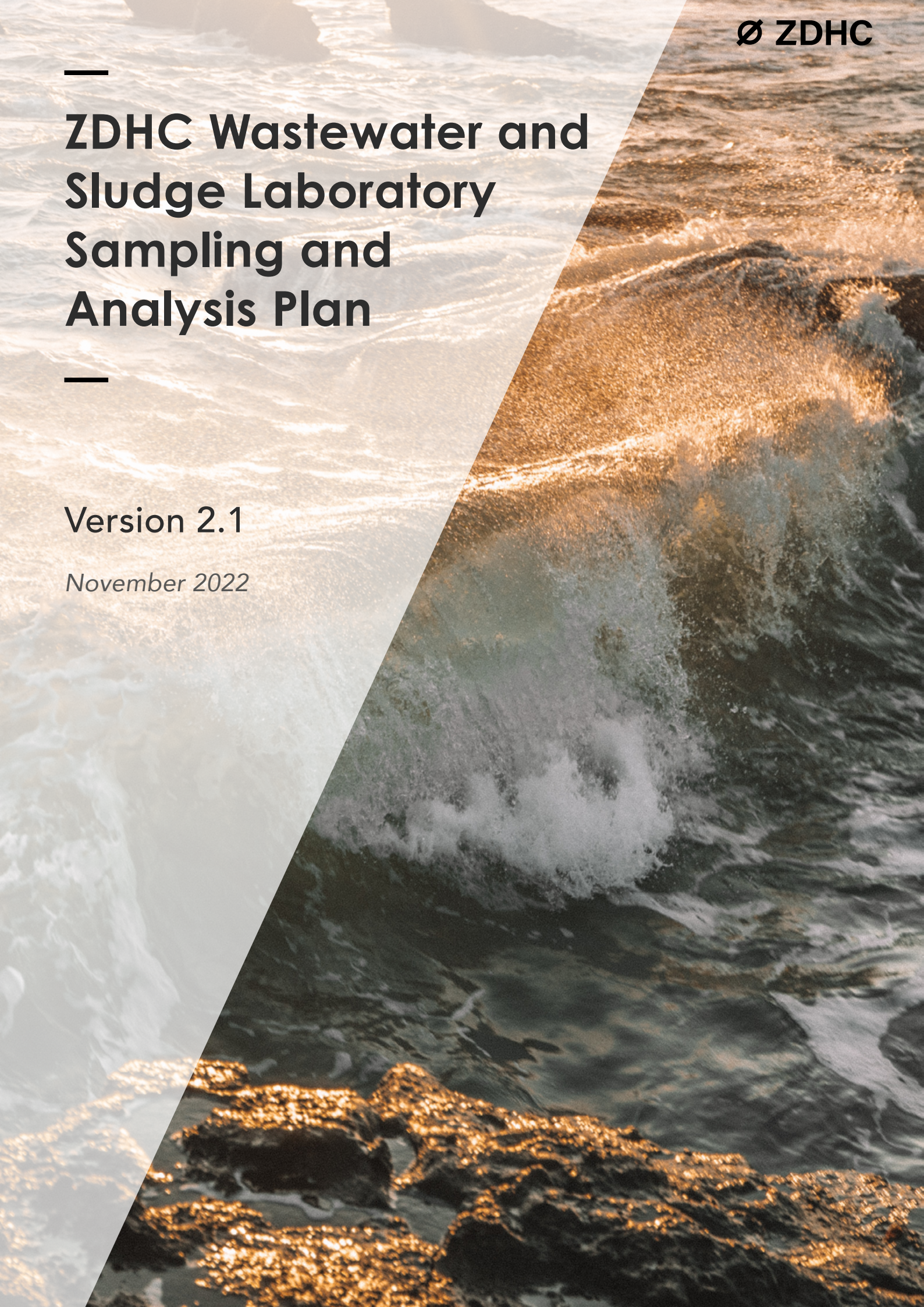
ZDHC

ZDHC Wastewater and Sludge Laboratory Sampling and Analysis Plan

Version 2.1

November 2022



Notes

The ZDHC Wastewater and Sludge Laboratory Sampling and Analysis Plan does not guarantee the following:

a. Compliance with, or take the place of, legal or regulatory requirements. Examples might include[1]: stricter legal, local or regional wastewater and sludge limits, or other requirements relating to the handling and disposal of sludges shall supersede any requirements as set forth in this document.
b. Compliance with, or conformance to, any national or international environmental or workplace safety requirements including, but not limited to, relevant regulations and/or standards.
c. Nor does this document replace any national or international environmental or workplace safety requirements including, but not limited to, regulations and/or standards.

It is not the intent of nor shall the ZDHC Foundation act as an agency reporting wastewater and sludge discharge data to governments or authorities having jurisdiction. It is expected that manufacturing facilities are accountable for reporting on their wastewater and sludge discharges in accordance with applicable laws and regulatory permits at all times. The ZDHC Wastewater and Sludge Laboratory Sampling and Analysis Plan is not intended nor can be used as a statement of legal requirements.

Disclaimers

ZDHC has made every reasonable effort to make sure that the content and information contained in this ZDHC Wastewater and Sludge Laboratory Sampling and Analysis Plan[2] is as accurate and correct as possible at the time of publication, ZDHC makes no claims, promises, or guarantees about the accuracy, completeness, or adequacy of the contents of this document.

In no event will ZDHC (and/or any related ZDHC majority-owned legal entities) or the Directors or staff thereof be liable, and ZDHC expressly disclaims any liability of any kind to any party for any loss, damage, or disruption caused:

a. By errors or omissions, whether such errors or omissions result from negligence, accident, or any other cause and/or;
b. From any use, decision made, or action taken or any other kind of reliance on the ZDHC Wastewater and Sludge Laboratory Sampling and Analysis Plan[2] by a reader or user of it and/or;
c. For any results obtained or not obtained from the use of the ZDHC Wastewater and Sludge Laboratory Sampling and Analysis Plan[2].

[1] This is non-exhaustive list.
[2] For the avoidance of doubt this Disclaimer applies to all related documents produced by ZDHC, specifically: ZDHC Wastewater Guidelines, ZDHC Sludge Reference Document, ZDHC Wastewater and Sludge Laboratory Sampling and Analysis Plan and ZDHC Wastewater Implementation Approach etc.

Introduction

This ZDHC Wastewater and Sludge Laboratory Sampling and Analysis Plan (hereafter referred to as "SAP") is one of the key documents supporting the implementation of the ZDHC Wastewater Guidelines (hereafter referred to as "WW Guidelines"). It does so by standardising procedures for laboratories to conduct sampling and analysis across the ZDHC Wastewater Guidelines, encompassing Textiles, Man-Made Cellulosic Fibres (MMCF) and Leather industry.

The SAP provides a detailed framework for laboratories to test to determine the concentration of parameters in wastewater and sludge. Only ZDHC Accepted Laboratories can perform testing and report results into the ZDHC Gateway. These laboratories must follow the WW Guidelines and the SAP, when performing, sampling, testing and reporting under the ZDHC Programme.

Detailed sample collection instructions and the ZDHC accreditation test are separate from this document and provided through the ZDHC Academy. Only ZDHC accredited samplers may collect wastewater and sludge samples.

Data Use

Wastewater and sludge data helps to promote the implementation of sustainable chemistry and best practices in the industry and can be used for critical decision making and strategic direction for manufacturing facilities. The laboratory must maintain the integrity of test data generated under the ZDHC Programme.

Contents

Revision History

In the spirit of continuous improvement, SAP will be reviewed and revised as needed to incorporate learnings and opportunities identified during the practical application and implementation of these procedures. This version has gone through significant changes listed in Table 1 below. For more details on the historical record of updates to the SAP refer to Appendix C: Expanded Revision History.

Table 1: Revision History of the ZDHC Wastewater and Sludge Laboratory Sampling and Analysis Plan

Version Number	Changes	Time of Publication
Version 2.1	• Added single grab sampling for homogenization tank • Updated Tables 3, 6, 7, 8, and 9 • Adjusted content in standard test method requirements for wastewater and sludge • Added test report requirements • Added Appendix D & E	November 2022
Version 2.0	• Added information for the parameters added with MRSL version 2.0 • Restructured content to avoid repeating information • Added information from the sludge task team • Added information from the Wastewater Council • Added information from the MMCF task team • Added information from the Leather task team • Changed from the EPA MDL and RL terminology to the ISO LOD and LOQ terminologies • Change guidance for collecting liquid sludge samples	November 2021
Previous Versions	See Appendix C: Expanded Revision History for more details	

Definition Terms

Visit the ZDHC Glossary to search for explanations on terminology used across this document and the ZDHC Foundation.

Related Work

This document is part of a set of guidelines and solutions provided by ZDHC. All stakeholders (Suppliers, manufacturing facilities, brands and retailers, and laboratories) are expected to follow the most current guidance documents and practical tools given below:

- ZDHC Wastewater Guidelines
- ZDHC Sludge Reference Document
- ZDHC Wastewater Industry Implementation Approach
- ZDHC Root Cause Analysis and Corrective Action Plan Template found in the Supplier Platform.
- ZDHC List of Accepted Laboratories for ZDHC Wastewater Guidelines Testing
- ZDHC Gateway
- ZDHC Manufacturing Restricted Substances List (ZDHC MRSL)
- USEPA 833-B-89-100: POTW Sludge Sampling and Analysis Guidance Document, United States Environmental Protection Agency 1989.
- ISO 5667- 13: Guidance on Sampling Sludge.
- ISO 5667- 10: Guidance on Sampling of Wastewater

Sample Collection

ZDHC has developed a sampling procedure and sampler training accessible through the ZDHC Academy. Its purpose is to promote consistent sampling and collection of field data. Samplers must complete the training and successfully pass a test at the end. The academy will assign a sampler accreditation number that must be provided with the reported analytical data.

All samplers that collect ZDHC samples must have the ZDHC accreditation sampler ID number. A reference check list of materials needed for sampling can be found in Appendix D.

Sample Locations

The WW Guidelines provide the sampling matrix, shown here in Table 2. The WW Guidelines acknowledges the difference between facilities with Direct, Indirect, Zero Liquid Discharge, and those with an 'Average Total Industrial wastewater generated, that is equal to or more than 15 m3/day'. The WW Guidelines apply to industrial wastewater. Where a Supplier combines their industrial wastewater with domestic wastewater, the resulting combined wastewater is classified as industrial wastewater, to which the Guidelines apply. Refer to the WW Guidelines for more information.

Sample Locations (continued)

Table 2a

Suppliers that generate on average, equal to, or more than 15m³ of industrial wastewater per day				
Test parameters and sample locations/ discharge types	**ZDHC MRSL[a]** Sample untreated wastewater and test Tables 1A-1T parameters	**ZDHC Heavy Metals** Sample effluent and test Table 2 parameters	**ZDHC Conventional and Anions** Sample effluent and test Table 3 parameters	**ZDHC Sludge** Sample sludge and test Table 4 parameters
Direct	Sample and test	Sample treated effluent and test	Sample and test	Sample and test against the chosen ZDHC sludge disposal pathway in accordance with the ZDHC Wastewater Guidelines
Indirect with pretreatment	Sample and test	Sample pre-treated effluent and only test[b] the following only: Arsenic, Cadmium, Chromium (VI), Lead, Mercury	No sample or testing required	Sample and test against the chosen ZDHC sludge disposal pathway in accordance with the ZDHC Wastewater Guidelines
Indirect without pretreatment	Sample and test[c]	Sample and only test[d] the following: Arsenic, Cadmium, Chromium (VI), Lead, Mercury	No sample or testing required	Not applicable, no sample or testing required
ZLD	Sample and test	No sample or testing required	No sample or testing required	Sample and test against the chosen ZDHC sludge disposal pathway in accordance with the ZDHC Wastewater Guidelines

[a] Excluding Heavy Metals.
[b] RCA/ CAP in the event of a detection.
[c] Composite sample is must.
[d] Composite sample is must. RCA/ CAP in the event of a detection.

Sample Locations (continued)

Table 2b

Suppliers that generate on average, less than 15m³ of industrial wastewater per day				
Test parameters and sample locations/ discharge types	**ZDHC MRSL[a]** Sample untreated wastewater and test Tables 1A-1T parameters	**ZDHC Heavy Metals** Sample effluent and test Table 2 parameters	**ZDHC Conventional and Anions** Sample effluent and test Table 3 parameters	**ZDHC Sludge** Sample sludge and test Table 4 parameters
Direct	No sample or testing required	Sample and test	Sample and test	No sample or testing required
Indirect with pretreatment	No sample or testing required	No sample or testing required	No sample or testing required	No sample or testing required
Indirect without pretreatment	No sample or testing required	No sample or testing required	No sample or testing required	No sample or testing required
ZLD	No sample or testing required	No sample or testing required	No sample or testing required	No sample or testing required

[a] Excluding Heavy Metals.

Sampling Specific to Wastewater

ZDHC Wastewater Parameters

The wastewater parameters for testing are listed in the ZDHC Wastewater Guidelines for Textiles, Leather, and Man-Made Cellulosic Fibres (MMCF).

Wastewater Sample Collection

1. Samples shall be taken by ZDHC trained and accredited samplers only. Laboratories shall nominate your samplers to undertake the training using the Solution Provider Platform.

2. Wastewater samples shall be collected as composite samples following ISO 5667 - 10 guidelines: "Guidance on Sampling of Wastewater".

3. 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, or a length of time that represents the entire production process cycle which could be more or less than 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]

4. If necessary, ZDHC approved sampling 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.

5. All of the sample containers will be filled from the same bulk composite sample. A minimum sample volume of 20-litres is required in order to fill all of the sample collection containers. Regarding the volume needed for the analysis, each laboratory shall ensure that the volume of water shipped will ensure duplicate tests and QC controls. The sampler shall coordinate the exact volume for testing with its laboratory.

6. Samples must be taken during a time representing continuous and normal production and continuous and normal wastewater treatment. Collect wastewater samples in a way that represents the entire production cycle. This may take a shorter or longer time than the specified 6-hour composite time. As part of a document control purpose, the facility management needs to confirm the fact that sample collection has been done during normal factory operation. The form could be found there.

7. Start the production cycle wastewater sampling after a time that compensates for the lag time in the effluent treatment system (ETP). For example, if the plant starts production at 8:00 AM and the lag time in the ETP is 3 hours, then ETP wastewater discharge sampling will start at 11:00 AM.

8. A sample collected when there is a homogenization tank – such as an equalization tank – with an average holding time of greater than 12-hours is also considered a composite sample if the volume of wastewater in the tank represents the production process/ cycle. This applies to both the untreated wastewater and the ETP effluent samples. The holding time is calculated by dividing the total operating volume of the tank by the average daily process water usage, multiplied by 24.

9. Samples must not be taken if the wastewater is diluted.

10. For a direct discharge facility the following parameters must be measured every hour during the composite sampling: pH, temperature, persistent foam, wastewater flow rate, total chlorine and dissolved oxygen. The hourly measurements will be reported with the field data report form, and the average will be reported with the ZDHC Gateway Electronic Data Reporting (EDR) template.

11. Wastewater flow rate (m^3/day) must be collected and reported with the laboratory test results using the EDR template. As per the ZDHC Sampler Training, collect flow rate data six times, over a six-hour period, to get the hourly average, before multiplying by 24 (hours), or the length of time the plant operated daily, to get m^3/day.

12. Appendix E provides access to the required ZDHC Wastewater Sampling Field Data Form and Representative Sample Declaration.

13. If a supplier has multiple discharge locations for industrial wastewater, samples must be taken and analysed for each discharge location.

14. Samples from multiple sample locations must be tested separately and not blended together.

15. Specific requirements for sampling Conventional Parameters and Metals (refer to WW Guidelines).
    - For Suppliers to be classified as Zero Liquid Discharge (ZLD) treatment system, they must meet ZDHC's definition of ZLD.

    - Sampling of Effluent:
      - » Sampling shall occur at a point closest to the location where the industrial wastewater leaves the property boundaries of the Supplier.
      - » This should be the same location used to obtain samples to demonstrate legal compliance.

    - Testing for Persistent Foam:
      - » Foam is a naturally occurring phenomenon in aeration basins in which biological wastewater treatment occurs. Samplers should include photographs of the foam they witnessed in the final lab report, along with the time and date of taking such photos. The foam colour should be similar to the liquid in the aeration basin, should dissipate quickly, and should be contained within the aeration basin.

[3] Longer composite sampling may be required to satisfy regulatory requirements. More information on temperature measurements can be found on Footnote B of Table 3 on the WW Guidelines.

If the foam is higher than 45 centimetres (by visual estimation) then it could result in permanent foam being discharged onto the surface of receiving waters and should be noted. For direct discharge facilities samplers should check for persistent foam on the surface of receiving waters at the point of discharge and the presence or absence of foam should be noted. This should be checked at the same location used for sampling the temperature difference. This test is to be done on-site by the sampler and should be checked at the same location used for ΔT sample checks.

- Testing for Temperature Difference:
  - » Testing for temperature difference is only applicable to Direct Discharge Facilities. Take the temperature of the discharged wastewater and the receiving body of water upstream. Subtract the temperature of the receiving body from the temperature of the discharge to give the delta temperature difference, which can be a positive or a negative value. The WW Guidelines discharge limits only refer to a positive value, which produces an overall increase in the temperature of the receiving body of water.

16. Utilising other test results for ZDHC WW Guidelines reporting:
    ZDHC supports Suppliers wishing to optimise sampling and testing to demonstrate both legal compliance and performance against the WW Guidelines for their applicable wastewater parameters wastewater parameters if certain conditions are met.

    This means, if Suppliers schedule both ZDHC and legal compliance sampling at the same time, the test results may only be utilised to report against the WW Guidelines if the laboratory is ZDHC Approved.

17. Trouble finding ZDHC Approved Laboratories in your area:
    Only ZDHC Approved Wastewater Laboratories are able to report against WW Guidelines. You can find an updated list of all approved ZDHC Approved Wastewater Laboratories here. If you are not able to find an approved laboratory in your area, you can guide your local wastewater testing laboratory to apply for acceptance via the Solution Provider Platform.

Wastewater Sample Containers and Preservatives

1. Table 3 presents standard sample collection containers and preservatives for the wastewater parameters specified in the WW 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 used at the laboratory.

3. A temperature indicator bottle should be included with each shipping container. The temperature indicator bottle will be clearly labelled. If the sample shipping time is short, such as across town, then collect a sub-sample from one of the sample containers and measure and report that as the temperature received at the lab.

4a. Field blanks shall be collected for the following parameter:
- Total Phosphorus
- Mercury
- Halogenated Solvents / Volatile Organic Compounds (VOC)
- Perfluorinated and Polyfluorinated Chemicals (PFCs)

4b. The field blanks shall use the same containers as the samples and will be filled with reagent grade laboratory water (ASTM D1193 or ISO 3696 water grade 1).

Table 3: Wastewater Sample Containers and Preservatives
(P= plastic, G= amber glass, FP= fluoropolymer)

Wastewater Parameter	**Sample Container Minimum Size**	**Standard Preservative** (verify with lab method to be used)
Shipping temperature of indicator bottle for all test parameters	calibrated thermometer to +/- 1C°	room temperature water
ZDHC Conventional including Anions		
Ammonia-Nitrogen	P,G,FP 500-ml	$H2SO_4$ < pH 2 keep cool - between 2˚C and 8˚ C
AOX	P,G,FP 500-ml	HNO_3 pH 1-2, keep cool - between 2˚C and 8˚ C
Biochemical Oxygen Demand 5-days concentration (BOD_5)	P,G,FP 1,000-ml	Keep cool between 2˚C and 8˚C
Chemical Oxygen Demand (COD)	P,G,FP 100-ml	$H2SO_4$ < pH 2 keep cool - between 2˚C and 8˚ C

Table 3: Wastewater Sample Containers and Preservatives

Wastewater Parameter	Sample Container Minimum Size	Standard Preservative (verify with lab method to be used)
ZDHC Conventional including Anions		
Chloride	P,G,FP 100-ml	keep cool - between 2˚C and 8˚ C
Colour [m-1] (436nm; 525nm; 620nm)	P,G,FP 500-ml	
Cyanide	P,FP 1000-ml	NaOH > pH12 0.1 ml of 10% Sodium Thiosulfate keep cool - between 2˚C and 8˚ C
Dissolved Oxygen (DO)	NA	Measured in the field
E.coli	P,G clean, sterile, non-reactive, 125-ml	0.1 ml of 10% Sodium Thiosulfate keep in the dark and cool between 2˚C and 8˚C
Oil and Grease	Glass, wide mouth PTFE lined lid 1,000-ml	HCl or $H2SO_4$ < pH 2 keep cool - between 2˚C and 8˚ C
Persistent Foam	NA	Measured in the field
pH	NA	
Phenol	P,G PTFE lined lid 500-ml	$H2SO_4$ < pH 2 keep cool - between 2˚C and 8˚ C
Temperature difference	NA	Measured in the field
Total Chlorine	NA	
Total Dissolved Solids (TDS)	P,G 200-ml	keep cool - between 2˚C and 8˚ C
Total Nitrogen	P,G,FP 100-ml	$H2SO_4$ < pH 2 keep cool - between 2˚C and 8˚ C
Total Phosphorus		$H2SO_4$ < pH 2 keep cool - between 2˚C and 8˚ C
Total Suspended Solids (TSS)	P,G 200-ml	keep cool - between 2˚C and 8˚ C
Sulfate	P,G,FP 100-ml	
Sulfide	P, FP 100-ml	4 drops 2N zinc acetate NaOH > pH 9 keep cool - between 2˚C and 8˚C
Sulfite	P,G,FP 100-ml	1-ml 2.5% EDTA keep cool - between 2˚C and 8˚C
ZDHC Heavy Metals		
Chromium (VI)	G acid washed 40-ml Brown Glass VOA vial	0.45µm filter in field, add buffer* to pH 9.0-9.5 keep cool - between 2˚C and 8˚C
Heavy Metals (Antimony, Arsenic, Barium, Cadmium, Chromium-total, Cobalt, Copper, Lead, Nickel, Selenium, Silver, Tin, Zinc)	P, G, FP acid washed 250-ml	HNO_3 < pH 2 keep cool - between 2˚C and 8˚C
Mercury	P, G, FP acid washed 500-ml	HNO_3 < pH 2 keep cool - between 2˚C and 8˚C
ZDHC MRSL		
Alkylphenol (AP) and Alkylphenol Ethoxylates (APEOs): including all isomers	G 1,000-ml FP lined lid for each parameter (12 total are needed)	keep cool - between 2˚C and 8˚C
Anti- Microbials & Biocides		
Chlorinated Parafins		
Chlorobenzenes and Chlorotoluenes		
Chlorophenols		
DMFa		
Restricted Aromatic Amines (Cleavable from Azo-colourants)		
Dyes – Carcinogenic or Equiv. Concern		
Dyes – Disperse (Sensitizing)		
Dyes – Navy Blue Colourant		
Flame Retardants		
Glycols / Glycol Ethers		

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

Table 3: Wastewater Sample Containers and Preservatives

Wastewater Parameter	Sample Container Minimum Size	Standard Preservative (verify with lab method to be used)
ZDHC MRSL (continued)		
Halogenated Solvents	Three x 40-ml amber VOA vial no headspace	HCl < pH 2 keep cool - between 2˚C and 8˚C
Organotin Compounds	G 1,000-ml acid washed FP lined lid	keep cool - between 2˚C and 8˚C
Other/Miscellaneous Chemicals	G 1,000-ml FP lined lid	
Perfluorinated and Polyfluorinated Chemicals (PFCs)	P 1,000-ml no FP lined lid	
Phthalates – including all other esters of ortho-phthalic acid	G 1,000-ml FP lined lid for each parameter (2 needed)	
Polycyclic Aromatic Hydrocarbons (PAHs)		
UV Absorbers	G 100-ml FP lined lid	keep cool - between 2˚C and 8˚C
Volatile Organic Compounds (VOC)	Three x 40-ml amber VOA vial no headspace	HCl or $H2SO_4$ or HNO_3 < pH 2 keep cool - between 2˚C and 8˚C
ZDHC MMCF Specific		
Acute Aquatic Toxicity; Luminus Bacteria	G 1,000-ml FP lined lid for each parameter	keep cool - between 2˚C and 8˚C
Acute Aquatic Toxicity; Fish Egg		
Acute Aquatic Toxicity; Daphne		
Acute Aquatic Toxicity; Algae		
Carbon Disulfide	Three x 40-ml amber VOA vial no headspace	HCl < pH 2 keep cool - between 2˚C and 8˚C
Total Hydrocarbons	Wide mouth G 1,000-ml FP lined lid	HCl or $H2SO_4$ < pH 2 keep cool - between 2˚C and 8˚C

Laboratory Required Reporting Limits and Standard Method for Analysis and Testing Wastewater

The ZDHC approved standard test methods and required reporting limits are presented in the ZDHC Wastewater Guidelines for Texiles, Leather and Man-Made Cellulosic Fibres (MMCF).

Standard Test Methods for Requirements for Wastewater

1. The accepted laboratory analytical methods for each wastewater parameter are based on requirements in the European Union, the United States of America, India, and China and are presented in the ZDHC wastewater guidelines. The analytical methods were selected in collaboration with the ZDHC laboratory Advisory Group (LAG).

2. With the exception of COD and colour an "equivalent" analytical methods can be used, such as those required by the regulatory agency in the region where the wet processing/manufacturing occurs. Equivalent methods must be pre-approved by ZDHC and/or the LAG. The pre-approval process is conducted so that data from one lab can be compared directly and equivalently to any other lab in the ZDHC programme.

3. An equivalent analytical method is defined by ZDHC as a method that has the fundamentally same sample collection (for example; sample container, preservative), sample preparation (for example; derivatisation, extraction, digestion), and analysis (for example; GC/MS, LC/MS-MS) and the same LOD & LOQ. The laboratory has to share with ZDHC relevant information to assess the equivalence. Alternatively, an analytical method may be accepted if a formal method validation process, using a representative matrix, has been successfully completed, and those results/data are shared by the laboratory with ZDHC.

4. The specified ZDHC methods for colour and Chemical Oxygen Demand (COD) must be used, without exceptions.

5. For some parameters, validated cuvette methods can be used alternatively, as indicated in WW Guidelines.

Sampling Specific to Sludge

ZDHC Sludge Parameters

Sludge parameters are listed in the ZDHC Wastewater Guidelines.

Sludge Sample Locations

1. Refer to the WW Guidelines and the ZDHC Sludge Reference Document to understand the main purpose of testing sludge and how to classify the sludge Disposal Pathways.

2. The Suppliers must identify, to qualified sampling personnel, the locations where sludge is generated and stored at the Supplier facility. The qualified sampling personnel will determine the proper sampling locations as per the guidance provided to them.

3. Sludge samples must be collected to be representative of the chosen ZDHC Disposal Pathways.

4. It may be necessary to collect various types of sludge samples throughout a Supplier's ETP, sludge types can include:
    a. Precipitation/flocculation/coagulation to remove organics
    b. Anaerobically digested secondary treated sludge
    c. Aerobically digested secondary treated sludge
    d. Primary treated sludge
    e. Biomass, secondary treated, and tertiary treated sludge
    f. Mechanically de-watered sludge
    g. Dried sludge
    h. Sludge generated from evaporation processes
    i. Ash from the incineration of any type of waste at an on-site incinerator

Sludge Sample Collection

1. Samples shall be taken by ZDHC trained and accredited samplers only. Laboratories nominate your samplers to train using the Solution Provider Platform.

2. Composite sludge samples are one sludge type taken over a period of time. The composite sludge sample can be taken from hopper, roll-off, or sludge storage areas. It must represent the facility's sludge production and storage cycle for the entire volume of that sludge type.

3. At facilities with on-site incineration and separately test two samples:
    - Residual incineration ash, and;
    - Composite sludge.

    These samples must be tested separately.

4. Sludge samples shall be collected as composite samples following: USEPA 833-B-89- 100[4]. The ISO 5667- 13 "Guidance on Sampling Sludge" document also provides reference sludge sampling guidance and more detailed information on sampling devices.

5. ISO 5667-13 "Guidance on Sampling Sludge" describes multiple sample collection devices.

6. The most appropriate way of sampling in any situation depends on several factors:
    - Safe access to the sampling point by personnel, and;
    - The practicality of installing and maintaining automatic equipment, if appropriate.

7. 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[5]. Therefore, manual composite sampling is required.

8. For collecting solid and semi-solid sludge samples:
    - 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.

    - 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.

[4] USEPA 833-B-89-100: POTW Sludge Sampling and Analysis Guidance Document, United States Environmental Protection Agency 1989.
[5] USEPA 833-B-89-100: POTW Sludge Sampling and Analysis Guidance Document, United States Environmental Protection Agency 1989.

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

- When sampling drying beds, divide each bed into quarters. From the centre 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.

- 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.

9. Collecting liquid sludge with high solids content:
   - Liquid sludges with low viscosity (of lower solids content) may not have sufficient dry matter to facilitate a truly representative analysis of constituents, e.g. metals, using the sludge analysis methods. Therefore, at the labs' discretion, these samples will be collected using the wastewater containers and preservatives, analysed like a wastewater sample, and reported as a sludge sample on a weight/volume basis (mg/L). The laboratory analyst can be consulted about the quantities of sludge required at the lab.

10. Collecting liquid sludge with a high solids content
    - All laboratory sample containers must 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 Quality Assurance samples. The sampler shall coordinate extra volume requirements with the laboratory.

    - Collect samples in a manner that represents the entire flow at the sampling point, over the entire sampling period[6].

    - These procedures should be followed when sampling from a tap[7]:
      - » Allow sufficient time following pump start-up to clear the line of stagnant sludge.
      - » 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.

    - To prevent solids separation in the sample, use glass, stirring rods, or stainless-steel spoons to mix the sample before splitting or transferring any portion of it to another container.

[6] USEPA 833-B-89-100: POTW Sludge Sampling and Analysis Guidance Document, United States Environmental Protection Agency 1989.
[7] USEPA 833-B-89-100: POTW Sludge Sampling and Analysis Guidance Document, United States Environmental Protection Agency 1989.

- 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.

- 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).

- 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 without clogging the flow.

- If the sludge solids tend to separate into different fractions, mix the samples adequately to obtain a representative sample. If they do not mix, collect separate samples. Some pollutant parameters are predominantly associated with the solid fraction, while others are associated with the liquid phase.

11. Sampling equipment must be made of materials that will not contaminate or react with the sludge and must have adequate capacity to avoid oxidation if the bottle is not completely filled. The best material choices are glass and stainless steel because they are relatively inert[9].

12. If available, sludge flux (weight/time) and/or sludge flow data (volume/time) must be collected and reported with the laboratory sample test report PDF. Typically, the sludge dewatering equipment is not operated 24/7 and will run 2 or 3 cycles per day depending on equipment sizing and sludge volume produced. Monitoring flow rates will not represent the daily operations and flows/generation of sludge. In such cases, sludge flux and flow data are not necessary to collect or record.

13. 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.

[9] USEPA 833-B-89-100: POTW Sludge Sampling and Analysis Guidance Document, United States Environmental Protection Agency 1989.

Sludge Sample Containers and Preservatives

1. Table 4 presents standard sample collection containers and preservatives for sludge samples generated from a wastewater effluent treatment plant.
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 used at the laboratory.
3. Caution should be exercised as 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[10].
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 and provide room for gases that may be produced[11].
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 is achieved by keeping the temperature between 2°C and 8°C.

Table 4: Sludge Sample Containers and Preservatives
(P= Plastic, G= Amber glass)

Sludge Parameter	Sample Container Minimum	Standard Preservative
ZDHC Conventional including Anions		
% Solids	125-ml P,G	keep cool - between 2˚C and 8˚C
Cyanide	P, G 1,000-ml wide mouth PTFE lined lid	NaOH > 12 pH, keep cool between 2˚C and 8˚C Approx 2-ml 10N NaOH
Feacal Coliform	P,G clean, sterile, non-reactive, 125-ml	0.1 ml of 10% Sodium Thiosulfate keep in the dark and cool between 2˚C and 8˚C
Paint Filter Test	250-ml P,G	keep cool - between 2˚C and 8˚C
ZDHC Total Metals		
Chromium (VI)	P, G acid washed 300-ml wide mouth	keep cool between 2˚C and 8˚C
Mercury	P, G acid washed 500-ml wide mouth	HNO_3 < pH 2 keep cool between 2˚C and 8˚C
Total Metals / Heavy Metals (Antimony, Arsenic, Barium, Cadmium, Chromium-total, Cobalt, Copper, Lead, Nickel, Selenium, Silver, Tin, Zinc)	P, G acid washed 1,000-ml wide mouth	HNO_3 < pH 2, keep cool between 2˚C and 8˚C
ZDHC MRSL		
Alkylphenol (AP) and Alkylphenol Ethoxylates (APEOs): including all isomers	Three G 1,000-ml PTFE lined lid wide mouth	0.008% $Na_2S_2O_3$ V/W keep cool between 2˚C and 8˚C
Chlorotoluenes		
Polycyclic Aromatic Hydrocarbons (PAHs)		
ZDHC MMCF Specific		
Adsorbable Organic Halogen Compounds, AOX, if requested	G, 300 ml wide mouth	As the dry solid sludge samples will be taken, preferably sludge cakes, there is no need for preservation of the sample. Sludge samples after collection shall be kept cool between 2˚C and 8˚C until sample preparation. Reference samples, if indicated, shall be stored in a climatized storeroom.
Extractable Organic Halogen Compounds, EOX		
Total Organic Carbon, TOC	G, 300 ml wide mouth	
Heavy metals	P,G acid washed 500-ml wide mouth	HNO_3 <pH 2 keep cool between 2˚C and 8˚C.

[10] ISO 5667- 13: Guidance on Sampling Sludge.
[11] USEPA 833-B-89-100: POTW Sludge Sampling and Analysis Guidance Document, United States Environmental Protection Agency 1989.

Standard Test Methods Requirements for Sludge

1. The accepted laboratory analytical methods for each sludge parameter are based on requirements in the European Union, the United States of America, India, and China and are presented in the ZDHC wastewater guidelines. The analytical methods were selected in collaboration with the laboratory Advisory Group (LAG).

2. An “equivalent” analytical method can be used, such as those required by the regulatory agency in the region where the wet processing/manufacturing occurs. Equivalent

methods must be pre-approved by ZDHC and/or the LAG. The pre-approval process is conducted so that data from one lab can be compared directly and equivalently to any other lab in the ZDHC programme.

3. All test results will be reported on a dry weight basis.

4. The required reporting limits were established with consideration to achieving these levels with good laboratory practices.

5. Laboratories will test all sludge samples for total metals, conventional sludge parameters, and certain organic MRSL compounds. If the total metals threshold values are exceeded, the laboratory will conduct leachate testing of the sludge for the metals that exceed the total metals threshold. The limits for conventional sludge parameters, organic MRSL compounds, leachate metals, and the total metals thresholds are shown in the WW Guidelines.

   Example methodology of applying the total metals threshold value for Arsenic:
   - Step 1: Conduct total metals analysis;
   - Step 2: Determine if the total metals results are greater than 10mg/kg for Arsenic on a dry weight basis;
   - Step 3: If greater than 10mg/kg, conduct a Toxicity Characteristic Leaching Procedure (TCLP) test;
   - Step 4: Analyse the TCLP extract for total Arsenic;
   - Step 5: Compare TCLP Arsenic results with the ZDHC TCLP limits.

Sample Holding Time

1. In general, minimising the time between sample collection and analysis will provide more reliable and representative analytical data.
2. Test results will be reported if the sample exceeds the maximum holding time[12]. Any test results for samples that exceeded the maximum holding time must be flagged with the following data qualifier: "Maximum holding time exceeded" in the ZDHC Gateway Electronic Data Reporting (EDR) template.
3. ZDHC encourages the use of local labs to meet short holding time requirements for some parameters as long as the following conditions are met:
   - The lab is ISO 17025 accredited for the parameters tested, and;
   - The lab must perform the quality assurance and quality control practices required for all ZDHC accepted labs. This includes the ZDHC specific data quality indicators that successfully comply with the ZDHC data quality objectives, and;
   - The laboratory reporting limits are at or below the aspirational limit values specified for wastewater, and at or below ZDHC reporting limits for MRSL wastewater and MRSL sludge, and;
   - The primary laboratory is responsible for data reporting and data quality for any sub-contracted labs used.

[12] Maximum Holding Time limits the time between sampling and the start of the sample's analysis.

Sample Holding Time Specific to Wastewater

Table 5 presents the recommended and maximum holding times for each of the wastewater testing parameters.

Table 5: Wastewater Sample Holding Times

Wastewater Parameter	Recommended Holding Time	Maximum Holding Time
ZDHC Conventional including Anions		
Ammonia-Nitrogen	7-days	28-days
AOX	-	6-months
Biochemical Oxygen Demand 5-days concentration (BOD_5)	6-hours	48-hours
Chemical Oxygen Demand (COD)	7-days	28-days
Chloride	-	28-days
Colour [m-1] (436nm; 525nm; 620nm)	-	48-hours
Cyanide	24-hours	14-days
Dissolved Oxygen (DO)	measure in the field	15-mins
E.coli	6-hours	24-hours
Oil and Grease	-	28-days
Persistent Foam	measure in the field	-
pH	measure in the field	6-hours
Phenol	24-hours	28-days
Temperature difference	measure in the field	15-mins
Total Chlorine	measure in the field	15-mins
Total Dissolved Solids (TDS)	24-hours	7-days
Total Nitrogen	-	28-days
Total Phosphorus	-	28-days
Total Suspended Solids (TSS)	24-hours	7-days

Table 5: Wastewater Sample Holding Times

Wastewater Parameter	Recommended Holding Time	Maximum Holding Time
ZDHC Conventional including Anions (continued)		
Sulfate	-	28-days
Sulfide	-	7-days
Sulfite	-	48-hours
ZDHC Heavy Metals		
Chromium (VI)	24-hours	28-days
Heavy Metals (Antimony, Arsenic, Barium, Cadmium, Chromium-total, Cobalt, Copper, Lead, Nickel, Selenium, Silver, Tin, Zinc)	28-days	6-months
Mercury	-	28-days
ZDHC MRSL		
Alkylphenol (AP) and Alkylphenol Ethoxylates (APEOs): Including All Isomers	-	**Extraction:** 7-days from collection **Analysis:** 40-days from extraction
Anti- Microbials & Biocides	-	
Chlorobenzenes and Chlorotoluenes	-	
Chlorinated Parafins	-	
Chlorophenols	-	
DMFa	-	
Restricted Aromatic Amines (Cleavable from Azo-colourants)	-	
Dyes – Carcinogenic or Equivalent Concern	-	**Extraction:** 7-days from collection **Analysis:** 40-days from extraction
Dyes – Disperse (Sensitizing)	-	
Dyes – Navy Blue Colourant	-	
Flame Retardants	-	
Glycols / Glycol Ethers	-	
Organotin Compounds	24-hours	
Other/Miscellaneous Chemicals	-	
Perfluorinated and Polyfluorinated Chemicals (PFCs)	-	
Phthalates – including all other esters of ortho-phthalic acid	-	
Polycyclic Aromatic Hydrocarbons (PAHs)	-	
UV Absorbers	-	
Halogenated Solvents	7-days	14-days
Volatile Organic Compounds (VOC)	7-days	14-days
ZDHC MMCF Specific		
Aquatic Toxicity; Luminus Bacteria, Fish egg, Daphne, or Algae	24-hours	48-hours
Carbon Disulfide	7-days	14-days
Total Hydrocarbon	-	28-days

Sample Holding Time Specific to Sludge

Table 6 presents the recommended and maximum holding times for each of the sludge testing parameters.

Table 6 – Sludge Sample Holding Time

Sludge Parameter	Recommended Holding Time	Maximum Holding Time
ZDHC Conventional including Anions (continued)		
% Solids	2-days	7-days
Cyanide	24-hours	14-days
Fecal Coliform	6-hours	24-hours*
Paint Filter Test	2-days	7-days
pH	15-mins	24-hours
ZDHC Heavy Metals		
Chromium (VI)	24-hours	28-days
Heavy Metals (Antimony, Arsenic, Barium, Cadmium, Chromium-total, Cobalt, Copper, Lead, Nickel, Selenium, Silver, Tin, Zinc)	28-days	6-months
Mercury	-	28-days
ZDHC MRSL		
Alkylphenol (AP) and Alkylphenol Ethoxylates (APEOs): Including All Isomers	-	**Extraction:** 7-days from collection **Analysis:** 40-days from extraction
Chlorotoluenes	-	
Polycyclic Aromatic Hydrocarbons (PAHs)	-	
ZDHC MMCF Specific		
Adsorbable Organic Halogen Comounds, AOX	7-days	14-days
Extractable Organic Halogen Compounds, EOX		
Total Organic Carbon, TOC		

* Fecal Coliform has a 24-hour holding time. It is acceptable to collect a grab sample for Fecal coliform and ship before the composite if that will satisfy the holding time.

Sample Shipments

1. Use a 24-hour (overnight) delivery service for samples shipped to a laboratory. If 24-hour delivery is not available, consider using a ZDHC Approved local laboratory to conduct a short hold time analysis.

2. To avoid shipping delays and compromising sample holding times, contact the shipping company before sample collection. The shipping company can help determine the appropriate customs arrangements that must be made.

3. Appendix B: Shipping and Customs Forms provides sample shipping forms that may help to avoid delays in customs.

4. Samples must 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 between 2°C and 8°C for the entire duration of transportation. Shipping containers that leak fluid, such as melting ice water, will likely be returned to the shipper.

5. The sample cool boxes must be sealed with custody tape, signed and dated by the sampling crew.

6. The sampler is responsible for handling, processing, and custody of the samples. This includes taking samples to the nearest servicing airport, bus station, or other carriers.

7. 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.

8. The sampling team must maintain physical custody or use custody seal tape on the sample cool boxes.

Sample Receipt, Handling, and Custody

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.
   - The laboratory shall use the shipping container temperature indicator bottle reading as the sample temperature.

   - To determine the temperature, invert the bottle several times, remove the cap, and insert a calibrated thermometer.

- Allow a minimum of three (3) minutes, but no greater than five (5) minutes prior to taking the measurement. The thermometer used shall be calibrated and capable of measuring within an accuracy of ±1°C.

- If a temperature indicator bottle is not present in the shipping container, an alternative means of determining shipping container temperature can be used.

- Under no circumstances shall a thermometer or any other device be inserted into a sample bottle to determine shipping container temperature. However, a small aliquot of the sample removed from the container can be used to measure temperature. This small aliquot must be discarded and not returned to the sample container.

- Other devices, such as an infrared thermometer, which can measure temperature, may be used if calibrated to ±1°C.

- The desired sample temperature when received at the laboratory is between 2°C and 8°C.
  - » If the sample temperature is greater than 8°C and less than 10°C, the laboratory shall note the issue and provide a remark with the laboratory sample test report PDF.
  - » 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. Each sample shipment requires a Chain of Custody log 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 protect the integrity of the sample by ensuring only authorised persons have custody of the sample. An example of a chain of custody form is presented in Appendix A: Example Chain of Custody Form. The sampling team must maintain physical custody or use custody seal tape on the sample cool boxes.

4. A document attesting that the sampler has been in the factory needs to be present signed both from the sampler and the customer (with stamp).

5. 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.

6. For wastewater and liquid type sludge, 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.
   - Measure pH using test strips, a hand-held electronic pen, or pH meter. To prevent sample contamination, measure the pH on a small aliquot of the sample removed from the container. This small aliquot must be discarded and not returned to the sample container.
   - Under no circumstances shall a strip or any device be inserted into a sample bottle for the purpose of determining pH.

Sample Storage

1. All samples will be stored under custody at 2˚C - 8˚C in the laboratory (unless otherwise specified by the standard test method).
2. The samples may be disposed of 60 days after the laboratory submits the final ZDHC Gateway Electronic Data Report (EDR).

Quality Systems

The minimum quality assurance measures for organic chemical analysis of wastewater and sludge are presented in Table 7.

Table 7: Minimum Quality Assurance Measures for Organic Chemical Analysis

Measure	Description	Target value	Frequency	Points to be checked (examples)	
A. Routine					
Method blank	Covering sample preparation and measurement	< LOD	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 of standards	
Internal Standard	For GC methods. Substance with physico-chemical properties similar to the analyte	50 – 150%	Every sample	Correction of injection error. Method specific: surrogate as alternative	Choice of internal standard or surrogate or a combination the reof 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	
Duplicate	Duplicate undergoing complete process	< 35 % RPD	1 per batch and every 20 samples	Reproducibility of method	
Matrix Spike Matrix Spike Duplicate (MS/MSD)	Spike into sample matrix (duplicate) undergoing complete process	±20% recovery and < 35% RPD	1 per batch and every 20 samples	Parameter recovery with sample matrix influence and reproducibility	

Table 7: Minimum Quality Assurance Measures for Organic Chemical Analysis

Measure	Description	Target value	Frequency	Points to be checked (examples)
B. For Method Validation				
Multi-Point Calibration	Min. 5-point calibration excl. origin	$r^2 \leq 0.990$	Validation	Linearity, working range
Recovery (LCS)	Extract the standard through the test procedure without matrix	Method and analyte specific		Recovery without influence of matrix
Repeatability (matrix spike replicate)	Matrix spike replicates under repeatability conditions			Robustness, recovery with matrix influence, UoM, general fitness for use
Limit of Detection	ISO/TS 13530:2009 4.4.3 4.4.7	Less than WWG RL Ideal: ≤ 1/2 WWG RL		LOD

Note:

- The general suitability of the analytical approach is demonstrated via method validation.
- Therefore, initial method validation is deemed to sufficiently cover most sample types, and a comparatively leaner Quality Control (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.

Quality Systems Specific to Wastewater

The quality assurance testing in Table 8 is required for each ZDHC wastewater parameters. This data may be requested and used by ZDHC to assess data quality and validate the analytical results.

Table 8: Required Quality Assurance Testing for Wastewater

DQI	Field Blank	Method Blank	Calibration Check*	Lab Duplicate	ISTD and Surrogate	Matrix Spike & Matrix Spike Duplicate
Frequency	**1 per Batch**	**1 per Batch**	**1 per Batch**	**1 in 20**	**Every Sample**	**1 in 20**
DQO	**< LOD**	**< LOD**	**+/-20%**	**+/-35%**	**Method Specific**	**20% Recovery 35% RPD**
ZDHC Conventional including Anions						
Ammonia-Nitrogen	-	X	X	X	-	X
AOX	-	X	X	X	-	X
Biochemical Oxygen Demand 5-days concentration (BOD_5)	-	X	X	X	-	-
Chemical Oxygen Demand (COD)	-	X	X	X	-	-
Chloride	-	X	X	X	-	-
Colour [m-1] (436nm; 525; 620nm)	-	X	X	X	-	-
Cyanide	-	X	X	X	-	X
Dissolved Oxygen (DO)	-	-	X	field test	-	-
E.coli	-	X	-	X	-	-
Oil and Grease	-	X	X	X	-	-
Persistent Foam	-	-	-	-	-	-

Table 8: Required Quality Assurance Testing for Wastewater

DQI	Field Blank	Method Blank	Calibration Check*	Lab Duplicate	ISTD and Surrogate	Matrix Spike & Matrix Spike Duplicate
Frequency	**1 per Batch**	**1 per Batch**	**1 per Batch**	**1 in 20**	**Every Sample**	**1 in 20**
DQO	**< LOD**	**< LOD**	**+/-20%**	**+/-35%**	**Method Specific**	**20% Recovery 35% RPD**
ZDHC Conventional including Anions (continued)						
pH	-	-	X	-	-	-
Phenol	-	X	X	X	-	X
Total Chlorine	-	-	X	field test	-	-
Temperature difference	-	-	-	-	-	-
Total Dissolved Solids (TDS)	-	-	X***	X	-	-
Total Nitrogen	-	X	X	X	-	X
Total Phosphorus	X	X	X	X	-	X
Total Suspended Solids (TSS)	-	-	X***	X	-	-
Sulfate	-	X	X	X	-	-
Sulfide	-	X	X	X	-	-
Sulfite	-	X	X	X	-	-
ZDHC Heavy Metals						
Chromium (VI)	-	X	X	X	-	X
Heavy Metals (Antimony, Arsenic, Barium, Cadmium, Chromium-total, Cobalt, Copper, Lead, Nickel, Selenium, Silver, Tin, Zinc)	-	X	X	X	X	X
Mercury	X	X	X	X	X	X
ZDHC MRSL						
Alkylphenol (AP) and Alkylphenol Ethoxylates (APEOs): Including All Isomers	-	X	X	X	X	X
Anti- Microbials & Biocides	-	X	X	X	X	X
Chlorinated Parafins	-	X	X	X	X	X
Chlorobenzenes and Chlorotoluenes	-	X	X	X	X	X
Chlorophenols	-	X	X	X	X	X
DMFa	-	X	X	X	X	X
Restricted Aromatic Amines (Cleavable from Azo-colourants)	-	X	X	X	X	X
Dyes – Carcinogenic or Equivalent Concern	-	X	X	X	X	X
Dyes – Disperse (Sensitizing)	-	X	X	X	X	X
Dyes – Navy Blue Colourant	-	X	X	X	X	X
Flame Retardants	-	X	X	X	X	X
Glycols / Glycol Ethers	-	X	X	X	X	X

* Calibration check conducted with a second source standard.
*** Check balance with reference weight.

Table 8: Required Quality Assurance Testing for Wastewater

DQI	Field Blank	Method Blank	Calibration Check*	Lab Duplicate	ISTD and Surrogate	Matrix Spike & Matrix Spike Duplicate
Frequency	**1 per Batch**	**1 per Batch**	**1 per Batch**	**1 in 20**	**Every Sample**	**1 in 20**
DQO	**< LOD**	**< LOD**	**+/-20%**	**+/-35%**	**Method Specific**	**20% Recovery 35% RPD**
ZDHC MRSL (continued)						
Halogenated Solvents	X	X	X	X	X	X
Organotin Compounds	-	X	X	X	X	X
Other/Miscellaneous Chemicals	-	X	X	X	X	X
Perfluorinated and Polyfluorinated Chemicals (PFCs)	X	X	X	X	X	X
Phthalates – including all other esters of ortho-phthalic acid	-	X	X	X	X	X
Polycyclic Aromatic Hydrocarbons (PAHs)	-	X	X	X	X	X
UV Absorbers	-	X	-	X	-	X
Volatile Organic Compounds (VOC)	X	X	X	X	X	X
ZDHC MMCF Specific						
Aquatic Toxicity; Luminous Bacteria, Fish egg, Daphne, or Algae	-	X	Reference Toxicant	X	-	-
Carbon Disulfide	X	X	X	X	X	-
Total Hydrocarbon	-	X	X	X	-	X

* Calibration check conducted with a second source standard.

Quality Systems Specific to Sludge

The quality assurance testing in Table 9 is required for each 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.

Table 9: Required Quality Assurance Testing for Sludge

DQI	Field Blank	Method Blank	Calibration Check*	Lab Duplicate	ISTD and Surrogate	Matrix Spike & Matrix Spike Duplicate
Frequency	**1 per Batch**	**1 per Batch**	**1 per Batch**	**1 in 20**	**Every Sample**	**1 in 20**
DQO	**< LOD**	**< LOD**	**+/-20%**	**+/-35%**	**Method Specific**	**20% Recovery 35% RPD**
ZDHC Conventional including Anions						
% Solids	-	-	X***	X	-	-
Cyanide	-	X	X	X	-	X
Feacal Coliform	-	-	-	X	-	-
Paint Filter Test	-	-	-	X	-	-
pH	-	-	X	X	-	-
ZDHC Heavy Metals						
Chromium (VI)	-	X	X	X	-	X
Heavy Metals (Antimony, Arsenic, Barium, Cadmium, Chromium-total, Cobalt, Copper, Lead, Nickel, Selenium, Silver, Tin, Zinc)	-	X	X	X	X	X
Mercury	X	X	X	X	X	X
ZDHC MRSL						
Alkylphenol (AP) and Alkylphenol Ethoxylates (APEOs): Including All Isomers	-	X	X	X	X	X
Chlorotoluenes	-	X	X	X	X	X

* Calibration check conducted with a second source standard.
*** Check balance with reference weight.

Table 9: Required Quality Assurance Testing for Sludge

DQI	Field Blank	Method Blank	Calibration Check*	Lab Duplicate	ISTD and Surrogate	Matrix Spike & Matrix Spike Duplicate
Frequency	**1 per Batch**	**1 per Batch**	**1 per Batch**	**1 in 20**	**Every Sample**	**1 in 20**
DQO	**< LOD**	**< LOD**	**+/-20%**	**+/-35%**	**Method Specific**	**20% Recovery 35% RPD**
ZDHC MRSL (continued)						
Polycyclic Aromatic Hydrocarbons (PAHs)	-	X	X	X	X	X
ZDHC MMCF Specific						
Adsorbable Organic Halogen Comounds, AOX	_	X	X	X	_	X
Extractable Organic Halogen Compounds, EOX	_	X	X	X	_	X
Heavy metals	Mercury	X	X	X	X	X
Total Organic Carbon, TOC	_	X	X	X	_	X

Test Report Requirements

Reports shall be in line with requirements of ISO 17025 and ZDHC Electronic Data Reporting (EDR) requirements shall contain at least, but not limited to:

- Factory Company Name
- Factory Address
- Sampling method
- Discharge type
- ZDHC sampler accreditation certification number
- Date and time of the beginning of sampling
- Date and time of the end of sampling
- Date Received Sample
- Testing period
- Sludge flux and/or sludge flow data if available
- A note if the sample temperature is greater than 8°C and less than 10°C when received from the laboratory
- A note if holding time has not been respected
- Subcontracted parameters
- Photos with relative time and date
- Remarks (if necessary)
- Include in the report the "ZDHC Wastewater Sampling Field Data Form and Representative Sample Declaration"

* Calibration check conducted with a second source standard.

Minimum Required Reporting Limits

The Level of Detection (LOD) for each parameter must be determined first. The LOD is established using ISO/TS 13530:2009 4.4.3. The procedure requires a complete, specific, and well-defined analytical method. All analytical method sample processing steps must be included when determining the LOD. The LOD for an analytical procedure may vary as a function of sample type.

The Level of Quantification (LOQ) will be established using ISO/TS 13530:2009 4.4.7.

ZDHC requires laboratories to provide their LOD and LOQ into the Solution Provider Platform. To be a ZDHC accepted laboratory, the laboratory LOQ must be at or lower than the ZDHC Aspirational limit (conventional and metals) and at or lower than the ZDHC MRSL wastewater reporting limit. If the ZDHC minimum LOQ cannot be achieved, an alternate method must be approved by ZDHC. Alternately, a sub-contracted laboratory can be used. The ZDHC minimum required LOQ's are presented in the ZDHC Wastewater Guidelines. These were established with consideration to achieving these levels with good laboratory practices.

Detect and Non-Detect Test Results

In order to report a Non-Detect (ND), the ND must include a numerical value that represents the Laboratory calculated LOQ for each parameter and where the Laboratory calculated LOQ is at or lower than the lowest ZDHC limits (e.g. MRSL wastewater, MRSL sludge and wastewater aspirations limits). Non-Detect is not allowed for certain parameters, including colour, pH and temperature.

Reporting Requirements

Only ZDHC Accepted Laboratories approved for ZDHC Wastewater Guidelines can perform sampling, testing, and report results into the ZDHC Gateway on behalf of the Suppliers.

Reporting means submitting test data/results onto the ZDHC Gateway – Wastewater Module. The integrity of the test data in the Gateway must be at its highest possible standard. This will, support the ZDHC Roadmap to Zero Programme in making scientific and data-driven decisions necessary to shape the future of our industry.

1. 1. All ZDHC Accepted Laboratories are expected to follow the data reporting requirements specified in the ZDHC Gateway Electronic Data Reporting (EDR) System Guidelines for wastewater and sludge.
2. 2. All test data must be reported using the EDR template generated in the ZDHC Gateway.
3. 3. The use of reporting formats other than those approved in the EDR will not be accepted.
4. 4. The following data qualifiers can be used when a numerical value is not entered for a parameter:
    - "Insufficient Sample" - not enough sample volume was provided.
    - "Not Requested" - used when the Supplier or their client did not request the analysis of this parameter.
    - "QA/QC" - sample analysis did not meet ZDHC data quality objectives.

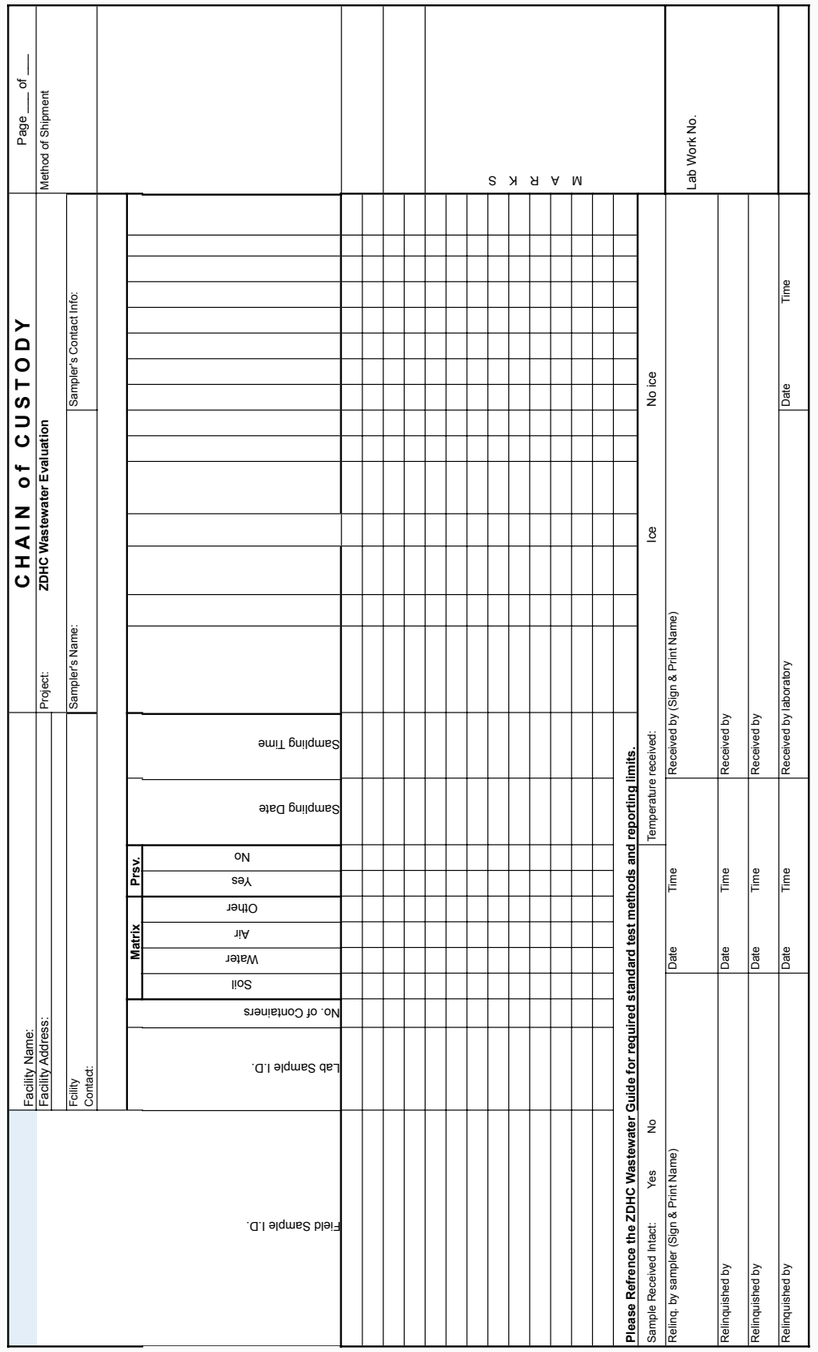
Data Validation

ZDHC routinely requests laboratory Quality Assurance/Quality Control information from randomly selected ZDHC Accepted Laboratories. The following information may be requested for data review:

- Calibration Curves
- Method Blank Instrument Reports
- Instrument Calibration Check Sample Reports
- Laboratory Control Sample Instrument Reports
- Laboratory Duplicate Instrument Reports
- Matrix Spike and Matrix Spike Duplicate Instrument Reports
- Sample Custody Documentation

The quality assurance and quality control results associated with the ZDHC sample 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.

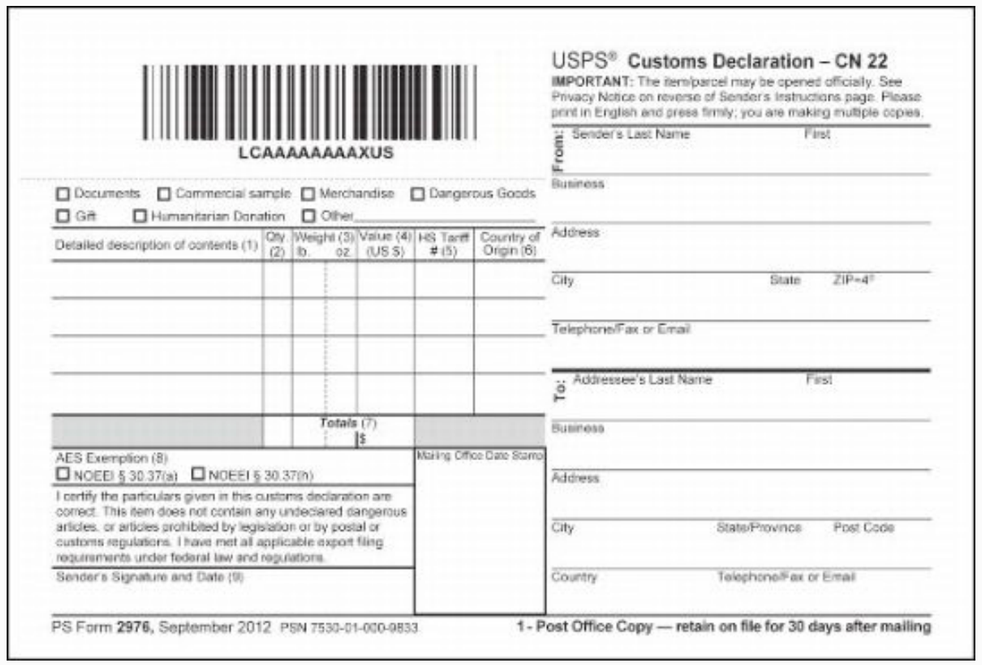
Appendix A
Example of Chain of Custody Form



Appendix B
Examples of Shipping and Customs Forms

The following are examples of forms to be 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 types of known hazardous material.
2. Customs declaration forms for various countries, such as the one presented below, can be found at this link.
3. Toxic Substance Control Act (TSCA) Certification. This form certifies that a sample is not a material which is hazardous to ship by air freight.



LCAAAAAAAAXUS

USPS® **Customs Declaration – CN 22**

IMPORTANT: The item/parcel may be opened officially. See Privacy Notice on reverse of Sender's Instructions page. Please print in English and press firmly; you are making multiple copies.

☐ Documents ☐ Commercial sample ☐ Merchandise ☐ Dangerous Goods
☐ Gift ☐ Humanitarian Donation ☐ Other

Detailed description of contents (1)	Qty (2)	Weight (3) lb.	Weight (3) oz	Value (4) (US $)	HS Tariff # (5)	Country of Origin (6)
		Totals (7)		$		

AES Exemption (8)
☐ NOEEI § 30.37(a) ☐ NOEEI § 30.37(h)

I certify the particulars given in this customs declaration are correct. This item does not contain any undeclared dangerous articles, or articles prohibited by legislation or by postal or customs regulations. I have met all applicable export filing requirements under federal law and regulations.

Sender's Signature and Date (9)

Mailing Office Date Stamp

From: Sender's Last Name First
Business
Address
City State ZIP+4®
Telephone/Fax or Email

To: Addressee's Last Name First
Business
Address
City State/Province Post Code
Country Telephone/Fax or Email

PS Form **2976**, September 2012 PSN 7530-01-000-9853 **1 - Post Office Copy — retain on file for 30 days after mailing**

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

Appendix C
Expanded Revision History

In the spirit of continuous improvement, the ZDHC Wastewater and Sludge Laboratory Sampling and Analysis Plan will be reviewed and revised as needed. The SAP has been edited to incorporate learnings and opportunities identified during the practical application and implementation over the past years. A historical record of the updates is given in Table 10 below.

Table 10: Expanded Revision History of the ZDHC Wastewater and Sludge Laboratory Sampling and Analysis Plan

Version Number	Changes	Time of Publication
Version 1.3	• Added sampling and analysis of conventional parameters specific to the ZDHC Leather Wastewater Guidelines Addendum. This includes: Faecal Coliform, Chloride, Sulfate and Total Dissolved Solids. • Added reference to and content from the ZDHC Wastewater and Sludge Sampling Procedure/Training. • Added guidance for composite wastewater sampling at facilities that do not have continuous production cycles. • Emphasised that the ZDHC specified methods for colour and Chemical Oxygen Demand must be used without exceptions. • Changed sample storage temperature from < 4°C to the ISO recommended temperature of 2°C to 8°C.	January 2021
Version 1.2	Added sampling and analysis of parameters specific to the ZDHC MMCF Wastewater Interim Guidelines.	April 2020
Version 1.1	• Added sampling and analysis procedures specific to sludge. • Improved sampling and analysis procedures for wastewater. • Ensured full alignment with ZDHC Wastewater Guidelines Version 1.1 requirements, including but not limited to standard method for analysis. • Changed the expected sample temperature and applied it to all relevant sections throughout the wastewater part of the document. • Changed the recommended holding time for halogenated solvents. • Adjusted the target value for Multi-Point Calibration. • Adjusted Calibration Check for Total Coliform. • Updated and clarified the Reporting and • Deliverable Requirements in Section 3.3.0 to align with latest development within ZDHC.	
Version 1.0	Initial publication of the ZDHC Wastewater Laboratory Sampling and Analysis Plan.	June 2019

Appendix D
Wastewater Sample Collection – Field Kit Check List

- Camera
- The following ZDHC sample collection forms:
    - Wastewater Sampling Request Form
    - Wastewater Sample Chain-of-Custody Form
    - Shipping and Customs Forms
    - Wastewater Sampling Field Data Form
    - Lab Sample Container List with preservatives
- Auto sampler with refrigeration capabilities
- Ice or cold packs, or Portable freezer / fridge with working range 1-4˚C if manual sampling is necessary and acceptable
- Ice or cold packs for shipping the samples
- ISO 17025 traceable thermometer for measuring sample temperature
- pH measurement equipment and supplies
    - Meter with temperature compensation capabilities. pH / LF temperature compensation: pH temperature compensation for indication of the pH value at the current temperature, with LF measurement converted to reference temperature of 20°C
    - Automatic Temperature Compensation (ATC) probe. This can be done manually if an ATC is not available.
    - high quality probe
    - buffer solutions 4, 7, and 10
    - laboratory control sample (LCS) or correlation testing sample with a known value
- Total Chlorine Measurement
    - For DPD test: Hand held meter, DPD reagent packets, Distilled water for rinsing, GEL standard to check meter calibration
- Dissolved Oxygen Measurement
    - For meter and probe: Hand held meter, oxygen probe, membrane kit for probe
- Lab sample container kit with preservatives
- Cold storage container (like a cooler) for shipping samples
- Facility information that has been requested ahead of sampling date:
    - Legal Discharge permit
    - Sampling locations – the crew may need multiple sample collection kits
    - Drawing of facility lay out that includes identifying sample collection points
    - Point of contact for the owner of the analytical data – for example a Brand that is paying for the testing.
- Safety equipment required by the lab, facility, brand, or others. This may include safety glasses, safety shoes, high visibility vest, hard hat, or other.
- ICE packs or ICE with zip-lock bags
    - Homogenization container 20 liter

Appendix E

ZDHC Wastewater Sampling Field Data Form and Representative Sample Declaration

Sampling Collection Information

Sampling Location:

Sampling Device Description/Owner:

Sampling Mode: ▫ Autosampler ▫ Manual

Start Time:

Stop Time:

Sampler Information

Date:

Sampler Name/Email:

Sampler ZDHC Accredited no.:

ZDHC Composite Sample Code:

ZDHC Wastewater Flow Device Dimensions				
Measurement (cm)	Meter	Pipe (O)	Flume (U)	Wier (V)
Diameter	NA			
Depth	NA	NA	NA	

ZDHC Wastewater Sampling - Facility Confirmation

The Wastewater samples have been collected under the facilitie's normal production scale and wastewater flow rate. The sampler listed below was on-site and collected the samples.

Facility Name:

Facility Representative Name:

Facility Representative Signature and stamp:

Sampler's Name:

Sampler's ZDHC Accreditation:

Sampler's Signature:

ZDHC Wastewater Sampling Field Testing QA/QC			
Parameter	LCS Known	LCS Measured	Accuracy %
pH			
Total Chlorine			

ZDHC Wastewater Sample Collection Field Test Measurements									
Sampling Time (Hours)	Temperature (°C)		pH (Units)	Dissolved Oxygen (mg/L)	Total Chlorine (mg/L)	Persistent Foam (Yes/No)	Wastewater Flow meter (L/min)	Alternate measured Flow	
	Wastewater Discharge	Receiving Water						Depth (cm)	Velocity (cm/sec)
0									
1									
2									
3									
4									
5									
6									
Ave*									

*reported with lab data