# Sampling and Analysis of Per- and Poly-fluorinated Substances

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# Glossary

| | | |
|---|---|---|
| AGDoH | - | Australian Government, Department of Health |
| APHA | - | American Public Health Association |
| AWWA | - | American Water Works Association |
| bgl | - | Below ground level |
| CLMG | - | Contaminated Land Management Guideline |
| ETFE | - | Ethylene tetrafluoroethylene |
| GC-MS | - | Gas Chromatography – Mass Spectrometry |
| HEPA | - | Heads of EPAs Australia and New Zealand |
| IANZ | - | International Accreditation New Zealand |
| LC-MS/MS | - | Liquid Chromatography – Mass Spectrometry/ Mass Spectrometry |
| MoH | - | Ministry of Health |
| MfE | - | Ministry for the Environment |
| NHDES | - | New Hampshire Department of Environmental Services |
| PFAS | - | Per & Poly Fluorinated Alkyl Substances |
| PFOA | - | Perfluorooctanoic Acid |
| PFOS | - | Perfluorooctane Sulphonic Acid / Perfluorooctane Sulfonate |
| PFHxS | - | Perfluorohexane Sulphonic Acid / Perfluorohexane Sulfonate |
| PTFE | - | Polytetrafluoroethylene |
| US EPA | - | United State Environmental Protection Agency |
| WA DER | - | Western Australia Department of Water and Environmental Regulation |
| WEF | - | Water Environment Forum |
| RPD | - | Relative Percentage Difference |

# 1 Introduction

The purpose of this document is to establish nationally consistent sampling protocols that, when adopted, help to ensure that the sampling processes undertaken in accordance with these protocols are robust and defensible.

Per- and Poly-fluroalkyl substances (PFAS) are a large group of over 3,000 man-made fluorine-containing substances which, due to their properties (which results in heat, stain, water and stick-resistance), are used in a wide range of consumer products.

PFAS have been used in water, oil and stain resistant coatings for textiles, paper products, carpets and cookware and to formulate some firefighting foams. They have a range of applications in: aerospace, photographic imaging, semiconductor, automotive, construction, electronics and aviation industries.

PFAS have been widely used globally and last for a long time before breaking down. Because of this, they are found in the environment world-wide, including in humans and animals. People are exposed to small amounts of some PFAS in everyday life, through food, dust, air, water and contact with consumer products that contain these compounds. PFAS accumulates in the bodies of a wide range of biota, including humans, and the half-life for retention in the body varies dependent on the biota from a few hours to multiple years.

For sampling purposes, they should be regarded as being ubiquitous and may be present in clothing, food packing materials, detergent and some cleaning products and within stain-repellent fabrics, including in vehicles. PFAS substances have been found in the environment in groundwater, surface water, soil and food products, both internationally and at a limited number of locations in New Zealand.

The human health and environmental guideline values used to assess the status of surface water, groundwater and potable water are very low due to PFAS's ability to accumulate in the body. Therefore, it is recommended that ultra-trace[1] sampling techniques based upon US EPA 1669 "clean hands/dirty hands" methodology should be adopted to ensure there is no accidental contamination or cross-contamination of the samples.

All contaminated site investigations and sampling exercises undertaken should be consistent with the guidance provided in the Ministry for the Environment's (the Ministry) Contaminated Land Management Guidelines No.s 1[2] & 5[3].

## 1.1 Sampling Methodology Guidance Documents

This document supports the Ministry's existing Contaminated Land Management Guidance and provides further information to help address the specific issues associated with testing ubiquitous substances at trace levels. Much of this guidance is based on the sampling protocols prepared by Pattle Delamore Partners Ltd (PDP) to support the New Zealand Defence Force PFAS investigations. The sampling protocols were developed in accordance with the recommendations contained within the following documents:

[1] For the purpose of this report, ultra-trace analysis refers to analysis undertaken to determine the concentration of a substance at level of approximately 500 ng/L (nanograms per litre) or less. Nanograms per litre is equivalent to parts per trillion (1 ppt or 1 in 1,000,000,000,000).

[2] Contaminated Land Management Guidelines No. 1: Reporting on contaminated sites in New Zealand, April 2011

[3] Contaminated Land Management Guidelines No. 5: Site investigation and analysis of soils, February 2004

### 1.1.1 US and European Guidance

- US Navy (2015) Field Sampling Protocols to Avoid Cross-Contamination During Water Sampling for Perfluorinated Compounds.
- NHDES (2017) Guidance on Sampling and Analysis for PFAS at Disposal Sites Regulated under the MCP.
- US EPA (1995) Method 1669: Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels.
- NHDES (2016) Perfluorinated Compound (PFAS) Sample Collection Guidance.
- NGA (2017) Groundwater and PFAS: State of Knowledge and Practice.
- CLU-IN (2018) Per- and Polyfluoroalkyl Substances (PFASs),Site Characterization and Analytical Methods
- US EPA (2015) SESDPROC-206-R3, Field Equipment Cleaning and Decontamination at the FEC

### 1.1.2 NZ and Australia Guidance

- NEMS 2017, DRAFT National Environmental Monitoring Standards, Water Quality Parts 1-4.
- Ministry of Health (MoH, 2017) Interim Guidance Level for Drinking Water, PFOA, PFOS and PFHxS.
- FSANZ 2017, Health Based Guidance Values for Per- and Poly-Fluoroalkyl Substances (PFAS)
- WA DER (2017), Interim Guidelines on the Assessment and Management of Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS)
- MOH/MFE (1997) Health and Environmental Guidelines for Selected Timber Treatment Chemicals.
- ARC/ECAN/GWRC (2016) An Update on Emerging Organic Contaminants of Concern for New Zealand with Guidance on Monitoring Approaches for Councils - Technical Report 2016/006
- HEPA (2018) PFAS National Environmental Management Plan

# 2 Limits of detection

Examples of the limits of detection which these sampling protocols are intended to support are:

1. Determine the presence or absence (less than 0.001 µg/l) of PFASs in groundwater from groundwater bores.
2. Determine the presence or absence (less than 0.001 µg/l) of PFASs in surface water.
3. Determine the presence or absence (less than 0.1 µg/kg) of PFASs in soils.
4. Determine the presence or absence (less than 0.1 µg/kg) of PFASs in sediments.

## 2.1 Environmental Guidelines

The guideline values presented in Table 1 may be used to evaluate the data collected as part of this project.

| Table 1: Human Health and Environmental Guidelines | | | | |
|---|---|---|---|---|
| **Media** | **PFOS / PFHxS** | **PFOA** | **Land Use / Environmental Value** | **Source** |
| Drinking Water | 0.07 µg/L | 0.56 µg/L | - | MoH[1] AGDoH [2] HEPA[3] |
| Non-potable water/contact recreational | 0.7 µg/L | 0.56 µg/L | - | AGDoH [2] HEPA[3] |
| Fresh and Marine water (Ecological receptors) | 0.00023 µg/L | 19 µg/L | 99% ecosystem protection | HEPA[3] |
| | 0.13 µg/L | 220 µg/L | 95% ecosystem protection | HEPA[3] WA DER[4] |
| | 31 µg/L | 1824 µg/L | 80% ecosystem protection | HEPA[3] WA DER[4] |
| Soil | 0.009 mg/kg | 0.1 mg/kg | Residential with garden/accessible soil | HEPA[3] |
| | 2 mg/kg | 20 mg/kg | Residential with minimal opportunities for soil access | HEPA[3] |
| | 1 mg/kg | 10 mg/kg | Public open spaces | HEPA[3] |
| | 20 mg/kg | 50 mg/kg | Industrial/commercial | HEPA[3] |
| Sediment | N/A | N/A | - | - |

Notes:

1 *Ministry of Health (MoH, 2017) Interim Guidance Level for Drinking Water, PFOA, PFOS and PFHxS.*

2 *Australian Government Department of Health (AGDoH, 2017) Health Based Guidance values for PFAS for Use in Site Investigations in Australia.*

3 *Heads of EPAs Australia and New Zealand (HEPA, 2018) PFAS National Environmental Management Plan*

4 *Draft ANZECC Australian and New Zealand Water Quality Guidelines reported in Government of Western Australia Department of Environmental Regulation (WA DER, updated 2017) Interim Guideline on the Assessment and Management of Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS) Contaminated Sites Guidelines.*

## 2.2 Analytical Detection Limits

For human health based assessments, the analytical detection limits for water samples should be lower than 0.007 µg/L (7 ng/L). Analytical detection has been set to be ten times lower than the lowest applicable guideline value (for water samples, the lowest value is the MoH interim level for drinking water). Therefore, ultra-trace sampling techniques are recommended for the collection of both groundwater and surface water samples.

For soil, sediment, food and biota sampling the limit of detection should be set at least five to ten times lower than the lowest standard/guideline value. The most protective of the environmental guidelines is currently set below the limit of detection for most commercial laboratories. It is therefore impractical to set an analytical detection limit for this scenario. When undertaking an environmental assessment, testing of the affected biota is the approach commonly undertaken to assess potential environmental effects directly.

## 2.3 Data Quality Indicators

To ensure that the data obtained during the investigation can provide information of suitable quality to meet the data quality objectives above, data quality indicators have been derived for the Quality Assurance / Quality Control (QA/QC) samples that will be collected, and are shown in Table 2.

**Table 2 Data Quality Indicator**

| Parameter | Data Quality Indicator | Rationale |
|---|---|---|
| Control water samples | Combined PFHxS and PFOS concentration less than 5 ng/L. | Less than 10% Drinking water outlined in the HEPA Guidelines[1].<br>Less than 10% Drinking water outlined in the MOH interim drinking water standard. |
| | Concentration of PFOA should be less than 50 ng/L | |
| Trip Blank | Combined PFHxS and PFOS concentration less than 5 ng/L. | |
| | Concentration of PFOA should be less than 50 ng/L. | |
| Rinsate Blank | Combined PFHxS and PFOS concentration less than 5 ng/L. | |
| | Concentration of PFOA should be less than 50 ng/L. | |
| Duplicates (water) | The %RPD between duplicate samples shall meet the level of precision determined by a Horwitz function[2]. | The level of precision will depend partly on the concentration of the substance, and partly on the analytical detection limit. Samples at very low concentration and close to the analytical detection limit will naturally have higher level of uncertainty associated with them than higher concentration samples. |

Notes:

1 *Heads of EPAs Australia and New Zealand, PFAS National Environmental Management Plan. January 2018*

2 *Horwitz and Albert (2006) "The Horwitz ratio (HorRat): A useful Index of Method Performance with respect to Precision", Assoc. Off. Anal. Chem., 189 pp 1095-1109*

# 3 Contaminants of Concern

## 3.1 Analysis Narrative

The analysis undertaken for assessments and comparisons with the human health and environmental guidelines are to be undertaken by an IANZ accredited laboratory using accredited methodologies consistent with the *US EPA METHOD 537, Version 1.1, Determination of Selected Perfluorinated Alkyl Acids in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS), September 2009 (US EPA Method 537)*.

The analytical suite needs to include, but is not limited to, the compounds listed in Table 3 as well as analysing both linear and branched isomers of PFOS and PFAS (reported as total PFOS and total PFOA). The list of target compounds in the analytical suite is based on the recommended analytical suite in the WA DER guidelines.

**Table 3 Minimum Analytical Suite for PFAS**

| Abbreviation | Compound Name | Abbreviation | Compound Name |
|---|---|---|---|
| PFOS | Perfluorooctane sulfonate | PFBS | Perfluorobutane sulfonate |
| PFOA | Perfluorooctanic acid | PFBA | Perfluorobutanoic acid |
| 6:2 FtS | 6:2 Fluorotelomer sulfonate | PFHxA | Perfluorohexanoic acid |
| 8:2 FtS | 8:2 Fluorotelomer sulfonate | PFHxS | Perfluorohexane sulfonate |
| PFHpA | Perfluoroheptoanoic acid | PFPeA | Perfluoropetanoic Acid |

All samples should be analysed by an IANZ accredited laboratory, or an overseas laboratory with similar accreditation, to meet the requirements of CLMG No. 5 (2004), MfE. All samples sent to the laboratory should use standard Chain of Custody procedures.

### 3.1.1 Other Analytical Methodologies

Other non-standard methods available to determine the concentration of PFAS in various media include Total Oxidisable Precursor Assay (TOPA) and Total Organic Fluorine Assay (TOFA). These methods are used to determine the concentration of per- fluorinated alkyl acids (PFAAs) precursors in the media to be analysed. At present there are no standardised TOPA or TOFA methods or regulatory guidance to confirm the appropriateness of the data produced.

#### *3.1.1.1 Total Oxidisable Precursor Assay*

TOPA data is used to interpret PFAS fate and transport in the environment. However, TOPA is currently considered as a screening method for understanding the potential implications of PFAA

precursors in the environment, but the following limitations of TOPA are to be recognised during the data interpretation:

- There is no standardized TOPA methodology or regulatory guidance confirming the data appropriateness.
- As the oxidation procedures are not contaminant selective, the presence of competing organic molecules within a sample may interfere with the complete oxidation of PFASs.
- TOPA does not quantify nor identify the structures of individual PFAA precursors nor can it be relied upon to quantify all of the fluorinated mass in a sample. As such TOPA results can only be used to estimate approximate significance of PFAA precursors in the environment and cannot be used to calculate the PFAS mass balance.
- TOPA and PFAS analytical suites do not detect all of the transient or metastable intermediates/transformation products.
- The oxidation process converts the PFAA precursors into per-fluorinated carboxylic acids only; this does not replicate some biotransformation processes that occur in the environment.
- TOPA is an aggressive methodology undertaken in laboratory controlled conditions and is therefore not indicative of the PFAS mass that is susceptible to oxidation in the natural environment. As such, the TOPA results represent a "worst-case" or potential scenario.

TOPA data can help with understanding the potential PFAS risk and it can provide valuable details regarding the carbon chain lengths of the PFAA precursors present at a site. TOPA involves converting all oxidisable PFAS compounds to PFAAs, which can then be detected using the US EPA Method 537. However, it should be noted that this method is still confined to what can be oxidized and the limited number of PFAA chemicals (C4 to C14) in the analytical method. Current analytical methods do not include all per-fluorinated carboxylic acids, therefore, not all end products are determined and included in potential PFAS risk evaluation.

The TOPA methodology is not currently considered to be as robust as the US EPA Method 537 and the results are deemed to be semi-quantitative at present. Worldwide, there are multiple research projects underway to refine this method to improve its accuracy and repeatability. At this time, MfE are not aware of any human health or environmental guidelines based on the TOPA methodology.

#### *3.1.1.2 Total Organic Fluorine Assay*

The TOFA method is carried out by release of fluorine from organic compounds and analytical determination of fluoride ion, but may not be suitable for all media types.

Release of fluorine can be achieved using different methods, including the combustion with oxygen in the furnace at 900–1000 °C. The fluorine can then be measured using a range of techniques including combustion ion chromatography and proton-induced gamma-ray emission. At this time we are not aware of any human health or environmental guidelines based on the TOFA method.

# 4 General Sampling Considerations

## 4.1 Collection of samples for ultra-trace/trace analysis

When analytical techniques are employed to analyse water samples to low parts per trillion (ppt) levels (ultra-trace) and soil samples to low parts per billion (ppb) levels (trace), given that PFAS are ubiquitous in the environment, special precautions are required to minimise the potential of

contamination of the samples. Sampling equipment and materials must be cleaned using high purity water and double bagged for protection.

Sample collection should use two or more person sampling teams, as described in US EPA Method 1669. One member of the two-person sampling team is designated as "Dirty Hands," and the second member of the team is designated as "Clean Hands."

Dirty Hands is responsible for the preparation of the sampling equipment (but does not handle the sample container itself), operation of any sampling equipment (ie, pumps), and for all other activities that do not involve direct contact with the sample (eg, writing notes, answering phone calls, cleaning up).

Clean Hands will handle all operations involving contact with the sample bottles and transfer of the samples from the sample collection device to the sample bottles.

For each sample collected, one replicate sample should be collected (ie, two sample bottles/jars must be filled from each location). The procedure for the collection of replicate samples must follow the same method used for the collection of the original sample.

All members of the team should wash their hands with water and soap before collecting samples.

Sampling teams should wear a new pair of disposable non-talc nitrile gloves as well as clean, lint-free outer clothing to protect samples from contamination by lint or dust.

Other team members can assist Clean Hands/Dirty Hands, and record information whilst not coming directly in contact with either the sampling equipment or media to be sampled.

**Note: Sampling personal must wear a new pair of disposable non-talc nitrile gloves at all times when handling apparatus, samples, and blanks. If Clean Hands touches (or even suspects that they have touched) another object, the ground, or other substances, the gloves may have been contaminated. If this occurs, the work must be halted and the gloves changed.**

## 4.2 Collection of samples not for ultra-trace/trace analysis

If the investigation does not seek to determine ultra-trace/trace levels of PFAS in an environmental media then more conventional sampling protocols may be appropriate. However, care should still be taken to eliminate sources of PFAS in sampling equipment, consumables and clothing to minimise, as far as practical, the potential for cross contamination to occur.

To minimise cross contamination during a sampling event, it is recommended that the sampling performed during any given day, and/or by any given team, should proceed from cleanest (or lowest concentration) to dirtiest (higher concentrations) sampling locations (NGA, 2017).

Sampling equipment such as bailers, tubing and gloves that cannot be decontaminated which have contacted potentially contaminated media cannot be re-used at another sampling location and must be disposed of after sampling. Water dippers, grab samplers, drilling/coring equipment, trowels and water quality meters must be decontaminated before they are re-used at another sampling location.

## 4.3 Materials to be avoided

Due to the widespread use of PFAS chemicals in consumer products, certain materials should not be used, or be within 3 metres of the sampling team during sampling and cannot be within the decontamination area. Equipment that contacts soil, sediment or surface water must not contain or be coated with Teflon®, PTFE or ETFE unless they are internal to the equipment and do not contact the external environment.

Appendix 1 lists material that should not be used during sample collection, or be present within the sample preparation/ equipment decontamination areas.

## 4.4 Control Water, Sampling Containers and Hold Times

### 4.4.1 Control water

Control water is a water of known quality and may comprise Type 1, distilled or potable water. For PFAS investigations, control water must be PFAS free. Control water can be either PFAS free water supplied by a laboratory or water that has been sampled, analysed and demonstrated to be PFAS free.

### 4.4.2 Sample bottles/containers

Samples shall only be collected in specially designated laboratory supplied plastic (polypropylene or high density polyethelene (HDPE)) sample containers, specific for PFAS analysis. Container lids cannot contain Teflon®, and glass containers shall not be used.

Type 1 or PFAS free water used for trip and rinsate blanks must be in plastic bottles, specific for PFAS/PFC analysis with unlined lids.

### 4.4.3 Chilly Bins

To avoid potential cross contamination, samples with high level of contamination and low level of contamination should be stored and transported in separate clean chilly bins. The concentration of PFAS in soils is generally expected to be higher than those found in water samples.

## 4.5 Considerations prior to sampling

To help evaluate the sample quality results, it is important to collect the following information:

- photos and notes of the sample location, including the physical state of any sampling infrastructure (eg, groundwater bore installations and casing);
- note the weather conditions;
- any other relevant information (eg, machinery operating near the sampling team); and,
- any potential contamination sources around, or in the vicinity of, the sampling location.

# 5 Water sampling

This section provides guidance on the procedures that should be used to sample groundwater bores and surface water. This section does not cover specific sampling methods (ie, low flow pump, bailer, tubing, etc), which should be tailored to the parameters required and the bore condition. Instead, it provides a broad overview of how to collect representative groundwater samples. Examples of specific protocols for the collection of water sample are provided in Appendix 3.

It is recommended that water sampling exercises are undertaken in general accordance with National Environmental Monitoring Standards (http://www.nems.org.nz/), taking note of the special precautions contained in this document to prevent cross contamination and preserve sample integrity.

## 5.1 Objectives of water samples

The key aim of groundwater sampling is to collect water that is representative of aquifer conditions. Water that has been sitting in the bore will slowly alter as it is exposed to the atmosphere, casing/screen material, etc. It is therefore necessary to ensure, where practicable, that samples are representative of the aquifer by purging the bore sufficiently.

Note that new bores or disused bores will require development prior to any sampling to ensure that groundwater flows effectively into the bore with minimal sediment. Methods to develop bores are not covered in this procedure as it is designed for the sampling of bores which are currently in use.

## 5.2 Calibration requirements when taking water samples

To obtain the field parameters, a multi-parameter Field Sampling Equipment (Optical Dissolved Oxygen (DO), electrical conductivity (EC), pH, redox potential, temperature and turbidity (FNU)) should be used. Prior to each sampling round, the field instrument will be calibrated using procedures detailed in the National Environmental Monitoring Standards, Water Quality Parts 1-4. The calibration data may be stored electronically on the instrument together with the time and date of calibration, and this should be downloaded from the instrument at the end of the project.

### 5.2.1 pH

At the start of each day, the pH of the meter should be calibrated with appropriate calibration solutions in accordance with the manufacturer's instructions. Dependent on the expected pH of the water to be sampled, a two or three point calibration using calibration solutions of pH 7, 4 and 9 or 10 (to cover the range of expected field measurements) should be undertaken. One of the calibration points needs to be pH 7. The meter should be verified against the calibration standards at the end of the day. Only new calibration[4] solution should be used to verify or calibrate the meter.

The sampling team member shall allow at least three minutes for the sensor to stabilise. pH should be within ±0.3 pH units of the temperature adjusted pH reading on the side of the calibration. If the pH reading is outside of this range, then the meter should be re-calibrated. pH mV values should also be monitored when calibrating. At a pH7, mV readings should be 0 +/- 30mV. If reading out of this range, the sensor needs replacing, even if calibrating properly.

### 5.2.2 Electrical Conductivity (EC)

At the start and end of each day the EC of the meter should be verified and, if necessary, the instrument calibrated with an appropriate calibration solution in accordance with the manufacturer's instructions. Only new calibration solutions should be used to verify or calibrate the meter.

When verifying EC sensors, only the specific conductivity reading should be used. The sampling team member shall allow the sensor to stabilise. Specific conductivity should be within the range ± 3% of the calibration standard. If the specific conductivity is outside of this range, then the meter should be re-calibrated.

[4] Which has not expired or been opened for longer than one month.

### 5.2.3 Dissolved Oxygen (DO)

A water-vapour saturated air verification check should be undertaken to verify the 100% saturation point at the start and end of each day.

Water-vapour saturated air verification is done by:

- Placing a clean, dry sensor in a vented vessel containing air.
- Placing a small amount of water in a sponge or a small amount of water which does not touch the sensor.
- When the reading has stabilised (allow five minutes), recording the DO reading.
- Checking the barometric pressure and dividing the actual barometer reading by 1,013 and then multiplying that number by 100. This is the figure that DO % saturation should read. If the reading is more or less than 5% of this value then re-calibrate the meter.

Barometric pressure and temperature should be recorded when validating and calibrating DO sensors.

## 5.3 Method of Sampling of Groundwater Bores

### 5.3.1 Regularly operated bores

Ideally, the best method (and therefore the first option for collecting the sample) is to obtain the water sample from an operating bore via a tap (see Section 4.3.3). If there is no tap in the immediate vicinity of the bore (or within 100m of the bore), then you will need to sample directly from the bore or the distribution pipe leading from it. Do not sample from downstream of any storage reservoir or connection to any other bore.

If a bore tap is not available, low-flow sampling using a peristaltic pump shall be used to collect a representative bore water sample directly from the bore using dedicated tubing in each well (see Section 4.3.4). Low flow sampling is to be utilised to minimise the turbidity within the sample (and therefore minimise the variability of the samples results) and minimise the amount of purge water that needs to be disposed of at each site. All tubing used to collect water samples must be single use, and must be disposed of following the sample collection.

A peristaltic pump should be used because none of the moving parts of the pump will come into contact with water sample. It, therefore, minimises the potential for cross-contamination between sampling locations. Groundwater of most interest during PFAS investigations is likely to be near surface aquifers and therefore within the sampling depth range of a peristaltic pump (maximum sampling depth of 7 to 8 m). PFAS compounds are not volatile and therefore should not present any degassing issues with the use of a peristaltic pump.

If the water level is deeper than the maximum sampling depth of the peristaltic pump, then another method, such as disposable bailer or a PFAS free bladder pump, can be used to collect the water sample (see Section 4.3.5). Electric submersible pumps, unless certified as PFAS free, are not recommend as most have PTFE motor seals and EFTE-coated motor cable.

**Note: Prior to taking each sample, all equipment to be used must have been decontaminated in accordance with the Decontamination Procedures (see Section 6).**

### 5.3.2 Bores which are not operating

If the bore is not operating, or is rarely used, then it will be necessary to run it to purge the bore and flush the system through. All non-operational bores should be purged prior to sampling to remove any standing water and replace it with fresh formation water. Purging is required because standing water in the well may not be chemically representative of groundwater in the aquifer.

The flushing time or well volumes removed required to reach stabilisation criteria will be dependent on the specific well design and the groundwater conditions. Stabilisation criteria are used to demonstrate that the water from the bore to be sampled is representative of the groundwater on site.

Purging of bore should follow the methods detailed in the National Environmental Monitoring Standards, Water Quality, Part 1 of 4: Sampling, Measuring, Processing and Archiving of Discrete Groundwater Quality Data, Version: 0.1 DRAFT, October 2017.

An example of the stabilisation criteria to be achieved prior to sampling groundwater are outlined in Table 4.

**Table 4: Stabilisation Criteria**

| **Parameter** | **Stabilisation criteria** |
|---|---|
| Electrical conductivity | ± 3 % |
| pH | ±0.1 pH units |
| Dissolved Oxygen | ± 0.3 mg/L |
| Temperature' | ± 3% |
| Turbidity | ± 10 for values greater than 50 FNU |

*Notes:*

*1. Temperature may not stabilise due to solar heating of the discharge line. You will need to make a determination whether or not to include temperature in stabilisation criteria.*

## 5.4 Surface Water Sampling

### 5.4.1 Selecting a Sample Location

The selection of surface water sampling locations should be based on the conceptual site model, but should also consider the following:

- Health and safety of the samplers;

- Depth of the surface water, with a preference for greater than 20 cm to avoid disturbing sediment during sample collection;
- In still water such as lakes, ponds, or reservoirs it is recommend that sampling is conducted in areas of well (better) mixed water that are away from weed beds; and,
- If waters are surface warmed or stratified, consideration should be given to the sampling depth.

### 5.4.2 Method of Sampling

Surface water samples should be collected in accordance with the recommendations contained in Appendix 1 of the *WA DER (2016) Interim Guideline on the Assessment and Management of Perfluoroalkyl and Polyfluoroalkyl Substances*. Ideally, water samples should be collected at least 10 cm from the bottom and 10 cm below surface water level. This is to avoid disturbing sediments which may contain elevated concentrations of PFAS and to avoid the collection of surface films. If the water depth is less than 20 cm, field staff should collect the sample in such a way to avoid collecting surface films and disturbing sediments. Field filtering of water samples is not recommended as PFAS can adsorb to filtration equipment.

Surface water samples may be collected using a grab sampler. The water grab samples will be collected mid-stream in the main flow and care will be taken not to disturb any of the sediment at the bottom of the stream. If any sediment does enter the sample container then the sample will immediately be discarded downstream of the sampling site and a new sampling container used to collect a new sample upstream of the area which had been disturbed.

In very shallow waters, surface water samples may be collected using a peristaltic pump if conditions allow. If the peristaltic pump is utilised for obtaining surface water samples, follow the procedures outlined for the use of this equipment to collect groundwater samples. The exception to the groundwater procedure is that samples should be collected from mid-stream, as close to mid-depth as is practicable (taking care not to disturb the bottom sediments). Field filtering of water samples is not recommended as PFAS can adsorb to filtration equipment.

### 5.4.3 Order of Activities

Physiochemical measurements using field-sampling equipment are to be undertaken within the watercourse after the water samples are collected and care should be taken to avoid disturbing sediments.

# 6 Soil and sediment sampling methodology

The guidance provide in this section provides the broad procedure that should be used to sample soils and sediment. This section does not cover specific sampling methods (ie, auger, drilling, trial pitting), which should be tailored to the parameters required and the soil/sediment conditions; instead, it provides a broad overview of how to collect representative samples. Specific protocols for the collection of soil samples are provided in Appendix 4.

## 6.1 Soil sampling methodology

Conventional soil drilling and core sampling techniques can generally be used to obtain samples for analysis of PFAS in accordance with *MoH/MfE (June 1997), Health and Environmental Guidelines for Selected Timber Treatment Chemicals*. The exception to this statement occurs particularly where

low PFAS concentrations are expected, at which time additional steps such as a 'Clean Hands/Dirty Hands' protocol may be required to ensure cross contamination does not occur and sample integrity is maintained.

The sampling should be undertaken in accordance with a documented field sampling plan and protocols and a health and safety plan. To sample surface and shallow strata, hand augering or other appropriate techniques may be used. Drilling or excavation using a backhoe may be necessary should difficult ground conditions be encountered, or excavations to depth be required.

Decontamination of drilling/sampling equipment must avoid the use of detergents unless they have been confirmed to be PFAS-free. Use Type 1, tap or deionised water (tested to ensure they are PFAS free) for decontaminating equipment. The use of Type 1 for decontaminating stainless steel equipment is not recommended as this is corrosive to stainless steel. See Section 9, below, for further information.

Soil core samples should be collected directly from single-use liners that must not be reused.

The field investigations may involve the recovery of soil samples. The following steps are to be undertaken during soil sampling:

- for surface soils, a shovel, hand trowel or hand auger may be used to collect samples
- for deeper soils, a hand auger or specialist drill rig may be used to collect discrete interval samples, or continuous coring samples, and
- field observations, including soil types, texture, colour and quality (presence of waste, staining, odours) are recorded for the depth of investigation.

PFAS, if present in soil samples, may be present in trace quantities and require very sensitive laboratory analytical procedures. Consequently, it is important that soil sampling procedures are such that the quality of the samples obtained is assured.

Samples should be collected in HDPE wide-mouth bottles, provided by the laboratory, and fitted with an unlined (no Teflon®), polypropylene screw cap. A minimum of 50 g of sample is required.

## 6.2 Sediment sampling methodology

Conventional sediment sampling and coring techniques and protocols can generally be used to obtain samples for analysis of PFAS. Where low PFAS concentrations are expected, additional precautionary steps, such as a 'Clean Hands/Dirty Hands' protocol may be required to prevent cross contamination and to maintain sample integrity.

For samples collected from shore or via wading, ensure that waders are constructed of fabric that has not been treated with waterproofing coatings. Sediment core samples must be collected directly from single-use liners that must not be reused.

Examples of three different sampling protocols typically used are detailed below:

- where the sediment is accessible and can hold its form without collapsing, a corer or 'Dormer Piston' sediment sampler could be used to take sediment samples;
- for sites where the sediment is accessible but either the sediment is sloppy and would not hold its form, or there is a high-density of tree roots or boulders and a corer or piston sampler would not be feasible. In this situation a stainless steel trowel could be used to remove surface samples;

- for sampling subtidal sediments, the depth from which the sample is required will dictate what specialist sampling equipment will be required to collect the sediment samples.

Samples should be collected in HDPE wide-mouth bottles, provided by the laboratory, and fitted with an unlined (no Teflon®), polypropylene screw cap. A minimum of 50 g of sample is required. Field observations, including sediment type, texture and colour should be recorded.

# 7 Biota sampling methodology

## 7.1 Biota sampling

Biota sampling may be undertaken should initial ground and surface water and/or soil sampling indicate the need to assess the potential human health and ecological risks from exposure to PFAS. The sampling methodology used will vary based on the type of biota being sampled.

The types of biota sampled will also depend on the specific site being investigated. These may include:

- fruit and vegetable samples
- pasture samples
- native plants
- animal products, from animals that graze in the investigation area, such as milk and flesh.
- backyard chicken eggs
- fish from local waterways and/or fisheries
- feral animals such as rabbits
- tissue samples.

Ensuring the laboratory analyses can meet the investigation data quality objectives will be dependent on the mass of the biota sampled. It is recommended that you discuss your data quality objectives with the laboratory to determine the mass of biota required for analysis.

Samples should be collected in HDPE wide-mouth bottles fitted with an unlined (no Teflon®), polypropylene screw cap or other appropriate PFAS free containers recommended by the laboratory.

Permits and other legislative requirements should be strictly adhered to before any biota sampling is undertaken.

# 8 Sampling Documents

All fieldwork documentation should be carried out in accordance with the procedures outlined below.

## 8.1 General Field Activities Documentation

All field data and observations will be recorded on field data sheets. All field data sheets will be prepared in permanent ink. All original copies of the field data sheets should be kept for future reference. Field sheets will provide the means for recording most field activity records and observations. The aim of the documentation within the field sheets is to allow future reconstruction of the field activities.

All aspects of sample collection shall be recorded on the field sheets. Records may include, but are not limited to, the following specific information:

- Project name and number
- Date, time, weather conditions
- Personnel present
- Sampling location
- Type of sample
- Sampling method
- Sample number and time of collection
- Depth of water
- Visual and olfactory descriptions
- Field measurements (pH, DO, EC, ORP, turbidity, and temperature)
- Photograph number (where applicable)
- Other information and observations.

An example of a specific field data sheet on which other field information and data may be collected and recorded is attached as Appendix 2.

Additional documentation related to the field activities that should be prepared include:

- Sampling plan
- Health and safety documentation
- Equipment calibration documentation.

# 9 Decontamination Procedures

All sampling equipment and measurement equipment will be decontaminated before and after each use.

The decontamination team members will put on a new pair of disposable non-talc nitrile gloves before decontaminating each piece of equipment;

No piece of decontaminated equipment shall be placed directly onto the ground. The equipment should be placed into new, clean, clear plastic bags. Once these bags have been used then they should not be reused;

An example of decontamination procedures that could be used for smaller field sampling equipment utilised at the site are detailed below:

  - Place three plastic buckets on a tarpaulin and half fill the first bucket with 2% PFAS free detergent/tap water, half fill the second bucket with tap water. The third bucket is for collecting the control (Type 1, tap or distilled) water rinsate, which is poured over the equipment.

- **DIRTY HANDS** removes encrusted materials, if any, by scraping, etc. Once this is completed, **DIRTY HANDS** will change disposable nitrile gloves.
- **DIRTY HANDS** scrubs equipment with brushes and 2% cleaning solution (PFAS free detergent mixed with potable water); and passes the cleaned equipment to "Clean hands."
- **CLEAN HANDS** does a potable water rinse.
- **CLEAN HANDS** does a control water rinse.
- **CLEAN HANDS** collects an equipment blank (as required by sampling plan).
- **CLEAN HANDS** places the decontaminated equipment into a clean clear plastic bag and seals it.

## 9.1 Disposal of Residual Material

All rinsate, purge water and water used to decontaminate equipment should be treated as PFAS contaminated water. All soils and non-reusable equipment should also be treated as PFAS contaminated material. All PFAS contaminated materials should be disposed of via an approved waste disposal facility. The results of the analyses could be used to determine the appropriate disposal method.

# 10 Quality Control Samples

As part of the QA/QC sampling program detailed in the sample plan, it is recommended that the following QA/QC be collected from each sampling round/sampling team:

- One blind duplicate sample will be collected per 20 samples
- One blind duplicate sample will be collected per sampling round for intra-laboratory analysis
- One rinsate blank per day will be collected from each type of field sampling equipment
- One equipment blank for each piece of sampling equipment will be collected per day
- One field blank will be collected per day
- One trip blank per sample consignment (ie, one for each chilly bin) will be collected.

Further information on the purpose of and the techniques for collecting these QA/QC samples is provided in the sections below.

## 10.1 Blanks

### 10.1.1 Field Blank

A field blank is collected as part of this project to determine if ambient conditions on site have impacted on sample integrity.

*10.1.1.1 How to Collect a Field Blank*

Type 1 water is ordered from the laboratory. Once on site, the bottle of Type 1 water is opened by **CLEAN HANDS** and is used to fill a sample bottle. It is important that the sample bottle is open for the same length of time that it would be open when collecting a sample of site water.

The field blank sample container is then labelled and sent to the laboratory with the other water samples.

### 10.1.2 Trip Blank

A trip blank is collected as part of this project to determine if the sample bottle preparation, delivery, handling and/or storage procedures have impacted on the sample integrity.

#### *10.1.2.1 How to Collect a Trip Blank*

A trip blank is ordered from the laboratory undertaking the analysis and supplying the sample bottles. It must be ordered in advance and arrive in the same chilly bin as the rest of the water sample bottles.

Upon receipt of the bottles, a member of the field sampling team shall inspect all the bottles to ensure that there are no breakages, and all the correct bottles/blanks have been provided. The trip blank shall be inspected to ensure there are no air bubbles or leaks in the container.

The trip blank is never opened, it stays with, and is returned with, the rest of the water sample bottles (ie, in the same chilly bin).

### 10.1.3 Rinsate / Equipment Blank

A rinsate blank or equipment blank is designed to verify the effectiveness of field equipment cleaning procedures. As PFAS are water soluble, a rinsate blank should be collected. Rinsate blanks are collected prior to sampling from field equipment, including single use equipment which is used sample media.

The frequency of equipment blank will be determined by the type and number of equipment used. It is recommended that one equipment blank is collected per item of equipment per day.

A rinsate blank is collected for any equipment that contacts the sampled media including:

- water level dip meter
- field sampling equipment
- water quality meter/s.

#### *10.1.3.1 How to Collect a Rinsate Blank*

A rinsate blank is collected immediately before equipment is to be used for sampling media. Laboratory supplied water is poured over the equipment that will come into contact with the sampled media and collected in a laboratory supplied water sample container.

The rinsate blank sample container is then labelled and sent to the laboratory with the other water samples.

#### *10.1.3.2 How to Collect an Equipment Blank*

An equipment blank is collected immediately after the item has been decontaminated. Laboratory supplied water is poured over the equipment that will come into contact with the sampled media and collected in a laboratory supplied water sample container.

The equipment blank sample container is then labelled and sent to the laboratory with the other water samples.

### 10.1.4 Duplicate Samples

A blind duplicate sample should be collected for all media types sampled. The duplicate samples shall be collected using the same methodology used to collect the original sample. Two samples must be collected for each duplicate.

The duplicate sample bottles are filled from the sample location in a manner that ensures that the chemistry is as close to identical as possible.

It is important that the blind duplicate sample is labelled so the laboratory cannot identify the sample as a duplicate or which sample it is a duplicate of.

*10.1.4.1 How to Collect a Duplicate Sample*

Two sample containers are opened simultaneously and each sample container is filled to approximately 20% of the volume of the bottle before the discharge of the sampling tap/pump/bailer is switched to the other sampling container. It may be necessary to turn the tap/pump speed down to near its lowest setting to do this. This process is then replicated until both sample containers are full.

# 11 Sample Management

## 11.1 Sample Labelling

Each sample container will be clearly labelled and marked with ink in the field. Samples collected from each sampling location should have unique sample numbers.

Sample labels will include the following information:

- Sample point number/designation
- Sampling date and time.

## 11.2 Chain of Custody Protocols

A Chain of Custody (COC) record will be utilised by field personnel to document possession of all samples collected for chemical analysis. The COC record may include, but is not limited to, the following information:

- Project name and number
- Name(s) of sampler(s)
- Sample type, identification number, and location
- Date and time of collection
- Number and type of containers
- Analyses required
- Signatures documenting change of sample custody.

The chilly bin containing the samples should be sealed with tape. During sampling events, partially filled and unfilled coolers will be kept within sight of the sample custodian or locked in a vehicle. The sample custodian will be a designated member of the sampling team.

The original COC record will accompany the samples to the analytical laboratory. A copy of the original COC record will be placed in the appropriate project file. Samples will be delivered to the laboratory promptly to ensure the specified holding times are met.

## 11.3 Keeping the Laboratory informed

Analysis of PFAS poses some challenges not seen with other environmental contaminants. These arise mainly from the analytical techniques that must be used.

LC-MS/MS analysis has a linear range of 800 (that is less than 3 orders of magnitude). Compare this to GC-MS analysis where the linear range is five to six orders of magnitude. As a result, many laboratories offer two different sample analysis methods as required, one to deal with samples where higher levels of contamination are expected, and a separate method for samples where lower normal levels are expected.

Some laboratories use a classification system (such as a traffic light system) to enable the sampling team to indicate the likely levels of contamination in the sample. Sample bottles may have labels affixed to facilitate identification.

## 11.4 Sample Shipment


To eliminate potential contamination of samples due to melting ice in chilly bins, re-useable ice block bottles will be provided for shipping samples. Do not use ice packs, blue ice, or frozen vegetables (as the packing material may contain PFAS). Frozen bags of ice can be used as a last resort but melt water within the chilly bin can saturate the sample bottles and make the labels unreadable.

PFAS have a range of volatility and although PFOS, PFOA and PFHXs have relatively low volatility, it is recommended that all samples be kept cool with ice, ideally at less than 4$^{o}$C, during sample transport and must be delivered to the laboratory for analysis within 14 days of collection.

Figure 1: Ice Block Bottle Example

# Appendix 1 - Known or suspected sources of sample contamination

**Table A-1: Known or commonly-suspected sources of environmental sample contamination during PFAS investigations are recommended practices and alternative(Clothing)**

| Product | Mitigation Practice | Alternative product or practice. |
|---|---|---|
| New clothing | Use clothes that have been washed previously. | Wash all field clothing a minimum of six times after purchase to remove surface coating before using at site. No fabric softeners to be used in wash cycle. If fabric softeners have been previously been used in washing machine, then run a rinse cycle before washing clothes. |
| Old field clothes. | Wash clothes. | Wash clothes at least three times to remove any PFAS residues that may be present from other site investigations. |
| Clothing with stain-resistant, rain-resistant, or water proof coatings/treated fabric (eg, Gore-Tex™). | Not to be used on-site. Not to be present in sampling/ decontamination or sample processing areas. | Avoid sampling in rain, if possible. Polyethylene, Vinyl or PVC clothing are acceptable. |
| Tyvek clothing with coatings or films to reduce permeability. | Not to be used on-site. Not to be present in sampling/decontamination or sample processing areas'. | Tyvek suits without coating or films<br>Cotton overalls. |
| Fast food wrappers, glad wrap, pre-wrapped food. | Not to be consumed on-site. Not to be present in sampling/decontamination or sample processing areas[1]. | Eat in designated area only which is physically separated from equipment storage, decontamination, and sample processing areas.<br>No eating in sampling areas. |

*Notes:*

*1. Entire sample collection and processing area, including vehicles used by sampling personal.*

| Table A-2: Known or commonly-suspected sources of environmental sample contamination during PFAS investigations are recommended practices and alternative (Sampling Equipment and Containers) | | |
|---|---|---|
| **Product** | **Mitigation Practice** | **Alternative product or practice** |
| Teflon™ containing or coated field equipment (tubing, bailers, o-rings, tape and plumbing paste). | Do not use at site. | HDPE or silicone tubing. Stainless steel, HDPE or polypropylene field equipment. If low density polyethylene (LDPE) piping is used it must be tested to ensure it is PFAS free. |
| Teflon™ lids on containers (for samples or rinsate water storage). | Do not use at site. | Use laboratory supplied containers for samples, trip blanks, and storage of Type 1 water.<br>Polypropylene lids for sample containers and polypropylene or HDPE containers for control water storage/transport. |
| Glass sample containers with lined lids. | Do not use at site. | Use laboratory supplied sample containers (PFAS adsorb strongly to glass). |
| Reusable chemical or gel ice packs (eg, Blue Ice). | Do not use at site. | Use laboratory supplied frozen water. |
| Detergents and decontamination solution. | Use only solutions which have been tested and verified to be free of PFAS. | Use water only triple rinse procedures if no verified detergents are available. |
| Aluminium foil or cling wrap (eg, Gladwrap™). | Do not use at site or wrap sampling equipment in these materials[1]. | Place cleaned equipment in zip lock bags. |
| Equipment or sample containers produced from recycled plastics | Do not use at site. | Equipment or sample containers produced from virgin plastics. |

*Notes:*

1. *Entire sample collection and processing area, including vehicles used by sampling personal.*

**Table A-3: Known or commonly-suspected sources of environmental sample contamination during PFAS investigations are recommended practices and alternative (Other materials)**

| Product | Mitigation Practice | Alternative product or practice |
|---|---|---|
| Self-sticky notes. | Do not use at site[1]. | Do not use. |
| Waterproof paper, notebooks and labels. | Do not use at site[1]. | Standard paper and paper labels. |
| Sunblock and insect repellent. | Many manufactured sunblocks and insect repents contain PFAS. | Avoid if possible. If necessary, use a 100% natural ingredient product. |
| Cosmetics, moisturizers, hand cream, etc. | Many of these products contain surfactants and may be a potential source of PFAS. | Use of these products should be avoided prior to a sampling event. |
| Decontamination water derived from the site. | Test prior to use to ensure that PFAS concentrations are below data quality objectives requirements. | Type 1 water or approved off-site water. |

*Notes:*

*1. Entire sample collection and processing area, including vehicles used by sampling personal.*

# Appendix 2 – An example Field Data Sheet

**PFAS SAMPLING FORM** (separate form for each primary sample)

| | |
|---|---|
| Location: | Job Number: |
| Sample Code | Land owner: (Name): |
| Address: | Date and time: |
| Weather: | |
| Sample point: tap / well / surface water | Sampled By: (Clean hands) (Dirty hands) |
| Description of sample point: | |
| Distance of sample point from bore: (m) | Site Photos taken? ☐ Yes ☐ No |
| Sampling equipment: | Drinking water supply: |
| Animals observed on site: Chickens / cows / sheep / pigs / goats / other …….. | |
| QA/QA Sample Codes: | |
| Duplicate | |
| Minimum volume between readings: 1 sample train volume (see formula below) | |
| Trip Blank | |
| Field Blank | |
| Rinsate Blank | |

**Key Stabilisation Criteria: NOTE: purge until well has stabilised using field parameters below (3 consecutive readings)**
**pH ± 0.1, EC ± 3%, T ± 3%, turbidity ± 10% of prior reading and ± 10 for values greater than 25 FNU**

TRANSFER FINAL READINGS TO STABILISATION FIELD SHEET

| | Time Elapsed | Time | Volume Removed (L) | pH | EC (µS/cm) | ORP (mV) | Dissolved Oxygen (mg/L) | Water Level (m)* | Turbidity (FNU) / Water Appearance[t] |
|---|---|---|---|---|---|---|---|---|---|
| Before | | | | | | | | | |
| During | | | | | | | | | |
| During | | | | | | | | | |
| During | | | | | | | | | |
| During | | | | | | | | | |
| During | | | | | | | | | |
| During | | | | | | | | | |
| During | | | | | | | | | |
| During | | | | | | | | | |
| During | | | | | | | | | |
| During | | | | | | | | | |

[t] CL=clear, CO=cloudy, TU=turbid, Sl=silty, SA=sandy

**Sample Train Volume Calculation (L)**
(length of sample tube x 3.141 x $d^2$ /4000) + flow through cell volume. Where d = internal diameter of sample tube in mm. Water sample internal ø = 6mm ≈ 30mL per meter

| | | | |
|---|---|---|---|
| Comments | | | |
| Analyses Required: PFAS suite | | | |
| Serial number of water quality sensor unit: | | | |
| Shake test — foam produced? | ☐ Yes ☐ No | | |
| COC form completed and checked? | ☐ Yes | Letter given to landowner? | ☐ Yes ☐ N/A |
| Location field sheet completed? | ☐ Yes | Well field sheet completed? | ☐ Yes ☐ N/A |
| Stabilisation criteria field sheet completed? | ☐ Yes | | |

* = needs to be recorded each time you take a set of parameters

## Appendix 3 – Examples of water sampling protocols

# Appendix 3a – tap sampling protocol

### *Tap Sampling procedure*

The methodology to be used to collect water samples from a tap using a 'Clean Hands/Dirty Hands' procedure in general accordance with US EPA Method 1669 is as follows:

1. Before putting on gloves, the sampling team removes the bags containing the gloves, 10 L bucket and the plastic groundsheet from the storage containers in which they are packed.
2. Select a flat suitable area for sampling and place groundsheet on the ground. Remove sampling equipment from the bags and place on the groundsheet. Place the decontamination equipment, and chilly bin onto the groundsheet.
3. **CLEAN HANDS** and **DIRTY HANDS** put on a new pair of disposable nitrile gloves.
4. **CLEAN HANDS** labels the preserved sample bottles and places them back into the zip lock plastic bags.
5. **DIRTY HANDS** opens the tap and allows the water to run for approximately two minutes into a bucket.
6. **DIRTY HANDS** undertakes the physicochemical measurements from the water collected into the bucket and records the readings and site observations.
7. **CLEAN HANDS** opens the sample and replicate bottles lids and collects the samples by alternately filling 25-33% of each bottle from the running tap.
8. **DIRTY HANDS** operates the tap to ensure the correct flow is maintained.
9. **CLEAN HANDS** replaces the lid on the sample bottles, returns the bottles to their inside bag, and zip-locks the bag.
10. **DIRTY HANDS** turns off the tap and places on a fresh set of gloves.
11. **CLEAN HANDS** then places the zipped bag into the outer bag held by **DIRTY HANDS**.
12. **DIRTY HANDS** zips the outer bag, places the double-bagged sample bottle into a clean chilly bin.

# Appendix 3b – Surface water sampling protocol

### *Surface Water Sample Collection Procedure*

The methodology to be used to collect surface water samples using a 'Clean Hands/Dirty Hands' procedure in accordance with US EPA Method 1669 is as follows:

1. Before putting on gloves, the sampling team removes the bags containing the gloves, 10 L bucket and plastic groundsheet from the storage containers in which they are packed.
2. Choose a flat suitable area for sampling and place groundsheet on the ground. Place the sampling and decontamination equipment, and chilly bin onto groundsheet.
3. **CLEAN HANDS** and **DIRTY HANDS** put on a new pair of disposable nitrile gloves.
4. **CLEAN HANDS** labels the preserved sample bottles and places them back into the zip lock plastic bags.
5. **DIRTY HANDS** opens the grab sampler.
6. **CLEAN HANDS** inserts an unpreserved bottle and removes the lid.
7. **DIRTY HANDS** selects a suitable sampling location. Ideally, the water should be more than 30 cm deep and the sample should be collected from mid-channel within the water course.
8. Once the sampler is in position, the water sample should be collected by pointing the opening of the 1000 mL sample bottle down and upstream of the sampler. Once the sample bottle is more than 15 cm below the surface water level and 15 cm above the bottom of the stream, the grab sampler (and sample bottle) is turned over so that water may flow into the bottle, and the sample is collected.
9. The sample bottle is then removed from the water, shaken and then the sample is discarded downstream of the sampler. Any formation of foam should be noted.
10. Steps 8 and 9 should be repeated three times before the final sample is collected in the unpreserved sample bottles.
11. **DIRTY HANDS** opens the might gripper
12. **CLEAN HANDS** removes the sample bottle.
13. **CLEAN HANDS** decants the water from the unpreserved bottle into the preserved sample bottle.
14. **CLEAN HANDS** replaces the lid on the samples bottle, returns the bottle to the inside bag, and seals the zip lock bag.
15. **DIRTY HANDS** places on a fresh set of gloves.
16. **CLEAN HANDS** then places the zipped bag into the outer bag held by **DIRTY HANDS**.
17. **DIRTY HANDS** places the zip lock bag within the chilly bin.
18. **Repeat** Steps 3 through 17 to collect replicate sample
19. **DIRTY HANDS** undertakes the physicochemical measurements from the water collected into the bucket.
20. **CLEAN HANDS** records the readings and site observations.

# Appendix 3c – Bore water sampling protocol - Peristaltic Pump

*Groundwater Sample Collection Procedure using a Peristaltic Pump*

Presuming that the bore is accessible, and must be sampled, and can be sampled via a peristaltic pump, the following procedure shall apply:

1. Before putting on gloves, the sampling team removes the bags containing the pump, silicone tubings[5], batteries, gloves, 10 L bucket and plastic groundsheet from the coolers or storage containers in which they are packed.
2. Choose a flat suitable area for sampling and place groundsheet on the ground. Place pump and battery, 10 L bucket and chilly bin onto groundsheet.
3. **CLEAN HANDS** and **DIRTY HANDS** put on a new pair of disposable nitrile gloves.
4. **DIRTY HANDS** measures the water level.
5. **DIRTY HANDS** removes the pump from its storage bag, and opens the bags containing the tubing.
6. **CLEAN HANDS** removes the tubing from the bags and installs the tubing while **DIRTY HANDS** holds the pump.
7. **CLEAN HANDS** installs the end of the silicone tubing over HDPE tubing line
8. **DIRTY HANDS** sets up the Field Sampling Equipment in the flow cell and inserts the other end of the silicone tubing into the flow cell.
9. Both **CLEAN HANDS** and **DIRTY HANDS** put on a new pair of disposable nitrile gloves.
10. **CLEAN HANDS** removes the sample bottle from the zip lock plastic bag and labels the sample bottle.
11. **DIRTY HANDS** turns the pump on.
12. Once the stabilisation criteria have been achieved (see Table 6).
13. **CLEAN HANDS** removes the sample and replicate bottles from the zip lock plastic bags.
14. **CLEAN HANDS** opens the sample and replicate bottles lids and collects the samples by alternately filling 25-33% of each bottle from the tubing.
15. **DIRTY HANDS** operates the pump to run so that the bottles are nearly filled.
16. **CLEAN HANDS** replaces the lids on the bottles, returns the bottles to the inside bag, and zip lock the bag.
17. **DIRTY HANDS** turns off the pump and places on a fresh set of gloves.
18. **CLEAN HANDS** then places the zipped bag into the outer bag held by **DIRTY HANDS**.
19. **DIRTY HANDS** seals the outer bag, places the double-bagged sample bottle into a clean ice cooled chilly bin.
20. Repeat Step 9 through 17 to take replicate sample.

[5] Dedicated silicon tubing is only used for a single site. It must not be reused for another site.

# Appendix 3d – Bore water sampling protocol - Bailer

*Sampling of a bore using bailers*

Sampling of the bore using a HDPE bailer is the last option if the sample cannot be collected either from a tap, or using the peristaltic pump.

1. Before putting on gloves, the sampling team removes the bailer, nylon line, 10 L bucket and plastic groundsheet from the coolers or storage containers in which they are packed.
2. Choose a flat suitable area for sampling and place groundsheet on the ground. Place 10 L bucket and chilly bin onto groundsheet.
3. **CLEAN HANDS** and **DIRTY HANDS** put on a new pair of disposable nitrile gloves.
4. **DIRTY HANDS** measures the water level.
5. **DIRTY HANDS** removes the bailer from its storage bag, and attaches the nylon line securely to the bailer.
6. **DIRTY HANDS** lowers the bailer slowly down the bore. Be careful not to dislodge dirt on the sides of the bore.
7. Once the bailer is full of water, **DIRTY HANDS** carefully raises the bailer slowly up the bore, being careful not to dislodge dirt on the sides of the bore.
8. **CLEAN HANDS** labels the preserved sample bottle.
9. Once the bailer is at the surface, **CLEAN HANDS** opens the sample bottle.
10. **CLEAN HANDS** then tilts the bailer to slowly decant the water into the sample bottle.
11. **CLEAN HANDS** replaces the lid on the bottle, returns the bottle to the inside bag, and seals the zip lock bag.
12. **DIRTY HANDS** puts down the bailer and places on a fresh set of gloves.
13. **CLEAN HANDS** then places the zipped bag into the outer bag held by **DIRTY HANDS**.
14. **DIRTY HANDS** seals the outer bag, places the double-bagged sample bottle into a clean ice cooled cooler.
15. **Repeat** Steps 3 through to 14 to collect replicate sample
16. **DIRTY HANDS** picks up the used bailer and line, and disposes of them.

## Appendix 4 – Example of soil sampling protocols

## Appendix 4a – Soil Sampling Protocol - Hand Auger Sampling

The following is an indicative procedure for recovery of soil samples by hand augering.

### *Shallow Samples*

- Establish a clean area immediately adjacent to the sample location, using a clean plastic groundsheet, on which all cleaned and double bagged equipment may be placed.
- Put on a new pair of disposable non-talc nitrile gloves.
- Remove a clean sampling trowel from the plastic bags. Always rest the trowel in the plastic bags not on the plastic groundsheet, whilst sampling.
- Remove grass etc. from the area to be sampled by hand or with the trowel.
- With the trowel remove soil to a depth of 100 mm from the sampling area and place directly in laboratory provided HDPE sample bottle.
- Depending on the analytical requirements, it may be appropriate to recover samples in more than one sample container, for example, recovery of separate samples for PCP and dioxin analyses where these are to be completed by different laboratories.
- Label each sample bottle. Record the details of the sampling location and other pertinent data. Complete a COC form for the samples.
- All samples shall be stored at <4 °C in a chilly bin whilst in the field or in transit.
- If no further samples are to be taken at the location, then replace any surface soil removed from the hole.

### *Deeper Samples*

- Establish a clean area immediately adjacent to the sample location, using a plastic groundsheet, on which all cleaned, and double bagged equipment may be placed.
- Change to a new pair of disposable non-talc nitrile gloves.
- Remove a new sampling trowel from the plastic bags Always rest the trowel in the plastic bags not on the plastic groundsheet, whilst sampling.
- Remove a pre-cleaned auger or a pre-cleaned shovel or crowbar from the plastic bags. Always rest the equipment on the plastic bags, not on the plastic groundsheet, whilst sampling.
- The deeper samples will be recovered by hand auger, taking care to select material such that the possibility for cross-contamination is minimised. In order to minimise the likelihood of smearing or cross-contamination between sampling depths, the initial sample will be recovered using a sampling spoon or 75 mm diameter auger. The hole will then be advanced using the 75 mm diameter auger before a narrower, for example, 62 mm diameter auger is used to recover the second sample. All equipment is cleaned in accordance with Section 6.0 of this guidance between each sample point.
- Label each sample container. Record the details of the sampling location and other pertinent data. Complete a COC form for the samples.

- Backfill the hole. If the hand auger hole approaches the water table or passes through an aquitard the hole may be sealed (eg, using bentonite pellets) to minimise contaminant migration.

It is noted that recovery of samples by hand auger is limited by practical considerations to a depth of approximately 2 m bgl, depending on soil type. In addition, the risk of cross contamination increases with sample depth when using a hand auger and therefore caution should be exercised when selecting this technique for sample recovery.

## Appendix 4b – Soil sampling protocol - Boreholes

Boreholes may be drilled to sample soil and/or groundwater where hand auger techniques are not appropriate. The hollow auger drilling technique, with sample recovery using a split barrel sampler, is commonly employed in assessing unconsolidated formations. Alternative drilling techniques include cable tool, mud rotary, air rotary and air hammer.

Techniques that involve the use of drilling fluids, or the introduction of other substances that may result in contamination of the bore **should be avoided where possible**. If drilling techniques requiring the use of drilling fluids (eg, water, mud, air) it must be ensured these are PFAS free. In addition, it is important to implement measures to reduce the potential for cross-contamination associated with the hydraulic oil commonly present as a mist in compressed air supplies.

Drilling

- The drill string will be steam-cleaned or water blasted with PFAS free water prior to commencing each borehole.
- All equipment used for drilling, augering, digging or extracting samples will be cleaned using the cleaning procedure specified in Section 6.0 prior to commencing the borehole and prior to obtaining each sample.
- Member of the field staff put on a new pair of disposable non-talc nitrile gloves
- Typically, samples of sub-surface material will be recovered from the depths specified in the sampling plan (although samples may be recovered from other depths as required).
- Every member of the field staff who will come into direct contact with the soil being sampled and the sampling bottles must change to a new pair of disposable non-talc nitrile gloves for collecting each sample.
- Label every sample jar.
- Each sample shall be recorded on the chain-of-custody documentation.
- All samples shall be stored at <4$^{o}$C in a chilly bin whilst in the field or in transit.
- Samples of sub-surface material will be recovered by driving a Split Barrel Sampler or other similar sampling device into undisturbed material.
- All boreholes will be sealed with cement grout or bentonite at the completion of drilling unless used to establish a groundwater monitoring well.

## Appendix 4c – Soil sampling protocol - Backhoe Testpits

A backhoe may be used to recover soil samples where ground conditions make the use of a hand auger impractical. The following precautions will apply:

- The backhoe bucket and boom will be steam cleaned or water blasted with PFAS free water prior to each test pit and at the end of each day's work, ensuring residual grease and oil are removed.
- The backhoe will be in good condition and free of oil or hydraulic fluid leaks.
- All equipment used for drilling, augering, digging or extracting samples will be cleaned using the cleaning procedure specified in Section 6.0 prior to commencing the trial pit and prior to obtaining each sample.
- Member of the field staff put on a new pair of disposable non-talc nitrile gloves.
- Samples will be recovered at depths as specified in the sampling plan. Additional samples may be recovered at the discretion of the field staff.
- Following excavation to the target depth, all loose dirt will be removed from the backhoe bucket and a sample representative of the material at the target depth will be recovered using the backhoe. Field staff must not enter the test pit greater than 1.0 m deep under any circumstances, unless it has been made safe in accordance with relevant occupational health and safety regulations.
- Every member of the field staff who will come into direct contact with the soil being sampled and the sampling bottles must change to a new pair of disposable non-talc nitrile gloves before collecting each sample.
- A sample will be recovered from the backhoe bucket using a cleaned sample spoon or trowel, taking care to select material that has not contacted the sides of the bucket. The sample will be placed in a cleaned HDPE container. In some circumstances samples may be recovered directly using a scoop, rather than from the backhoe bucket.
- Every sample/container will be labelled.
- Chain-of-custody documentation will be completed for each sample.
- All soil samples to be analysed for organic constituents shall be stored at <4$^{o}$C in a chilly bin whilst in the field or in transit.