ENFORCEABLE CONSENT AGREEMENT
FOR
ENVIRONMENTAL TESTING FOR
OCTAMETHYLCYCLOTETRASILOXANE (D4) (CASRN 556-67-2)

Docket No. EPA-HQ-OPPT-2012-0209
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Date: February 6, 2014

Contains No Confidential Business Information

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I. INTRODUCTION

A. Under the authority of Section 4 of the Toxic Substances Control Act (TSCA), 15 U.S.C. § 2603, and 40 C.F.R. Part 790 of the Agency's implementing regulations, the United States Environmental Protection Agency [hereinafter "EPA" or "Agency"] and, Dow Corning Corporation, Evonik Corporation, Momentive Performance Materials USA Inc., Shin-Etsu Silicones of America, Inc., and Wacker Chemical Corporation [hereinafter individually a "Signatory Company" and collectively "the Signatory Companies"] enter into this Enforceable Consent Agreement for certain environmental testing [hereinafter "this ECA"]. As used in this ECA, the term "Parties" shall refer jointly to EPA and the Signatory Companies, and the term "Party" shall refer individually to one or the other.

II. CHEMICALS SUBJECT TO THE ECA

This ECA requires testing for presence of octamethylcyclotetrasiloxane, Chemical Abstracts Service Registry Number (CASRN) 556-67-2 [hereinafter referred to as "D4"] in specified wastewater treatment plant (WWTP) influent and effluent discharges, receiving streams and environmental matrices at method detection limits specified in the test standards in Appendices 4-8 of this document.

III. OBLIGATIONS OF THE SIGNATORY COMPANIES

The Signatory Companies are responsible for complying with the terms of this ECA. The Signatory Companies recognize that to implement this ECA, EPA will issue an order under Section 4 of TSCA that incorporates the terms of this ECA. The Signatory Companies agree that all terms of this ECA will take effect on the date of publication of the notice in the Federal Register announcing the issuance of the Order that incorporates this ECA. All applicable time periods will be treated as beginning on that publication date.

The Signatory Companies shall submit a draft Study Plan and Quality Assurance Project Plan ("QAPP") to carry out the environmental testing program set forth in Section VII and Appendices 1- 8. The Signatory Companies shall conduct environmental testing in accordance with the Final Study Plan and Final QAPP that will be developed based on EPA's review of the Signatory Companies' draft submissions. Following completion of environmental testing, the Signatory Companies shall submit a Final Report to EPA.

Sections VI through IX provide more details about the testing that will be accomplished under this ECA ("Testing Program").

IV. PRINCIPAL TEST SPONSOR

A. To facilitate implementation of the Testing Program, the Signatory Companies have appointed the Silicones Environmental, Health, and Safety Center (SEHSC), 700 2nd Street NE, Washington DC 20002, 202-249-7000, as the Principal Test Sponsor of this Testing Program.

B. The Signatory Companies will provide EPA with written notice should they elect to designate a different Principal Test Sponsor.

C. EPA and the Signatory Companies recognize that the Principal Test Sponsor has no legal responsibility for complying with this ECA. The role of the Principal Test Sponsor is to assist in coordinating and administering testing under this ECA and in communicating with EPA about study plans, protocols, analytical methods, schedules, reports, and other aspects of the testing program. Responsibility for complying with the ECA rests at all times with the individual Signatory Companies.

V. PURPOSE OF THE TESTING PROGRAM

The purpose of the Testing Program is to conduct environmental monitoring to characterize specified sources and pathways of release of D4 to the environment and resulting exposure of aquatic and sediment dwelling organisms to D4.

Through the Testing Program, the Signatory Companies will develop environmental testing data for D4 in the vicinity of manufacturing and processing (including product formulating) sites and WWTPs in the United States. EPA believes that the Testing Program will generate data useful to the Agency to assess D4 exposures and risks to sediment dwelling and aquatic organisms.

VI. SCOPE OF THE TESTING PROGRAM

The Testing Program is described in Section VII. Sampling and analysis will be conducted in accordance with the test standards described in Section VIII ("Test Standards") and documented in the required submissions described in Section IX (i.e., Study Plan, QAPP, Interim Progress Reports, and Final Report).

VII. DESCRIPTION OF TESTING PROGRAM

A. As described further in Appendix 1 to this ECA, environmental testing will be conducted on samples collected at four (4) direct discharge locations operated by certain Signatory Companies. For each of the four locations described in Appendix 1, there will be two (2) testing events. In particular, each facility's WWTP's effluent will be sampled and analyzed for D4. Sediment, surface water and biota (benthic and fish species) in the receiving waters will also be sampled and analyzed for D4. The test standards described in Appendices 4, 5, 7 and 8 shall be used for testing.

B. As described further in Appendix 2 to this ECA, environmental testing will be conducted on samples collected at five (5) WWTP locations that use activated sludge to treat wastewater from indirect discharge sites that include D4 processors (including product formulators). For each of the locations described in Appendix 2, there will be two (2) testing events involving the collection and analysis for D4 of samples of the following: WWTP influent, WWTP effluent, WWTP biosolids, receiving stream surface water, receiving stream sediment, and receiving stream biota (benthic and fish species). The test standards described in Appendices 4, 5, 6, 7 and 8 shall be used for testing.

C. As described further in Appendix 3 to this ECA, environmental testing will be conducted on samples collected at five (5) WWTP locations receiving less than 15% of wastewater from industrial facilities and, preferably, no wastewater from D4 manufacturing or processing (including product formulation) sites. For each of the locations described in Appendix 3, there will be two (2) testing events involving the collection and analysis for D4 of samples of the following: WWTP influent, WWTP effluent, WWTP biosolids, receiving stream surface water, receiving stream sediment, and receiving stream biota (benthic and fish species). The test standards described in Appendices 4, 5, 6, 7 and 8 shall be used for testing.

Following completion of the environmental testing described in paragraphs A-C above, the Signatory Companies will provide EPA with a report summarizing the results.

VIII. STANDARDS FOR CONDUCTING TESTING

A. Environmental testing shall be conducted in accordance with the Test Standards described in Appendices 4, 5, 6, 7, and 8 to this ECA. Preferably, all samples should be analyzed for D4 at one commercial testing laboratory that has appropriate expertise with the D4 analyses of samples of the types collected in this testing program when the analysis occurs, unless there are unforeseen circumstances such as lack of laboratory availability as noted in 40 C.F.R. § 790.68(b)(2)(iii).

1. Certain provisions of Test Standards are considered to be mandatory and are referred to as "requirements." These requirements are identified by the use of the words "shall," "will," or "must" in the text of the Test Standard and delineate a test requirement to be followed or met.

2. Provisions that are not mandatory, and are therefore only recommended, are identified by the use of "should" statements. If such "should" provisions are not followed, the Signatory Companies will not be deemed by EPA to be in violation and will not be subject to penalties or other enforcement actions and this will not, in and of itself, cause the resulting data to be deemed invalid.

B. The Signatory Companies and EPA will consult in good faith to consider the need for Test Standard modifications if either EPA or the Signatory Companies desire such modifications. Modifications to the Test Standards, if any, will be governed by 40 C.F.R. § 790.68.

C. As specified in the Test Standards in Appendices 4, 5, 6, 7, and 8, all testing required by this ECA shall be in accordance with the EPA Good Laboratory Practice (GLP) regulations found at 40 C.F.R. Part 792.

IX. SCHEDULE, STUDY PLANS, TESTING, AND REPORTS

The schedule and deliverables for the Testing Program are described below. EPA and the Signatory Companies recognize that in some instances modifications to the described schedule may be required given the uncertainties (such as weather, sampling/analytical issues, logistics, *etc.*) inherent in performing the field sampling and environmental testing contemplated by this

Testing Program. Modifications to the schedule, if any, will be made according to the procedures set out in 40 C.F.R. § 790.68.

A. Study Plan

The Signatory Companies will submit a Study Plan prepared pursuant to this ECA to EPA at least forty-five (45) days prior to the initiation of testing in accordance with 40 C.F.R. § 790.62 and no more than one hundred twenty (120) days after the effective date of the ECA. The content of the Study Plan submitted to EPA will comply with 40 C.F.R. § 790.62(b). Modifications to the study plan will be governed by the procedures of 40 C.F.R. § 790.62(c). The Study Plan will become part of the official record (docket number EPA-HQ-OPPT-2012-0209). EPA shall approve the Study Plan at the same time QAPP approval is required if it meets the requirements of this ECA and 40 C.F.R. § 790.62(b). The Study Plan shall become the "Final Study Plan" when approved by EPA.

The Signatory Companies shall submit a QAPP to EPA within one hundred eighty (180) days of the Effective Date of this ECA and at least forty-five (45) days prior to the initiation of testing. The QAPP must be prepared in accordance with EPA guidance.[1] The QAPP shall include complete information on the Test Standards to be used. If multiple commercial testing laboratories are used for different environmental media and environmental matrices tested, the QAPP will address inter-laboratory variability of D4 analyses. EPA shall approve the QAPP within 60 days of receipt of the QAPP if it meets the requirements of this ECA and is consistent with EPA guidance noted above.

B. Testing

The Testing Program shall commence (i.e., initiation of field work) after the Study Plan and QAPP have been approved by EPA. The testing program shall commence no later than sixty (60) days after the study plan and QAPP have been approved. Testing (*i.e.*, collection and analysis of all samples) shall be completed within three hundred sixty (360) days after testing commences, unless the schedule is modified, as described above and in Section X.

C. Interim Progress Reports

The Signatory Companies will submit Interim Progress Reports to EPA informing the Agency of the progress of the Testing Program. An Interim Progress Report is required one hundred eighty (180) days after the Effective Date specified in Section XXII.A of this ECA and every one hundred eighty (180) days thereafter until the Signatory Companies have fulfilled all obligations under Section VII of this ECA. Interim Progress Reports shall include a summary of work completed to date, any proposed changes in protocols or schedule, raw data (as defined in 40 C.F.R. § 792.3) and any other matters affecting progress of testing. No further reporting is required of the Signatory Companies to satisfy any potential reporting obligations that might arise under Section 8(e) of TSCA with respect solely to the data being generated under this ECA

[1] USEPA Guidance for Quality Assurance Project Plans, EPA QA/G-5, prepared by: Office of Environmental Information, EPA (December 2002) - http://www.epa.gov/quality/qs-docs/g5-final.pdf.

once the Interim Progress Reports and the Environmental Monitoring Report are submitted to the Agency in accordance with this ECA.

D. Final Report

No later than one hundred fifty (150) days following completion of the required environmental testing (*i.e.*, collection and analysis of the data), the Signatory Companies shall submit to EPA an environmental monitoring report ("Final Report"). This Final Report shall include a description of monitoring performed, summary of test results, raw data, laboratory analyses, and quality assurance/quality control information, as per 40 C.F.R. §792.185. Records shall be retained per 40 C.F.R. §792.195.

This Final Report is intended to be released to the public. If the Signatory Companies believe that any of this information should be submitted under a confidentiality claim, then a confidential version should be submitted in accordance with Section XIII of this agreement. However, in such event EPA may choose to initiate a review of the confidentiality claim in accordance with EPA confidentiality regulations at 40 C.F.R. § 2.306(d) and (e) and Sections 14(a) and 14(b) of TSCA, 15 U.S.C. § 2613(a)-(b), in order to ensure that the necessary information is made available to the public.

The Signatory Companies will document all Quality Assurance/Quality Control work done as part of the Testing Program. The Signatory Companies will electronically submit all of the raw data (as defined in 40 C.F.R. § 792.3) produced during the Testing Program.

X. MODIFICATIONS TO THE ECA

Modifications to this ECA, if any, shall be made in accordance with the modification procedures contained in 40 C.F.R. § 790.68.

Modifications to any Study Plan under this ECA shall be governed by the procedures of 40 C.F.R. § 790.62(c).

XI. FAILURE TO COMPLY WITH ECA

The Signatory Companies acknowledge that, as specified in 40 C.F.R. § 790.65, a violation of this ECA shall constitute a "prohibited act" under section 15(1) of TSCA, 15 U.S.C. § 2614(1) and shall trigger all provisions applicable to a violation of section 15. In addition, noncompliance with this ECA could result in a citizen's civil action. The Signatory Companies further acknowledge that 40 C.F.R. § 790.65 provides additional information regarding the implications of failing to comply with an enforceable consent agreement.

XII. EPA MONITORING OF ECA TESTING

EPA may conduct monitoring activities, such as laboratory inspections and/or study audits of the monitoring, sampling, and/or testing conducted under this ECA in accordance with the authority and procedures in Section 11 of TSCA, 15 U.S.C. § 2610. In the event that this monitoring contributes to delays in the completion of any activities required under this

ECA, the parties may seek modification in the scope of testing performed under the consent order or test schedule in accordance with 40 C.F.R. § 790.68.

XIII. SUBMISSIONS TO EPA AND CONFIDENTIALITY OF INFORMATION

A. All data submitted to EPA under this ECA will be identified by the Docket Number "EPA-HQ-OPPT-2012-0209" and the name "Testing Consent Order for Octamethylcyclotetrasiloxane (D4) CASRN: 556-67-2." All submissions under this ECA will be provided to EPA at the address specified in 40 C.F.R. § 790.5 in a readily downloadable electronic format.

B. Any document submitted to EPA that contains data or information for which a Signatory Company makes a claim of confidentiality shall be submitted as two separate versions. One version (the confidential business information (CBI) version) shall be complete, with the information being claimed as confidential marked in the manner described under 40 C.F.R. § 790.7. The other, public version shall be identical in all respects except that all of the information claimed as confidential shall be redacted. EPA will place only the public version in the Agency's docket. The complete version will be treated in accordance with EPA confidentiality regulations in 40 C.F.R. Part 2 and 40 C.F.R. § 790.7. Data or other information that are considered to be CBI must not be submitted electronically to EPA by e-mail. Any part or all of data or other information claimed as CBI must be so marked. If the CBI submission is on diskette or CD ROM, the outside of the diskette or CD ROM shall be marked as CBI and the specific information that is CBI shall be identified electronically within the diskette or CD ROM.

C. EPA shall not disclose information marked as CBI except in accordance with procedures set forth in 40 C.F.R. Part 2 and 40 C.F.R. § 790.7. Any claims of confidentiality for information submitted under this Testing Program shall be made under the terms of 40 C.F.R. § 790.7. Information claimed as confidential shall be treated in accordance with the procedures in 40 C.F.R. Part 2 and with Section 14 of TSCA, 15 U.S.C. § 2613. If no claim of confidentiality is made and substantiated in accordance with 40 C.F.R. § 790.7(c) by the submitter of the information at the time of submission, the information will be deemed by EPA, in accordance with 40 C.F.R. § 790.7, to be public, and may be made available to the public without further notice to the submitter.

XIV. PUBLICATION AND DISCLOSURE OF TESTING RESULTS

A. All results of testing conducted pursuant to this ECA shall be announced to the public by EPA in accordance with procedures specified in Section 4(d) of TSCA, 15 U.S.C. § 2603(d).

B. Disclosure by EPA of data generated pursuant to this ECA to the public or other government agencies shall be governed by Section 14(b) of TSCA, 15 U.S.C. § 2613(b), and 40 C.F.R. Part 2.

C. Public availability of the Final Report and other data generated pursuant to this ECA is not intended to, and does not create an ownership interest or right to use the Final Report, the underlying data or other information provided by the Signatory Companies pursuant to this ECA for commercial purposes in any entity that is not a Signatory Company.

XV. OTHER RESPONSIBILITIES OF THE SIGNATORY COMPANIES

A. The Signatory Companies are bound by the terms of this ECA and the provisions of 40 C.F.R. §§ 790.62 and 790.65.

B. The Signatory Companies shall comply with the notification requirements of Section 12(b)(1) of TSCA, 15 U.S.C. 2611(b)(1) and 40 C.F.R. Part 707, subpart D, if they export or intend to export D4. Any other person who exports or intends to export D4 is subject to the above cited export notification requirements.

C. If D4 becomes subject to a rule promulgated under TSCA Section 5(a)(2), 15 U.S.C. 2604(a)(2), governing significant new uses of D4 then the Signatory Companies will be subject to the data submission requirements imposed by section 5(b)(1)(A) of TSCA, 15 U.S.C. 2604(b)(1)(A), as if the testing under this ECA had been required by a TSCA Section 4 test rule.

XVI. RESPONSIBILITY FOR THE ACTIONS OF UNRELATED THIRD PARTIES

The Signatory Companies shall make a good faith effort to secure the cooperation of third parties (such as WWTP operators) as needed to complete the Testing Program under this ECA. However the Signatory Companies are not responsible for the actions of third parties and shall not be held liable for any inability to secure needed cooperation and/or permission to conduct the environmental testing specified under this ECA at locations owned, operated, and/or controlled by non-parties to this ECA.

XVII. FORCE MAJEURE

A Signatory Company shall not be held liable for any failure to perform its obligations under this ECA that is caused by circumstances beyond its control or the control of any entity controlled by the Signatory Company, including any contractors and subcontractors, that the Signatory Company could not have prevented through the exercise of reasonable due diligence.

XVIII. DISPUTE RESOLUTION

The Parties shall use their best efforts informally and in good faith to resolve any disputes that may arise concerning the interpretation or application of the provisions of this ECA, including those involving the Study Plan or QAPP.

XIX. SEVERABILITY OF ECA PROVISIONS

In the event that one or more provisions of this ECA is determined by a court decision to be unenforceable, the remaining provisions of this ECA will not be presumed to be valid, and EPA will either initiate a rulemaking proceeding to require testing or publish in the Federal Register its reason for not initiating such a proceeding.

XX. FINAL AGENCY ACTION

For purposes of 5 U.S.C. § 704, publication of the Federal Register notice announcing the issuance of the Order incorporating this ECA constitutes final agency action.

XXI. PUBLIC RECORD

EPA has established a public record which will contain this ECA, the Order that incorporates this ECA, the Federal Register notice announcing issuance of the Order incorporating this ECA, and any and all relevant information, subject to the confidentiality provisions of section 14(b) of TSCA, 40 C.F.R. Part 2, and 40 C.F.R. § 790.7. The official record for this ECA, including the public version, which does not include any information claimed as CBI, has been established under docket control number EPA-HQ-OPPT-2012-0209.

XXII. EFFECTIVE DATE AND TERM

A. Effective Date: This ECA takes effect on the date of publication in the Federal Register of the notice announcing the issuance of the Order that incorporates this ECA, which shall follow final approval and signature of the ECA by the Parties. This ECA may be signed in separate counterparts. This ECA will not be effective unless signed by each of the Signatory Companies and EPA. EPA will codify a reference to the substance in the Testing Program in subpart C of 40 C.F.R. Part 799.

B. Term: Obligations of the Signatory Companies under this ECA, other than record retention obligations under 40 C.F.R. § 792.195, as applicable, will cease when any one of the following occurs:

1. The Signatory Companies have provided EPA with all of the deliverables specified under this ECA.

2. A court determines that the relevant provisions of this ECA are unenforceable as described in Section XIX of this ECA and 40 C.F.R. § 790.60(a)(14).

3. Non-performance of the specific obligation is excused due to Force Majeure as described in Section XVII.

XXIII. RIGHTS OF THE SIGNATORY COMPANIES

By signing this ECA, the Signatory Companies waive their right to challenge EPA's authority to assess penalties for violations of this ECA. This waiver does not affect any other rights that the Signatory Companies may have under TSCA with respect to this ECA or to D4 testing beyond this ECA, including, but not limited to:

1. the right to contest whether a violation of this ECA has occurred,

2. the right to contest the amount of any penalty assessed for alleged violations of this ECA, and

3. the right to seek judicial review of any administrative enforcement decision pertaining to this ECA or of any EPA rule that imposes requirements to test D4.

XXIV. RESERVATION OF RIGHTS BY SIGNATORY COMPANIES

The Signatory Companies are not admitting that the requirements of Section 4 of TSCA for promulgating a test rule to generate the data and information required by this ECA have been satisfied. The Signatory Companies are also not admitting that Section 4 of TSCA provides EPA with authority to require generation of some of the data and information the Signatory Companies will provide to EPA through this ECA.

XXV. NOTICES

A. Whenever under the terms of this ECA notice is required to be given or a report or other document is required to be submitted to a Party, it shall be directed to the individuals and addresses specified below, unless otherwise specified in this ECA.

B. Any changes in the individuals or addresses referenced in Section XXV.A of this ECA shall be made by written notice to all Parties.

C. All documents submitted pursuant to this ECA shall be deemed submitted on the date of postmark or placed in the hands of a commercial courier service for overnight delivery. Hand-delivered documents are deemed submitted upon receipt at the appropriate address specified in Section XXV.A. Electronically transmitted documents are deemed submitted upon transmission.

XXVI. IDENTITY OF THE SIGNATORY COMPANIES AND PRINCIPAL TEST SPONSOR

A. The Principal Test Sponsor is the Silicones Environmental, Health and Safety Center (SEHSC), 700 2nd Street NE Washington DC 20002.

B. The Signatory Companies subject to this ECA are:

Dow Corning Corporation
Corporate Center
PO Box 994
Midland, MI 48686

Evonik Corporation
PO Box 1299
Hopewell, VA 23860

Momentive Performance Materials USA Inc.
260 Hudson River Road
Waterford, NY 12188

Shin-Etsu Silicones of America, Inc.

1150 Damar Drive
Akron, OH 44305

Wacker Chemical Corporation
3301 Sutton Road
Adrian, MI 49221

XXVII. SIGNATURES

Each undersigned representative of the Parties to this ECA certifies that he or she is fully authorized by the Party represented to enter into the terms and conditions of this ECA and to execute and legally bind that Party to it.

Date: _____ 3/28/2014

Jim Jones, Assistant Administrator, Office of Chemical Safety and Pollution Prevention
United States Environmental Protection Agency

SIGNATURES (Continued)

Date: 11 FEB 2014

Linda Kennan, Vice President, Corporate Stewardship
Dow Corning Corporation
Mail # CO1320
PO Box 994
Midland, MI 48686-0994

SIGNATURES (Continued)

Date: 2-7-14

Reinhold Brand, Senior Vice President & General Manager
Consumer Specialties North America
Evonik Corporation
PO Box 1299
Hopewell, VA 23860

Date: 7 feb 2014

Russell Mait, Director EHSQ
Consumer Specialties North America
Evonik Corporation
PO Box 1299
Hopewell, VA 23860

SIGNATURES (Continued)

Date: Feb. 24, 2014 Karen E Koster

Karen E. Koster, Executive Vice President - Environmental Safety and Health
Momentive Performance Materials USA Inc.
260 Hudson River Road
Waterford, NY 12188

SIGNATURES (Continued)

Date: Feb. 07, 2014 _____

Jun Hamuro, President/CEO
Shin-Etsu Silicones of America, Inc.
1150 Damar Drive
Akron, OH 44305

SIGNATURES (Continued)

Date: 2/7/2014 _____

Dr. Ingomar Kovar, President /CEO
Wacker Chemical Corporation
3301 Sutton Road
Adrian, MI 49221

Date: 2-7-14 _____

Thomas Degnan, Vice President Human Resources and Site Services
Wacker Chemical Corporation
3301 Sutton Road
Adrian, MI 49221

APPENDIX 1 - Environmental Testing at D4 Direct Discharge Sites

Direct discharge sites are D4 manufacturing and/or processing sites that discharge process wastewater into the environment after on-site treatment. The four (4) D4 direct discharge sites operated by Signatory Companies that directly discharge process wastewater into the environment after onsite wastewater treatment that will be monitored for D4 under this ECA are:

Dow Corning Carrollton Plant
4770 Highway 42
East Carrollton, KY 41008

MPM Silicones, LLC
Waterford Plant
260 Hudson River Road
Waterford, NY 12188

MPM Silicones, LLC
Sistersville Plant
10851 Energy Highway
Friendly, WV 26146

Wacker Adrian Plant
3301 Sutton Road
Adrian, MI 49221

A general process description of the industrial plant operations involving D4 shall be provided. A more detailed description, including a written narrative and process flow diagram(s) of the wastewater treatment system employed at the sites shall also be provided (*e.g.*, at a minimum consistent with what was provided in each facility's discharge permit application). At each of these sites, wastewater treatment effluent, receiving stream surface water, receiving stream sediment and receiving stream biota shall be sampled and analyzed for D4 in accordance with the Test Standards provided in Appendices 4, 5, 7 and 8. These appendices provide details on sampling locations, sample collection procedures, sample handling procedures and sample analysis (method detection limit and limit of quantification). Total effluent flow rate shall be recorded and reported.

Samples shall be taken during two testing events at least three (3) months apart. The exact duration between sampling events for each site shall be determined in a detailed Sampling Plan included in the Study Plan and QAPP.

Samples shall be collected during normal plant operations and during such times that effluent flow rates from the wastewater treatment system are representative of the normal plant operations.

Samples shall be taken during typical weather conditions and not until at least three (3) days after an unusual weather event such as a heavy rain storm. Samples shall be collected at a time

when the rate of D4 release is expected to be representative of the typical rate of release of D4 for that site.

A detailed Sampling Plan shall be prepared for each site and included as part of the overall Study Plan submitted to EPA. The Sampling Plans shall include (with appropriate references to Test Standards and QAPP):

- map and detailed description of testing locations
- sampling grids
- sampling timing and schedule
- sampling objectives and robust experimental design
- number and type of samples to be collected
- sampling protocols, including loss-free methods for collection, storage, and analysis of samples, and standard operating procedures
- access requirements
- site characterization for benthic invertebrate and fish sampling, including the species that are expected to be collected for analysis

The Study Plan shall address training of sample collection personnel in sampling protocols and the special handling requirements associated with D4, the qualifications of contract laboratory vendor(s), and method validation for all matrices to be sampled (*e.g.*, sediment, water, biota).

APPENDIX 2 - Environmental Testing for Indirect Discharge Sites

Indirect discharge sites are D4 processing sites (including product formulation sites) that discharge process wastewater to offsite WWTPs. Testing shall be conducted for D4 at five (5) WWTP locations receiving wastewater from D4 processors (including product formulators). The WWTP locations will be chosen based on the following criteria:

- All wastewater treatment sites selected for monitoring must be currently processing wastewater from one or more industrial sites known to be a D4 processor or formulator as documented through industrial user surveys or by other readily available information. The WWTP influent shall reasonably be expected to contain D4 based on industrial user surveys or other readily available information. The approximate relative contribution of wastewater being treated from industrial sources and wastewater treated from residential sources shall be provided for all wastewater treatment sites selected for monitoring.

- All wastewater treatment sites selected for monitoring shall use activated sludge for wastewater treatment. Sites selected may follow activated sludge treatment with secondary clarification and/or disinfection (but no other forms of additional treatment unless agreed to by EPA).

- All wastewater treatment sites selected for monitoring shall release wastewater to riverine systems, not the marine (ocean environment).

- Privately owned wastewater treatment works may be selected for monitoring provided their treatment processes are similar to publicly owned treatment works.

- Wastewater treatment sites selected for monitoring should have effluent discharge rates that are relatively large when compared to the receiving bodies flow rate (low dilution).

- Consideration should be given to geography when selecting wastewater treatment sites for testing. Ideally, the sites selected should be in different regions of the country.

The Study Plan shall detail the factors that were used to select each of the sites for testing and shall provide an explanation of why D4 is expected in the influents. A summary of each WWTP's NPDES permit (*e.g.*, location, industrial inputs, compliance issues, changes in facility structure or operation, *etc.*) as well as a summary of available data on historical (i.e., within previous 5 years) effluent conditions (*e.g.*, annual flow, dissolved oxygen, temperature, pH, suspended solids, biological oxygen demand, *etc.*) shall be included in the Study Plan.

A description of the industrial activity at the D4 processor or formulator sites that indirectly discharge to the WWTPs shall be provided for such sites controlled by signatory companies.

This information shall be requested (and reported, if obtained) from D4 processor or formulator sites that are not controlled by the signatory companies. A more detailed description, including a written narrative and process flow diagram(s), of the wastewater treatment systems employed at the WWTPs shall also be provided (*e.g.*, consistent with what was provided in each facility's discharge permit application).

Prior to including a specific location in the Study Plan, the Signatory Companies shall secure, as necessary and appropriate, a letter of cooperation/access from the person with control of the location. These letters will be included in the Study Plan.

At each of the five (5) WWTP locations, the WWTP influent, WWTP effluent, WWTP biosolids, receiving stream surface water, receiving stream sediment, and receiving stream biota shall be sampled and analyzed for D4 in accordance with the Test Standards provided in Appendices 4 - 8. These appendices provide details on sampling locations, sample collection procedures, sample handling procedures and sample analysis (method detection limit and limit of quantification).

Samples shall be taken during two testing events at least three (3) months apart. The exact duration between sampling events for each site shall be determined in a detailed Sampling Plan included in the Study Plan and QAPP.

Samples shall be collected during normal plant operations and during such times that effluent flow rates from the wastewater treatment system are representative of the normal plant operations.

Samples shall be taken during typical weather conditions and not until at least three (3) days after an unusual weather event such as a heavy rain storm. Samples shall be collected at a time when the rate of D4 release is expected to be representative of the typical rate of release of D4 for that site.

A detailed Sampling Plan shall be prepared for <u>each</u> site and included as part of the Study Plan submitted to EPA. The Sampling Plans shall include (with appropriate references to Test Standards and QAPP):

- map and detailed description of testing locations
- sampling grids
- sampling timing and schedule
- sampling objectives and robust experimental design
- number and type of samples to be collected
- sampling protocols including loss-free methods for collection, storage, and analysis of samples, standard operating procedures
- access requirements
- site characterization for benthic invertebrate and fish sampling, including the species that are expected to be collected for analysis

The Study Plan shall address the training of sample collection personnel in sampling protocols and the special handling requirements associated with D4, the qualifications of contract laboratory vendor(s), and method validation for all matrices to be sampled (*e.g.*, water, sediment, biosolids, biota).

APPENDIX 3 - Environmental Testing for Primarily Non-Industrial Wastewater Treatment Plants

This Appendix addresses D4 testing at WWTP locations that receive less than 15% of wastewater from industrial facilities, and, preferably, no wastewater from D4 manufacturing or processing (including product formulation) sites. The intent of the testing specified below is to develop a greater understanding of environmental releases of D4 emanating from the down-the-drain uses of D4 in various consumer products post-treatment by a WWTP. Testing shall be conducted for D4 at five (5) WWTPs. The WWTP locations will be chosen based on the following criteria:

- All wastewater treatment sites selected for monitoring shall use activated sludge for wastewater treatment. Sites selected may follow activated sludge treatment with secondary clarification and/or disinfection (but no other forms of additional treatment unless agreed to by EPA).

- The influent to the WWTP shall contain less than 15% of wastewater from industrial sources by volume and, preferably, no wastewater from D4 manufacturing, processing, or formulating sites, as documented through industrial user surveys or by other readily available information.

- All wastewater treatment sites selected for monitoring shall release wastewater to riverine systems, not the marine (ocean environment).

- Wastewater treatment sites selected for monitoring should have effluent discharge rates that are relatively large when compared to the receiving bodies flow rate (low dilution).

- Consideration should be given to geography when selecting wastewater treatment sites for testing. Ideally, the sites selected should be in different regions of the country.

The Study Plan shall detail the factors that were used to select each of the sites for testing. A summary of each WWTP's NPDES permit (*e.g.*, location, industrial inputs, compliance issues, changes in facility structure or operation, *etc.*) as well as a summary of publicly available data on historical (i.e., within previous 5 years) effluent conditions (*e.g.*, annual flow, dissolved oxygen, temperature, pH, suspended solids, biological oxygen demand, *etc.*) shall be included in the Study Plan.

A detailed description, including a written narrative and process flow diagram(s) of the wastewater treatment systems employed at the WWTPs shall be provided (*e.g.*, consistent with what was provided in each facility's discharge permit application).

Prior to including a specific location in the Study Plan, the Signatory Companies shall secure, as necessary and appropriate, a letter of cooperation/access from the person with control of the location. These letters will be included in the Study Plan.

At each of the five (5) WWTP locations, the WWTP influent, WWTP effluent, WWTP biosolids, receiving stream surface water, receiving stream sediment, and receiving stream biota shall be sampled and analyzed for D4 in accordance with the Test Standards provided in Appendices 4 - 8. These appendices provide details on sampling locations, sample collection procedures, sample handling procedures and sample analysis (method detection limit and limit of quantification).

Samples shall be taken during two testing events at least three (3) months apart. The exact duration between sampling events for each site shall be determined in a detailed Sampling Plan included in the Study Plan and QAPP.

Samples shall be collected during normal plant operations and during such times that effluent flow rates from the wastewater treatment system are representative of the normal plant operations.

Samples shall be taken during typical weather conditions and not until at least three (3) days after an unusual weather event such as a heavy rain storm. Samples shall be collected at a time when the rate of D4 release is expected to be representative of the typical rate of release of D4 for that site.

A detailed Sampling Plan shall be prepared for <u>each</u> site and included as part of the Study Plan submitted to EPA. The Sampling Plans shall include (with appropriate reference to Test Standards and QAPP):

- map and detailed description of testing locations
- sampling grids
- sampling timing and schedule
- sampling objectives and robust experimental design
- number and type of samples to be collected
- sampling protocols, including loss-free methods for collection, storage, and analysis of samples, standard operating procedures
- access requirements
- site characterization for benthic invertebrate and fish sampling, including the species that are expected to be collected for analysis

The Study Plan shall address training of sample collection personnel in sampling protocols and the special handling requirements associated with D4, the qualifications of contract laboratory vendor(s), and method validation for all matrices to be sampled (*e.g.*, water, sediment, biosolids, biota).

APPENDIX 4 - Testing Standard for the Collection, Sample Handling, Transfer and Analysis of Influent and Effluent Samples for D4

Synopsis:

This testing standard provides guidelines for the collection and analysis of environmental samples for D4 in support of a Testing Program detailed in this ECA. This standard cites the requirements for the sampling of influent and effluent as described in Section VII of the ECA and Appendices 1, 2, and 3, and identifies specific guidelines and references that will be used in the preparation of site-specific Sampling Plans for the collection/analysis of influent and effluent samples, which will be included in a Study Plan and QAPP for the Testing Program. This standard addresses:

1. When to collect influent and effluent samples
2. Where to collect influent and effluent samples
3. Special considerations during sample collection to avoid sample contamination
4. How to collect and process influent and effluent samples
5. How to analyze influent and effluent samples for D4 and the appropriate method detection limit and limit of quantification

Requirements for sampling influents and effluents:

Appendices 1 – 3 of this ECA state that:

> "Samples shall be taken during two testing events at least three (3) months apart. The exact duration between sampling events for each site shall be determined in a detailed Sampling Plan included in the Study Plan and QAPP."
>
> "Samples shall be collected during normal plant operations and during such times that effluent flow rates from the wastewater treatment system are representative of the normal plant operations."
>
> "Samples shall be taken during typical weather conditions and not until at least three (3) days after an unusual weather event such as a heavy rain storm. Samples shall be collected at a time when the rate of D4 release is expected to be representative of the typical rate of release of D4 for that site."

Establishment of the appropriate time for sampling events:

At each site, two sampling events will be undertaken that are scheduled to be a minimum of three months apart and during normal plant operations and weather conditions. Normal operating conditions will be established by consulting with the operator of each WWTP, indirect and direct discharge facility. The criteria or means that are used by the facilities to determine normal operating conditions will be documented in the site-specific Sampling Plans. Confirmation will be obtained that the subject facility is operating under normal conditions prior to commencing sampling at a given location. In addition, sampling would not take place

within three (3) days of unusual weather events. The date and time of the most recent precipitation occurrence for each sampling event will be recorded.

Establishment of the location for influent sample collection:

For the sites where influent is to be tested, influent samples should be collected at the headworks of the WWTP. The exact location for collection of an influent sample will be facility-specific and specified in the WWTP's discharge permit. Each site-specific Sampling Plan shall include a basis for determining the appropriate sampling location.

Establishment of the location for effluent sample collection:

At each site, effluent samples shall be collected at the regulated compliance point per the WWTP's discharge permit. Each site-specific Sampling Plan shall include a complete description of the effluent discharge portions of the WWTP, including the established sampling location.

Special considerations for the sampling and handling of influent and effluent samples for D4:

Cyclic volatile methyl siloxane (cVMS) materials, such as D4, are widely used in consumer products and may be present in personal care products, commercial products, and lubricants, and may be components of antifoams widely used in WWTPs. If these products are used by individuals during any part of the preparation for or during any aspect of the field sampling event or laboratory analysis sample contamination by D4 volatilizing from the user could occur. To avoid the significant potential for sample contamination during collection, processing, storage, and analysis for D4 in environmental matrices, preventative measures should be implemented to the extent possible in the field. For example, field and laboratory personnel shall be required to refrain from using any personal care products that may contain any cVMS materials (e.g., sun-block, sun-screen, hand lotion, antiperspirants, etc.) while preparing for or conducting any field activities to minimize the possibility for contamination with D4. Specific requirements for collecting and handling influent and effluent samples aimed at preventing sample contamination by sources of D4 that are not specific to the WWTP or direct discharge site shall be specified in the Study Plan and QAPP.

Collection of influent and effluent samples for analysis of D4:

The exact method for collection of influent and effluent samples is a site-specific determination primarily dependent on the accessibility and configuration of the headworks of the WWTP for influent sampling and the compliance point for effluent sampling. Influent and effluent samples will be collected as grab samples and not composite samples due the expected high degree of volatilization of D4 from aqueous samples. For each site, procedures for collecting grab samples of influent and effluent will be based on USEPA 2013 (Wastewater Sampling, Section 4, Sample Types and Section 6, Manual Sampling, pp. 14-15, 20), USEPA 2004 (NPDES Compliance Inspection Manual, Section 5B, Sampling Procedures and Techniques, pp. 5-3 to 5-7), Knoerr 2013 (Sample Collection section), and APHA 1999 (Part 1060 Collection and

Preservation of Samples, pp.48-62) if appropriate given the site-specific circumstances. This guidance identifies the factors involved in determination of the most appropriate sampling methods for influents and effluents. The exact collection methods for influent and effluent samples will be detailed in the Study Plan and QAPP.

Specific requirements for sample container preparation, sample handling, sample preservation, shipping and storage of samples should be essentially the same across all sites. Immediately prior to each sampling event at each site, the laboratory that will analyze the samples shall prepare clean (new, never used) glass sample containers in sufficient numbers for all influent and effluent samples to be analyzed for D4, for all quality assurance samples, and for retain samples. The sample containers will be prepared by pre-washing with hexane, adding low density polyethylene (LDPE) sorbent into the containers, providing polytetrafluoroethylene (PTFE) tape to assist in sealing the containers (as described in Knoerr 2013, Sample Collection section), as well as providing labels. The laboratory will ship all sample containers with adequate packing materials in coolers to each site. The coolers will also contain chain-of-custody forms that will accompany the sample containers from the laboratory to the field and back to the laboratory.

Figure 1 provides a schematic that describes the quality assurance and D4 study samples to be taken at each influent and effluent sampling location on the day of sampling at a given site. At each influent and effluent location seven grab samples (two quality assurance samples and five D4 study samples) will be taken. Influent and effluent flow rates shall be recorded at the time of sampling and reported.

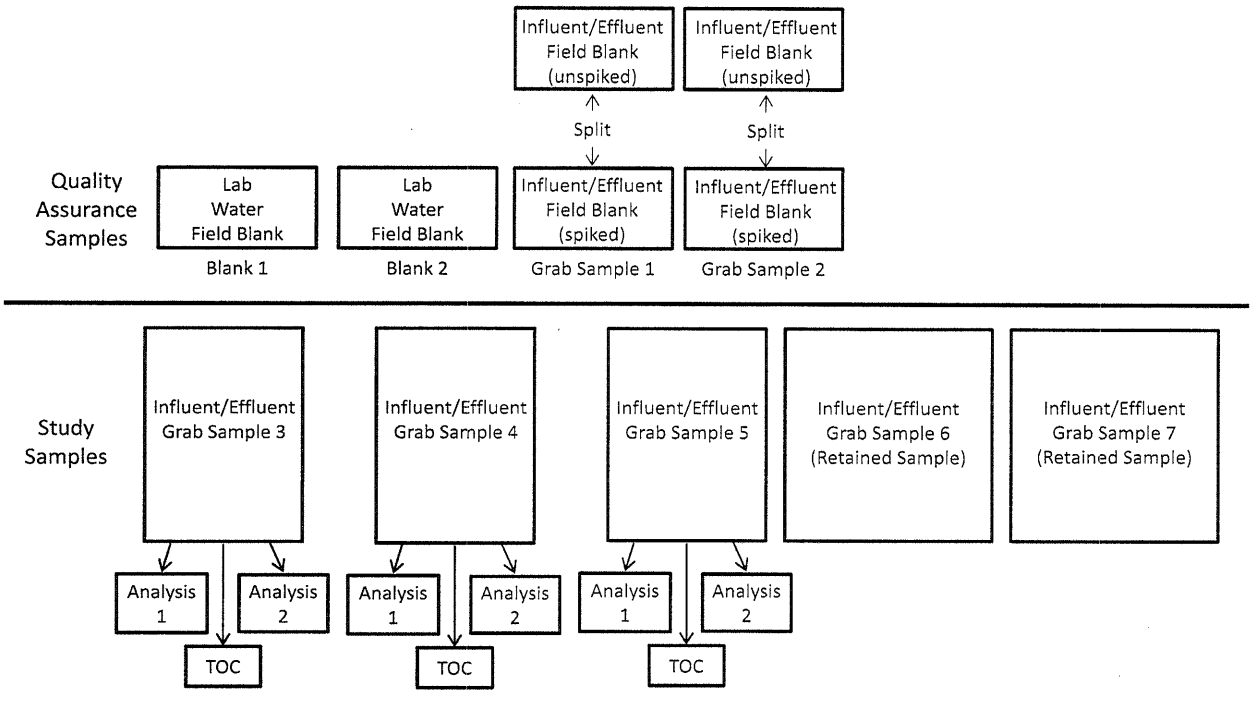

Figure 1. Schematic diagram of samples taken while monitoring for D4 in influent and effluent at wastewater treatment plants.

Grab samples 3, 4 and 5 will be divided to provide two duplicates for analysis of D4. The duplicate samples shall be processed and analyzed as individual samples for D4. Duplicate samples are used to evaluate between-sample variability and precision. Additionally, an aliquot of each of the three samples will be used for Total Organic Carbon (TOC) analysis. The TOC analyses shall follow procedures equivalent to APHA 1999 Part 5310, Total Organic Carbon (TOC). While this guidance (APHA 1999) provides several methods that could be used for the analysis of TOC, the exact method and instrumentation that will be used will be determined by the analytical laboratory that will conduct the analyses and documented in the Study Plan and QAPP. Grab samples 6 and 7 will serve as retain samples. These retain samples would be analyzed if a primary sample container arrives broken at the laboratory, but otherwise would be retained in a refrigerator for later analysis if a sample becomes compromised during collection or processing. The retain samples will be kept until Quality Assurance has been verified and may be analyzed for D4 as necessary.

In addition to the study samples used to determine D4 concentrations in influent and effluent, several samples will be analyzed for quality assurance purposes. Grab samples 1 and 2 will serve as field blank/field spike samples. The field blank/field spike samples will be split into two parts. One part will be analyzed for D4 as is (field blank) and the second part will be spiked with a known amount of D4 and then analyzed (field spike). The field blank/field spike samples will be used to evaluate contamination bias resulting from sample collection, processing, transport, storage and analysis. During each influent and effluent sampling event at a given site, two laboratory blanks will also be prepared. The two laboratory blanks shall be created from two samples of laboratory-grade water having concentrations of D4 below the Limit of Quantification (LOQ) and shall be taken into the field and processed like an influent or effluent sample. The laboratory blanks will be used to evaluate contamination bias resulting from collection, processing, transport, storage, and analysis of samples. Specific requirements for preparation, processing, and analysis of the quality assurance samples shall be detailed in the Study Plan and the QAPP.

Sealed sample containers will be packed into coolers with blue-ice or water ice, and taken back to the laboratory or shipped back to the laboratory using an overnight express shipping company. All sample collection methods and sample handling procedures will be detailed in the Study Plan and QAPP.

Analysis of influent and effluent samples for D4:

All influent and effluent samples and accompanying quality assurance samples shall be analyzed for D4 at one commercial testing laboratory that has appropriate expertise with the D4 analyses to be conducted when the analysis occurs, unless there are unforeseen circumstances such as lack of laboratory availability as noted in 40 C.F.R. § 790.68(b)(2)(iii). The commercial laboratory will validate a method for the analysis of D4 in the influent and effluent samples that shall be adapted from the analytical method specified in Knoerr (2013). The Knoerr (2013) analytical method utilizes pieces of LDPE film to act as a sorbent and partial barrier to prevent loss of analyte to the headspace of the sample container. Immediately after collection, a water sample is placed into a container containing pieces of LDPE, which adsorbs

the D4. In the laboratory, the water sample and the LDPE sorbent are solvent extracted and processed for analysis with GC-MS.

The Method Detection Limit (MDL) is the concentration of a constituent in a sample, that when processed through the complete analytical method, can be measured and reported with 99% probability that it is greater than 0 or statistically different from a blank. The MDL is a measure of a method's ability to quantify a constituent in a sample matrix. During method development, the Knoerr (2013) analytical method for D4 achieved a matrix-specific MDL of 0.037 μg/L which shall be achieved for influent and effluent testing. The specific level of detection shall be based on the LOQ which shall be 3 times the MDL. EPA recognizes that a laboratory may have difficulties achieving the specified MDL. In this event, the signatory companies shall seek a modification as per 40 C.F.R. § 790.68.

Compliance with Good Laboratory Practice Requirements:

All field work related specifically to the collection, handling, and transfer of influent and effluent samples should be conducted in accordance with USEPA's GLP regulations (see 40 C.F.R. Part 792). All analytical work, including analysis of D4 and TOC, shall be conducted in accordance with USEPA's GLP regulations (see 40 C.F.R. Part 792). The QAPP shall be prepared according to USEPA guidance (USEPA 2002).

REFERENCES

USEPA 2013. Wastewater Sampling, Section 4 Sample Types, Section 6 Manual Sampling. Operating Procedure No. SESDPROC-306-R3. US Environmental Protection Agency, Region 4. February, 2013.

USEPA 2004. NPDES Compliance Inspection Manual, Section 5B, Sampling Procedures and Techniques . EPA 305-X-04-001, US Environmental Protection Agency, July, 2004.

Knoerr SM. 2013. NON REGULATED STUDY: Development of Collection, Storage and Analysis Procedures for the Quantification of D4, D5, and D6 in Waste Water Treatment Plant Effluent and Surface Water Samples. Dow Corning Corporation, HES Study No. 11936-108, April 18, 2013.

APHA 1999. Standard Methods for the Examination of Water and Wastewater, Part 1060, Collection and Preservation of Samples. American Public Health Association, American Water Works Association, Water Environment Federation.

APHA 1999. Standard Methods for the Examination of Water and Wastewater, Part 5310 C. Total Organic Carbon (TOC). American Public Health Association, American Water Works Association, Water Environment Federation. Public Health Association, American Water Works Association, Water Environment Federation.

USEPA 2002 Guidance for Quality Assurance Project Plans, EPA QA/G-5, prepared by: Office of Environmental Information, EPA (December 2002) - http://www.epa.gov/quality/qs-docs/g5-final.pdf.

APPENDIX 5 - Testing Standard for the Collection, Sample Handling, Transfer and Analysis of Surface Water Samples for D4

Synopsis:

This testing standard provides guidelines for the collection and analysis of environmental samples for D4 in support of a Testing Program detailed in this ECA. This standard cites the requirements for the sampling of surface water as described in Section VII of the ECA and Appendices 1, 2, and 3, and identifies specific guidelines and references that will be used in the preparation of site-specific Sampling Plans for the collection/analysis of surface water samples, which will be included in a Study Plan for the Testing Program. This standard addresses:

1. When to collect surface water samples
2. Where to collect surface water samples
3. Special considerations during sample collection to avoid sample contamination
4. How to collect and process surface water samples
5. How to analyze surface water samples for D4 and the appropriate method detection limit and limit of quantification (LOQ)

Requirements for sampling surface (receiving) waters:

Appendices 1 – 3 of this ECA state that:

> "Samples shall be taken during two testing events at least three (3) months apart. The exact duration between sampling events for each site shall be determined in a detailed Sampling Plan included in the Study Plan and QAPP."
>
> "Samples shall be collected during normal plant operations and during such times that effluent flow rates from the wastewater treatment system are representative of the normal plant operations."
>
> "Samples shall be taken during typical weather conditions and not until at least three (3) days after an unusual weather event such as a heavy rain storm. Samples shall be collected at a time when the rate of D4 release is expected to be representative of the typical rate of release of D4 for that site."

Establishment of the appropriate time for sampling events:

At each site, two sampling events will be undertaken that are scheduled to be a minimum of three months apart and during normal plant operations and weather conditions. Normal operating conditions will be established by consulting with the operator of each WWTP, indirect and direct discharge facility. The criteria or means that are used by the facilities to determine normal operating conditions will be documented in the site-specific Sampling Plans. Confirmation will be obtained that the subject facility is operating under normal conditions

prior to commencing sampling at a given location. In addition, sampling would not take place within three (3) days of unusual weather events. The date and time of the most recent precipitation occurrence for each sampling event will be recorded.

Establishment of the location for surface water sample collection:

At each site, surface water samples should be collected at approximately the same location and roughly the same time as benthic organisms are collected which is described in Appendix 8

Special considerations for the sampling and handling of water samples for D4:

cVMS materials, such as D4, are widely used in consumer products and may be present in personal care products, commercial products, and lubricants, and may be components of antifoams widely used in WWTPs. If these products are used by individuals during any part of the preparation for or during any aspect of the field sampling event or laboratory analysis, sample contamination by D4 volatilizing from the user could occur. To avoid the potential for sample contamination during collection, processing, storage, and analysis for D4 in environmental matrices, preventative measures should be implemented to the extent possible in the field. For example, field and laboratory personnel shall be required to refrain from using any personal care products that may contain any cVMS materials (e.g., sun-block, sun-screen, hand lotion, antiperspirant, etc.) while preparing for or conducting any field activities to minimize the possibility for contamination with D4. Specific requirements for collecting and handling surface water samples aimed at preventing sample contamination by sources of D4 that are not specific to the WWTP or direct discharge site shall be specified in the Study Plan.

Collection of surface water samples for analysis of D4:

The exact method for collection of surface water samples is a site-specific determination. During preparation of the site-specific Sampling Plans, the physical nature (e.g., width, depth, flow) of the receiving water will be determined and used to guide the selection of the appropriate method of sample collection. For each site, collection procedures for surface water samples shall be based, as appropriate to the characteristics of the receiving water, on USEPA 1994 (SOP #2013, Section 7.3 Sample Collection, pp. 3-4) (USEPA 1994). This guidance identifies the several main types of collection devices that are used to collect aqueous samples. The exact collection method for surface water samples will be detailed in the Study Plan and QAPP.

Specific requirements for sample container preparation, sample handling, sample preservation, shipping and storage of samples should be essentially the same across all sites. Immediately prior to each sampling event at each site, the laboratory that will analyze the samples shall prepare clean (new, never used) glass sample containers in sufficient numbers for all surface water samples to be analyzed for D4, for all quality assurance samples, and for retain samples. The sample containers will be prepared by pre-washing with hexane, adding LDPE sorbent into the containers and providing PTFE tape to assist in sealing the containers (as described in Knoerr 2013, Sample Collection section), as well as providing labels. The laboratory will ship all sample containers with adequate packing materials in coolers to each site. The coolers will

also contain chain-of-custody forms that will accompany the sample containers from the laboratory to the field and back to the laboratory.

Figure 2 provides a schematic that describes the quality assurance and D4 study samples to be taken at each surface water sampling location on the day of sampling at a given site. At each surface water location seven grab samples (two quality assurance samples and five D4 study samples) will be taken.

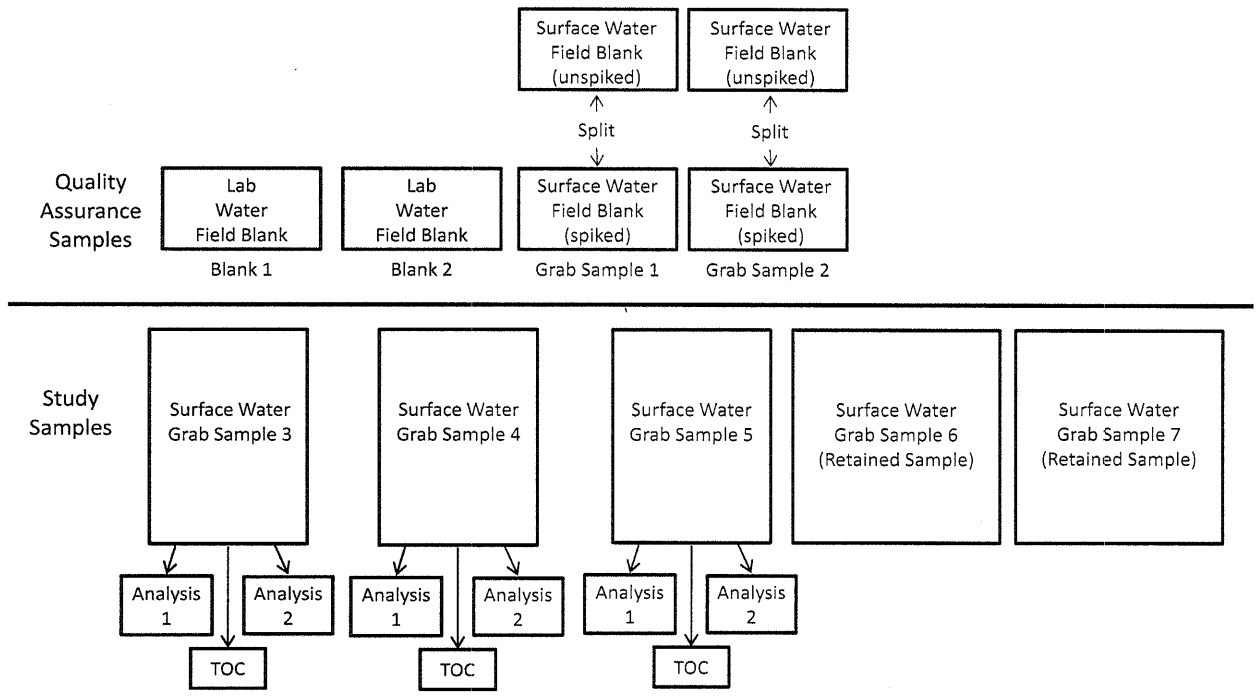

Figure 2. Schematic diagram of samples taken while monitoring for D4 in surface water near wastewater treatment plants.

Grab samples 3, 4 and 5 will be divided to provide two duplicates for analysis of D4. The duplicate samples shall be processed and analyzed as individual samples for D4. Duplicate samples are used to evaluate between-sample variability and precision. Additionally, an aliquot of each of the three samples will be used for TOC analysis. The TOC analyses shall follow procedures equivalent to APHA 1999 Part 5310, Total Organic Carbon (TOC). While this guidance (APHA 1999) provides several methods that could be used for the analysis of TOC, the exact method and instrumentation that will be used will be determined by the analytical laboratory that will conduct the analyses and documented in the Study Plan and QAPP. Grab samples 6 and 7 will serve as retain samples. These retain samples would be analyzed if a primary sample container arrives broken at the laboratory, but otherwise would be retained in a refrigerator for later analysis if a sample becomes compromised during collection or processing. The retain samples will be kept until Quality Assurance has been verified and may be analyzed for D4 as necessary.

In addition to the study samples used to determine D4 concentrations in surface water, several samples will be analyzed for quality assurance purposes. Grab samples 1 and 2 will serve as field

blank/field spike samples. The field blank/field spike samples will be split into two parts. One part will be analyzed for D4 as is (field blank) and the second part will be spiked with a known amount of D4 and then analyzed (field spike). The field blank/field spike samples will be used to evaluate contamination bias resulting from sample collection, processing, transport, storage and analysis. During each surface water sampling event at a given site, two laboratory blanks will also be prepared. The two laboratory blanks shall be created from two samples of laboratory-grade water having concentrations of D4 below the LOQ and shall be taken into the field and processed like a surface water sample. The laboratory blanks will be used to evaluate contamination bias resulting from collection, processing, transport, storage, and analysis of samples. Specific requirements for preparation, processing, and analysis of the quality assurance samples shall be detailed in the Study Plan and the QAPP.

Sealed sample containers will be packed into coolers with blue-ice or water ice, and taken back to the laboratory or shipped back to the laboratory using an overnight express shipping company. All sample collection methods and sample handling procedures will be detailed in the Study Plan and QAPP.

Analysis of surface water samples for D4:

All surface water samples and accompanying quality assurance samples shall be analyzed for D4 at one commercial testing laboratory that has appropriate expertise with the D4 analyses to be conducted when the analysis occurs, unless there are unforeseen circumstances such as lack of laboratory availability as noted in 40 C.F.R. § 790.68(b)(2)(iii). The commercial laboratory will validate a method for the analysis of D4 in the surface water samples that shall be adapted from the analytical method specified in Knoerr (2013). The Knoerr (2013) analytical method utilizes pieces of LDPE film to act as a sorbent and partial barrier to prevent loss of analyte to the headspace of the sample container. Immediately after collection, a water sample is poured into a container containing pieces of LDPE, which adsorbs the D4. In the laboratory, the water sample and the LDPE sorbent are solvent extracted and processed for analysis with GC-MS.

The MDL is the concentration of a constituent in a sample, that when processed through the complete analytical method, can be measured and reported with 99% probability that it is greater than 0 or statistically different from a blank. The MDL is a measure of a method's ability to quantify a constituent in a sample matrix. During method development, the Knoerr (2013) analytical method for D4 achieved a matrix-specific MDL of 0.037 μg/L and which shall be achieved for surface water testing. The specific level of detection shall be based on the LOQ which shall be 3 times the MDL. EPA recognizes that a laboratory may have difficulties achieving the specified MDL. In this event, the signatory companies shall seek a modification as per 40 C.F.R. § 790.68.

Compliance with Good Laboratory Practice Requirements:

All field work related specifically to the collection, handling, and transfer of surface water samples should be conducted in accordance with USEPA's GLP regulations (see 40 C.F.R. Part 792). All analytical work, including analysis of D4 and TOC, shall be conducted in

accordance with USEPA's GLP regulations (see 40 C.F.R. Part 792). The QAPP shall be prepared according to USEPA guidance (USEPA 2002).

REFERENCES

USEPA 2006. Compilation of EPA Mixing Zone Documents, Modeling Documents, pp. 9-13. EPA 823-R-06-003, July, 2006.

USEPA 1994. Surface Water Sampling, Section 7.3 Sample Collection. U.S. Environmental Protection Agency, SOP#: 2013, 11/17/94, REV. #: 0.0

Knoerr SM, Durham JA. 2013. NON REGULATED STUDY: Development of Collection, Storage and Analysis Procedures for the Quantification of D4, D5, and D6 in Waste Water Treatment Plant Effluent and Surface Water Samples. Dow Corning Corporation, HES Study No. 11936-108, April 18, 2013.

APHA 1999. Standard Methods for the Examination of Water and Wastewater, Part 5310 C. Total Organic Carbon (TOC). American Public Health Association, American Water Works Association, Water Environment Federation.

USEPA 2002. Guidance for Quality Assurance Project Plans, EPA QA/G-5, prepared by: Office of Environmental Information, EPA - http://www.epa.gov/quality/qs-docs/g5-final.pdf.

APPENDIX 6 - Testing Standard for the Collection, Sample Handling, Transfer and Analysis of Biosolids Samples for D4

Synopsis:

This testing standard provides guidelines for the collection and analysis of environmental samples for D4 in support of a Testing Program detailed in this ECA. This standard cites the requirements for the sampling of biosolids as described in Section VII of the ECA and Appendices 2 and 3 and identifies specific guidelines and references that will be used in the preparation of site-specific Sampling Plans for the collection/analysis of biosolids samples, which will be included in a Study Plan and QAPP for the Testing Program. The standard addresses:

1. When to collect biosolids samples
2. Where to collect biosolids samples
3. Special considerations during sample collection to avoid sample contamination
4. How to collect and process biosolids samples
5. How to analyze biosolids samples for D4 and the appropriate method detection limit and limit of quantification

Requirements for sampling biosolids:

Appendices 1-3 of this ECA state that:

> "Samples shall be taken during two testing events at least three (3) months apart. The exact duration between sampling events for each site shall be determined in a detailed Sampling Plan included in the Study Plan and QAPP."
>
> "Samples shall be collected during normal plant operations and during such times that effluent flow rates from the wastewater treatment system are representative of the normal plant operations."
>
> "Samples shall be taken during typical weather conditions and not until at least three (3) days after an unusual weather event such as a heavy rain storm. Samples shall be collected at a time when the rate of D4 release is expected to be representative of the typical rate of release of D4 for that site."

Establishment of the appropriate time for sampling events:

At each site, two sampling events will be undertaken that are scheduled to be a minimum of three months apart and during normal plant operations and weather conditions. Normal operating conditions will be established by consulting with the operator of each WWTP to be tested. The criteria or means that are used by the facilities to determine normal operating conditions will be documented in the site-specific Sampling Plans. Confirmation will be obtained that the subject facility is operating under normal conditions prior to commencing

sampling at a given location. In addition, sampling would not take place within three (3) days of unusual weather events.

Establishment of the location for biosolids sample collection:

At each site, the chosen location for collection of biosolids samples shall be immediately after dewatering before onsite storage, as practicable, and shall be established in the site specific Sampling Plans.

Special considerations for the sampling and handling of biosolids samples for D4:

cVMS materials, such as D4, are widely used in consumer products and may be present in personal care products, commercial products, and lubricants, and may be components of antifoams widely used in WWTPs. If these products are used by individuals during any part of the preparation for or during any aspect of the field sampling event or laboratory analysis, sample contamination by D4 volatilizing from the user could occur. To avoid the potential for sample contamination during collection, processing, storage, and analysis for D4 in environmental matrices, preventative measures should be implemented to the extent possible in the field. For example, field and laboratory personnel shall be required to refrain from using any personal care products that may contain cVMS materials (e.g., sun-block, sun-screen, hand lotion, antiperspirants, etc.) while preparing for or conducting any field activities to minimize the possibility for contamination with D4. Specific requirements for collecting and handling biosolids samples aimed at preventing sample contamination by sources of D4 that are not specific to the WWTP shall be specified in the Study Plan and QAPP.

Collection of biosolids samples for analysis of D4:

The exact method for collection of biosolids samples is a site-specific determination. During preparation of the site-specific Sampling Plans, the general consistency of the biosolids will be established. The consistency of the biosolids will guide the methods used for sampling. For each site, collection procedures for biosolids samples shall be based, as appropriate to the characteristics of the biosolids, on techniques described in USEPA 1989 (Section 2.2 Sample Point Selection and Section 2.3 Sample Collection, pp. 2-4 to 2-14). The guidance identifies sample collection devices and techniques for collection of subsamples that will make up composite samples. The exact collection method for biosolids samples will be detailed in the Study Plan and QAPP.

Specific requirements for sample container preparation, sample handling, sample preservation, shipping and storage of samples should be essentially the same across all sites. Immediately prior to each sampling event at each site, the laboratory that will analyze the samples shall prepare clean (new, never used) pre-weighed glass sample containers in sufficient numbers for all biosolids samples to be analyzed for D4, for all quality assurance samples, and for retain samples. The sample containers will be prepared by pre-washing with hexane, providing PTFE tape to assist in sealing the containers, as well as providing labels. The laboratory will ship all sample containers with adequate packing materials in coolers to each site. The coolers will also

contain chain-of-custody forms that will accompany the sample containers from the laboratory to the field and back to the laboratory.

Figure 3 provides a schematic that describes the quality assurance and D4 study samples to be taken at each biosolids sampling location on the day of sampling at a given site. At each biosolids location, seven composited biosolids samples (two quality assurance samples and five D4 study samples) will be taken. During each sampling event for biosolids at a given site, all quality assurance samples and D4 samples will be prepared as described in Powell and Woodburn (2009).

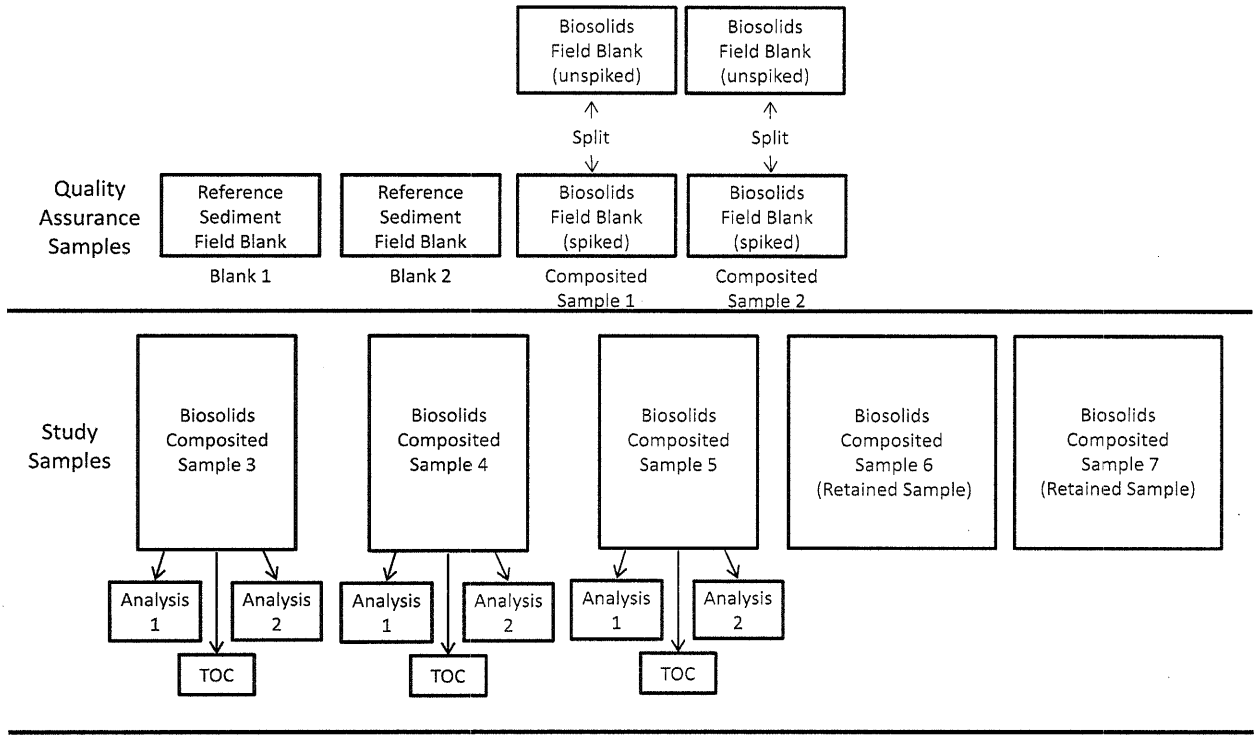

Figure 3. Schematic diagram of samples taken while monitoring for D4 in biosolids near wastewater treatment plants.

Composited biosolids samples 3, 4 and 5 will be divided to provide two duplicates for analysis of D4. The duplicate samples shall be processed and analyzed as individual samples for D4. Duplicate samples are used to evaluate between-sample variability and precision. In addition, a separate aliquot shall be taken from each of the three biosolids samples and separately stored for analysis of total organic carbon and water content. Following the general procedures of Powell 2010, the additional aliquots shall be analyzed by carbon coulometry or an equivalent method for total carbon, total inorganic carbon, and total organic carbon, and loss-on-ignition for total water content and total organic matter content. Composited biosolids samples 6 and 7 will serve as retain samples. These retain samples would be analyzed if a primary sample container arrives at the laboratory compromised or broken, but otherwise would be retained in a refrigerator for later analysis if a sample becomes compromised during collection or processing. The retain samples will be kept until Quality Assurance has been verified and may be analyzed for D4 as necessary.

In addition to the study samples used to determine D4 concentrations in biosolids, several samples will be analyzed for quality assurance purposes. Composited biosolids samples 1 and 2 shall be split, one half of each sample shall be spiked in the field with a known amount of D4. The field spiked biosolids samples will be used to evaluate loss of D4 during collection, processing, transport, storage, and analysis of samples, and to evaluate analytical bias. Two reference sediment samples having concentrations of D4 below the LOQ for this matrix shall be taken into the field and processed like biosolids samples. Reference sediment will be used because of the expectation that any WWTP biosolids may contain D4. The reference sediment samples will be used to evaluate contamination bias resulting from collection, processing, transport, storage, and analysis of samples. Specific requirements for preparation, processing, and analysis of the quality assurance samples shall be detailed in the Study Plan and the QAPP.

Sealed sample containers will be packed into coolers with blue-ice or water ice, and taken back to the laboratory or shipped back to the laboratory using an overnight express shipping company. All sample collection methods and sample handling procedures will be detailed in the Study Plan and QAPP.

Analysis of Biosolids Samples for D4:

All biosolids samples and accompanying quality assurance samples shall be analyzed for D4 at one commercial testing laboratory that has appropriate expertise with the D4 analyses to be conducted when the analysis occurs, unless there are unforeseen circumstances such as lack of laboratory availability as noted in 40 C.F.R. § 790.68(b)(2)(iii). The commercial laboratory will validate a method for the analysis of D4 in the biosolids samples that shall be adapted from the analytical method used in Powell (2010)

The MDL is the concentration of a constituent in a sample, that when processed through the complete analytical method, can be measured and reported with 99% probability that it is greater than 0 or statistically different from a blank. The MDL is a measure of a method's ability to quantify a constituent in a sample matrix. Powell (2010) determined an MDL up to 3.7 ng/g (wet weight, ww) for sediment which shall be applied for biosolids. The specific level of detection shall be based on the LOQ which shall be 3 times the MDL. All measurements of D4 concentration in biosolids shall include sufficient information to perform a wet weight to dry weight conversion and shall report concentrations in terms of dry weight. EPA recognizes that a laboratory may have difficulties achieving the specified MDL. In this event, the signatory companies shall seek a modification as per 40 C.F.R. § 790.68.

Compliance with Good Laboratory Practice Requirements:

All field work related to the collection, handling, and transfer of biosolids samples should be conducted in accordance with USEPA's GLP regulations (see 40 C.F.R. Part 792). All analytical work, including analysis of D4 and TOC, shall be conducted in accordance with USEPA's GLP regulations (see 40 C.F.R. Part 792). The QAPP shall be prepared according to USEPA guidance (US EPA 2002).

REFERENCES

US EPA (1989): WWTP Sludge Sampling and Analysis Guidance Document, Section 2.2 Sample Point Selection and Section 2.3 Sample Collection. EPA 833-B-89-100, August, 1989.

Powell, D.E. 2010. Bioaccumulation and Trophic Transfer of Cyclic Volatile Methylsiloxane (cVMS) Materials in the Aquatic Marine Food Webs of the Inner and Outer Oslofjord, Norway. HES Study No: 11060-108. Health and Environmental Sciences, Dow Corning Corporation, Auburn, MI.

Powell DE, Woodburn KB. 2009. Trophic Dilution of Cyclic Volatile Methylsiloxane (cVMS) Materials in a Temperate Freshwater Lake. Dow Corning Corporation, HES Study No. 10771-108.

USEPA 2002. Guidance for Quality Assurance Project Plans, EPA QA/G-5, prepared by: Office of Environmental Information, EPA (December 2002) - http://www.epa.gov/quality/qs-docs/g5-final.pdf.

APPENDIX 7 - Testing Standard for the Collection, Sample Handling, Transfer and Analysis of Sediment Samples for D4

Synopsis:

This testing standard provides direction for the collection and analysis of environmental samples for D4 in support of a Testing Program detailed in this ECA. This standard cites the requirements for the sampling of sediment as described in Section VII of the ECA and Appendices 1, 2, and 3, and identifies specific guidelines and references that will be used in the preparation of site-specific Sampling Plans for the collection/analysis of sediment samples, which will be included in a Study Plan and QAPP for the Testing Program. The standard addresses:

1. When to collect sediment samples
2. Where to collect sediment samples
3. Special considerations during sample collection to avoid sample contamination
4. How to collect and process sediment samples
5. How to analyze sediment samples for D4 and the appropriate method detection limit and limit of quantification

Requirements for sampling sediments:

Appendices 1 -3 of this ECA state that:

> "Samples shall be taken during two testing events at least three (3) months apart. The exact duration between sampling events for each site shall be determined in a detailed Sampling Plan included in the Study Plan and QAPP."
>
> "Samples shall be collected during normal plant operations and during such times that effluent flow rates from the wastewater treatment system are representative of the normal plant operations."
>
> "Samples shall be taken during typical weather conditions and not until at least three (3) days after an unusual weather event such as a heavy rain storm. Samples shall be collected at a time when the rate of D4 release is expected to be representative of the typical rate of release of D4 for that site."

Establishment of the appropriate time for sampling events:

At each site, two sampling events will be undertaken that are scheduled to be a minimum of three months apart and during normal plant operations and weather conditions. Normal operating conditions will be established by consulting with the operator of each WWTP, indirect discharge facility and direct discharge facility. The criteria or means that are used by the facilities to determine normal operating conditions will be documented in the site-specific Sampling Plans. Confirmation will be obtained that the subject facility is operating under

normal conditions prior to commencing sampling at a given location. In addition, sampling would not take place within three (3) days of unusual weather events.

Establishment of the location for sediment sample collection:

At each site, sediment samples from the receiving water body shall be collected at approximately the same location where benthic organisms are collected for D4 analysis as described in Appendix 8.

Special considerations for the sampling and handling of sediment samples for D4:

cVMS materials, such as D4, are widely used in consumer products and may be present in personal care products, commercial products, and lubricants, and may be components of antifoams widely used in WWTPs. If these products are used by individuals during any part of the preparation for or during any aspect of the field sampling event or laboratory analysis, sample contamination by D4 volatilizing from the user could occur. To avoid the potential for sample contamination during collection, processing, storage, and analysis for D4 in environmental matrices, preventative measures should be implemented to the extent possible in the field. For example, field and laboratory personnel shall be required to refrain from using any personal care products that may contain cVMS materials (e.g., sun-block, sun-screen, hand lotion, antiperspirant, etc.) while preparing for or conducting any field activity to minimize the possibility for contamination with D4. Specific requirements for collecting and handling sediment samples aimed at preventing sample contamination by sources of D4 that are not specific to the WWTP or direct discharge site shall be specified in the Study Plan and QAPP.

Collection of sediment samples for analysis of D4:

The exact method for collection of sediment samples is a site-specific determination. During preparation of the site-specific Sampling Plans, the physical nature (e.g., width, depth, flow) of the receiving water will be determined and used to guide the selection of the appropriate method of sample collection. For each site, collection procedures for sediment samples shall be based, as appropriate to the characteristics of the receiving water, on techniques described in USEPA 1994 (SOP# 2016, Sections 2-5,7, pp. 1-7) and USEPA (2001) (Chapter 3, pp. 3-1 to 3-17). This guidance identifies the several main types of collection devices that are used to collect sediment samples. The exact collection method for sediment samples will be detailed in the Study Plan and QAPP.

Specific requirements for sample container preparation, sample handling, sample preservation, shipping and storage of samples should be essentially the same across all sites. Immediately prior to each sampling event at each site, the laboratory that will analyze the samples shall prepare clean (new, never used) pre-weighed glass sample containers in sufficient numbers for all sediment samples to be analyzed for D4, for all quality assurance samples, and for retain samples. The sample containers will be prepared by pre-washing with hexane, providing PTFE tape to assist in sealing the containers, as well as providing labels. The laboratory will ship all sample containers with adequate packing materials in coolers to each site. The coolers will also

contain chain-of-custody forms that will accompany the sample containers from the laboratory to the field and back to the laboratory.

Figure 4 provides a schematic that describes the quality assurance and D4 study samples to be taken at each sediment sampling location on the day of sampling at a given site. At each sediment location seven sediment samples (two quality assurance samples and five D4 study samples) will be taken in accordance with the sample collection procedures set out in the Study Plan.

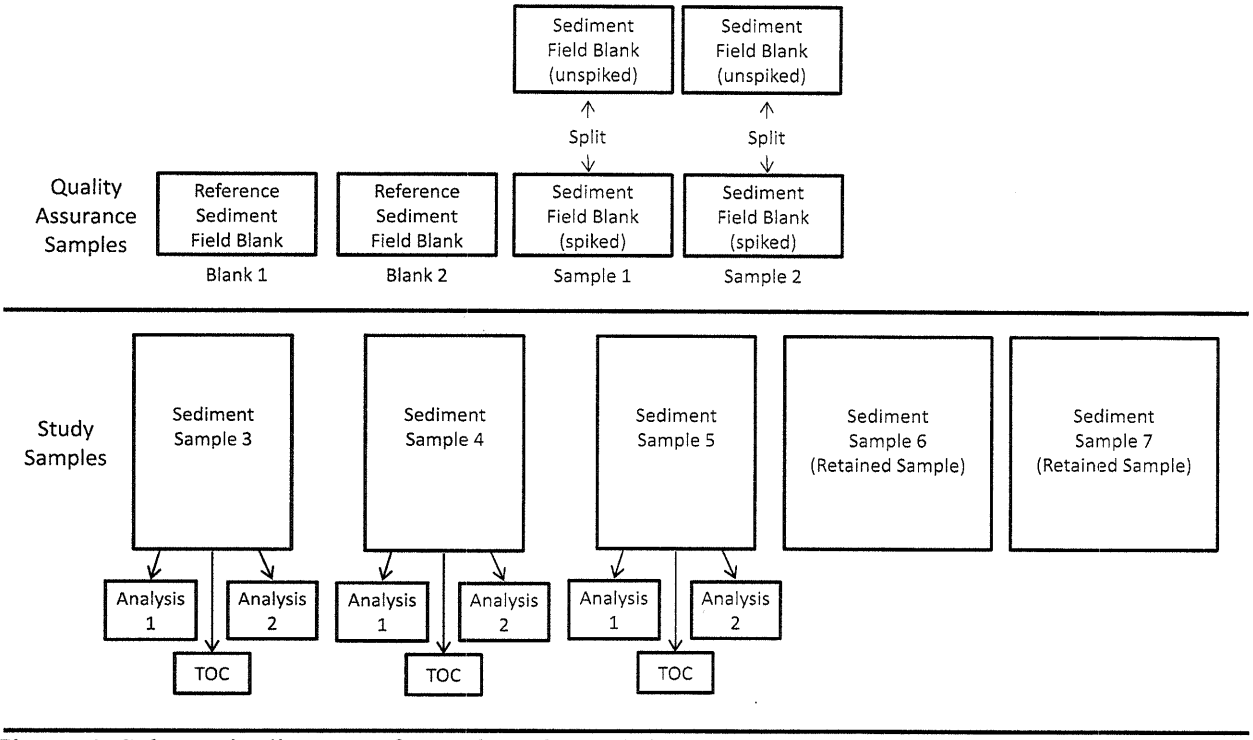

Figure 4. Schematic diagram of samples taken while monitoring for D4 in sediment near wastewater treatment plants.

Sample collection, storage and preparation will follow Powell and Woodburn (2009) with each sample being placed in a plastic bag, homogenized, then placed directly into a glass jar, and then capped.

Sediment samples 3, 4 and 5 will be divided to provide two duplicates for analysis of D4. The duplicate samples shall be processed and analyzed as individual samples for D4. Duplicate samples are used to evaluate between-sample variability and precision. After each sediment sample is homogenized in the field, a separate aliquot shall be taken from each sample and separately stored for analysis of total organic carbon (TOC) and water content. Following the general procedures of Powell and Woodburn (2009, Characterization of Sediments, p. 10) these additional samples shall be analyzed by carbon coulometry or an equivalent method for total carbon, total inorganic carbon, and total organic carbon, and loss-on- ignition for total water content and total organic matter content. Sediment samples 6 and 7 will serve as retain samples. These retain samples would be analyzed if a primary sample container arrives broken

at the laboratory, but otherwise would be retained in a refrigerator for later analysis if a sample becomes compromised during collection or processing. The retain samples will be kept until Quality Assurance has been verified and may be analyzed for D4 as necessary.

In addition to the study samples used to determine D4 concentrations in sediment, several samples will be analyzed for quality assurance purposes. Sediment samples 1 and 2 shall be split, one half of each sample shall be spiked in the field with a known amount of D4. The field spiked sediment samples will be used to evaluate loss of D4 during collection, processing, transport, storage, and analyses of samples, and to evaluate analytical bias. Specific requirements for preparation, processing, and analysis of field blanks, field spikes, and duplicate samples shall be detailed in the Study Plan and the QAPP. Two reference sediment samples having concentrations of D4 below the LOQ for this matrix shall be taken into the field and processed like sediment samples. The reference sediment samples will be used to evaluate contamination bias resulting from collection, processing, transport, storage, and analysis of samples.

Sealed sample containers will be packed into coolers with blue-ice or water ice and taken back to the laboratory or shipped back to the laboratory using an overnight express shipping company. All sample collection methods and sample handling procedures will be detailed in the Study Plan and QAPP.

Analysis of Sediment Samples for D4:

All sediment samples and accompanying quality assurance samples shall be analyzed for D4 at one commercial testing laboratory that has appropriate expertise with D4 analyses to be conducted when the testing occurs, unless there are unforeseen circumstances such as lack of laboratory availability as noted in 40 C.F.R. § 790.68(b)(2)(iii). The commercial laboratory will validate a method for the analysis of D4 in sediment samples that shall be adapted from the analytical method specified in Powell (2010).

The MDL is the concentration of a constituent in a sample, that when processed through the complete analytical method, can be measured and reported with 99% probability that it is greater than 0 or statistically different from a blank. The MDL is a measure of a method's ability to quantify a constituent in a sample matrix. The method for analyzing D4 in sediment reported by Powell (2010) is deemed the appropriate method for achieving an MDL up to 3.7 ng/g (wet weight, ww) and shall be achieved for sediment. The specific level of detection shall be based on the LOQ which shall be 3 times the MDL. All measurements of D4 concentration in sediment shall include sufficient information to perform a wet weight to dry weight conversion and shall report concentrations in terms of dry weight. EPA recognizes that a laboratory may have difficulties achieving the specified MDL. In this event, the signatory companies shall seek a modification as per 40 C.F.R. § 790.68.

Compliance with Good Laboratory Practice Requirements:

All field work related specifically to the collection, handling, and transfer of sediment samples should be conducted in accordance with USEPA's GLP regulations (see 40 C.F.R. Part 792). All analytical work, including analysis of D4 and lipid content, shall be conducted in accordance with USEPA's GLP regulations (see 40 C.F.R. Part 792). The QAPP shall be prepared according to USEPA guidance (USEPA 2002).

REFERENCES

USEPA 1994. Sediment Sampling, Sections 2-5 and 7. U.S. Environmental Protection Agency, SOP#: 2016, 11/17/94, REV. #: 0.0– See attached

USEPA 2001. Methods for Collection, Storage and Manipulation of Sediments for Chemical and Toxicological Analysis: Technical Manual, Chapter 3 and Appendix E. US Environmental Protection Agency, EPA 823-B-01-002, October, 2001.

Powell, D.E. 2010. Bioaccumulation and Trophic Transfer of Cyclic Volatile Methylsiloxane (cVMS) Materials in the Aquatic Marine Food Webs of the Inner and Outer Oslofjord, Norway. HES Study No: 11060-108. Health and Environmental Sciences, Dow Corning Corporation, Auburn, MI.

Powell DE, Woodburn KB. 2009. Trophic Dilution of Cyclic Volatile Methylsiloxane (cVMS) Materials in a Temperate Freshwater Lake. Dow Corning Corporation, HES Study No. 10771-108.

USEPA 2002. Guidance for Quality Assurance Project Plans, EPA QA/G-5, prepared by: Office of Environmental Information, EPA (December 2002) - http://www.epa.gov/quality/qs-docs/g5-final.pdf.

APPENDIX 8 - Testing Standard for the Collection, Sample Handling, Transfer and Analysis of Biota Samples for D4

Synopsis:

This testing standard provides guidelines for the collection and analysis of environmental samples for D4 in support of a Testing Program detailed in this ECA. This standard cites the requirements for the sampling of biota as described in Section VII of the ECA and Appendices 1, 2 and 3, and identifies specific guidelines and references that will be used in the preparation of site-specific Sampling Plans for the collection/analysis of biota samples, which will be included in a Study Plan and QAPP for the Testing Program. The standard addresses:

1. When to collect biota samples
2. Where to collect biota samples
3. Special considerations during sample collection to avoid sample contamination
4. How to collect and process biota samples
5. How to analyze biota samples for D4 and the appropriate method detection limit and limit of quantification

Requirements for sampling biota:

> Biota sampled shall include benthic species collected in sediment of the receiving water body and two species of fish, if practicable, of different trophic guilds, in the receiving water body."

Appendices 1-3 of this ECA state that:

> "Samples shall be taken during two testing events at least three (3) months apart. The exact duration between sampling events for each site shall be determined in a detailed Sampling Plan included in the Study Plan and QAPP."
>
> "Samples shall be collected during normal plant operations and during such times that effluent flow rates from the wastewater treatment system are representative of the normal plant operations."
>
> "Samples shall be taken during typical weather conditions and not until at least three (3) days after an unusual weather event such as a heavy rain storm. Samples shall be collected at a time when the rate of D4 release is expected to be representative of the typical rate of release of D4 for that site."

Establishment of the appropriate time for sampling events:

At each site, two sampling events will be undertaken that are scheduled to be a minimum of three months apart and during normal plant operations and weather conditions. Normal operating conditions will be established by consulting with the operator of each WWTP, indirect and direct discharge facility. The criteria or means that are used by the facilities to determine normal operating conditions will be documented in the site-specific Sampling Plans. Confirmation will be obtained that the subject facility is operating under normal conditions prior to commencing sampling at a given location. In addition, sampling would not take place within three (3) days of unusual weather events.

Establishment of the location for collection of benthic organisms and fish:

At each site, benthic organisms shall be collected as close as reasonably possible to the effluent outfall provided adequate mixing of the discharge and receiving water has occurred and where adequate benthic organism sample masses are obtained. Each site specific sampling plan will identify where the effluent and receiving stream are adequately mixed and the basis for the determination. At each site fish, surface water and sediment shall also be collected at approximately the same location.

Special considerations for the sampling and handling of biota samples for D4:

cVMS materials, such as D4, are widely used in consumer products and may be present in personal care products, commercial products, and lubricants, and may be components of antifoams widely used in WWTPs. If these products are used by individuals during any part of the preparation for or during any aspect of the field sampling event or laboratory analysis, sample contamination by D4 volatilizing from the user could occur. To avoid the potential for sample contamination during collection, processing, storage, and analysis for D4 in environmental matrices, preventative measures should be implemented to the extent possible in the field. For example, field and laboratory personnel shall be required to refrain from using any personal care products that may contain cVMS materials (e.g., sun-block, sun-screen, hand lotion, antiperspirants, etc.) while preparing for or conducting any field activities to minimize the possibility for contamination with D4. Specific requirements for collecting and handling biota samples aimed at preventing sample contamination by sources of D4 that are not specific to the WWTP or direct discharge shall be specified in the Study Plan and QAPP.

Collection of benthic organism samples for analysis of D4 and lipid content:

The exact method for collection of sediment samples from which benthic invertebrates will be collected is a site-specific determination. During preparation of the site-specific Sampling Plans, the physical nature (e.g., width, depth, flow) of the receiving water will be determined and used to guide the selection of the appropriate method of sample collection. For each site, collection procedures for sediment samples shall be based, as appropriate to the characteristics of the receiving water, on techniques described in Powell and Woodburn (2009, Sample Collection, p. 9) and USEPA (2003a, Sections 5.2 Sampling for Community Samples and 5.3 Sampling for Analytical Measurements). This guidance identifies collection procedures that

may be used to collect sediment samples from which benthic invertebrates will be collected. For each site, the exact method for collecting benthic organisms will be detailed in the site-specific Sampling Plans and QAPP.

Specific requirements for sample container preparation, sample handling, sample preservation, shipping and storage of samples should be essentially the same across all sites. Immediately prior to each sampling event at each site, the laboratory that will analyze the samples shall prepare clean (new, never used) pre-weighed glass sample containers in sufficient numbers for all benthic organism samples to be analyzed for D4. The sample containers will be prepared by pre-washing with hexane and providing PTFE tape to assist in sealing the containers, as well as providing labels. The laboratory will ship all sample containers with adequate packing materials in coolers to each site. The coolers will also contain chain-of-custody forms that will accompany the sample containers from the laboratory to the field and back to the laboratory.

Figure 5 provides a schematic that describes benthic organism samples to be taken at each sampling location. Five composited samples shall be prepared. Samples 1, 2 and 3 shall be divided into three parts. Two of the parts will serve as duplicates for D4 analysis and one part will be analyzed for lipid content. The duplicates shall be processed and analyzed as individual samples for D4. Duplicate samples are used to evaluate between-sample variability and precision. Samples 4 and 5 will be retained for analysis as needed. These retain samples would be analyzed if a primary sample container arrives broken at the laboratory, but otherwise would be retained in a freezer for later analysis if a sample becomes compromised during collection or processing. The retain samples will be kept until Quality Assurance has been verified and may be analyzed for D4 as necessary.

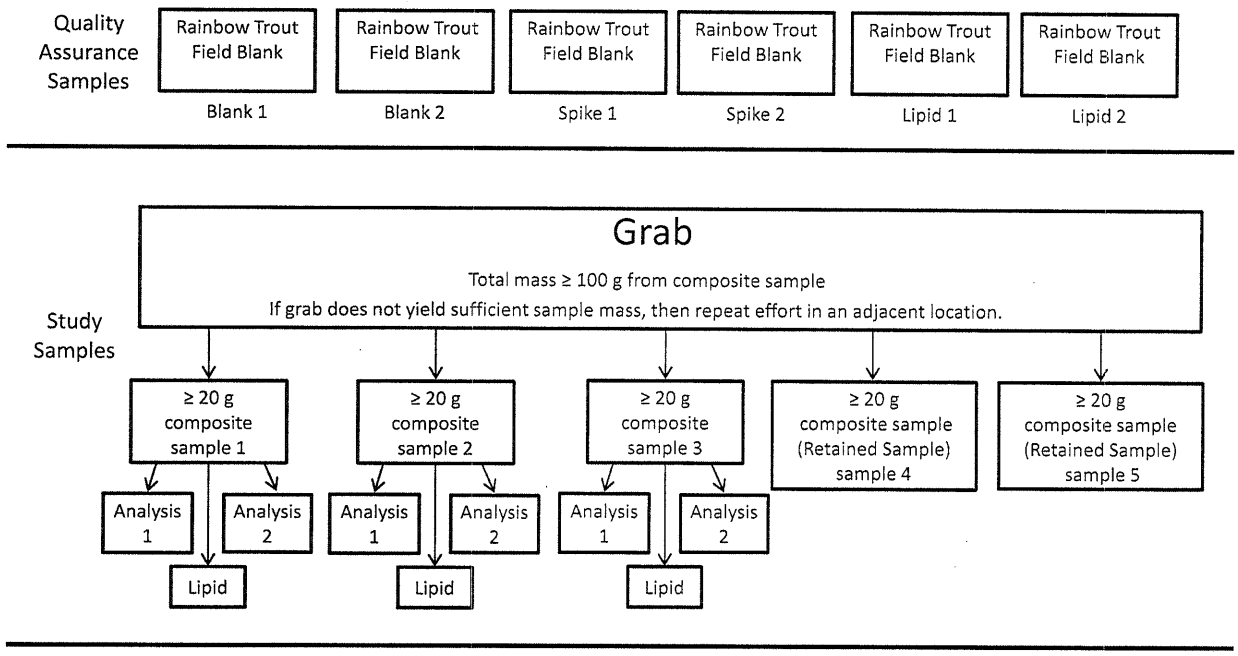

Figure 5. Schematic diagram of samples taken while monitoring for D4 in benthic organisms near wastewater treatment plants.

Sediment containing benthic organisms will be obtained such that sufficient mass of benthic organisms are obtained for the required analyses. Benthic organisms will be separated from the sediment and five composite samples shall be prepared by randomly dividing the collected organisms into glass containers and freezing prior to shipment. Prior to preparing composite samples, the taxa represented in the sample will be noted at the lowest level possible. Frozen samples will be packed into coolers with dry ice and taken back to the laboratory or shipped back to the laboratory using an overnight express shipping company.

It should be noted that it is often not possible to obtain sufficient mass of benthic organisms to both analyze for chemical concentration and to prepare quality assurance samples. Because of this, rainbow trout purchased from a commercial fish hatchery will be used as surrogate material to use to prepare quality assurance samples to use during preparation of benthos samples.

During each sampling event at a given site, two field blanks and two field spikes will be prepared as follows. Rainbow trout tissue purchased from a commercial fish hatchery will be ground into a homogenous mixture. Samples of the ground rainbow trout will be prepared in the laboratory prior to sample collection and shipped to the field. Prior to shipping to the field, the ground rainbow trout samples will be analyzed and shown to have concentrations of D4 below the LOQ for this matrix. Serving as field blanks, two reference ground rainbow trout samples will be opened during preparation of the composite samples of benthic organisms. The reference rainbow trout samples will be used to evaluate contamination bias resulting from collection, processing, transport, storage, and analysis of benthos samples. In addition, two of the ground rainbow trout samples shall be spiked in the field with a known amount of D4. The field spiked samples of ground rainbow trout will be used to evaluate loss of D4 during collection, processing, transport, storage, and analysis of the benthos samples, and to evaluate analytical bias. Sample collection procedures as well as specific requirements for sample container preparation, sample preservation, shipping and storage of the samples will be detailed in Study Plan and QAPP.

Lipid analysis will be performed on two ground rainbow trout field blanks. The method for analysis of lipid content of the composited benthic organism samples will be the same as used for fish. Procedures equivalent to Powell and Woodburn (2009) Characterization of Fish and Benthic Macroinvertebrates, p. 11 shall be used to measure lipid contents in the benthic organism samples.

Specific requirements for monitoring site location preparation, processing, and analysis of field blanks, field spikes, and duplicate samples shall be detailed in the Study Plan and QAPP.

Collection of fish samples for analysis of D4:

The exact method for collection of fish is a site-specific determination. During preparation of the site-specific Sampling Plans, the physical nature (e.g., width, depth, flow) of the receiving

water will be determined and used to guide the selection of the appropriate method of sample collection. For each site, collection procedures will be based, as appropriate to the characterization of the receiving water, on USEPA 2003a (Section 7.0 Procedures, pp. 3-5) and Powell and Woodburn (2009, Sample Collection, p. 8). This guidance identifies two main types of fish collection methods for relatively shallow and slow moving water and gives direction on choice of method, general practices, and other considerations for the field work. For each site, the exact collection method for fish samples will be detailed in the site-specific Sampling Plans and QAPP.

Specific requirements for sample container preparation, sample handling, sample preservation, shipping and storage of samples should be essentially the same across all sites. Immediately prior to each sampling event at each site, the laboratory that will analyze the samples shall prepare clean (new, never used) pre-weighed glass sample containers and polyethylene food storage bags in sufficient numbers for all fish samples to be analyzed for D4, for all quality assurance samples, and for retain samples. The sample containers will be prepared by pre-washing with hexane and providing PTFE tape to assist in sealing the containers, as well as providing labels. The laboratory will ship all sample containers and polyethylene bags with adequate packing materials in coolers to each site. The coolers will also contain chain-of-custody forms that will accompany the sample containers from the laboratory to the field and back to the laboratory.

On the day of field sampling at a given site, fish shall be collected and sorted by species. The taxonomic identification of each fish species shall be noted. Two species of fish from different trophic guilds, if practicable, collected in sufficient mass such that individual or composite samples can be prepared for the analysis of D4, shall be selected. If adequate quantities of fish from different trophic guilds are not available the two most abundant species will be selected. Information about the life history of the two species selected shall be included in study reports. The individual fish will be measured for length and weight.

Figure 6 provides a schematic that describes fish samples to be taken at each sampling location. For each of the two species, five individual fish or composited samples shall be prepared and frozen. In the laboratory three of the samples shall be thawed, homogenized and divided into three parts. Two of the parts will serve as duplicates for D4 analysis and one part will be analyzed for lipid content. The duplicates shall be processed and analyzed as individual samples for D4. Duplicate samples are used to evaluate between-sample variability and precision.

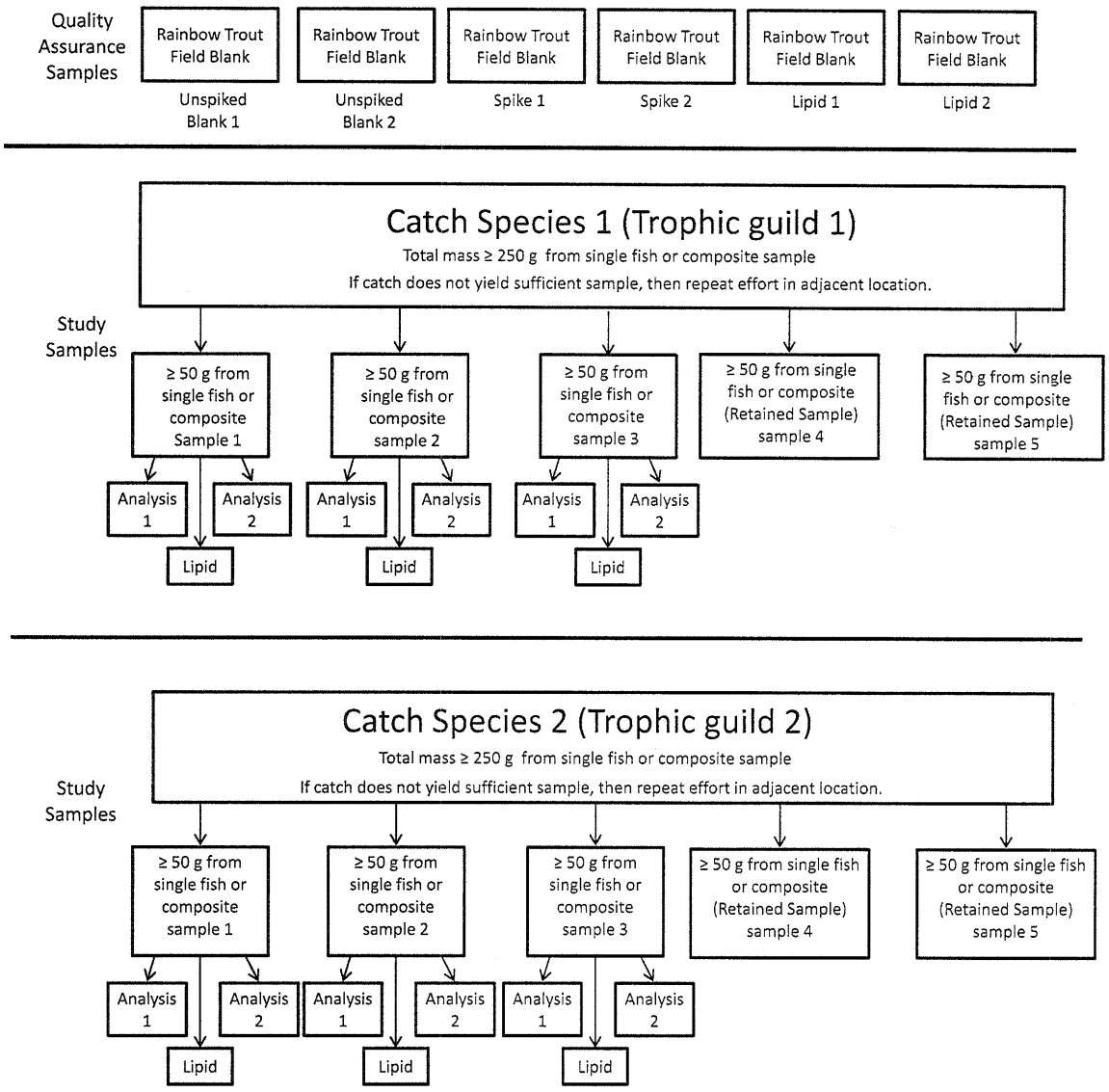

Figure 6. Schematic diagram of samples taken while monitoring for D4 in fish near wastewater treatment plants.

Two of the five samples will be retained for analysis as needed. These retain samples would be analyzed if a primary sample container arrives broken at the laboratory, but otherwise would be retained in a freezer for later analysis if a sample becomes compromised during collection or processing. The retain samples will be kept until Quality Assurance has been verified and may be analyzed for D4 as necessary.

During each sampling event at a given site, two field blanks and two field spikes will be prepared as follows. Rainbow trout purchased from a commercial fish hatchery will be ground into a homogenous mixture. Samples of the ground fish will be prepared in the laboratory prior to sample collection and shipped to the field. Prior to shipping to the field, the ground fish samples will be analyzed and shown to have concentrations of D4 below the LOQ for this matrix. Serving as field blanks, two reference ground fish samples will be processed like field

samples. The reference fish samples will be used to evaluate contamination bias resulting from collection, processing, transport, storage, and analysis of fish samples. In addition, two of the ground fish samples shall be spiked in the field with a known amount of D4. The field spiked samples of ground fish will be used to evaluate loss of D4 during collection, processing, transport, storage, and analysis of fish samples, and to evaluate analytical bias. Specific requirements for preparation, processing, and analysis of quality assurance samples shall be detailed in the Study Plan and the QAPP.

Individual fish will be doubly bagged using polyethylene bags and frozen prior to shipment. Composited fish will be placed in sample containers and frozen prior to shipment. Frozen samples will be packed into coolers with dry ice and taken back to or shipped back to the laboratory using an overnight express shipping company. Sample collection methods as well as specific requirements for sample container preparation, sample handling, sample preservation, shipping and storage of the samples will be detailed in the Study Plan and QAPP.

In the laboratory, as part of the processing of the fish samples prior to analysis, fish will be ground up and homogenized. Lipid content shall be analyzed using procedures equivalent to Powell and Woodburn (2009) Characterization of Fish and Benthic Macroinvertebrates, p. 11.

Analysis of Biota Samples for D4:

All biota samples and accompanying quality assurance samples shall be analyzed for D4 at one commercial testing laboratory that has appropriate expertise with the D4 analyses to be conducted when the analysis occurs, unless there are unforeseen circumstances such as lack of laboratory availability as noted in 40 C.F.R. § 790.68(b)(2)(iii). The commercial laboratory will validate a method for the analysis of D4 in biota samples that shall be adapted from the analytical method specified in Powell and Woodburn (2009, Analysis of Cyclic Volatile Methylsiloxane (cVMS) Materials section, Extraction of Fish and Benthic Macroinvertebrates sub- section, p. 13, and Quality Control, p. 14). The Powell and Woodburn (2009) analytical method involves extraction of aliquots of homogenized biota samples and quality assurance samples followed by quantification using GC-MS.

The MDL is the concentration of a constituent in a sample, that when processed through the complete analytical method, can be measured and reported with 99% probability that it is greater than 0 or statistically different from a blank. The MDL is a measure of a method's ability to quantify a constituent in a sample matrix. The method for analyzing D4 in biota reported by Campbell 2010; Durham 2010a and 2010 b; Kaj 2005; Powell 2010a and 2010 b; and Powell and Woodburn (2009) is deemed the appropriate method for an MDL of 0.2 to 3.0 ng/g (wet weight, ww). An MDL up to a value not exceeding 3.0 ng/g (wet weight, ww) shall be applied for biota. The specific level of detection shall be based on the LOQ which shall be 3 times the MDL. EPA recognizes that a laboratory may have difficulties achieving the specified MDL. In this event, the signatory companies shall seek a modification as per 40 C.F.R. § 790.68.

Compliance with Good Laboratory Practice Requirements:

All field work related specifically to the collection, handling, and transfer of biota samples should be conducted in accordance with USEPA's GLP regulations (see 40 C.F.R. Part 792). All analytical work, including analysis of D4 and lipid content, shall be conducted in accordance with USEPA's GLP regulations (see 40 C.F.R. Part 792). The QAPP shall be prepared according to USEPA guidance (USEPA 2002).

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