any other cuttings separation device whose NAF-cuttings waste is discharged to the ocean. NAF-cuttings wastestreams not directly discharged to the ocean (e.g., NAF-cuttings generated from shake shakers and sent to a cuttings dryer for additional processing) do not require sampling and analysis.

1.2 The collected samples shall be representative of each NAF-cuttings discharge. Operators shall conduct sampling to avoid the serious consequences of error (*i.e.,* bias or inaccuracy). Operators shall collect NAF-cuttings samples near the point of origin and before the solids and liquid fractions of the stream have a chance to separate from one another. For example, operators shall collect shale shaker NAF-cuttings samples at the point where NAF-cuttings are coming off the shale shaker and not from a holding container downstream where separation of larger particles from the liquid can take place.

1.3 Operators shall provide a simple schematic diagram of the solids control system and sample locations to the NPDES permit controlling authority.

2.0 Type of Sample and Sampling Frequency

2.1 Each NAF-cuttings, fines, or accumulated solids discharge has an associated mass percent NAF base fluid retained on cuttings value (%BF) and mass NAF-cuttings discharge fraction (X) for each sampling interval (*see* Section 2.4 of this addendum). Operators shall collect a single discrete NAF-cuttings sample for each NAF-cuttings waste stream discharged to the ocean during every sampling interval.

2.2 Operators shall use measured depth in feet from the Kelly bushing when samples are collected.

2.3 The NAF-cuttings samples collected for the mass fraction analysis (*see* Equation 6, appendix 7 of subpart A of this part) shall also be used for the retort analysis (*see* Equations 1-5, appendix 7 of subpart A of this part).

2.4 Operators shall collect and analyze at least one set of NAF-cuttings samples per day while discharging. Operators engaged in fast drilling (*i.e.,* greater than 500 linear NAF feet advancement of drill bit per day) shall collect and analyze one set of NAF-cuttings samples per 500 linear NAF feet of footage drilled. Operators are not required to collect and analyze more than three sets of NAF-cuttings samples per day (*i.e.,* three sampling intervals). Operators performing zero discharge of all NAF-cuttings (*i.e.,* all NAF cuttings, fines, or accumulated solids retained for no discharge) shall use the following periods to count sampling intervals:

(1) One sampling interval per day when drilling is less than 500 linear NAF feet advancement of drill bit per day; and

(2) one sampling interval per 500 linear NAF feet of footage drilled with a maximum of three sampling intervals per day.

2.5 The operator shall measure the individual masses (F_i, kg) and sum total mass (G, kg) (*see* Equation 6, appendix 7 of subpart A of this part) over a representative period of time (e.g., <10 minutes) during steady-state conditions for each sampling interval (*see* Section 2.4 of this addendum). The operator shall ensure that all NAF-cuttings are capture for mass analysis during the same sampling time period (e.g., <10 minutes) at approximately the same time (*i.e.,* all individual mass samples collected within one hour of each other).

2.6 Operators using Best Management Practices (BMPs) to control NAF-cuttings discharges shall follow the procedures in Addendum B to appendix 7 of subpart A of 40 CFR 435.

3.0 Sample Size and Handling

3.1 The volume of each sample depends on the volumetric flow rate (cm^3/s) of the NAF-cuttings stream and the sampling time period (e.g., <10 minutes). Consequently, different solids control equipment units producing different NAF-cuttings waste streams at different volumetric flow rates will produce different size samples for the same period of time. Operators shall use appropriately sized sample containers for each NAF-cuttings waste stream to ensure no NAF-cuttings are spilled during sample collection. Operators shall use the same time period (e.g., <10 minutes) to collect NAF-cuttings samples from each NAF-cuttings waste stream. Each NAF-cuttings sample size shall be at least one gallon. Operators shall clearly mark each container to identify each NAF-cuttings sample.

3.2 Operators shall not decant, heat, wash, or towel the NAF-cuttings to remove NAF base fluid before mass and retort analysis.

3.3 Operators shall first calculate the mass of each NAF-cuttings sample and perform the mass ratio analysis (*see* Equation 6, appendix 7 of subpart A of this part). Operators with only one NAF-cuttings discharge may skip this step (*see* Section 4.c.4, appendix 7 of subpart A of this part).

3.4 Operators shall homogenize (e.g., stirring, shaking) each NAF-cuttings sample prior to placing a sub-sample into the retort cup. The bottom of the NAF-cuttings sample container shall be examined to be sure that solids are not sticking to it.

3.5 Operators shall then calculate the NAF base fluid retained on cuttings using the retort procedure (*see* Equations 1-5, appendix 7 of subpart A of this part). Operators shall start the retort analyses no more than two hours after collecting the first individual mass sample for the sampling interval .

3.6 Operators shall not discharge any sample before successfully completing the mass and retort analyses [*i.e.*, mass balance requirements (*see* Section 4.b, appendix 7 of subpart A of this part) are satisfied]. Operators shall immediately re-run the retort analyses if the mass balance requirements (*see* Equation 4, appendix 7 of subpart A of this part) are not within a tolerance of 5% (*see* Section 4.b, Equation 4, appendix 7 of subpart A of this part).

4.0 Calculations

4.1 Operators shall calculate a set of mass percent NAF base fluid retained on cuttings values (%BF) and mass NAF-cuttings discharge fractions (X) for each NAF-cuttings waste stream (*see* Section 1.1 of this addendum) for each sampling interval (*see* Section 2.4 of this addendum) using the procedures outlined in appendix 7 of subpart A of this part.

4.2 Operators shall tabulate the following data for each individual NAF-cuttings sample:

(1) Date and time of NAF-cuttings sample collection;

(2) time period of NAF-cuttings sample collection (*see* Section 3.1 of this addendum);

(3) mass and volume of each NAF-cuttings sample;

(4) measured depth (feet) at NAF-cuttings sample collection (*see* Section 2.2 of this addendum);

(5) respective linear feet of hole drilled represented by the NAF-cuttings sample (feet); and

(6) the drill bit diameter (inches) used to generate the NAF-cuttings sample cuttings.

4.3 Operators shall calculate a single total mass percent NAF base fluid retained on cuttings value ($\%BF_T$) for each sampling interval (*see* Section 2.4 of this addendum) using the procedures outlined in appendix 7 of subpart A of this part.

4.4 Operators shall tabulate the following data for each total mass percent NAF base fluid retained on cuttings value ($\%BF_T$) for each NAF-cuttings sampling interval:

(1) Date and starting and stopping times of NAF-cuttings sample collection and retort analyses;

(2) measured depth of well (feet) at start of NAF-cuttings sample collection (*see* Section 2.2 of this addendum);

(3) respective linear feet of hole drilled represented by the NAF-cuttings sample (feet);

(4) the drill bit diameter (inches) used to generate the NAF-cuttings sample cuttings; and

(5) annotation when zero discharge of NAF-cuttings is performed.

4.5 Operators shall calculate the weighted mass ratio averaged over all NAF well sections ($\%BF_{well}$) using the procedures outlined in appendix 7 of subpart A of this part.

4.6 Operators shall tabulate the following data for each weighted mass ratio averaged over all NAF well sections ($\%BF_{well}$) for each NAF well:

(1) Starting and stopping dates of NAF well sections;

(2) measured depth (feet) of all NAF well sections;

(3) total number of sampling intervals (*see* Section 2.4 and Section 2.6 of this addendum);

(4) number of sampling intervals tabulated during any zero discharge operations;

(5) total volume of zero discharged NAF-cuttings over entire NAF well sections; and

(6) identification of whether BMPs were employed (*see* Addendum B of appendix 7 of subpart A of this part).

Addendum B to Appendix 7 to Subpart A of Part 435—Best Management Practices (BMPs) for use with API Recommended Practice 13B-2

1.0 Overview of BMPs

1.1 Best Management Practices (BMPs) are inherently pollution prevention practices. BMPs may include the universe of pollution prevention encompassing production modifications, operational changes, material substitution, materials and water conservation, and other such measures. BMPs include methods to prevent toxic and hazardous pollutants from reaching receiving waters. Because BMPs are most effective when organized into a comprehensive facility BMP Plan, operators shall develop a BMP in accordance with the requirements in this addendum.

1.2 The BMP requirements contained in this appendix were compiled from several Regional permits, an EPA guidance document (*i.e.*, Guidance Document for Developing Best Management Practices (BMP)" (EPA 833-B-93-004, U.S. EPA, 1993)), and draft industry BMPs. These common elements represent the appropriate mix of broad directions needed to complete a BMP Plan along with specific tasks common to all drilling operations.

1.3 Operators are not required to use BMPs if all NAF-cuttings discharges are monitored in accordance with appendix 7 of subpart A of this part.

2.0 BMP Plan Purpose and Objectives

2.1 Operators shall design the BMP Plan to prevent or minimize the generation and the potential for the discharge of NAF from the facility to the waters of the United States through normal operations and ancillary activities. The operator shall establish specific objectives for the control of NAF by conducting the following evaluations.

2.2 The operator shall identify and document each NAF well that uses BMPs before starting drilling operations and the anticipated total feet to be drilled with NAF for that particular well.

2.3 Each facility component or system controlled through use of BMPs shall be examined for its NAF-waste minimization opportunities and its potential for causing a discharge of NAF to waters of the United States due to equipment failure, improper operation, natural phenomena (e.g., rain, snowfall).

2.4 For each NAF wastestream controlled through BMPs where experience indicates a reasonable potential for equipment failure (e.g., a tank overflow or leakage), natural condition (e.g., precipitation), or other circumstances to result in NAF reaching surface waters, the BMP Plan shall include a prediction of the total quantity of NAF which could be discharged from the facility as a result of each condition or circumstance.

3.0 BMP Plan Requirements

3.1 The BMP Plan may reflect requirements within the pollution prevention requirements required by the Minerals Management Service (*see* 30 CFR 250.300) or other Federal or State requirements and incorporate any part of such plans into the BMP Plan by reference.

3.2 The operator shall certify that its BMP Plan is complete, on-site, and available upon request to EPA or the NPDES Permit controlling authority. This certification shall identify the NPDES permit number and be signed by an authorized representative of the operator. This certification shall be kept with the BMP Plan. For new or modified NPDES permits, the certification shall be made no later than the effective date of the new or modified permit. For existing NPDES permits, the certification shall be made within one year of permit issuance.

3.3 The BMP Plan shall:

3.3.1 Be documented in narrative form, and shall include any necessary plot plans, drawings or maps, and shall be developed in accordance with good engineering practices. At a minimum, the BMP Plan shall contain the planning, development and implementation, and evaluation/reevaluation components. Examples of these components are contained in “Guidance Document for Developing Best Management Practices (BMP)” (EPA 833-B-93-004, U.S. EPA, 1993).

3.3.2 Include the following provisions concerning BMP Plan review.

3.3.2.1 Be reviewed by permittee's drilling engineer and offshore installation manager (OIM) to ensure compliance with the BMP Plan purpose and objectives set forth in Section 2.0.

3.3.2.2 Include a statement that the review has been completed and that the BMP Plan fulfills the BMP Plan purpose and objectives set forth in Section 2.0. This statement shall have dated signatures from the permittee's drilling engineer and offshore installation manager and any other individuals responsible for development and implementation of the BMP Plan.

3.4 Address each component or system capable of generating or causing a release of significant amounts of NAF and identify specific preventative or remedial measures to be implemented.

4.0 BMP Plan Documentation

4.1 The operator shall maintain a copy of the BMP Plan and related documentation (e.g., training certifications, summary of the monitoring results, records of NAF-equipment spills, repairs, and maintenance) at the facility and shall make the BMP Plan and related documentation available to EPA or the NPDES Permit controlling authority upon request.

5.0 BMP Plan Modification

5.1 For those NAF wastestreams controlled through BMPs, the operator shall amend the BMP Plan whenever there is a change in the facility or in the operation of the facility which materially increases the generation of those NAF-wastes or their release or potential release to the receiving waters.

5.2 At a minimum the BMP Plan shall be reviewed once every five years and amended within three months if warranted. Any such changes to the BMP Plan shall be consistent with the objectives and specific requirements listed in this addendum. All changes in the BMP Plan shall be reviewed by the permittee's drilling engineer and offshore installation manager.

5.3 At any time, if the BMP Plan proves to be ineffective in achieving the general objective of preventing and minimizing the generation of NAF-wastes and their release and potential release to the receiving waters and/or the specific requirements in this addendum, the permit and/or the BMP Plan shall be subject to modification to incorporate revised BMP requirements.

6.0 Specific Pollution Prevention Requirements for NAF Discharges Associated with Cuttings

6.1 The following specific pollution prevention activities are required in a BMP Plan when operators elect to control NAF discharges associated with cuttings by a set of BMPs.

6.2 Establishing programs for identifying, documenting, and repairing malfunctioning NAF equipment, tracking NAF equipment repairs, and training personnel to report and evaluate malfunctioning NAF equipment.

6.3 Establishing operating and maintenance procedures for each component in the solids control system in a manner consistent with the manufacturer's design criteria.

6.4 Using the most applicable spacers, flushes, pills, and displacement techniques in order to minimize contamination of drilling fluids when changing from water-based drilling fluids to NAF and vice versa.

6.5 A daily retort analysis shall be performed (in accordance with appendix 7 to subpart A of part 435) during the first 0.33 X feet drilled with NAF where X is the anticipated total feet to be drilled with NAF for that particular well. The retort analyses shall be documented in the well retort log. The operators shall use the calculation procedures detailed in appendix 7 to subpart A of part 435 (*see* Equations 1 through 8) to determine the arithmetic average ($\%BF_{well}$) of the retort analyses taken during the first 0.33 X feet drilled with NAF.

6.5.1 When the arithmetic average ($\%BF_{well}$) of the retort analyses taken during the first 0.33 X feet drilled with NAF is less than or equal to the base fluid retained on cuttings limitation or standard (*see* §§ 435.13 and 435.15), retort monitoring of cuttings may cease for that particular well. The same BMPs and drilling fluid used during the first 0.33 X feet shall be used for all remaining NAF sections for that particular well.

6.5.2 When the arithmetic average ($\%BF_{well}$) of the retort analyses taken during the first 0.33 X feet drilled with NAF is greater the base fluid retained on cuttings limitation or standard (*see* §§ 435.13 and 435.15), retort monitoring shall continue for the following (second) 0.33 X feet drilled with NAF where X is the anticipated total feet to be drilled with NAF for that particular well. The retort analyses for the first and second 0.33 X feet shall be documented in the well retort log.

6.5.2.1 When the arithmetic average ($\%BF_{well}$) of the retort analyses taken during the first 0.66 X feet (*i.e.*, retort analyses taken from first and second 0.33 X feet) drilled with NAF is less than or equal to the base fluid retained on cuttings limitation or standard (*see* §§ 435.13 and 435.15), retort monitoring of cuttings may cease for that particular well. The same BMPs and drilling fluid used during the first 0.66 X feet shall be used for all remaining NAF sections for that particular well.

6.5.2.2 When the arithmetic average ($\%BF_{well}$) of the retort analyses taken during the first 0.66 X feet (*i.e.*, retort analyses taken from first and second 0.33 X feet) drilled with NAF is greater than the base fluid retained on cuttings limitation or standard (*see* §§ 435.13 and 435.15), retort monitoring shall continue for all remaining NAF sections for that particular well. The retort analyses for all NAF sections shall be documented in the well retort log.

6.5.3 When the arithmetic average ($\%BF_{well}$) of the retort analyses taken over all NAF sections for the entire well is greater that the base fluid retained on cuttings limitation or standard (*see* §§ 435.13 and 435.15), the operator is in violation of the base fluid retained on cuttings limitation or standard and shall submit notification of these monitoring values in accordance with NPDES permit requirements. Additionally, the operator shall, as part of the BMP Plan, initiate a reevaluation and modification to the BMP Plan in conjunction with equipment vendors and/or industry specialists.

6.5.4 The operator shall include retort monitoring data and dates of retort-monitored and non-retort-monitored NAF-cuttings discharges managed by BMPs in their NPDES permit reports.

6.6 Establishing mud pit and equipment cleaning methods in such a way as to minimize the potential for building-up drill cuttings (including accumulated solids) in the active mud system and solids control equipment system. These cleaning methods shall include but are not limited to the following procedures.

6.6.1 Ensuring proper operation and efficiency of mud pit agitation equipment.

6.6.2 Using mud gun lines during mixing operations to provide agitation in dead spaces.

6.6.3 Pumping drilling fluids off of drill cuttings (including accumulated solids) for use, recycle, or disposal before using wash water to dislodge solids.

[66 FR 6901, Jan. 22, 2001; 66 FR 30811, June 8, 2001]

Appendix 8 to Subpart A of Part 435—Reference C_{16}-C_{18} Internal Olefin Drilling Fluid Formulation

The reference C_{16}-C_{18} internal olefin drilling fluid used to determine the drilling fluid sediment toxicity ratio and compliance with the BAT sediment toxicity discharge limitation (*see* § 435.13) and NSPS (*see* § 435.15) shall be formulated to meet the specifications in Table 1 of this appendix.

Drilling fluid sediment toxicity ratio = 4-day LC_5. of C_{16}-C_{18} internal olefin drilling fluid/4-day LC_5. of drilling fluid removed from drill cuttings at the solids control equipment as determined by EPA Method 1644: "Method for Conducting a Sediment Toxicity Test with *Leptocheirus plumulosus* and Non-Aqueous Drilling Fluids or Synthetic-Based Drilling Muds" after sediment preparation procedures specified in EPA Method 1646, which are published as appendices to Subpart A of this part and in "Analytic Methods for the Oil and Gas Extraction Point Source Category," EPA-821-R-11-004. See § 435.11(ee) and (uu).

Table 1—Properties for Reference C_{16}-C_{18} IOs SBF Used in Discharge Sediment Toxicity Testing

Mud weight of SBF discharged with cuttings (pounds per gallon)	Reference C_{16}-C_{18} IOs SBF (pounds per gallon)	Reference C_{16}-C_{18} IOs SBF synthetic to water ratio (%)
8.5-11	9.0	75/25
>11-14	11.5	80/20
>14	14.5	85/15
Plastic Viscosity (PV), centipoise (cP)	12-30	
Yield Point (YP), pounds/100 sq. ft	10-20	
10-second gel, pounds/100 sq. ft	8-15	
10-minute gel, pounds/100 sq. ft	12-30	
Electrical stability, V	>300	

[66 FR 6901, Jan. 22, 2001, as amended at 77 FR 29845, May 18, 2012]

Subpart B [Reserved]

Subpart C—Onshore Subcategory

§ 435.30 Applicability; description of the onshore subcategory.

The provisions of this subpart are applicable to those facilities engaged in the production, field exploration, drilling, well completion and well treatment in the oil and gas extraction industry which are located landward of the inner boundary of the territorial seas as defined in 40 CFR 125.1(gg) and which are not included within subpart D, E, or F, *Provided, however,* That the applicability of this subpart to (a) facilities in existence on April 13, 1979 or thereafter engaged in the production, field exploration, drilling, well completion and well treatment in the oil and gas extraction industry which are located on land and which would have been considered "coastal" as defined under the interim final regulations for this industry (40 CFR 435.41, 41 FR 44942, October 13, 1976) or which are (b) located in the Santa Maria Basin of California is suspended.

(Secs. 301, 304(b) and 501 of the Clean Water Act as amended, 33 U.S.C. 1251 *et seq.*)

[44 FR 22075, Apr. 13, 1979, as amended at 47 FR 31555, July 21, 1982]

§ 435.31 Specialized definitions.

For the purpose of this subpart:

(a) The general definitions, abbreviations, and methods of analysis set forth in 40 CFR part 401 shall apply to this subpart.

§ 435.32 Effluent limitations guidelines representing the degree of effluent reduction attainable by the application of the best practicable control technology currently available.

Except as provided in §§ 125.30 through 125.32, any existing point source subject to this subpart shall achieve the following effluent limitations representing the degree of effluent reduction attainable by the application of the best practicable control technology currently available (BPT): there shall be no discharge of waste water pollutants into navigable waters from any source associated with production, field exploration, drilling, well completion, or well treatment (*i.e.*, produced water, drilling muds, drill cuttings, and produced sand).

[60 FR 33966, June 29, 1995]

§ 435.33 Pretreatment standards for existing sources (PSES).

(a) ***PSES for wastewater from unconventional oil and gas extraction.*** Except as provided in 40 CFR 403.7 and 403.13, any existing source subject to this section, must achieve the following pretreatment standards for existing sources (PSES).

(1) There shall be no discharge of wastewater pollutants associated with production, field exploration, drilling, well completion, or well treatment for unconventional oil and gas extraction (including, but not limited to, drilling muds, drill cuttings, produced sand, produced water) into publicly owned treatment works.

(2) For the purposes of this section,

(i) ***Unconventional oil and gas*** means crude oil and natural gas produced by a well drilled into a shale and/or tight formation (including, but not limited to, shale gas, shale oil, tight gas, tight oil).

(ii) ***Drill cuttings*** means the particles generated by drilling into subsurface geologic formations and carried out from the wellbore with the drilling fluid.

(iii) ***Drilling mud*** means the circulating fluid (mud) used in the rotary drilling of wells to clean and condition the hole and to counterbalance formation pressure.

(iv) ***Produced sand*** means the slurried particles used in hydraulic fracturing, the accumulated formation sands, and scales particles generated during production. Produced sand also includes desander discharge from the produced water waste stream, and blowdown of the water phase from the produced water treating system.

(v) ***Produced water*** means the fluid brought up from the hydrocarbon-bearing strata during the extraction of oil and gas, and includes, where present, formation water, injection water, and any chemicals added downhole or during the oil/water separation process.

(3) ***Compliance deadline for existing sources.*** Existing sources discharging into publicly owned treatment works on or between April 7, 2015 and June 28, 2016, shall comply with the PSES by August 29, 2019. All other existing sources shall comply by August 29, 2016.

(b) ***PSES for Wastewater from Conventional Oil and Gas Extraction.*** [Reserved]

[81 FR 41857, June 28, 2016, as amended at 81 FR 88127, Dec. 7, 2016]

§ 435.34 Pretreatment standards for new sources (PSNS).

(a) ***PSNS for wastewater from unconventional oil and gas extraction.*** Except as provided in 40 CFR 403.7 and 403.13, any new source with discharges subject to this section must achieve the following pretreatment standards for new sources (PSNS).

(1) There shall be no discharge of wastewater pollutants associated with production, field exploration, drilling, well completion, or well treatment for unconventional oil and gas extraction (including, but not limited to, drilling muds, drill cuttings, produced sand, produced water) into publicly owned treatment works.

(2) For the purposes of this section, the definitions of unconventional oil and gas, drill cuttings, drilling muds, produced sand, and produced water are as specified in § 435.33(b)(2)(i) through (v).

(b) ***PSNS for Wastewater from Conventional Oil and Gas Extraction.*** [Reserved]

[81 FR 41857, June 28, 2016]

Subpart D—Coastal Subcategory

Source: 61 FR 66125, Dec. 16, 1996, unless otherwise noted.

§ 435.40 Applicability; description of the coastal subcategory.

The provisions of this subpart are applicable to those facilities engaged in field exploration, drilling, well production, and well treatment in the oil and gas industry in areas defined as "coastal." The term "coastal" shall mean:

(a) Any location in or on a water of the United States landward of the inner boundary of the territorial seas; or

(b)

(1) Any location landward from the inner boundary of the territorial seas and bounded on the inland side by the line defined by the inner boundary of the territorial seas eastward of the point defined by 89°45' West Longitude and 29°46' North Latitude and continuing as follows west of that point:

Direction to west longitude	Direction to north latitude
West, 89°48'	North, 29°50'.
West, 90°12'	North, 30°06'.
West, 90°20'	South, 29°35'.
West, 90°35'	South, 29°30'.
West, 90°43'	South, 29°25'.
West, 90°57'	North, 29°32'.
West, 91°02'	North, 29°40'.
West, 91°14'	South, 29°32'.
West, 91°27'	North, 29°37'.
West, 91°33'	North, 29°46'.
West, 91°46'	North, 29°50'.

Direction to west longitude	Direction to north latitude
West, 91°50'	North, 29°55'.
West, 91°56'	South, 29°50'.
West, 92°10'	South, 29°44'.
West, 92°55'	North, 29°46'.
West, 93°15'	North, 30°14'.
West, 93°49'	South, 30°07'.
West, 94°03'	South, 30°03'.
West, 94°10'	South, 30°00'.
West, 94°20'	South, 29°53'.
West, 95°00'	South, 29°35'.
West, 95°13'	South, 29°28'.
East, 95°08'	South, 29°15'.
West, 95°11'	South, 29°08'.
West, 95°22'	South, 28°56'.
West, 95°30'	South, 28°55'.
West, 95°33'	South, 28°49'.
West, 95°40'	South, 28°47'.
West, 96°42'	South, 28°41'.
East, 96°40'	South, 28°28'.
West, 96°54'	South, 28°20'.
West, 97°03'	South, 28°13'.
West, 97°15'	South, 27°58'.
West, 97°40'	South, 27°45'.
West, 97°46'	South, 27°28'.
West, 97°51'	South, 27°22'.
East, 97°46'	South, 27°14'.
East, 97°30'	South, 26°30'.
East, 97°26'	South, 26°11'.

(2) East to 97°19' West Longitude and Southward to the U.S.-Mexican border.

§ 435.41 Specialized definitions.

For the purpose of this subpart:

(a) Except as provided below, the general definitions, abbreviations and methods of analysis set forth in 40 CFR part 401 shall apply to this subpart.

(b) ***Average of daily values for 30 consecutive days*** means the average of the daily values obtained during any 30 consecutive day period.

(c) ***Base fluid*** means the continuous phase or suspending medium of a drilling fluid formulation.

(d) ***Base fluid retained on cuttings*** as applied to BAT effluent limitations and NSPS refers to the "Determination of the Amount of Non-Aqueous Drilling Fluid (NAF) Base Fluid from Drill Cuttings by a Retort Chamber (Derived from API Recommended Practice 13B-2)", EPA Method 1674, which is published as an appendix to Subpart A of this part and in "Analytic Methods for the Oil and Gas Extraction Point Source Category," EPA-821-R-11-004. See paragraph (mm) of this section.

(e) ***Biodegradation rate*** as applied to BAT effluent limitations and NSPS for drilling fluids and drill cuttings refers to the "Protocol for the Determination of Degradation of Non Aqueous Base Fluids in a Marine Closed Bottle Biodegradation Test System: Modified ISO 11734:1995," EPA Method 1647, supplemented with "Procedure for Mixing Base Fluids With Sediments," EPA Method 1646. Both EPA Method 1646 and 1647 are published as appendices to Subpart A of this part and in "Analytic Methods for the Oil and Gas Extraction Point Source Category," EPA-821-R-11-004. See paragraph (mm) of this section.

(f) ***Cook Inlet*** refers to coastal locations north of the line between Cape Douglas on the West and Port Chatham on the east.

(g) ***Daily values*** as applied to produced water effluent limitations and NSPS means the daily measurements used to assess compliance with the maximum for any one day.

(h) ***Deck drainage*** means any waste resulting from deck washings, spillage, rainwater, and runoff from gutters and drains including drip pans and work areas within facilities subject to this subpart.

(i) ***Development facility*** means any fixed or mobile structure subject to this subpart that is engaged in the drilling of productive wells.

(j) ***Dewatering effluent*** means wastewater from drilling fluids and drill cuttings dewatering activities (including but not limited to reserve pits or other tanks or vessels, and chemical or mechanical treatment occurring during the drilling solids separation/recycle/disposal process).

(k) ***Diesel oil*** refers to the grade of distillate fuel oil, as specified in the American Society for Testing and Materials Standard Specification for Diesel Fuel Oils D975-91, that is typically used as the continuous phase in conventional oil-based drilling fluids. This incorporation by reference was approved by the Director of the Federal Register in accordance with 5 U.S.C. 552(a) and 1 CFR part 51. Copies may be obtained from the American Society for Testing and Materials, 100 Barr Harbor Drive, West Conshohocken, PA 19428. Copies may be inspected at the National Archives and Records Administration (NARA). For information on the availability of this material at NARA, call 202-741-6030, or go to: *http://www.archives.gov/federal_register/code_of_federal_regulations/ibr_locations.html.* A copy may also be inspected at EPA's Water Docket, 1200 Pennsylvania Ave. NW., Washington, DC 20460.

(l) ***Domestic waste*** means the materials discharged from sinks, showers, laundries, safety showers, eye-wash stations, hand-wash stations, fish cleaning stations, and galleys located within facilities subject to this subpart.

(m) ***Drill cuttings*** means the particles generated by drilling into subsurface geologic formations and carried out from the wellbore with the drilling fluid. Examples of drill cuttings include small pieces of rock varying in size and texture from fine silt to gravel. Drill cuttings are generally generated from solids control equipment and settle out and accumulate in quiescent areas in the solids control equipment or other equipment processing drilling fluid (*i.e.*, accumulated solids).

(1) ***Wet drill cuttings*** means the unaltered drill cuttings and adhering drilling fluid and formation oil carried out from the wellbore with the drilling fluid.

(2) ***Dry drill cuttings*** means the residue remaining in the retort vessel after completing the retort procedure specified in EPA Method 1674, which is published as an appendix to Subpart A of this part and in "Analytic Methods for the Oil and Gas Extraction Point Source Category," EPA-821-R-11-004. See paragraph (mm) of this section.

(n) ***Drilling fluid*** means the circulating fluid (mud) used in the rotary drilling of wells to clean and condition the hole and to counterbalance formation pressure. Classes of drilling fluids are:

(1) ***Water-based drilling fluid*** means the continuous phase and suspending medium for solids is a water-miscible fluid, regardless of the presence of oil.

(2) ***Non-aqueous drilling fluid*** means the continuous phase and suspending medium for solids is a water-immiscible fluid, such as oleaginous materials (e.g., mineral oil, enhanced mineral oil, paraffinic oil, C_{16}-C_{18} internal olefins, and C_8-C_{16} fatty acid/2-ethylhexyl esters).

(i) ***Oil-based*** means the continuous phase of the drilling fluid consists of diesel oil, mineral oil, or some other oil, but contains no synthetic material or enhanced mineral oil.

(ii) ***Enhanced mineral oil-based*** means the continuous phase of the drilling fluid is enhanced mineral oil.

(iii) ***Synthetic-based*** means the continuous phase of the drilling fluid is a synthetic material or a combination of synthetic materials.

(o) ***Enhanced mineral oil*** as applied to enhanced mineral oil-based drilling fluid means a petroleum distillate which has been highly purified and is distinguished from diesel oil and conventional mineral oil in having a lower polycyclic aromatic hydrocarbon (PAH) content. Typically, conventional mineral oils have a PAH content on the order of 0.35 weight percent expressed as phenanthrene, whereas enhanced mineral oils typically have a PAH content of 0.001 or lower weight percent PAH expressed as phenanthrene.

(p) ***Exploratory facility*** means any fixed or mobile structure subject to this subpart that is engaged in the drilling of wells to determine the nature of potential hydrocarbon reservoirs.

(q) ***Formation oil*** means the oil from a producing formation which is detected in the drilling fluid, as determined by the GC/MS compliance assurance method, EPA Method 1655, when the drilling fluid is analyzed before being shipped offshore, and as determined by the RPE method, EPA Method 1670, when the drilling fluid is analyzed at the offshore point of discharge. The GC/MS compliance assurance method and the RPE method approved for use with this part are published as appendices to Subpart A of this part and in "Analytic Methods for the Oil and Gas Extraction Point Source Category," EPA-821-R-11-004. See paragraph (mm) of this section. Detection of formation oil by the RPE method may be confirmed by the GC/MS compliance assurance method, and the results of the GC/MS compliance assurance method shall supersede those of the RPE method.

(r) ***Garbage*** means all kinds of victual, domestic, and operational waste, excluding fresh fish and parts thereof, generated during the normal operation of coastal oil and gas facility and liable to be disposed of continuously or periodically, except dishwater, graywater, and those substances that are defined or listed in other Annexes to MARPOL 73/78. A copy of MARPOL may be inspected at EPA's Water Docket, 1200 Pennsylvania Ave. NW., Washington, DC 20460.

(s) ***M9IM*** means those offshore facilities continuously manned by nine (9) or fewer persons or only intermittently manned by any number of persons.

(t) ***M10*** means those offshore facilities continuously manned by ten (10) or more persons.

(u) ***Maximum*** as applied to BAT effluent limitations and NSPS for drilling fluids and drill cuttings means the maximum concentration allowed as measured in any single sample of the barite for determination of cadmium and mercury content.

(v) ***Maximum for any one day*** as applied to BPT, BCT and BAT effluent limitations and NSPS for oil and grease in produced water means the maximum concentration allowed as measured by the average of four grab samples collected over a 24-hour period that are analyzed separately. Alternatively, for BAT and NSPS the maximum concentration allowed may be determined on the basis of physical composition of the four grab samples prior to a single analysis.

(w) ***Minimum*** as applied to BAT effluent limitations and NSPS for drilling fluids and drill cuttings means the minimum 96-hour LC_{50}. value allowed as measured in any single sample of the discharged waste stream. *Minimum* as applied to BPT and BCT effluent limitations and NSPS for sanitary wastes means the minimum concentration value allowed as measured in any single sample of the discharged waste stream.

(x)

(1) ***New source*** means any facility or activity of this subcategory that meets the definition of "new source" under 40 CFR 122.2 and meets the criteria for determination of new sources under 40 CFR 122.29(b) applied consistently with all of the following definitions:

(i) ***Water area*** as used in "site" in 40 CFR 122.29 and 122.2 means the water area and water body floor beneath any exploratory, development, or production facility where such facility is conducting its exploratory, development or production activities.

(ii) ***Significant site preparation work*** as used in 40 CFR 122.29 means the process of surveying, clearing or preparing an area of the water body floor for the purpose of constructing or placing a development or production facility on or over the site.

(2) "New Source" does not include facilities covered by an existing NPDES permit immediately prior to the effective date of these guidelines pending EPA issuance of a new source NPDES permit.

(y) ***No discharge of free oil*** means that waste streams may not be discharged that contain free oil as evidenced by the monitoring method specified for that particular stream, e.g., deck drainage or miscellaneous discharges cannot be discharged when they would cause a film or sheen upon or discoloration of the surface of the receiving water; drilling fluids or cuttings may not be discharged when they fail EPA Method 1617 (Static Sheen Test), which is published as an appendix to Subpart A of this part and in "Analytic Methods for the Oil and Gas Extraction Point Source Category," EPA-821-R-11-004. See paragraph (mm) of this section.

(z) Parameters that are regulated in this subpart and listed with approved methods of analysis in Table 1B at 40 CFR 136.3 are defined as follows:

(1) ***Cadmium*** means total cadmium.

(2) ***Chlorine*** means total residual chlorine.

(3) ***Mercury*** means total mercury.

(4) ***Oil and Grease*** means total recoverable oil and grease.