

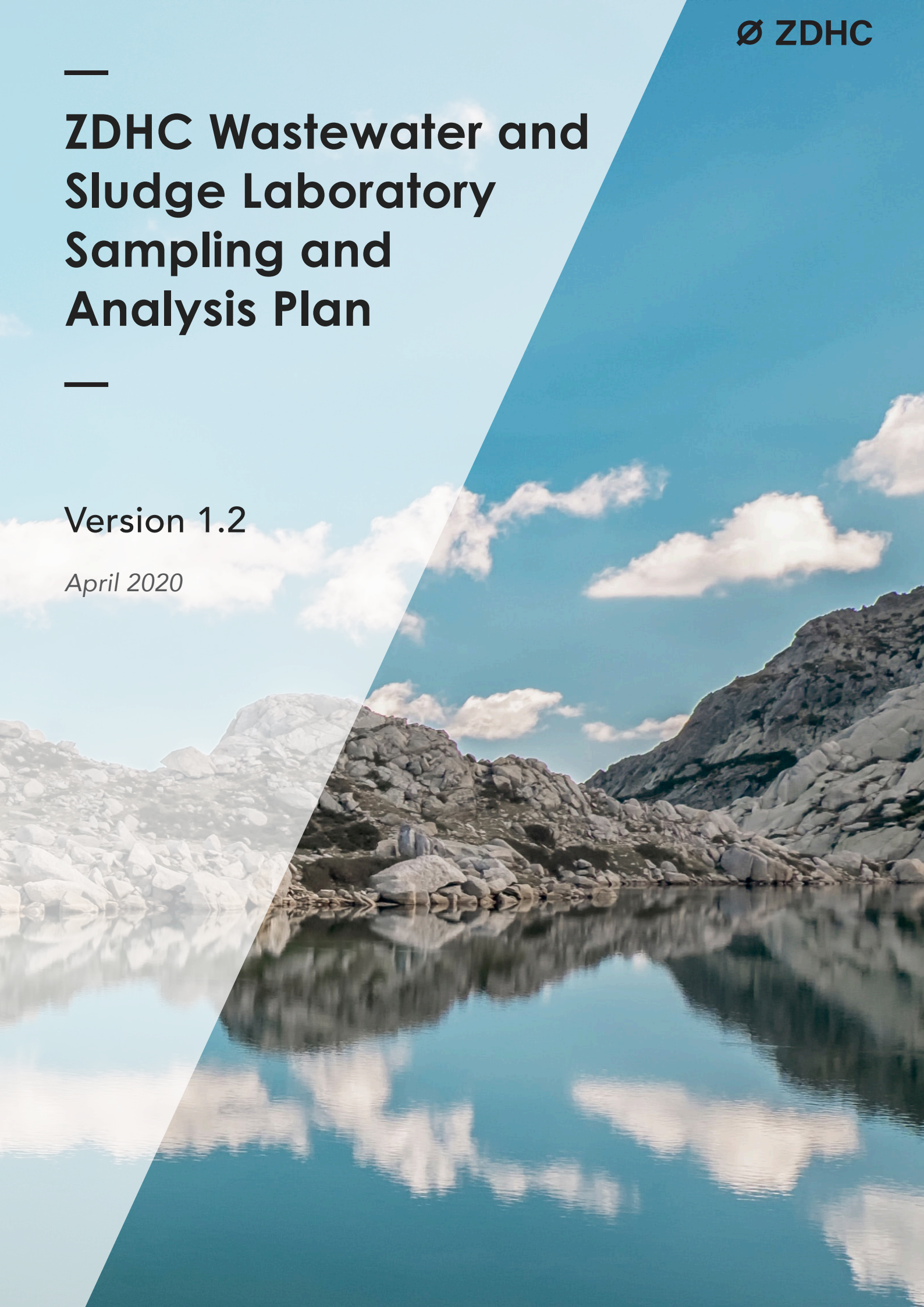
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# ZDHC Wastewater and Sludge Laboratory Sampling and Analysis Plan

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Version 1.2

*April 2020*



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# 1.0.0 Revision History

In the spirit of continuous improvement, the ZDHC Wastewater and Sludge Laboratory Sampling and Analysis Plan (SAP) will be reviewed on a regular basis and revised as needed to incorporate learnings and opportunities identified during the practical application and implementation of these procedures. A historical record of updates to the SAP is noted in the figure below.

Figure 1: Revision History

| Version Number | Changes   | Time of Publication |
|----------------|---|---------------------|
| Version 1.0    | Initial publication of the ZDHC Wastewater Laboratory Sampling and Analysis Plan.   | June 2019           |
| Version 1.1    | <div><div>1. Added sampling and analysis procedures specific to sludge.</div><div>2. Improved sampling and analysis procedures for wastewater.<div><div>▪ Ensured full alignment with ZDHC Wastewater Guidelines Version 1.1 requirements, including but not limited to standard method for analysis.</div><div>▪ Changed the expected sample temperature and applied it to all relevant sections throughout the wastewater part of the document.</div><div>▪ Changed the recommended holding time for halogenated solvents – see Figure 3.</div><div>▪ Adjusted the target value for Multi-Point Calibration in Figure 4.</div><div>▪ Adjusted Calibration Check for Total Coliform in Figure 5.</div><div>▪ Updated and clarified the Reporting and Deliverable Requirements in Section 3.3.0 to align with latest development within ZDHC.</div></div></div></div> | August 2019         |
| Version 1.2    | <div><div>1. Added sampling and analysis of parameters specific to the ZDHC MMCF Waste-water interim guidelines.<div><div>▪ Parameters added for Wastewater: Toxicity (Luminous Bacteria Toxicity, or Fish egg Toxicity, or Daphne Toxicity or Algae Toxicity), Total Hydrocar-bons and Carbon disulphide in Figures 2, 3, and 5.</div><div>▪ Parameters added for Sludge: Heavy metals, Total Organic Carbon (TOC), Extractable Organic Halogen Compounds (EOX), Adsorbable Organic Halogen Compounds (AOX) in Figure 6, 7, and 9.</div></div></div></div>   | April 2020          |

# 2.0.0 Introduction

The ZDHC Roadmap to Zero Programme takes a holistic approach to tackling the issue of hazardous chemicals in the global textile, apparel, footwear and leather industry. This holistic approach starts with the management of input chemistries, the management of day-to-day chemical use at production facilities (**suppliers**), and the management of effluent generated and discharged by suppliers.

With regards to effluent management, the ZDHC Wastewater Guidelines (always refer to the latest version, publicly available on the [ZDHC website](#)) are in place to harmonise wastewater parameters, limit values and test methods, as well as requirements for sampling, testing and reporting.

This is an attempt to encourage and enable the industry, in particular brands, suppliers and testing laboratories, to work towards the same set of expectations.

This ZDHC Wastewater and Sludge Laboratory Sampling and Analysis Plan (SAP) document is one of the key elements to support implementation of the ZDHC Wastewater Guidelines. It does so by standardising procedures for laboratories to conduct sampling and analysis.

## Purpose

This SAP provides a detailed framework for laboratories to perform sampling and testing to determine the concentration of parameters in wastewater and sludge.

## Data Uses

Wastewater and sludge test data helps to promote the implementation of sustainable chemistry and best practices in the industry.

The laboratory must be aware of the importance of maintaining the integrity of test data generated under the ZDHC Programme. The test data may be used to make major decisions regarding manufacturing facilities.

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## 3.0.0 Wastewater

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### 3.1.0 Sampling for Wastewater

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#### 3.1.1 Types of Samples and Sampling Points/Locations

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Please refer to the ZDHC Wastewater Guidelines (WWG) for types of samples and sampling points/locations. The types of samples to be collected will depend on the testing option decided upon by the brand and supplier (manufacturing facility), but limited to the two testing options identified in the WWG. The WWG acknowledges the difference between facilities with a direct discharge, indirect discharge and on-site zero liquid discharge treatment plant. Important to note: to streamline efforts within the value chain, sampling, testing and reporting as per the WWG and as requested by one ZDHC Brand is a valid test. This test will and should be accepted by all ZDHC Brands.

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#### 3.1.2 Wastewater Sample Collection

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1. Samples shall be taken by qualified laboratory personnel. Wastewater samples shall be collected as composite samples following ISO 5667 - 10 guidelines: "Water Quality Sampling Guidance for the preservation and handling of water samples".
2. Sampling using calibrated and refrigerated auto samplers is preferred. To ensure representative samples, composite sampling must be performed for no less than six (6) hours, with no more than one (1) hour between discrete samples. Each discrete sample shall be of equal volume. The composite sample container must be cooled during sampling.
3. If necessary, laboratory personnel can collect discrete samples by hand for no less than six (6) hours, with no more than one (1) hour between discrete samples. Each discrete sample shall be of equal volume and combined to produce one composite sample. The composite sample container must be cooled during sampling.

4. All of the laboratory sample containers will be filled from the same bulk composite sample. A minimum sample volume of 20 litres is needed to fill all the containers. The laboratory may require extra volume for QA samples. The sampler shall coordinate extra volume requirements with the laboratory.
5. Samples must be taken during a time that represents continuous and normal production and continuous and normal wastewater treatment. For example, if the supplier starts production, and the wastewater treatment system doesn't reach equilibrium for one hour, then wastewater sampling must be delayed for that length of time.
6. Samples must not be taken if the wastewater is diluted, for example, by heavy rainfall.
7. Wastewater flow data (volume/time) must be collected and reported with the laboratory test results.

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#### 3.1.3 Wastewater Sample Containers and Preservatives

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1. *Figure 2* presents standard sample collection containers and preservatives for the wastewater parameters specified in the ZDHC Wastewater Guidelines.
2. The appropriate sample collection container and preservative can vary depending on the standard test method used. Therefore, verify the proper container and preservative with the test method being used at the laboratory.

Figure 2: Wastewater Sample Containers and Preservatives

| Wastewater Parameter                | Sample Container<br>Minimum Size             | Standard Preservative<br>(verify with lab method to be used)                              |
|-------------------------------------|--|---|
| Conventional                        |  |   |
| Temperature                         | NA   | Measured in the field   |
| TSS                                 | P, G 200-ml                                  | cool < 4°C  |
| COD                                 | P, G, FP 100-ml                              | H <sub>2</sub> SO <sub>4</sub> < pH 2<br>cool < 4°C                                       |
| Total-N                             | P, G, FP 100-ml                              | H <sub>2</sub> SO <sub>4</sub> < pH 2<br>cool < 4°C                                       |
| pH                                  | NA   | cool < 4°C  |
| Colour [m-1]<br>(436nm; 525; 620nm) | P, G, FP 500-ml                              | cool < 4°C  |
| BOD5                                | P, G, FP 1,000-ml                            | cool < 4°C  |
| Ammonium-N                          | P, G, FP 500-ml                              | H <sub>2</sub> SO <sub>4</sub> < pH 2<br>cool < 4°C                                       |
| Total-P                             | P, G, FP 100-ml                              | H <sub>2</sub> SO <sub>4</sub> < pH 2<br>cool < 4°C                                       |
| AOX                                 | P, G, FP 500-ml                              | 0.1 ml of 10% Sodium<br>Thiosulfate, H <sub>2</sub> SO <sub>4</sub> < pH 2,<br>cool < 4°C |
| Oil and Grease                      | Glass, wide mouth PTFE<br>lined lid 1,000-ml | HCl or H <sub>2</sub> SO <sub>4</sub> < pH 2<br>cool < 4°C                                |
| Phenols                             | P, G PTFE lined lid 500-ml                   | H <sub>2</sub> SO <sub>4</sub> < pH 2<br>cool < 4°C                                       |
| Total Coliform<br>[bacteria/100ml]  | P, G clean, sterile,<br>non-reactive, 125-ml | 0.1 ml of 10%<br>Sodium Thiosulfate<br>cool < 4°C do not freeze                           |
| Persistent foam                     | NA   | Measured in the field   |
| Cyanide                             | P, FP 1,000-ml                               | NaOH > 12 pH, 0.1 ml of 10%<br>Sodium Thiosulfate,<br>cool < 4°C                          |

|  |  |  |
|--|--|--|
| Sulfide  | P, FP 100-ml                                 | 4 drops 2N zinc acetate,<br>NaOH > pH9<br>cool < 4°C                 |
| Sulfite  | P, G, FP 100-ml                              | 1-ml 2.5% EDTA, 0.5 g zinc<br>acetate<br>cool < 4°C                  |
| Luminous Bacteria Toxicity,<br>or Fish egg Toxicity, or Daph-<br>ne Toxicity or Algae Toxicity | P,G,FP 1,000-ml                              | cool, < 6°C  |
| Total Hydrocarbon  | Glass, wide mouth PTFE<br>lined lid 1,000-ml | HCl or H <sub>2</sub> SO <sub>4</sub> < pH 2 cool < 6°C              |
| Carbon disulphide  | Three x 40-ml amber VOA<br>vial no headspace | HCl < pH 2 cool < 6°C  |
| Shipping temperature<br>indicator bottle   | calibrated thermometer<br>to +/- 1C°         | room temperature water   |
| Metals   |  |  |
| Antimony, Chromium-total<br>Cobalt, Copper, Nickel<br>Silver, Zinc, Arsenic<br>Cadmium, Lead   | P, G, FP acid washed 250-ml                  | HNO <sub>3</sub> < pH 2  |
| Chromium (VI)  | G acid washed 40-ml Brown<br>Glass VOA vial  | 0.45µm filter in field, add<br>buffer * to pH 9.0-9.5,<br>cool < 4°C |
| Mercury  | P, G, FP acid washed 500-ml                  | HNO <sub>3</sub> < pH 2<br>cool < 4°C                                |

| ZDHC MRSL V1.1  |  |                                |
|---|--|--------------------------------|
| AP and APEOs:<br>Including All Isomers                              | G 1,000-ml PTFE lined lid                    | cool < 4°C                     |
| Chlorobenzenes and<br>Chlorotoluenes                                | G 1,000-ml PTFE lined lid                    | cool < 4°C                     |
| Chlorophenols   | G 1,000-ml PTFE lined lid                    | cool < 4°C                     |
| Dyes – Azo (Forming<br>Restricted Amines)                           | G 1,000-ml PTFE lined lid                    | cool < 4°C                     |
| Dyes – Carcinogenic or<br>equivalent Concern                        | G 1,000-ml PTFE lined lid                    | cool < 4°C                     |
| Dyes – Disperse (Sensitising)                                       | G 1,000-ml PTFE lined lid                    | cool < 4°C                     |
| Flame Retardants  | G 1,000-ml PTFE lined lid                    | cool < 4°C                     |
| Glycols   | G 1,000-ml PTFE lined lid                    | cool < 4°C                     |
| Halogenated Solvents  | Three x 40-ml amber VOA<br>vial no headspace | HCl < pH 2<br>cool < 4°C       |
| Organotin Compounds   | G 1,000-ml acid washed<br>PTFE lined lid     | 1M HCl to pH 2-3<br>cool < 4°C |
| Perfluorinated and<br>Polyfluorinated Chemicals<br>(PFCs)           | P 1,000-ml <u>NO</u> PTFE lined<br>lid       | cool < 4°C                     |
| Otho-Phthalates –<br>Including all ortho esters of<br>phthalic acid | G 1,000-ml PTFE lined lid                    | cool < 4°C                     |
| Polycyclic Aromatic<br>Hydrocarbons                                 | G 1,000-ml PTFE lined lid                    | cool < 4°C                     |
| Volatile Organic Compounds<br>(VOC)                                 | Three x 40-ml amber VOA<br>vial no headspace | HCl < pH 2<br>cool < 4°C       |

\* Buffer = EPA Method 218.6. Dissolve 33g of ammonium sulphate in 75-ml of ASTM D1103 Type 1 or ISO 3696 water,  
add 6.5-ml of ammonium hydroxide. Dilute to 100-ml with ASTM D1103 Type-1 or ISO 3696 water.

P= plastic, G= amber glass, FP= fluoropolymer

3. A temperature indicator bottle shall be included with each shipping container. The temperature indicator bottle will be clearly labelled.
4. Field blanks shall be collected for the following parameters:
  - a. Total-P
  - b. Coliform
  - c. Mercury
  - d. Halogenated Solvents
  - e. Volatile Organic Compounds (VOC)
5. The field blanks shall use the same containers as the samples and will be filled with ultra-pure laboratory grade water (ASTM D1193 or ISO 3696).

### 3.1.4 Wastewater Sample Custody

Each sample shipment requires a Chain of Custody log that is maintained from the time of collection, during the entire analytical process, and until sample disposal. A Chain of Custody document provides a record of sample transfer from person to person. This document helps to protect the integrity of the sample by ensuring only authorised persons have custody of the sample. An example Chain of Custody form is presented in *Appendix A*. The sampling team must maintain physical custody, or use custody seal tape on the cool boxes, until the samples are handed off to the shipping company or laboratory.

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### 3.1.5 Wastewater Sample Shipments

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1. Use an a 24-hour (overnight) delivery service for samples that are shipped to a laboratory.
2. To avoid shipping delays and compromising sample holding times, contact the shipping company prior to sample collection. The shipping company can help determine the appropriate customs arrangements that must be made.
3. *Appendix B* provides sample shipping forms that may help to avoid delays in customs.
4. Samples will be shipped in cool boxes with sufficient insulation and artificial refrigerant ("blue ice"), or ice contained in double zip-lock bags, to maintain a sample temperature of less than 4°C for the duration of transportation. Shipping containers that leak fluid, such as melting ice water, will likely be returned to the shipper.
5. Containers should be held upright during shipment. Use bubble wrap around individual glass containers and use adequate packing material to prevent movement during shipment, cushion from shock, and reduce the risk of leakage.
6. The sampler shall be responsible for all handling, processing, and custody of the samples, including taking samples to the nearest servicing airport, bus station, or other carrier.

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### 3.2.0 Laboratory Analysis/Testing for Wastewater

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#### 3.2.1 Wastewater Sample Receipt, Handling, and Custody

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1. The laboratory shall be available to receive sample shipments at any time the delivery service is operating, including weekends.
2. The sample temperature shall be measured and recorded immediately upon opening the shipping container, and prior to unpacking the samples or removing the packing material.
  - a. The laboratory shall use the shipping container temperature indicator bottle reading as the sample temperature.
  - b. To determine the temperature, invert the bottle several times, remove the cap, and insert a calibrated thermometer.
  - c. Allow a minimum of three (3) minutes, but not greater than five (5) minutes prior to taking the measurement. The thermometer used shall be calibrated and capable of measuring within an accuracy of  $\pm 1^{\circ}\text{C}$ .
  - d. If a temperature indicator bottle is not present in the shipping container, an alternative means of determining shipping container temperature can be used.
  - e. Under no circumstances shall a thermometer or any other device be inserted into a sample bottle for the purpose of determining shipping container temperature.
  - f. Other devices (e.g. infrared thermometer), which can measure temperature may be used if they are calibrated to  $\pm 1^{\circ}\text{C}$
  - g. The desired sample temperature when it is received at the laboratory is 4°C or less.
    - i. If the sample temperature is greater than 4°C and less than 10°C, the laboratory shall note the issue and provide an exception report with the sample test report.

- ii. If the sample temperature exceeds 10°C when received at the laboratory, the laboratory shall contact the client and inform them of the temperature deviation. The client may decide not to perform testing on these samples.

3. The pH for all aqueous/water sample containers received by the laboratory shall be measured and recorded at the laboratory to demonstrate that proper preservation was performed.
  - a. Measure pH using test strips, an electronic hand-held pen, or pH meter. To prevent sample contamination, measure the pH on a small aliquot of the sample removed from the container.
  - b. Under no circumstances shall a strip or any device be inserted into a sample bottle for the purpose of determining pH.
4. If the laboratory encounters problems with samples or related documentation (e.g. mixed media, sample pH, sample documentation and paperwork such as Traffic Report/Chain-of-Custody), the laboratory shall immediately contact the sampler for a resolution.

### 3.2.2 Wastewater Sample Holding Time

1. In general, minimising the time between sample collection and analysis will provide more reliable and representative analytical data.
2. *Figure 3* presents both the recommended and maximum holding times for each of the wastewater testing parameters.
3. If a sample exceeds the holding time the test results will be reported. However, any test results that exceed the holding time must be flagged with the following data qualifier: "Maximum holding time exceeded. Red flag in the ZDHC Gateway - Wastewater Module. Probable error in results due to the holding time."

Figure 3: Wastewater Sample Holding Times

| Wastewater Parameter  | Recommended Holding Time | Maximum Holding Time |
|---|--------------------------|----------------------|
| <b>Conventional</b>   |                          |                      |
| Temperature   | measure in the field     | 15 minutes           |
| TSS   | 24 hours                 | 7 days               |
| COD   | 7 days                   | 28 days              |
| Total-N   | -                        | 28 days              |
| pH  | measure in the field     | 6 hours              |
| Colour [m-1]<br>(436nm; 525nm; 620nm)   | -                        | 48 hours             |
| BOD5  | 6 hours                  | 48 hours             |
| Ammonium-N  | 7 days                   | 28 days              |
| Total-P   | -                        | 28 days              |
| AOX   | -                        | 6 months             |
| Oil and Grease  | -                        | 28 days              |
| Phenols   | 24 hours                 | 28 days              |
| Total Coliform<br>[bacteria/100ml]  | 6 hours                  | 24 hours             |
| Persistent foam   | measure in the field     | -                    |
| Cyanide   | 24 hours                 | 14 days              |
| Sulfide   | -                        | 7 days               |
| Sulfite   | -                        | 48 hours             |
| Luminus Bacteria Toxicity, or<br>Fish egg Toxicity, or Daphne<br>Toxicity or Algae Toxicity | 6 hours                  | 48 hours             |
| Total Hydrocarbon   | -                        | 28 days              |
| Carbon disulphide   | 7 days                   | 14 days              |
| <b>Metals</b>   |                          |                      |
| Trace Metals  | 28 days                  | 6 months             |
| Chromium (VI)   | 24 hours                 | 28 days              |
| Mercury   | -                        | 28 days              |



| ZDHC MRSL V1.1  |          |                   |
|---|----------|-------------------|
| Alkylphenol (AP) and Alkylphenol Ethoxylates (APEOs): Including All Isomers | -        | 7 days to extract |
| Chlorobenzenes and Chlorotoluenes   | -        | 7 days to extract |
| Chlorophenols   | -        | 7 days to extract |
| Dyes – Azo (Forming Restricted Amines)                                      | -        | 7 days to extract |
| Dyes – Carcinogenic or Equivalent Concern                                   | -        | 7 days to extract |
| Dyes – Disperse (Sensitising)   | -        | 7 days to extract |
| Flame Retardants  | -        | 7 days to extract |
| Glycols   | -        | 7 days to extract |
| Halogenated Solvents  | 7 days   | 14 days           |
| Organotin Compounds   | 24 hours | 7 days            |
| Perfluorinated and Polyfluorinated Chemicals (PFCs)                         | -        | 7 days to extract |
| Otho-Phthalates – Including all ortho esters of phthalic acid               | -        | 7 days to extract |
| Polycyclic Aromatic Hydrocarbons (PAHs)                                     | -        | 7 days to extract |
| Volatile Organic Compounds (VOC)  | 7 days   | 14 days           |

### 3.2.3 ZDHC Wastewater Parameters

The wastewater parameters are listed in the ZDHC Wastewater Guidelines document, *Appendix A Tables 1A-1B and Tables 2A-2N*.

### 3.2.4 Standard Test Methods for Wastewater

- The ZDHC approved standard test methods are presented in the ZDHC Wastewater Guidelines, *Appendix A Tables 1A-1B and Tables 2A-2N*.
- The methods are based on requirements in the European Union, the United States of America, and China. Alternate methods, such as those required by the regulatory agency in the region where the wet processing/manufacturing occurs, may be used with prior approval from ZDHC, with exceptions for colour and COD. For more information refer to ZDHC Wastewater Guidelines section 9.6.0.
- Testing for persistent foam.
  - Foam is a naturally occurring phenomena in aeration basins that enable biological wastewater treatment. To ensure accurate accounting of foam, laboratory personnel are expected to take a digital photo of the foam they witness within the wastewater treatment system. They should include photographs of the foam they witnessed in the final laboratory report, along with the time and date of taking such photos.
  - The presence of foam is acceptable and meets the requirements of the Guidelines if its colour is similar to the liquid in the aeration basin, dissipating, no thicker than 45 centimetres (by visual estimation) and is contained within the aeration basin.
  - If the foam is higher than 45 centimetres (by visual estimation) or is not contained within the aeration basin, then it does not meet the requirements of the Guidelines.

3.2.5 Required Reporting Limits for Wastewater

- 1. The minimum required reporting limits are presented in the ZDHC Wastewater Guidelines, *Appendix A Tables 1A-1B and Tables 2A-2N*. They are also based on the ZDHC discharge limits, which were established with consideration to achieving these levels with good laboratory practices. If the ZDHC reporting limits cannot be achieved, an alternate method or a sub-contract laboratory must be used.
- 2. The Method Detection Limit (MDL) for each parameter must be determined first and is used to establish the reporting limit. The MDL will be established using ISO/TS 13530:2009 4.4.3.
- 3. The Reporting Limit (RL) will be established using ISO/TS 13530:2009 4.4.7.
- 4. Non-detected test results will be reported using the calculated RL for each parameter and not the ZDHC discharge limit.

3.2.6 Quality Systems

- 1. The minimum quality assurance measures for organic chemical analysis of wastewater and sludge are presented in *Figure 4*.

Figure 4: Minimum Quality Assurance Measures for Organic Chemical Analysis

| Measure           | Description                                 | Target value | Fre-quency  | Points to be checked (examples)   |
|-------------------|---|--------------|-------------|---|
| A. Routine        |   |              |             |   |
| Method blank      | Covering sample preparation and measurement | < MDL        | 1 per batch | Cleanliness of laboratory glassware and equip-ment                            |
| Calibration Check | An independently sourced/prepared standard  | ± 20 %       | 1 per batch | Check instrument condition/drift, clean and re-calibrate, stability standards |

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|   |   |                 |                          |   |   |
|---|---|-----------------|--------------------------|---|---|
| Internal Standard   | For GC methods. Substance with physico-chemical properties similar to the analyte | 50 – 150%       | every sample             | Correction of injection error.<br>Method specific: surrogate as alternative   | Choice of internal standard or surrogate or a combination thereof is method/analyte dependent |
| Surrogate   | Substance which has similar physico-chemical properties to the analyte            | Method specific | Every sample             | Check sample preparation procedure and internal standard correction.<br>Method specific: internal standard as alternative |   |
| <b>B. In case of problematic samples</b><br>(e.g. internal standard recovery too low, phase separation issues etc.) |   |                 |                          |   |   |
| Duplicate   | Duplicate undergoing complete process   | < 35 % RPD      | Problematic samples only | Flag results  |   |
| Matrix Spike<br>Matrix Spike<br>Duplicate   | spike onto sample matrix (duplicate) undergoing complete process                  | Method specific | Problematic samples only | Flag results  |   |

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| C. For method validation               |  |   |            |  |
|--|--|---|------------|--|
| Multi-Point Calibration                | Min. 5-point calibration excl. origin                          | $r^2 \geq 0.995$                                  | Validation | Linearity, working range   |
| Recovery (LCS)                         | Extract the standard through the test procedure without matrix | Method and analyte specific                       | Validation | Recovery without influence of matrix                                     |
| Repeatability (matrix spike replicate) | Matrix spike replicates under repeatability conditions         | Method and analyte specific                       | Validation | Robustness, recovery with matrix influence, UoM, general fitness for use |
| Limit of Detection                     | ISO/TS 13530:2009 4.4.3 4.4.7                                  | $\leq$ WWG RL<br>Ideal: $\leq \frac{1}{2}$ WWG RL | Validation | MDL<br>RL  |

**Note:**

- General suitability of the analytical approach is demonstrated via method validation.
- Matrix to be encountered for wastewater and sludge analysis is less diverse/concentrated than for process chemicals (ZDHC MRSL).
- Therefore, initial method validation is deemed to sufficiently cover most sample types and a comparatively leaner QC programme is applied.
- Specific, problematic sample matrices, which are not covered by the validation, require additional QC measures.
- In case of conflict, quality assurance measures specified by the applied standard, the accreditation body or local authority shall prevail.

2. The quality assurance testing in *Figure 5* is required for each of the ZDHC wastewater parameters. This data may be requested and used by ZDHC to assess data quality and validate the analytical results.

Figure 5 – Required Quality Assurance Testing for Wastewater

| DQI                              | Field Blank | Method Blank | Calibration Check* | Lab duplicate | ISTD and Surrogate |
|----------------------------------|-------------|--------------|--------------------|---------------|--------------------|
| Frequency                        | 1 per Batch | 1 per Batch  | 1 per Batch        | 1 in 20       | Every Sample       |
| DQO                              | < MDL       | < MDL        | +/- 20%            | +/- 35%       | Method Specific    |
| Conventional                     |             |              |                    |               |                    |
| Temperature                      | -           | -            | -                  | -             | -                  |
| TSS                              | -           | -            | X                  | X             | -                  |
| COD                              | -           | X            | X                  | X             | -                  |
| Total-N                          | -           | X            | X                  | X             | -                  |
| pH                               | -           | -            | X                  | -             | -                  |
| Colour [m-1] (436nm; 525; 620nm) | -           | X            | X                  | -             | -                  |
| BOD5                             | -           | X            | X                  | -             | -                  |
| Ammonium-N                       | -           | X            | X                  | X             | -                  |
| Total-P                          | X           | X            | X                  | X             | -                  |
| AOX                              | -           | X            | X                  | X             | -                  |
| Oil and Grease                   | -           | X            | X                  | X             | -                  |
| Phenols                          | -           | X            | X                  | X             | -                  |
| Total Coliform [bacteria/100ml]  | X           | X            | -                  | X             | -                  |
| Persistent foam                  | -           | -            | -                  | -             | -                  |
| Cyanide                          | -           | X            | X                  | X             | -                  |
| Sulfide                          | -           | X            | X                  | X             | -                  |
| Sulfite                          | -           | X            | X                  | X             | -                  |

|  |   |   |   |   |   |
|--|---|---|---|---|---|
| Luminus Bacteria Toxicity or Fish egg Toxicity, or Daphne Toxicity or Algae Toxicity | - | X | X | X | - |
| Total Hydrocarbon  | - | X | X | X | - |
| Carbon disulphide  | X | X | X | X | X |
| <b>Metals</b>  |   |   |   |   |   |
| Metals   | - | X | X | X | X |
| Chromium (VI)  | - | X | X | X | X |
| Mercury  | X | X | X | X | X |
| <b>ZDHC MRSL V1.1</b>  |   |   |   |   |   |
| Alkylphenol (AP) and Alkylphenol Ethoxylates (APEOs): Including All Isomers          | - | X | X | X | X |
| Chlorobenzenes and Chlorotoluenes  | - | X | X | X | X |
| Chlorophenols  | - | X | X | X | X |
| Dyes – Azo (Forming Restricted Amines)   | - | X | X | X | X |
| Dyes – Carcinogenic or equivalent Concern  | - | X | X | X | X |
| Dyes – Disperse (Sensitising)  | - | X | X | X | X |
| Flame Retardants   | - | X | X | X | X |
| Glycols  | - | X | X | X | X |
| Halogenated Solvents   | X | X | X | X | X |
| Organotin Compounds  | - | X | X | X | X |
| Perfluorinated and Polyfluorinated Chemicals (PFCs)                                  | - | X | X | X | X |
| Otho-Phthalates – Including all ortho esters of phthalic acid                        | - | X | X | X | X |
| Polycyclic Aromatic Hydrocarbons (PAHs)  | - | X | X | X | X |
| Volatile Organic Com-pounds (VOC)  | X | X | X | X | X |

\* calibration check conducted with a second source standard

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### 3.2.7 Wastewater Sample Storage

1. All samples will be stored under custody at less than 4°C and above freezing 0°C (unless otherwise specified by the standard test method).
2. The samples may be disposed of 60 days after the final laboratory report is issued.

### 3.3.0 Reporting and Deliverable Requirements

1. Reporting<sup>1</sup> here means the submission of test data/results onto the ZDHC Gateway – Wastewater Module by ZDHC Accepted Laboratories on behalf of suppliers. It is vital that the integrity of test data in the Gateway is at its highest possible standard. This will, among other things, support the ZDHC Roadmap to Zero Programme in making scientific and data driven decisions necessary to shape the future of our industry.
2. All test data must be reported using the ZDHC Gateway Electronic Data Reporting (EDR) System. The EDR guidelines and reporting template are publicly available on the ZDHC website. Important to note: at the time of release of this SAP document in August 2019, the feature is under development, with an expected rollout in 2020 (exact date to be determined).
3. Once the ZDHC EDR is rolled out and fully implemented, the use of reporting formats other than those approved will be deemed non-conformance. Such data is unacceptable and resubmission in the specified format will be required.
4. Between the release of this SAP document in August 2019 and the rollout of the ZDHC EDR, all ZDHC Accepted Laboratories are expected to follow the data reporting requirements specified in the ZDHC Gateway Data Reporting Interim Guidelines for wastewater and sludge, available on the [ZDHC website](#).

<sup>1</sup> For more information please read the latest version of the ZDHC Wastewater Guidelines and the ZDHC Gateway User Terms and Conditions document.

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## 3.4.0 Data Validation

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- ZDHC routinely requests laboratory QA/QC information from randomly selected ZDHC Accepted Laboratories. The following information may be requested for data review:
  - a. Calibration Curves
  - b. Method Blank Instrument Reports
  - c. Calibration Check Sample Instrument Reports
  - d. Laboratory Control Sample Instrument Reports
  - e. Laboratory Duplicate Instrument Reports
  - f. Matrix Spike and Matrix Spike Duplicate Instrument Reports
  - g. Sample Custody Documentation
  
- The quality assurance results reported with the sample results will be assessed by ZDHC to validate the analytical data. Quality assurance results that fail to meet ZDHC guidelines may result in the rejection of sample results.

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## 4.0.0 Sludge

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### 4.1.0 Sampling for Sludge

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#### 4.1.1 Sludge Sampling Points/Locations

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1. Please refer to the ZDHC Wastewater Guidelines (WWG) for the definition of sludge and the main purpose of testing sludge. Depending on the chosen testing option described in the WWG Section 9, sludge samples should be collected.
  
2. The suppliers must identify, to qualified laboratory personnel, the points where sludge is generated and stored. The qualified laboratory personnel will make a determination as to the proper sampling locations.
  
3. Sludge samples will be collected. These will be representative of all sludges generated by the supplier's ETP (Effluent Treatment Plant) that are disposed of or reused.
  
4. It may be necessary to collect various types of sludge samples throughout a given supplier's ETP, including:
  - a. Any Liquid Sludge Waste (not to be confused with wastewater) containing low or high amounts of solids.
  - b. Anaerobically Digested Sludge
  - c. Aerobically Digested Sludge
  - d. De-watered Sludge Cake
  - e. Primary Sludge
  - f. Tertiary Sludge
  - g. Biomass Sludge (Secondary Sludge)
  - h. Compost Product
  - i. Dried Sludge Solid Waste
  - j. Incinerator Ash

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## 4.1.2 Sludge Sample Collection

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1. Samples shall be taken by qualified personnel from the ZDHC Accepted Laboratories. Sludge samples shall be collected as composite samples following: USEPA 833-B-89-100 “POTW Sludge Sampling and Analysis Guidance Document”. The ISO 5667- 13 “Guidance on Sampling Sludge” document also provides reference sludge sampling guidance and more detailed information on sampling devices.
2. The most appropriate way of sampling in any situation depends on several factors:
  - c. safe access to the sampling point by personnel.
  - d. the practicality of installing and maintaining automatic equipment, if appropriate.
  - e. the practicalities of safely interrupting a stream of moving liquid sludge or cake when manually sampling and the nature of the chamber or tank design with respect to stratification of liquid sludges.
3. In general, automatic sampling devices, which are widely used for wastewater streams, do not work well for sludge streams because of the solids content and viscosity of sludges.<sup>2</sup> Therefore, manual composite sampling may be required.
4. ISO 5667-13 describes multiple sample collection devices.
5. For collecting solid sludge samples<sup>3</sup>:
  - a. When sampling heaps of air-dried sludge lifted from drying beds or stockpiles of sludge cake, it is important to obtain portions of sludge from throughout the mass and not just from the surface layer.
  - b. For either de-watered cakes, dried sludge powder or compost product, combine equal amounts collected at various locations/depths for each grab sample. This will obtain a more representative composite sample.
  - c. To produce a sample from multiple sample locations (e.g. two or more de-watering units), combine the grab samples from each location (equal amounts or weighted, based on flow or solids flux data) in a plastic or stainless steel bucket

<sup>2</sup>USEPA 833-B-89-100: POTW Sludge Sampling and Analysis Guidance Document

<sup>3</sup>ISO 5667- 13: Guidance on Sampling Sludge

and thoroughly mix the sample (with a scoop or spoon). Then transfer it to sample containers.

- d. When sampling drying beds, divide each bed into quarters. From the center of each quarter, collect a single core sample through the entire depth of the sludge using a coring device. Usually a small amount of sand will be collected; avoid large amounts of sand. Combine and thoroughly mix in a plastic or stainless steel bucket and transfer to sample containers.
  - e. A sample shall be collected as one composite sample of that sludge type. The composite sample shall represent the entire volume of that sludge type. A sampling grid pattern may be needed, and core samples may be required to obtain a representative sample. Collect samples in a manner that represents the entire sludge volume.
6. For collecting liquid sludge samples:
    - a. It should be noted that thin liquid sludges (of lower solids content) require the preparation of relatively large volumes of the sampled material to provide sufficient dry matter to facilitate a truly representative analysis of constituents, e.g. metals. The analyst should always be consulted as to the quantities of sludge required, and the sample reduced accordingly in the field before returning to the laboratory.<sup>4</sup>
    - b. To ensure representative samples, composite sampling must be performed for no less than six (6) hours, with no more than one (1) hour between discrete samples. Each discrete sample shall be of equal volume.
    - c. All of the laboratory sample containers will be filled from the same bulk composite sample. A minimum sample volume of six (6) litres is needed to fill all the containers. The laboratory may require extra volume for QA samples. The sampler shall coordinate extra volume requirements with the laboratory.
    - d. Collect samples in a manner that represents the entire flow at the sampling point over the entire sampling period<sup>5</sup>.
    - e. These procedures should be followed when sampling from a tap<sup>6</sup>:
      - Allow sufficient time following pump startup to clear the line of stagnant sludge.

<sup>4</sup>ISO 5667- 13: Guidance on Sampling Sludge

<sup>5</sup>USEPA 833-B-89-100: POTW Sludge Sampling and Analysis Guidance Document

<sup>6</sup>USEPA 833-B-89-100: POTW Sludge Sampling and Analysis Guidance Document

- Allow sludge to flow from the tap for several seconds prior to sampling. This will flush out stagnant sludge and solids accumulated in the tap.<sup>6</sup>
  - f. Before drawing a sludge sample, rinse each piece of sampling equipment three (3) times with sample to reduce the chance of contamination from the previous grab.
  - g. To prevent solids separation in the sample, use glass, PTFE-coated stirring rods, or stainless steel spoons to mix the sample before splitting or transferring any portion of it to another container.
  - h. With sludge processing trains, samples from taps on the discharge side of sludge pumps are well mixed since flow at this point in the system is turbulent with minimal solids separation within the flow stream.
  - i. If a sample is drawn from a tap on a pipe containing sludge that is distant from the sludge pumps, the average flow velocity through the pipe should be greater than 2 feet per second (fps). Average velocities of less than 2 fps result in solids separation and settling, and affect sample solids content, depending on the location of the tap (top, side or bottom of the pipe).
  - j. Given a choice, a tap on the side of the pipe is preferable. In addition, the tap should be a large size to encourage draw from the entire cross-section of flow when fully open.
  - k. If the sludge solids tend to separate into different fractions care must be given to mixing the samples adequately to obtain a representative sample. If the fractions cannot be mixed, then separate samples are to be collected. This is because some pollutant parameters, such as metals, are predominantly associated with the solids fraction while others, such as dissolved organics, are associated with the liquid phase.
7. Sampling equipment must be made of materials which will not contaminate or react with the sludge. The best material choices are Teflon, glass, and stainless steel because they are relatively inert.<sup>7</sup>
  8. Sludge flux (weight/time) and/or flow data volume/time, if available, must be collected and reported with the analytical results.

<sup>7</sup>USEPA 833-B-89-100: POTW Sludge Sampling and Analysis Guidance Document

9. The facility shall provide all necessary assistance to the sampler. Including but not limited to:
  - access to all relevant areas.
  - provision of information e.g. flow rates, facility layout, flow path, processes.
  - relocation of parts of solid sludge piles where needed to access deeper layers.
  - provision of safety gear and warnings on any specific hazards present.

### 4.1.3 Sludge Sample Containers and Preservatives

1. *Figure 6* presents standard sample collection containers and preservatives for sludge samples generated from a wastewater/effluent treatment plant (ETP).
2. The appropriate sample collection container and preservative can vary depending on the analytical procedure used. Therefore, verify the proper container and preservative with the analytical method being used at the laboratory.
3. Caution should be exercised since containers can become pressurised due to gas production in wastewater sludges and explosive situations can occur. Care should be taken, particularly when glass containers are used, to prevent a build-up of gas pressure and to minimise the dispersion of fragments if an explosion occurs.<sup>8</sup>
4. A temperature indicator bottle shall be included with each shipping container to measure the temperature of samples at their time of arrival at the laboratory. The temperature indicator bottle will be clearly labelled.
5. When collecting samples, fill the container to 4/5 full to enable expansion of samples when they are frozen and provide room for gases that may be produced.<sup>9</sup>
6. For solid sludge samples (cake, powder, ash), adding a chemical preservative is generally not useful since the preservative does not usually penetrate the sludge matrix. Preservation consists of chilling to 4°C.<sup>10</sup>

<sup>8</sup>ISO 5667- 13: Guidance on Sampling Sludge

<sup>9</sup>USEPA 833-B-89-100: POTW Sludge Sampling and Analysis Guidance Document

<sup>10</sup>USEPA 833-B-89-100: POTW Sludge Sampling and Analysis Guidance Document

Figure 6: Sludge Sample Containers and Preservatives

| Sludge Parameter  | Sample Container<br>Minimum Size              | Standard Preservative<br>(verify with lab method to<br>be used)        |
|---|---|--|
| Anions  |   |  |
| Cyanide   | P, G 1,000-ml wide mouth<br>PTFE lined lid    | NaOH > 12 pH, < 13 pH,<br>cool < 4°C<br>approx 2-ml 10N NaOH           |
| Metals  |   |  |
| Trace Metals  | P, G acid washed 1,000-ml<br>wide mouth       | HNO <sub>3</sub> < pH 2  |
| Chromium (VI)   | P, G acid washed 300-ml wide<br>mouth         | cool < 4°C   |
| Mercury   | P, G acid washed 500-ml wide<br>mouth         | "HNO <sub>3</sub> < pH 2<br>cool < 4°C                                 |
| ZDHC MRSL V1.1  |   |  |
| Alkylphenol (AP) and Alkyl-<br>phenol Ethoxylates (APEOs):<br>Including all Isomers | Three G 1,000-ml PTFE lined<br>lid wide mouth | 0.008% Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> V/W<br>cool < 4°C |
| Chlorobenzenes and Chloro-<br>toluenes  |   |  |
| Dyes – Azo (Forming Re-<br>stricted Amines)   |   |  |
| Dyes – Carcinogenic or<br>Equivalent Concern  |   |  |
| Dyes – Disperse (Sensitising)   |   |  |
| Flame Retardants  |   |  |
| Glycols   |   |  |
| Otho-Phthalates – Including<br>all ortho esters of Phthalic<br>Acid                 |   |  |
| Polycyclic Aromatic Hydro-<br>carbons (PAHs)  |   |  |

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|  |   |  |
|--|---|--|
| Perfluorinated and Polyfluorinated Chemicals (PFCs)    | G 1,000-ml <u>NO</u> PTFE lining wide mouth   | 0.008% Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> V/W<br>cool < 4°C   |
| Chlorophenols  | G 1,000-ml PTFE lining wide mouth             | H2SO4, pH <2 0.008%<br>Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> V/W,<br>cool < 4°C  |
| Organotin Compounds                                    | G 1,000-ml acid washed PTFE lining wide mouth | 1M HCl to pH 2-3<br>cool < 4°C   |
| Halogenated Solvents                                   | Three x 40-ml VOA vial, no headspace          | 1:1 HCl pH <2 , 0.008%<br>Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> V/W<br>cool < 4°C<br>dark  |
| Volatile Organic Compounds (VOC)                       |   |  |
| ZDHC MMCF  |   |  |
| Heavy metals   | P, G 1000 ml wide mouth                       | "As the dry solid sludge samples will be taken, preferably sludge cakes, there is no need for preservation of the sample.<br><br>Sludge samples after collection shall be kept cool until sample preparation. Reference samples, if indicated, shall be stored in a climatized storeroom." |
| Total Organic Carbon, TOC                              | G, 300 ml wide mouth                          |  |
| Extractable Organic Halogen Compounds, EOX             | G, 300 ml wide mouth                          |  |
| Adsorbable Organic Halogen Comounds, AOX, if requested | G, 300 ml wide mouth                          |  |

P= plastic, G= amber glass

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#### 4.1.4 Sludge Sample Custody

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Each sample shipment requires a Chain of Custody log that is maintained from the time of collection, during the entire analytical process, and until sample disposal. A Chain of Custody document provides a record of sample transfer from person to person. This document helps to protect the integrity of the sample by ensuring only authorised persons have custody of the sample. An example Chain of Custody form is presented in *Appendix A*. The sampling team must maintain physical custody, or use custody seal tape on the cool boxes, until the samples are handed off to the shipping company or laboratory.

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#### 4.1.5 Sludge Sample Shipments

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1. Use a 24-hour (overnight) delivery service for samples that are shipped to a laboratory.
2. To avoid shipping delays and compromising sample holding times, contact the shipping company prior to sample collection. The shipping company can help determine the appropriate customs arrangements that must be made.
3. *Appendix B* provides sample shipping forms that may help to avoid delays in customs.
4. Samples will be shipped in cool boxes with sufficient insulation and artificial refrigerant ("blue ice"), or ice contained in double zip-lock bags, to maintain a sample temperature of less than 4°C for the duration of transportation. Shipping containers that leak fluid, such as melting ice water, will likely be returned to the shipper.
5. Containers should be held upright during shipment. Use bubble wrap around individual glass containers and use adequate packing material to prevent movement during shipment, cushion from shock, and reduce the risk of leakage.
6. The sampler shall be responsible for all handling, processing, and custody of the samples, including taking samples to the nearest servicing airport, bus station, or other carrier.

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### 4.2.0 Laboratory Analysis/Testing for Sludge

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#### 4.2.1 Sludge Sample Receipt, Handling, and Custody

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1. The laboratory shall be available to receive sample shipments at any time the delivery service is operating, including weekends.
2. The sample temperature shall be measured and recorded immediately upon opening the shipping container, and prior to unpacking the samples or removing the packing material.
  - a. The laboratory shall use the shipping container temperature indicator bottle reading as the sample temperature.
  - b. To determine the temperature, invert the bottle several times, remove the cap, and insert a calibrated thermometer.
  - c. Allow a minimum of three (3) minutes, but not greater than five (5) minutes prior to taking the measurement. The thermometer used shall be calibrated and capable of measuring within an accuracy of  $\pm 1^{\circ}\text{C}$ .
  - d. If a temperature indicator bottle is not present in the shipping container, an alternative means of determining shipping container temperature can be used.
  - e. Under no circumstances shall a thermometer or any other device be inserted into a sample bottle for the purpose of determining shipping container temperature.
  - f. Other devices (e.g. infrared thermometer), which can measure temperature may be used if they are calibrated to  $\pm 1^{\circ}\text{C}$ .
  - g. The desired sample temperature when it is received at the laboratory is 4°C or less.
    - i. If the sample temperature is greater than 4°C and less than 10°C, the laboratory shall note the issue and provide an exception report with the sample test report.
    - ii. If the sample temperature exceeds 10°C when received at the laboratory, the laboratory shall contact the client and inform them of the temperature deviation. The client may decide not to perform testing on these samples.
3. If the laboratory encounters problems with samples or related documentation (e.g. mixed media, sample pH, sample documentation and paperwork such as Traffic Report/Chain-of-Custody), the laboratory shall immediately contact the sampler for a resolution.

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4.2.2 Sludge Sample Holding Time

- 1. In general, minimising the time between sample collection and analysis will provide more reliable and representative analytical data.
- 2. Figure 7 presents both the recommended and maximum holding times for each of the sludge testing parameters.
- 3. If a sample exceeds the holding time the test results will be reported. However, any test results for samples that exceeded the maximum holding time must be flagged with the following data qualifier:  
"Maximum holding time exceeded. Red flag in the ZDHC Gateway – Wastewater Module. Probable error in results due to the holding time"

Figure 7 – Sludge Sample Holding Time

| Sludge Parameter   | Recommended Holding Time | Maximum Holding Time                 |
|--|--------------------------|--------------------------------------|
| Anions   |                          |                                      |
| Cyanide  | 24 hours                 | 14 days                              |
| Metals   |                          |                                      |
| Trace Metals   | 28 days                  | 6 months                             |
| Chromium (VI)  | 24 hours                 | 28 days                              |
| Mercury  | -                        | 28 days                              |
| ZDHC MRSL V1.1   |                          |                                      |
| Alkylphenol (AP) and Alkyl-phenol Ethoxylates (APEOs): Including all Isomers | -                        | 7 days to extract & 40 days analysis |
| Chlorobenzenes and Chloro-toluenes   | -                        | 7 days to extract & 40 days analysis |

|   |          |                                      |
|---|----------|--------------------------------------|
| Chlorophenols   | -        | 7 days to extract & 40 days analysis |
| Dyes – Azo (Forming Restricted Amines)                        | -        | 7 days to extract & 40 days analysis |
| Dyes – Carcinogenic or Equivalent Concern                     | -        | 7 days to extract & 40 days analysis |
| Dyes – Disperse (Sensitising)                                 | -        | 7 days to extract & 40 days analysis |
| Flame Retardants  | -        | 7 days to extract & 40 days analysis |
| Glycols   | -        | 7 days to extract & 40 days analysis |
| Halogenated Solvents  | 7 days   | 14 days                              |
| Organotin Compounds   | 24 hours | 7 days                               |
| Perfluorinated and Polyfluorinated Chemicals (PFCs)           | -        | 7 days to extract & 40 days analysis |
| Otho-Phthalates – Including all ortho esters of Phthalic Acid | -        | 7 days to extract & 40 days analysis |
| Polycyclic Aromatic Hydrocarbons (PAHs)                       | -        | 7 days to extract & 40 days analysis |
| Volatile Organic Compounds (VOC)                              | 7 days   | 14 days                              |
| ZDHC MMCF   |          |                                      |
| Heavy metals  | 28 days  | 6 month                              |
| Total Organic Carbon, TOC                                     | 7 days   | 14 days                              |
| Extractable Organic Halogen Compounds, EOX                    | 7 days   | 14 days                              |
| Adsorbable Organic Halogen Comounds, AOX, if requested        | 7 day    | 14 days                              |

4.2.3 ZDHC Sludge Parameters

The sludge parameters are listed in the ZDHC Wastewater Guidelines document *Appendix A Table 3*.

4.2.4 Required Reporting Limits and Standard Test Methods for Sludge

- 1. The ZDHC approved standard analytical/test methods and required reporting limits for each of the sludge parameters are presented in the ZDHC Wastewater Guidelines, see *Appendix A Table 3*.
- 2. All test results will be reported on a dry-weight basis.
- 3. The required reporting limits are based on the ZDHC discharge limits, which were established with consideration to achieving these levels with good laboratory practices.
- 4. The methods are based on requirements in the European Union, the United States of America, and China. Alternate methods, such as those required by the regulatory agency in the region in which the wet manufacturing occurs, may be used with prior ZDHC approval.

4.2.5 Quality Systems

- 1. The minimum quality assurance measures for organic chemical analysis of wastewater and sludge are presented in *Figure 8*.

Figure 8: Minimum Quality Assurance Measures for Organic Chemical Analysis

| Measure           | Description   | Target value    | Frequency    | Points to be checked<br>(examples)   |   |
|-------------------|---|-----------------|--------------|--|---|
| A. Routine        |   |                 |              |  |   |
| Method blank      | Covering sample preparation and measurement                                       | < MDL           | 1 per batch  | Cleanliness of laboratory glassware and equipment  |   |
| Calibration Check | An independently sourced/prepared standard  | ± 20 %          | 1 per batch  | Check instrument condition/drift, clean and re-calibrate, stability standards  |   |
| Internal Standard | For GC methods. Substance with physico-chemical properties similar to the analyte | 50 – 150%       | Every sample | Correction of injection error.<br>Method specific: surrogate as alternative  | Choice of internal standard or surrogate or a combination thereof is method/analyte dependent |
| Surrogate         | Substance which has similar physico-chemical properties to the analyte            | method specific | Every sample | Check sample preparation procedure and internal standard correction. Method specific: internal standard as alternative |   |

| B. In case of problematic samples<br>(e.g. internal standard recovery too low, phase separation issues etc.) |  |   |                           |  |
|--|--|---|---------------------------|--|
| Duplicate  | Duplicate undergoing complete process  | < 35 % RPD  | Prob-lematic samples only | Flag results   |
| Matrix Spike Duplicate   | Spike onto sample matrix (duplicate) undergoing complete process               | Method specific                                   | Prob-lematic samples only | Flag results   |
| C. For method validation   |  |   |                           |  |
| Multi-Point Calibration  | Min. 5-point calibration excl. origin  | $r^2 \geq 0.995$                                  | Validation                | Linearity, working range   |
| Recovery (LCS)   | Extract the standard through the test procedure without matrix                 | Method and analyte specific                       | Validation                | Recovery without influence of matrix                                     |
| Repeatability (matrix spike replicate)   | Matrix spike replicates under repeatability conditions                         | Method and analyte specific                       | Validation                | Robustness, recovery with matrix influence, UoM, general fitness for use |
| Limit of Detection   | Reference to ZDHC Wastewater Guidelines; various methodologies can be applied. | $\leq$ WWG RL<br>Ideal: $\leq \frac{1}{2}$ WWG RL | Validation                | Sensitivity, LoD, LoQ  |

Note:

- General suitability of the analytical approach is demonstrated via method validation.
  - Matrix to be encountered for wastewater and sludge analysis is less diverse/concentrated than for process chemicals (ZDHC MRSL).
  - Therefore, initial method validation is deemed to sufficiently cover most sample types and a comparatively leaner QC program is applied.
  - Specific, problematic sample matrices, which are not covered by the validation, require additional QC measures.
  - In case of conflict, quality assurance measures specified by the applied standard, the accreditation body, or local authority shall prevail.
2. The quality assurance testing in *Figure 9* is required for each of the ZDHC sludge parameters. This data will be reported with the sample results and used by ZDHC to assess data quality and validate the analytical data.

Figure 9 – Required Quality Assurance Testing for Sludge

| Parameter   | Field Blank | Method Blank | Calibration Check* | Lab Duplicate | ISTD and Surrogate |
|---|-------------|--------------|--------------------|---------------|--------------------|
| <b>Anions</b>   |             |              |                    |               |                    |
| Cyanide   | -           | X            | X                  | X             | -                  |
| <b>Metals</b>   |             |              |                    |               |                    |
| Trace Metals  | -           | X            | X                  | X             | X                  |
| Chromium (VI)   | -           | X            | X                  | X             | -                  |
| Mercury   | X           | X            | X                  | X             | -                  |
| <b>ZDHC MRSL V1.1</b>   |             |              |                    |               |                    |
| Alkylphenol (AP) and Alkylphenol Ethoxylates (APEOs): Including all Isomers | -           | X            | X                  | X             | X                  |

\* calibration check conducted with a second source standard



|  |   |   |   |   |   |
|--|---|---|---|---|---|
| Chlorobenzenes and Chlorotoluenes                              | - | X | X | X | X |
| Chlorophenols  | - | X | X | X | X |
| Dyes – Azo (Forming Restricted Amines)                         | - | X | X | X | X |
| Dyes – Carcinogenic or Equivalent Concern                      | - | X | X | X | X |
| Dyes – Disperse (Sensitising)                                  | - | X | X | X | X |
| Flame Retardants   | - | X | X | X | X |
| Glycols  | - | X | X | X | X |
| Halogenated Solvents   | X | X | X | X | X |
| Organotin Compounds  | - | X | X | X | X |
| Perfluorinated and Polyfluorinated Chemicals (PFCs)            | - | X | X | X | X |
| Ortho-Phthalates – Including all ortho esters of Phthalic Acid | - | X | X | X | X |
| Polycyclic Aromatic Hydrocarbons (PAHs)                        | - | X | X | X | X |
| Volatile Organic Compounds (VOC)                               | X | X | X | X | X |
| <b>ZDHC MMCF</b>   |   |   |   |   |   |
| Heavy metals   | - | x | x | x | x |
| Total Organic Carbon, TOC                                      | x | x | x | x | x |
| Extractable Organic Halogen Compounds, EOX                     | x | x | x | x | x |
| Adsorbable Organic Halogen Compounds, AOX, if requested        | x | x | x | x | x |

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## 4.2.6 Sludge Sample Storage

1. All samples will be stored under custody at or less than 4°C and above freezing 0°C (unless otherwise specified by the analytical method).
2. The samples may be disposed of 60 days after the final laboratory report is issued.

## 4.3.0 Reporting and Deliverable Requirements

Reporting<sup>11</sup> here means the submission of test data/results onto the ZDHC Gateway – Wastewater Module by ZDHC Accepted Laboratories on behalf of suppliers. It is vital that the integrity of test data in the Gateway is at its highest possible standard. This will, among other things, support the ZDHC Roadmap to Zero Programme in making scientific and data driven decisions necessary to shape the future of our industry.

1. All test data must be reported using the ZDHC Gateway Electronic Data Reporting (**EDR**) System. The EDR guidelines and reporting template are publicly available on the ZDHC website. **Important to note:** at the time of release of this SAP document in August 2019, the feature is under development, with an expected rollout in 2020 (exact date to be determined).
2. Once the ZDHC EDR is rolled out and fully implemented, the use of reporting formats other than those approved will be deemed non-conformance. Such data is unacceptable and resubmission in the specified format will be required.
3. Between the release of this SAP document in August 2019 and the rollout of the ZDHC EDR, all ZDHC Accepted Laboratories are expected to follow the data reporting requirements specified in the ZDHC Gateway Data Reporting Interim Guidelines for wastewater and sludge, available on the ZDHC website.

<sup>11</sup>For more information please read the latest version of the ZDHC Wastewater Guidelines and the ZDHC Gateway User Terms and Conditions document.

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4.4.0 Data Validation

- ZDHC routinely requests laboratory QA/QC information from randomly selected ZDHC Accepted Laboratories. The following information may be requested for data review:
  - a. Calibration Curves
  - b. Method Blank Instrument Reports
  - c. Calibration Check Sample Instrument Reports
  - d. Laboratory Control Sample Instrument Reports
  - e. Laboratory Duplicate Instrument Reports
  - f. Matrix Spike and Matrix Spike Duplicate Instrument Reports
  - g. Sample Custody Documentation
- The quality assurance results reported with the sample results will be assessed by ZDHC to validate the analytical data. Quality assurance results that fail to meet the ZDHC guidelines may result in the rejection of sample results.

Appendix A  
Example Chain of Custody Form

|   |                                     |                                 |  |        |   |  |
|---|-------------------------------------|---------------------------------|--|--------|---|--|
| Sample I.D.   | Facility Name:<br>Facility Address: |                                 | Project:<br>ZDHC Wastewater Evaluation |        | Page ____ of ____<br>Method of Shipment |  |
|   | Facility Contact                    |                                 | Sampler's Name:                        |        | Sampler's Contact Info:                 |  |
|   | Lab Sample No.                      |                                 | No. of Containers                      |        | Matrix                                  |  |
|   | Soil                                |                                 | Water                                  |        | Air                                     |  |
|   | Other                               |                                 | Yes                                    |        | No                                      |  |
|   | Sampling Date                       |                                 | Sampling Time                          |        | Temperature received:                   |  |
|   | Ice                                 |                                 | No ice                                 |        | Turn Around Time (working days)         |  |
|   | M                                   |                                 | A                                      |        | R                                       |  |
|   | K                                   |                                 | S                                      |        | Special Detection Unit/Reporting        |  |
|   | S                                   |                                 | M                                      |        | Lab Work No.                            |  |
| Please Reference the ZDHC Wastewater Guide for required standard test methods and reporting limits. |                                     |                                 |  |        |   |  |
| Sample Received Intact: Yes No  |                                     | Date                            |  | Time   |   |  |
| Relinq. by sampler (Sign & Print Name)  |                                     | Received by (Sign & Print Name) |  | No ice |   |  |
| Relinquished by   |                                     | Date                            |  | Time   |   |  |
| Relinquished by   |                                     | Date                            |  | Time   |   |  |
| Relinquished by   |                                     | Date                            |  | Time   |   |  |

Appendix B

Shipping and Customs Forms

If the following forms are completed and accompany the samples during international shipment, the chance for shipping delays in customs will be minimised:

- 1. Safety Data Sheet (SDS) for water samples. This illustrates that the wastewater samples are not some type of known hazardous material. Search on Google to find some publicly available examples.
- 2. Customs declaration forms for various countries, such as the one presented below, can be found at this link: <https://www.bing.com/images/search?q=Cus-toms+Declaration+Form+PDF&FORM=IDINTS>

|  |                                    |  |  |                 |  |
|--|------------------------------------|--|--|-----------------|--|
| <b>CUSTOMS DECLARATION</b>   |                                    | May be opened officially   |  | <b>CN 22</b>    |  |
| Designated operator  |                                    | Important! See instructions on the back                                      |  |                 |  |
| <input type="checkbox"/> Gift  | <input type="checkbox"/> Documents | <input type="checkbox"/> Commercial sample<br><input type="checkbox"/> Other |  |                 |  |
| Quantity and detailed description of contents (1)  |                                    | Weight (in kg)   |  | Value (3)       |  |
|  |                                    |  |  |                 |  |
| For commercial items only<br>If known, HS tariff number (4)<br>and country of origin of goods (5)  |                                    | Total weight (in kg) (6)   |  | Total value (7) |  |
|  |                                    |  |  |                 |  |
| I, the undersigned, whose name and address are given on the item, certify that the particulars given in this declaration are correct and that this item does not contain any dangerous article or articles prohibited by legislation or by postal or customs regulations.<br>Date and sender's signature (8) |                                    |  |  |                 |  |

TOXIC SUBSTANCE CONTROL ACT (TSCA)

CERTIFICATION

Date: \_\_\_\_\_

(CHECK ONE SECTION ONLY)

POSITIVE CERTIFICATION:

“I CERTIFY THAT ALL CHEMICAL SUBSTANCES IN THIS SHIPMENT COMPLY WITH ALL APPLICABLE RULES OR ORDERS UNDER TSCA AND THAT I AM NOT OFFERING A CHEMICAL SUBSTANCE FOR ENTRY IN VIOLATION OF TSCA OR ANY APPLICABLE RULE OR ORDER THEREUNDER.”

- OR -

NEGATIVE CERTIFICATION:

“I CERTIFY THAT ALL CHEMICALS IN THIS SHIPMENT ARE NOT SUBJECT TO TSCA.”

COMPANY NAME: \_\_\_\_\_

COMPANY ADDRESS: \_\_\_\_\_

AUTHORIZED NAME: \_\_\_\_\_

AUTHORIZED SIGNATURE: \_\_\_\_\_

TITLE: \_\_\_\_\_

FEDERAL EXPRESS AWB#: \_\_\_\_\_

RETURN TO: \_\_\_\_\_

IF THE CERTIFIER IS UNSURE IF THEIR CHEMICAL SUBSTANCE IS SUBJECT TO TSCA COMPLIANCE, CONTACT THE ENVIRONMENTAL PROTECTION AGENCY, TSCA, ASSISTANCE OFFICE, WASHINGTON, D.C. (202) 544-1404 BETWEEN 8:30 AM AND 5:00 PM EST.

REVISED May 7, 1990

Toxic.392

