



Government of **Western Australia**  
Department of **Water**

*Looking after all our water needs*

# Surface water sampling methods and analysis – technical appendices

Standard operating procedures for water sampling-methods and analysis

*Looking after all our water needs*

Department of Water

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# 1 Introduction

This document is the third and final in a series of three associated publications addressing surface water sampling programs. The other two are:

- *Water quality monitoring program design: A guideline to the development of surface water quality monitoring programs*
- *Field sampling guidelines: A guideline for field sampling for surface water quality monitoring programs.*

The purpose of this publication is to promote a consistent approach for field measurements and sampling techniques. It provides information on how to collect water samples to analyse for different water quality parameters that can be measured in the field and by laboratory analysis. The information includes how water samples are collected correctly and consistently for field and laboratory analysis, and how to store, preserve and transport samples to enable effective analysis by a testing laboratory.

This information is based on standards recommended in Australian/New Zealand Standards for Water Quality Sampling (AS/NZS 5667.1:1998), and methods described by the *Standard methods for the examination of water and waste water*, American Public Health Association, (APHA, 1998). This publication is designed to provide accurate, standardised methodology for those involved in developing water quality monitoring programs.

It has been prepared in conjunction and/or consultation with:

- methods described in AS/NZS 5667.1:1998 (AS/NZS, 1998), AS/NZS 5667.12:1999 (AS/NZS, 1999), and APHA (1998)
- the National Measurement Institute (NMI)
- the Water Science Branch and Water Information Branch, Department of Water; and
- the Swan Catchment Council.

This document includes methods for *in situ* parameters where measurements are directly determined in the field and other parameters in which samples are collected for analysis by external analytical laboratories.

'Holding time' refers to the maximum storage time between sample collection and analysis by the laboratory. Unless otherwise indicated, these guidelines are taken from the AS/NZS 5667.1:1998. Where the Australian/New Zealand standards have proven impractical to implement, non-standard guidelines are given instead, denoted by a superscripted dollar sign (\$). These were derived experimentally for the CSIRO and the Waters and Rivers Commission by Hosking Chemical Services, and will provide reliable results when adhered to. In any conditions where the standards cannot be followed, the onus is on the sampling manager to establish the validity of the sample storage and handling techniques by experimental means. This includes storage times for samples from auto samplers.



Despite the care taken in the preparation of this publication, there may be acceptable alternatives to the methods given to sample for various water quality variables. It is strongly recommended that this publication be used as a guide only. If there is any doubt as to the correct method for sampling any variable, you must check with the accredited and independently audited laboratory you have selected to carry out the analysis of your samples to be certain that you are using the most suitable method(s) that will yield the most accurate and reliable data.

## 2 General sampling procedures

### 2.1 General equipment

Use only specified equipment, including sample containers and other sampling equipment. In particular, laboratory supplied containers must be used as specified: the use of alternative sample containers or sampling methods will make the sample unusable and the laboratory may reject incorrect samples.

### 2.2 Equipment calibrating, cleaning and maintenance

Ensure that sampling equipment is clean and is maintained in good working order before use and at the end of sampling. Generally, you will not need to clean sampling equipment thoroughly, apart from rinsing it at the end of each sampling trip. However, if a site that is particularly contaminated (e.g. if there is an algal bloom, or the site smells strongly of hydrocarbons, sewage or something else) is sampled the equipment must be rinsed prior to sampling at the next site; or ideally leave that site until the end of the sampling run in order to avoid cross contamination with subsequent samples. Keep some spare deionised/distilled/filtered water for this purpose. Equipment must be cleaned periodically to prevent a build-up of dirt. To do this:

- 1 rinse the equipment well in tap water
- 2 clean with De-Con 90 (a phosphate free detergent)
- 3 rinse well with tap water
- 4 rinse three times with de-ionised water
- 5 allow to dry.

Ensure all field measurement instruments are fully calibrated before starting sampling (pre-field) and again once all sampling has been completed (post-field). The results of the calibration should be marked in a calibration information box on the field observations form (FOF).

It is preferable to use new, pre-cleaned sampling containers to store samples, but if existing ones need to be re-used, rinse with detergent (De-Con 90 is recommended), then very thoroughly wash and rinse with deionised or distilled water. De-Con 90 is an antibacterial/microbial reagent and is useful for cleaning and/or decontaminating glassware, ceramics, rubbers, plastics, stainless steel and ferrous metals. De-Con 90 is not suitable for use on non-ferrous metals, notably aluminium and zinc, or on polycarbonate. Other washing solvents include dilute hydrochloric acid (HCl) (0.1 moles/L HCl), which can remove metal contaminants, and dilute ethanol or methanol (5% in distilled water) which can be used to remove organic contaminants (only important if sampling for metals or organic parameters).

**Important:** It is essential that the containers are washed and rinsed very thoroughly with deionised or distilled water after using any of the above described solvents to remove completely any trace of these solvents before sampling commences.

The deionised/distilled/filtered water unit must be checked to ensure it is well cleaned and maintained and serviced regularly. Be aware that when using deionised or distilled or filtered water for blanks and for rinsing equipment, that this water is free of contaminants. Ensure that dispensers of this water are maintained regularly and filters cleaned to ensure that they produce non-contaminated water. A good practice is to purchase deionised water from the analytical laboratory you are using for sample analysis.

### 3 Laboratories

While the rest of this document gives detailed standard operating procedures for collecting, handling and storing samples, there are subtle differences between different laboratories; for example, different laboratories may require different sample volumes for the same chemical measurement. When developing a program **it is essential** that the analytical laboratory is consulted regarding all aspects of sample handling and storage (e.g. sample volume, container type and even use of preservatives). Because of the difference in the analytical techniques used by different laboratories, it is also very important that a laboratory that is both accredited by the National Association of Testing Authorities and that has also been independently audited by the Department of Water is selected.

Below are the names of some the laboratories available to supply analytical services. Please note that not all laboratories use comparable analysis methods, so enquire with the QA officer in the Measurement and Water Information Branch as to which laboratories are able to provide which analyses, to ensure the data remains of sufficiently high quality to go onto the WIN database.

**National Measurements Institute (NMI)**

Australian Resources Research Centre (ARRC)

26 Dick Perry Ave

Kensington WA 6151

Phone: +61 (08) 9368 8400

Web: <<http://www.measurement.gov.au>>

**Australian Laboratory Services (ALS)**

10 Hod Way

Malaga WA 6090

Phone: +61 (08) 9209 7655

E-mail: [perth@alsenviro.com](mailto:perth@alsenviro.com)

**Marine and Freshwater Research Laboratory (MAFRL)**

Environmental Science

Murdoch University

South St

Murdoch WA 6150

Phone: +61 (08) 9360 6907

Web: <<http://www.scieng.murdoch.edu.au/centres/mafrl/>>

**Chemistry Centre (WA)**

125 Hay Street

East Perth WA 6004

Phone: +61 (08) 9222 3333

Web: <<http://www.doir.wa.gov.au/CCWA/index.asp>>

**Path West WA**

Foods and Waters Unit

Ground Floor, J Block, Hospital Avenue

Nedlands WA 6009

Phone: +61 (08) 9346 3000

Web: <<http://www.pathwest.com.au/>>

## 4 Common field measured parameters

### 4.1 Electrical Conductivity

Electrical conductivity is the measure of the ability of water to conduct an electric current and depends upon the number of ions or charged particles in the water, and is measured by passing a current between two electrodes (a known distance apart) that are placed into a sample of water. The unit of measurement for electrical conductivity is expressed in either micro Siemens per centimetre ( $\mu\text{S}/\text{cm}$ ) or milli Siemens per centimetre ( $\text{mS}/\text{cm}$ ).

Electrical conductivity determinations are useful in aquatic studies because they provide a direct measurement of dissolved ionic matter in the water. Low values are characteristic of high-quality, low-nutrient waters. High values of conductance can be indicative of salinity problems but also are observed in eutrophic waterways where plant nutrients (fertiliser) are in greater abundance. Very high values are good indicators of possible polluted sites. A sudden change in electrical conductivity can indicate a direct discharge or other source of pollution into the water. However, electrical conductivity readings do not provide information on the specific ionic composition and concentrations in the water.

**Table 1 Sampling procedures for electrical conductivity**

Collection technique using hand-held meter – <i>in situ</i> field measurement	Meter should be kept in gentle motion through the water column while a reading is being taken. Allow several minutes for the meter to stabilise. Ideally, measurements should be made about 10 cm below the water surface (and then about 10 cm above the sediment surface); however, this is not always possible in shallow water bodies. A mid water column reading will be sufficient in these cases.
Sample collection technique for laboratory analysis at 25°C	Unfiltered sample
Volume	125 mL
Container	Plastic <sup>A</sup> Bottle cap must have a teflon liner Use new pre-cleaned bottles
Collection technique	Direct collection into sample bottle or transfer into a sample bottle from collection vessel. Ensure sample bottle is pre-rinsed three times with sample water (3 × 20 mL) before final collection.
Treatment to assist preservation	Refrigerate at 1–4°C, do not freeze
Filling technique	Excessive turbulence should be avoided to minimise presence of air bubbles in the sample. Fill container completely to the top to exclude air. The sample must be free of air bubbles and capped tightly.
Maximum sample holding time and storage conditions	Analyse within 24 hours for samples of low conductivity, i.e. below 20 $\mu\text{S}/\text{cm}$ . Other samples can be held for one month if sample is kept refrigerated at 1–4°C and stored in an airtight container.

Units of measurement	$\mu\text{S/cm}$ (or $\text{mS/cm}$ ).
Analysis method	Conductivity is measured electrometrically with (or without) temperature compensation and is calibrated against a standard solution of potassium chloride. <i>Measurement of Conductivity Method 2510</i> (APHA, 1998).
Comments	It is preferable to perform this test in the field.

<sup>A</sup> Plastic sample bottles should not be made from low-density polyethylene (LDPE) as these tend to leak. Appropriate sample container plastics are high-density polyethylene (HDPE), polypropylene, polycarbonate or a fluoropolymer (e.g. teflon).

## 4.2 Dissolved oxygen (DO)

Dissolved oxygen analysis measures the amount of gaseous oxygen ( $\text{O}_2$ ) dissolved in an aqueous solution. Oxygen dissolved in water by diffusion from the surrounding air, by aeration (rapid movement), and as a product of photosynthesis. The dissolved oxygen analysis should be performed immediately and in situ. Therefore, this is a field test that should be performed on site.

Dissolved oxygen can be expressed either as a concentration (in  $\text{mg/L}$ ), which is an absolute value, or as percentage saturation, which is an expression of the proportion of dissolved oxygen in the water relative to the maximum concentration of oxygen that water at a particular temperature, pressure, and salinity can dissolve. The amount of dissolved oxygen in water is largely dependant upon the water temperature; colder water can carry more dissolved oxygen than warmer water. When in equilibrium with the atmosphere, at this maximum concentration the water is said to be saturated or at 100% saturation of dissolved oxygen.

**Table 2 Sampling procedures for dissolved oxygen**

Collection technique using hand-held meter – <i>in situ</i> field measurement	Meter should be kept in gentle motion through the water column while a reading is being taken. Excessive turbulence should be avoided to minimise presence of air bubbles in the water, near the measurement cell. Allow several minutes for the meter to stabilise Ideally measurements should be made about 10 cm below the water surface (and then about 10 cm above the sediment surface); however, this is not always possible in shallow water bodies. A mid water column reading will be sufficient in these cases.
Units of measurement	$\text{mg/L}$ (dissolved oxygen concentration) or % (saturation)
Comments	This test must be done in the field

## 4.3 pH

The pH of a solution is the concentration of hydrogen ions, expressed as a negative logarithm. It reflects the acidity or alkalinity of a solution, in this case water. Water with a pH of 7 is neutral; lower pH levels indicate increasing acidity, while pH levels higher than 7 indicate increasingly alkaline solutions.

It is important to consider the effects of pH on other potential toxicants; e.g. the bioavailability of heavy metals.

**Table 3 Sampling procedures for pH**

Collection technique using hand-held meter – <i>in situ</i> field measurement	Meter should be kept in gentle motion through the water column while a reading is being taken. Allow several minutes for the meter to stabilise. Ideally, measurements should be made about 10 cm below the water surface (and then about 10 cm above the sediment surface); however, this is not always possible in shallow water bodies. A mid water column reading will be sufficient in these cases.
Sample collection technique for laboratory analysis	Unfiltered sample
Volume	125 mL
Container	Plastic <sup>A</sup> Bottle cap must have a teflon liner Use new pre-cleaned bottles
Collection technique	Direct collection into sample bottle or transfer into a sample bottle from collection vessel. Ensure sample bottle is pre-rinsed three times with sample water (3 × 20 mL) before final collection.
Treatment to assist preservation	Refrigerate at 1–4°C, do not freeze
Filling technique	Excessive turbulence should be avoided to minimise presence of air bubbles near the measurement cell or in the sample. Fill container completely to the top to exclude air. The sample must be free of air bubbles. Cap tightly.
Maximum sample holding time and storage conditions	Analyse directly as soon as possible after sample is collected and preferably in the field, but within 6 hours if the sample is refrigerated at 1–4°C, do not freeze.
Units of measurement	Standard pH units
Analysis method	pH is measured electrochemically using a combination electrode (glass plus reference electrode) and is calibrated against two or three commercially available buffer solutions. Electrometric method for pH value analysis 4500-H <sup>+</sup> B (APHA, 1998)
Comments	It is preferable to perform this test in the field, <i>in situ</i> .

<sup>A</sup> Plastic sample bottles should not be made from low-density polyethylene (LDPE) as these tend to leak. Appropriate sample container plastics are high-density polyethylene (HDPE), polypropylene, polycarbonate or a fluoropolymer (e.g. teflon).



## 4.4 Salinity

In measuring the salinity of water, we consider the concentration of salt dissolved in the water. Concentrations are usually expressed in parts per thousand (PPT) which can also be denoted by the symbol ‰ (per mille). These are the classes of salinity we use for water:

- fresh water – less than 5 ‰
- brackish water – from 5 ‰ to 25 ‰
- saline water – from 25 ‰ to 36 ‰
- super-saline (or hyper-saline) water – greater than 36 ‰ (more saline than seawater).

Open ocean salinities are generally in the range between 32 ‰ and 37 ‰.

**Table 4 Sampling procedures for salinity**

Collection technique using hand-held meter – <i>in situ</i> field measurement	Meter should be kept in gentle motion through the water column while a reading is being taken. Allow several minutes for the meter to stabilise. Ideally, measurements should be made about 10 cm below the water surface (and then about 10 cm above the sediment surface); however, this is not always possible in shallow water bodies. A mid water column reading will be sufficient in these cases.
Sample collection technique for laboratory analysis	Unfiltered sample
Volume	200 mL
Container	Plastic <sup>A</sup> Bottle cap must have a teflon liner Use new pre-cleaned bottles
Collection technique	Direct collection into sample bottle or transfer into a sample bottle from collection vessel. Ensure sample bottle is pre-rinsed three times with sample water (3 × 20 mL) before final collection.
Treatment to assist preservation	Refrigerate at 1–4°C, do not freeze
Filling technique	Excessive turbulence should be avoided to minimise presence of air bubbles in the sample or between the electrodes of the measurement cell. Fill container completely to the top to exclude air. The sample must be free of air bubbles. Cap tightly.
Maximum sample holding time and storage conditions	Analyse directly as soon as possible after sample is collected, but within 24 hours if the sample is refrigerated at 1–4°C, do not freeze.
Units of measurement	Parts per thousand (‰)
Comments	It is preferable to perform this test in the field.

<sup>A</sup> Plastic sample bottles should not be made from low-density polyethylene (LDPE) as these tend to leak. Appropriate sample container plastics are high-density polyethylene (HDPE), polypropylene, polycarbonate or a fluoropolymer (e.g. teflon).

## 4.5 Temperature

Temperature can be measured using a thermometer with a range of 0–50°C or a suitable electronic thermometer. The probe (or thermometer) is placed in the water to be measured. The temperature is measured after the reading has stabilised: this may take several minutes.

Since the solubility of dissolved oxygen decreases with increasing water temperature, high water temperatures limit the availability of dissolved oxygen for aquatic life. In addition, water temperature regulates various biochemical reaction rates that influence water quality. Heat sources and sinks to a water body include incident solar radiation, back radiation, evaporative cooling and heat conduction, thermal dischargers (e.g. cooling water from power plants), tributary inflows and groundwater discharge.

**Table 5 Sampling procedures for temperature**

Collection technique using hand-held meter – <i>in situ</i> field measurement	Meter should be kept in gentle motion through the water column while a reading is being taken. Allow several minutes for the reading to stabilise. Ideally, measurements should be made about 10 cm below the water surface (for surface measurements).
Units of measurement	Degrees Celsius (°C)
Comments	This test must be performed in the field.

## 4.6 Turbidity

Turbidity in water is caused by suspended and colloidal matter such as clay, silt, finely divided organic and inorganic matter, and plankton and other microscopic organisms. Turbidity is a measure of the clarity of a water body and is an optical measurement that compares the intensity of light scattered by a water sample with the intensity of light scattered by a standard reference suspension. It is commonly recorded in nephelometric turbidity units (NTUs).

Methods for both *in situ* and lab analysed turbidity measurements are given below. It is important to note that the *in situ* probes are prone to inaccuracy in very shallow waters (<0.5 m) and so for catchment-based projects in shallow streams, it is strongly recommended that a water sample is taken for laboratory analysis to most accurately determine turbidity.

See also “4.7 Secchi disk depth”.

**Table 6 Sampling procedures for turbidity**

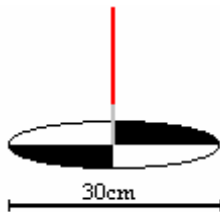
Collection technique using hand-held meter	Meter should be kept in gentle motion through the water column while a reading is being taken. Allow several minutes for the reading to stabilise. Measurements using probes must be made at least 1 m below the water surface and deeper in clear waters to ensure that there is no influence from ambient light.
Sample collection technique for laboratory analysis	Unfiltered sample
Sample requirements	Unfiltered sample
Volume	250 mL
Container	Plastic <sup>A</sup> or glass Use new pre-cleaned bottles
Collection technique	Direct collection into sample bottle or transfer into a sample bottle from collection vessel. Ensure sample bottle is pre-rinsed three times with sample water (3 × 20 mL) before final collection. It is important not to increase the turbidity of the water while collecting a sample, so do not disturb the bottom or the aquatic plants.
Treatment to assist preservation	Store container in dark Refrigerate at 1–4°C, do not freeze
Filling technique	Excessive turbulence should be avoided to minimise presence of air bubbles in the water. Fill to just below shoulder of the bottle.
Maximum sample holding time and storage conditions	Analyse directly as soon as possible after sample is collected and preferably in the field (only if you have an accurate probe, measuring accurately), but within 24 hours if the sample is refrigerated at 1–4°C. Keep cold but do not freeze.
Units of measurement	NTU (nephelometric turbidity units)
Comments	Freezing must be avoided, as irreversible changes in turbidity will occur if the sample is frozen.

<sup>A</sup> Plastic sample bottles should not be made from low-density polyethylene (LDPE) as these tend to leak. Appropriate sample container plastics are high-density polyethylene (HDPE), polypropylene, polycarbonate or a fluoropolymer (e.g. teflon).

## 4.7 Secchi disk depth

The Secchi disc is a simple device for measuring the depth of light penetration into a body of water for comparative purposes. Secchi disc depth gives a rough approximation of how turbid the water is. The use of Secchi discs is normally restricted to measurements in coastal and inland waters, as the clarity of open ocean waters is very difficult to measure.

A Secchi disc consists of a circular white plate made of any non-corrosive rigid material, and is usually a diameter of  $30 \pm 1$  cm. To reduce the effects of currents on the angle of view, a mass of  $3.0 \pm 0.5$  kg is suspended below the centre of the disc on a rigid rod 15 cm long. The disc is painted with quadrants in flat black and flat white waterproof paints. The disc is normally attached to a non-stretch rope, which has been marked at appropriate intervals of depth with waterproof markings. As the waters to be measured will be of variable clarity, judgement should be made as to the scale of measurement to be used. In turbid waters, markings at 10 cm intervals would be appropriate, whereas in clearer waters, markings at 50 cm intervals would be adequate.



**Figure 1: A Secchi disk**

Generally, where the disc cannot be seen (disappearance of the black and white quadrants) is where effective light penetration is extinguished.

Secchi disk depth is a measure of the limit of vertical visibility in the upper water column, and is therefore a direct function of water clarity. High Secchi depth readings correspond to high water clarity. Conversely, low Secchi depth readings are indicative of reduced water clarity that is often associated with the presence of suspended particles and algal blooms. Low Secchi transparency measurements are also indicative of limited light penetration and limited primary production. It is important to note here that highly coloured waters (e.g. with tannins) will also have low Secchi transparency, but this is not necessarily an indicator of poor water quality.

It is important to remember that the Secchi disk is prone to error if strong flows and clouds casting shade are present. Optimal conditions for measuring Secchi disc depth are as follows:

- clear sky
- sun directly overhead – if the sun is not directly overhead, make sure that the sun is at your back to minimise reflection from the sun on the water
- measurements to be taken on the protected side of the boat, with minimal waves or ripples
- the same person should record Secchi disc depth during the sampling day, to ensure consistency across the readings
- if the conditions vary from this ideal situation, record any differences in field notes on the field observations form.



#### How to take a Secchi depth reading.

- 1 The sampler must wear sunglasses.
- 2 Tie the end of the rope onto a float (e.g. a bucket) to prevent accidental loss of the disc.
- 3 Lower the disc into the water in a position away from shadow and record the depth at which the black/white interface on the disc just disappears from sight. Raise the disc until it just becomes visible and record this depth to the nearest 10 cm, then lower it just to the point where the disc disappears again. The depths at disappearance and reappearance are averaged and referred to as the Secchi disc depth.

## 5 Laboratory analysed parameters

### 5.1 Total suspended solids (TSS)

Total suspended solids (TSS) are defined as the portion of total solids in a water sample retained by a glass fibre (GF/C) filter of pore size  $>2\text{ }\mu\text{m}$ . This pore size can vary so please check with your analytical lab, however please note that the WIN database has nominated a pore size of  $0.45\text{ }\mu\text{m}$ . Once the filter has been dried at  $103\text{--}105^{\circ}\text{C}$  and weighed, the amount of total suspended solids is recorded in units of mg/L.

**Table 7 Sampling procedures for total suspended solids**

Sample requirements	Unfiltered sample
Volume	1 L
Container	Plastic <sup>A</sup> Use new pre-cleaned bottles
Collection technique	Direct collection into sample bottle or transfer into a sample bottle from collection vessel. Ensure sample bottle is pre-rinsed three times with sample water ( $3 \times 20\text{ mL}$ ) before final collection. It is important not to increase the turbidity of the water while collecting a sample, so do not disturb the bottom or the aquatic plants.
Treatment to assist preservation	Refrigerate at $1\text{--}4^{\circ}\text{C}$ , do not freeze
Filling technique	Excessive turbulence should be avoided to minimise presence of air bubbles in the water. Fill to the shoulder of bottle.
Maximum sample holding time and storage conditions	Analyse directly as soon as possible after sample is collected, but within 24 hours if the sample is refrigerated at $1\text{--}4^{\circ}\text{C}$ . Do not hold samples longer than 7 days Keep cold but do not freeze Alternative holding time is 3 days at $4^{\circ}\text{C}$ <sup>D</sup>
Units of measurement	mg/L (mg total suspended solids/L)
Analysis method	Total suspended solids dried at $105^{\circ}\text{C}$ 2540-D. (APHA, 1998) Method also in accordance with AS 3550.4:1990 Sample is filtered through a glass fibre (GF/C) filter of nominal pore size (WIN has nominated a pore size of $0.45\text{ }\mu\text{m}$ ). The Gooch crucible, filter and the retained material is dried at $105^{\circ}\text{C}$ . TSS is determined as the weight of the retained material.
Comments	Take care not disturb bottom sediments or plants during collection.

<sup>A</sup> Plastic sample bottles should not be made from low-density polyethylene (LDPE) as these tend to leak. Appropriate sample container plastics are high-density polyethylene (HDPE), polypropylene, polycarbonate or a fluoropolymer (e.g. teflon).

<sup>D</sup> Guideline experimentally derived by Hosking Chemical Services for CSIRO and the Waters and Rivers Commission.

## 5.2 Volatile suspended solids (VSS)

Volatile suspended solids (VSS) are defined as the portion of total suspended solids (TSS) that are lost on ignition (heating to 550°C). This information is useful to the treatment plant operator as it gives an approximation of the amount of organic matter present in the solid fraction of wastewater, activated sludge or industrial wastes. It is sometimes referred to as Loss on Ignition (LOI).

**Table 8 Sampling procedures for volatile suspended solids**

Sample requirements	Unfiltered sample
Volume	2 L
Container	Plastic <sup>A</sup> Use new pre-cleaned bottles
Collection technique	Direct collection into sample bottle or transfer into a sample bottle from collection vessel. Ensure sample bottle is pre-rinsed three times with sample water (3 × 20 mL) before final collection. It is important not to increase the turbidity of the water while collecting a sample, so do not disturb the bottom or the aquatic plants.
Treatment to assist preservation	Refrigerate at 1–4°C, do not freeze
Filling technique	Excessive turbulence should be avoided to minimise presence of air bubbles in the water. Fill to the shoulder of bottle.
Maximum sample holding time and storage conditions	Analyse directly as soon as possible after sample is collected, but within 24 hours if the sample is refrigerated at 1–4°C. Do not hold samples longer than 7 days Keep cold but do not freeze Alternative holding time is 3 days at 4°C <sup>D</sup>
Units of measurement	mg/L (mg volatile suspended solids/L)
Analysis method	Volatile solids ignited at 550°C 2540-E. (APHA, 1998) Method also in accordance with AS 3550.4:1990 Sample is filtered through an ashless glass fibre (GF/C) filter of nominal pore size (WIN has nominated a pore size of 0.45 µm). The Gooch crucible, filter and the retained material is dried at 105°C weighed and then ignited at 550°C. The sample is then cooled and reweighed. VSS is determined as the weight of the lost material on ignition at 550°C compared to constant weight at 105°C.
Comments	Take care not disturb bottom sediments or plants during collection. VSS and TSS can be collected in the same 2 L container for analysis.

<sup>A</sup> Plastic sample bottles should not be made from low-density polyethylene (LDPE) as these tend to leak. Appropriate sample container plastics are high-density polyethylene (HDPE), polypropylene, polycarbonate or a fluoropolymer (e.g. teflon).

<sup>D</sup> Guideline experimentally derived by Hosking Chemical Services for CSIRO and the Waters and Rivers Commission.

## 5.3 Total nitrogen (TN)

Total nitrogen includes all forms of nitrogen, such as (in order of decreasing oxidation state) nitrate, nitrite, ammonia and organic nitrogen. The concentration of nitrogen can be used to assess nutrient status in waterways. Enrichment by nitrogenous compounds may lead to related problems (such as nuisance or toxic algal blooms), although some waterways are naturally high in nitrogen and/or other key nutrients. Some sources of nitrogen enrichment may include fertilizers (in both rural and urban areas), animal wastes (e.g. from farms and feed lots), sewage, nitrogen fixing plants, and in some instances, lightning.

**Table 9 Sampling procedures for total nitrogen**

Sample requirements	Unfiltered sample
Volume	200 mL
Container	Plastic <sup>A</sup> Use new pre-cleaned bottles
Collection technique	Direct collection into sample bottle or transfer into a sample bottle from collection vessel. Ensure sample bottle is pre-rinsed three times with sample water (3 × 20 mL) before final collection.
Treatment to assist preservation	Refrigerate at 1–4°C or freeze and store in the dark
Filling technique	Fill to just below shoulder of the bottle
Maximum sample holding time and storage conditions	Analyse within 24 hours if sample is kept refrigerated at 1–4°C Analyse within 30 days if kept frozen below -20° Alternative holding time is 7 days at 4°C <sup>D</sup>
Units of measurement	mg/L (mg nitrogen/L)
Analysis method	Persulphate digestion method 4500-N C. (APHA, 1998), and the automated cadmium reduction method 4500-NO <sub>3</sub> <sup>-</sup> F (APHA, 1998)
Comments	Samples for TN and TP determination can be collected in the same 250 mL container.

<sup>A</sup> Plastic sample bottles should not be made from low-density polyethylene (LDPE) as these tend to leak. Appropriate sample container plastics are high-density polyethylene (HDPE), polypropylene, polycarbonate or a fluoropolymer (e.g. teflon).

<sup>D</sup> Guideline experimentally derived by Hosking Chemical Services for CSIRO and the Waters and Rivers Commission.



## 5.4 Total phosphorus (TP)

Phosphorus occurs in natural waters and in wastewaters almost solely as phosphates. These are classified as orthophosphates ( $\text{PO}_4^{3-}$ ), condensed phosphates (pyro-, meta-, and other polyphosphates), and organically bound phosphates. They occur in solution, in particle or detritus, or in the bodies of aquatic organisms (APHA, 1998). Sources of phosphorus enrichment may include some detergents, fertilisers (in both rural and urban areas), animal faeces (e.g. from farms and feed lots), sewage and some industrial wastes. High levels of phosphorus and/or other key nutrients may lead to related problems such as nuisance or toxic algal blooms, although some waterways are naturally eutrophic (nutrient enriched).

**Table 10 Sampling procedures for total phosphorus**

Sample requirements	Unfiltered sample
Volume	200 mL
Container	Plastic <sup>A</sup> Use new pre-cleaned bottles
Collection technique	Direct collection into sample bottle or transfer into a sample bottle from collection vessel. Ensure sample bottle is pre-rinsed three times with sample water (3 × 20 mL) before final collection.
Treatment to assist preservation	Refrigerate at 1–4°C or freeze; and store in the dark
Filling technique	Fill to just below shoulder of the bottle
Maximum sample holding time and storage conditions	Immediate analysis is preferable, but analyse within 24 hours if sample is kept refrigerated at 1–4°C and stored in the dark. Analyse within 30 days if kept frozen below -20°C Alternative holding time is 7 days at 4°C <sup>D</sup>
Units of measurement	mg/L (mg phosphorus/L)
Analysis method	Persulphate digestion method 4500-P B.5. (APHA, 1998), and the automated ascorbic acid reduction method 4500-P F. (APHA, 1998)
Comments	Samples for TN and TP determination can be collected in the same 250 mL container.

<sup>A</sup> Plastic sample bottles should not be made from low-density polyethylene (LDPE) as these tend to leak. Appropriate sample container plastics are high-density polyethylene (HDPE), polypropylene, polycarbonate or a fluoropolymer (e.g. teflon).

<sup>D</sup> Guideline experimentally derived by Hosking Chemical Services for CSIRO and the Waters and Rivers Commission.

## 5.5 Total oxidised nitrogen ( $\text{NO}_x\text{-N}$ ), [Nitrate ( $\text{NO}_3^-$ ) + Nitrite ( $\text{NO}_2^-$ )]

Total oxidised nitrogen is the sum of the nitrate ( $\text{NO}_3^-$ ) and nitrite ( $\text{NO}_2^-$ ) expressed as concentrations in mg/L nitrogen. Additionally, the nitrate and nitrite species can be determined separately.

*Nitrite* is an intermediate form of nitrogen and is generally short-lived as it is rapidly oxidised to nitrate.

*Nitrate* is an essential plant nutrient and its levels in natural waterways are typically low (less than 1 mg/L). Excessive amounts of nitrate can cause water quality problems and accelerate eutrophication, altering the densities and types of aquatic plants found in affected waterways. Some bacteria mediate the conversion of nitrate into gaseous nitrogen through a process known as denitrification, and this can be a useful process reducing levels of nitrate in waterways.

**Table 11 Sampling procedures for total oxidised nitrogen**

Sample requirements	Filtered sample <sup>A</sup>
Volume	125 mL
Container	Plastic <sup>B</sup> Use new pre-cleaned bottles
Collection technique	The sample can be collected in a clean sample container prior to filtration. Filtered sample is placed into a different sample bottle, after rinsing. Ensure sample bottle is pre-rinsed three times with filtered sample water (3 × 20 mL) before final collection.
Filtration technique	Filter the sample through 0.45 µm pore diameter cellulose acetate (membrane) filter <sup>C</sup> .
Treatment to assist preservation	Refrigerate at 1–4°C or freeze and store in the dark
Filling technique	Fill to just below shoulder of the bottle
Maximum sample holding time and storage conditions	Analyse within 24 hours if sample is kept refrigerated at 1–4°C Analyse within 30 days if kept frozen below -20°C Alternative holding time is 1–3 days at 4°C <sup>D</sup>
Units of measurement	mg/L (mg oxidised nitrogen as nitrogen/L)
Analysis method	Automated cadmium reduction method 4500-NO <sub>3</sub> -F (APHA, 1998)
Comments	If determining nitrite species, the sample may be refrigerated (< 4°C) upon collection and analysed as soon as possible thereafter. If the sample is frozen, the analysis must occur within 2 days of collection. Samples for determining NO <sub>x</sub> -N, NH <sub>4</sub> -N /NH <sub>3</sub> -N, soluble reactive phosphorus and dissolved organic nitrogen can be collected in the same 250 mL container.

<sup>A</sup> Samples should be filtered as soon as possible after sample collection, preferably on site. Filter paper should be washed with sample first prior to filtration. Do not re-use filter paper.

<sup>B</sup> Plastic sample bottles should not be made from low-density polyethylene (LDPE) as these tend to leak. Appropriate sample container plastics are high-density polyethylene (HDPE), polypropylene, polycarbonate or a fluoropolymer (e.g. teflon).

<sup>C</sup> Optional: If the sample has high particulate matter content then it may be necessary to pre-filter using a glass fibre filter paper (GFC 1.2 µm).

<sup>D</sup> Guideline experimentally derived by Hosking Chemical Services for CSIRO and the Waters and Rivers Commission.

## 5.6 Nitrogen as ammonia/ammonium (NH<sub>3</sub>-N/NH<sub>4</sub>-N)

Ammonia nitrogen and ammonium nitrogen species are determined using the same analytical method. Analytically they are the same species. Ammonia and ammonium exist in equilibrium in aqueous solution. In alkaline solutions the predominant species is ammonia (NH<sub>3</sub>), while ammonium (NH<sub>4</sub><sup>+</sup>) predominates at lower pH. During the analysis the pH is adjusted to alkaline, thereby converting almost all the ammonia to ammonium.

Sources of ammonia include fertilizers and the mineralisation (decomposition) of organic matter.

**Table 12 Sampling procedures for nitrogen as ammonia/ammonium**

Sample requirements	Filtered sample <sup>A</sup>
Volume	125 mL
Container	Plastic <sup>B</sup> or glass Use new pre-cleaned bottles
Collection technique	The sample can be collected in a clean sample container prior to filtration. Filtered sample is placed into a different sample bottle, after rinsing. Ensure sample bottle is pre-rinsed three times with filtered sample water (3 × 20 mL) before final collection.
Filtration technique	Filter the sample through 0.45 µm pore diameter cellulose acetate (membrane) filter <sup>C</sup> .
Treatment to assist preservation	Refrigerate at 1–4°C or freeze and store in the dark
Filling technique	Fill to just below shoulder of the bottle
Maximum sample holding time and storage conditions	Analyse within 24 hours if sample is filtered and kept refrigerated at 1–4°C Analyse within 30 days if filtered and kept frozen below -20°C Alternative holding time is 1–3 days at 4°C <sup>D</sup>
Units of measurement	mg/L (mg N/L)
Analysis method	Automated phenate method 4500-NH <sub>3</sub> G. (APHA, 1998)
Comments	Store in an area free from contamination as ammonia vapour may permeate the walls of HDPE. Samples for determining NH <sub>4</sub> -N /NH <sub>3</sub> -N, NO <sub>x</sub> -N, soluble reactive phosphorus and dissolved organic nitrogen can be collected in the same 250 mL container.

<sup>A</sup> Samples should be filtered as soon as possible after sample collection, preferably on site. Filter paper should be washed with sample first prior to filtration. Do not re-use filter paper.

<sup>B</sup> Plastic sample bottles should not be made from low-density polyethylene (LDPE) as these tend to leak. Appropriate sample container plastics are high-density polyethylene (HDPE), polypropylene, polycarbonate or a fluoropolymer (e.g. teflon).

<sup>C</sup> Optional: If the sample has high particulate matter content then it may be necessary to pre-filter using a glass fibre filter paper (GFC 1.2 µm).

Guideline experimentally derived by Hosking Chemical Services for CSIRO and the Waters and Rivers Commission.

## 5.7 Soluble reactive phosphorus (SRP) or PO<sub>4</sub>-P

Soluble reactive phosphorus (SRP) describes the dissolved phosphates that respond to colorimetric tests without preliminary hydrolysis or oxidative digestion of the sample and are termed 'reactive phosphorus'. Reactive phosphorus is largely a measure of orthophosphate (PO<sub>4</sub><sup>3-</sup>); however, a small fraction of any condensed phosphate present is usually hydrolysed unavoidably in the analytical procedure.

Reactive phosphorus occurs as both dissolved and suspended phosphorus. Sources include natural cycling of phosphorus but also fertilisers, detergents and soil erosion, which can carry particulate bound phosphate into waterways.

Note: Do not use the term 'filterable reactive phosphorus' (FRP) and soluble reactive phosphorus (SRP) interchangeably, as the term 'filterable' has different meanings in different contexts and with different laboratories, e.g. at NMI, total filterable solids' is the residue left on filter paper after filtering a solution; but applied to other analytes the term 'filterable' means 'soluble'. Soluble reactive phosphorus (SRP) is the correct term to be used.

**Table 13 Sampling procedures for soluble reactive phosphorus**

Sample requirements	Filtered sample <sup>A</sup>
Volume	125 mL
Container	Plastic <sup>B</sup> or glass Use new pre-cleaned bottles
Collection technique	The sample can be collected in a clean sample container prior to filtration. Filtered sample is placed into a different sample bottle, after rinsing. Ensure sample bottle is pre-rinsed three times with filtered sample water (3 × 20 mL) before final collection.
Filtration technique	Filter sample through 0.45 µm pore diameter cellulose acetate (membrane) filter <sup>C</sup>
Treatment to assist preservation	Refrigerate at 1–4°C or freeze and store in the dark
Filling technique	Fill to just below shoulder of the bottle
Maximum sample holding time and storage conditions	Analyse within 24 hours if sample is kept refrigerated at 1–4°C Analyse within 30 days if kept frozen below -20°C Alternative holding time is 1–3 days at 4°C <sup>D</sup>
Units of measurement	mg/L (mg phosphorus/L)
Analysis method	Automated ascorbic acid reduction method 4500-P F. (APHA, 1998)
Comments	Samples for determining soluble reactive phosphorus, NO <sub>x</sub> -N, NH <sub>4</sub> -N /NH <sub>3</sub> -N and dissolved organic nitrogen can be collected in the same 250 mL container.

<sup>A</sup> Samples should be filtered as soon as possible after sample collection, preferably on site. Filter paper should be washed with sample first prior to filtration. Do not re-use filter paper.

<sup>B</sup> Plastic sample bottles should not be made from low-density polyethylene (LDPE) as these tend to leak. Appropriate sample container plastics are high-density polyethylene (HDPE), polypropylene, polycarbonate or a fluoropolymer (e.g. teflon).

<sup>C</sup> Optional: If the sample has high particulate matter content then it may be necessary to pre-filter using a glass fibre filter paper (GFC 1.2 µm).

<sup>D</sup> Guideline experimentally derived by Hosking Chemical Services for CSIRO and the Waters and Rivers Commission.

## 5.8 Total organic nitrogen (TOrgN)

Total organic nitrogen may be calculated from the concentrations of total nitrogen, nitrite, nitrate and ammonium nitrogen, by subtracting the concentrations of inorganic fractions of nitrogen, namely nitrite and nitrate ( $\text{NO}_x$ ) and ammonium nitrogen ( $\text{NH}_3\text{-N}/\text{NH}_4\text{-N}$ ) from the total nitrogen (TN) concentration:

i.e.  $\text{TOrgN} = \text{TN} - (\text{NO}_x + \text{NH}_3\text{-N}/\text{NH}_4\text{-N})$ .

## 5.9 Total Kjeldahl nitrogen (TKN)

Kjeldahl nitrogen is a term used to describe all dissolved nitrogen in the tri-negative oxidation state (e.g. ammonium, ammonia, urea, amines, amides, etc) and therefore comprises all the dissolved nitrogen except for some inorganic species (nitrite and nitrate) and organic compounds (azo- compounds, nitriles, oximes, etc). The Kjeldahl method hydrolyses all the amino nitrogen to ammonium, which is then measured by the ammonium/ammonia method.

Assuming that the concentrations of many of the other nitrogen species are very low, the TKN concentration is therefore approximately equal to the TN concentration less the nitrite and nitrate concentrations. Or alternatively the TKN concentration is approximately equal to the sum of the total organic nitrogen and ammonia/ammonium as nitrogen concentrations.

Many analytical laboratories do not actually measure TKN using the Kjeldahl method (unless specifically requested); instead TKN (total) is calculated by subtracting nitrate and nitrite from total nitrogen (TN) on an unfiltered sample.

The Kjeldahl determination is rarely used because it is not as precise as the persulphate digestion method used to calculate TN. It also uses mercuric sulphate–sulphuric acid digest, leaving mercury as an undesirable waste product.

If a value of TKN is necessary ask for it on the COC. Be sure to confirm beforehand with the lab that this is for the calculated value (which should be free, assuming you are already paying for TN and  $\text{NO}_x$  (nitrite and nitrate) analyses).

## 5.10 Dissolved organic nitrogen (DOrgN)

Dissolved organic nitrogen (DOrgN) is calculated by analysing TN in a filtered sample and then subtracting the  $\text{NH}_3\text{-N}/\text{NH}_4\text{-N}$  and  $\text{NO}_x\text{-N}$  (i.e. the dissolved inorganic fractions of nitrogen) from the result.

Until recently DOrgN could not be accurately measured; it was calculated and therefore prone to greater error. Previously DOrgN was not thought to be a significant portion of the total nitrogen in a system compared to inorganic fractions of nitrogen. However, research has shown that in fact DOrgN is; and that it can be readily utilised by some nuisance algal species. In light of this, it is important that we quantify this previously ignored fraction of nitrogen.

**Table 14 Sampling procedures for dissolved organic nitrogen**

Sample requirements	Filtered sample <sup>A</sup>
Volume	125 mL
Container	Plastic <sup>B</sup> Use new pre-cleaned bottles
Collection technique	The sample can be collected in a clean sample container prior to filtration. Filtered sample is placed into a different sample bottle, after rinsing. Ensure sample bottle is pre-rinsed three times with filtered sample water ( $3 \times 20$ mL) before final collection.
Filtration technique	Filter sample through $0.45 \mu\text{m}$ pore diameter cellulose acetate (membrane) filter <sup>C</sup>
Treatment to assist preservation	Refrigerate at $1\text{--}4^\circ\text{C}$ or freeze and store in the dark
Filling technique	Fill to the shoulder of bottle
Maximum sample holding time and storage conditions	Analyse within 24 hours if sample is filtered and kept refrigerated at $1\text{--}4^\circ\text{C}$ Analyse within 30 days if filtered and kept frozen below $-20^\circ\text{C}$ Alternative holding time is 1–3 days at $4^\circ\text{C}$ <sup>D</sup>
Units of measurement	mg/L (mg DOrgN as nitrogen/L)
Analysis method	Total nitrogen by persulphate digestion method 4500-N C. (APHA, 1998) and the automated cadmium reduction method 4500- $\text{NO}_3^-$ F (APHA, 1998) Nitrate by the automated cadmium reduction method 4500- $\text{NO}_3^-$ F (APHA, 1998) Ammonia by the automated phenate method 4500- $\text{NH}_3$ G. (APHA, 1998)
Comments	Samples for determining dissolved organic nitrogen, $\text{NH}_4\text{-N}/\text{NH}_3\text{-N}$ , $\text{NO}_x\text{-N}$ and soluble reactive phosphorus can be collected in the same 250 mL container.

<sup>A</sup> Samples should be filtered as soon as possible after sample collection, preferably on site. Filter paper should be washed with sample first prior to filtration. Do not re-use filter paper.

<sup>B</sup> Plastic sample bottles should not be made from low-density polyethylene (LDPE) as these tend to leak. Appropriate sample container plastics are high-density polyethylene (HDPE), polypropylene, polycarbonate or a fluoropolymer (e.g. teflon).

<sup>C</sup> Optional: If the sample has high particulate matter content then it may be necessary to pre-filter using a glass fibre filter paper (GFC  $1.2 \mu\text{m}$ ).

<sup>D</sup> Guideline experimentally derived by Hosking Chemical Services for CSIRO and the Waters and Rivers Commission.

## 5.11 Chlorophyll-a, b, c, and Phaeophytin-a

The chlorophyll-a, b, c, and phaeophytin-a are all photosynthetic pigments and their concentrations in water can be used to estimate phytoplankton biomass. The concentrations are determined from the filtered remnants of a water sample.

Natural and anthropogenic factors (e.g. nutrients, light and temperature) can affect the biomass of a phytoplankton community and in turn chlorophyll-a concentrations. High chlorophyll-a concentrations are often the result of elevated nutrient concentrations.

**Table 15 Sampling procedures for chlorophyll-a, b, c and phaeophytin-a**

Sample requirements	Filtered sample <sup>A</sup>
Volume	Collect 2 L sample initially for filtration; place filtered remnants in a ~10.5 cm × 6 cm yellow seed envelope.
Container	Plastic <sup>B</sup> Use new pre-cleaned bottles If necessary, bottles should be washed in phosphate-free detergent and rinsed three times with tap water and three times with deionised water. Sample is collected on a new (uncontaminated) glass fibre (GF/C) filter paper (GFC 1.2 µm), then stored in a small yellow seed envelope.
Collection technique	The sample is collected on a new glass fibre (GF/C) filter paper (GFC 1.2 µm) after filtration of a known volume of sample. The pigments are extracted from the paper in the laboratory.
Filtration technique	Rinse all individual parts of the filter tower with de-ionised water <sup>C</sup> . This is done prior to use and in between sites. Assemble filter tower, placing a glass fibre (GF/C) filter onto filter membrane using tweezers. Attach electric pump vacuum hose (or hand held vacuum pump if not available) to vacuum port adaptor. Samples and filter papers should not come into contact with the skin, as oil and dirt can contaminate samples. Rinse a 500 mL measuring cylinder with 10 mL sample water three times, and then accurately measure 500 mL of sample water into the measuring cylinders. Two 500 mL samples are filtered. A total volume of 1000 mL should be poured through the filter paper. Do not wash filter paper with sample prior to filtration. If the filter paper becomes blocked, return the remaining water sample from the top of the funnel to the measuring cylinder and record the volume. Large, accurately measured volumes of water filtered minimise the errors in the determination. The minimum volume to be filtered is 500 mL. If the filter paper is blocked prior to 500 mL being filtered, return the remaining sample to the measuring cylinder and disassemble the filter tower and remove the chlorophyll paper. Replace with a new GFC, reassemble the tower and return the remaining water sample from the measuring cylinder. It is acceptable to have several GFC filter papers for the chlorophyll analysis. Record the number of GF/C papers on the chain of custody. More filter papers increase the error of the measurement. Record to the nearest 5 mL the volume that is filtered through the filter paper onto a chain of custody form, field observation form or other documentation. The laboratory requires this information when analysing the sample. Using tweezers, place another GFC filter paper over the first and fold the filter paper in half, and then into quarters. Place the filter papers into the appropriately labelled seed envelope with the site written on it.

Treatment to assist preservation	Refrigerate the filter paper in the seed envelope at 1–4°C or freeze nad store in the dark
Filling technique	Store the sample on the filter paper in a small yellow seed envelope.
Maximum sample holding time and storage conditions	Analyse within 24 hours if sample is kept refrigerated at 1–4°C in the dark Analyse within 30 days if kept frozen below -20°C in the dark
Units of measurement	µg/L
Analysis method	Chlorophyll by spectrophotometric method 10200 H. (APHA, 1998)

<sup>A</sup> *Samples should be filtered as soon as possible after sample collection, preferably on site. Do not wash filter paper with sample prior to filtration. Do not re-use filter paper.*

<sup>B</sup> *Plastic sample bottles should not be made from low-density polyethylene (LDPE) as these tend to leak. Appropriate sample container plastics are high-density polyethylene (HDPE), polypropylene, polycarbonate or a fluoropolymer (e.g. teflon).*

<sup>C</sup> *Care must be taken in the use of deionised water for rinsing equipment. Care must be taken that this water is not contaminated in anyway, and it must be ensured that dispensers of this water are regularly maintained and cleaned to ensure that they produce non-contaminated water. A good practice is purchase deionised water from the analysis laboratory you're using.*



## 5.12 Total organic carbon (TOC)

The total organic carbon (TOC) concentration represents all the carbon covalently bonded in organic molecules and so is not filtered. Total organic carbon does not take into account the oxidation state of the organic matter, and does not measure other organically bound elements, such as nitrogen and hydrogen, and inorganics that can contribute to the oxygen demand measured by biological oxygen demand (BOD). Drinking water TOC concentrations range from less than 100 µg/L to more than 25 mg/L. Wastewaters may contain very high levels of organic carbon (>100mg/L).

Until recently the sample bottle was directly filled with no rinsing but upon consulting NMI in attempting to sample total and dissolved organic carbon using the same standard techniques (as the two parameters are often compared) it was decided to rinse the sample bottles three time prior to sample collection, as is the practice for dissolved organic carbon sample collection.

**Table 16 Sampling procedures for total organic carbon**

Sample requirements	Unfiltered sample
Volume	125 mL
Container	Glass – brown (amber) container Cap must have teflon-lined insert Use new pre-cleaned bottles that are free from organics
Collection technique	Ensure sample bottle is pre-rinsed three times with sample water (3 × 20 mL) before final collection.
Treatment to assist preservation	Refrigerate at 1–4°C, do not freeze Store in the dark
Filling technique	Pre-rinse three times with sample water Fill container completely to the top to exclude air. The sample must be free of air bubbles. Ideally the sample is acidified by adding 10% sulphuric acid (H <sub>2</sub> SO <sub>4</sub> ) in the field until the pH is < 2. This is often not possible in the field.
Maximum sample holding time and storage conditions	Test should be carried out as soon as possible after collection. Keep refrigerated at 1–4°C and stored in dark. Do not freeze If acidified, holding time is 7 days Alternative holding time is 3 days at 4°C (no acidification) <sup>D</sup>
Units of measurement	mg/L (mg carbon/L or µg non-purgeable organic carbon/L)
Analysis method	Total organic carbon by high temperature combustion and IR detection, method 5310 (APHA, 1998)
Comments	Inorganic carbon must be purged before analysis, hence volatile organic species will be lost. Report as non-purgeable organic carbon.

<sup>D</sup> Guideline experimentally derived by Hosking Chemical Services for CSIRO and the Waters and Rivers Commission.

## 5.13 Dissolved organic carbon (DOC)

Dissolved organic carbon (DOC), represents all the soluble organic carbon (or carbon covalently bonded in organic molecules) that can pass through a 0.45 µm pore diameter filter.

Dissolved total inorganic carbon (TIC, or DIC) represents the carbonate ( $\text{CO}_3^{2-}$ ), bicarbonate ( $\text{HCO}_3^-$ ) and dissolved carbon dioxide ( $\text{CO}_2$ ) present in a sample. Interference of DIC in the measurement of DOC is removed by acidifying the sample to a pH of less than 2 thus converting all carbonates to  $\text{CO}_2$ . The  $\text{CO}_2$  gas produced is purged from the sample prior to DOC analysis. In this process of  $\text{CO}_2$  purging from the sample, volatile organic carbon present in the sample will also be removed; therefore, only non-purgeable organic carbon will be determined in the DOC measurement).

**Table 17 Sampling procedures for dissolved organic carbon**

Sample requirements	Filtered sample <sup>A</sup>
Volume	125 mL
Container	Glass – brown (amber) container Cap must have teflon-lined insert Use new pre-cleaned bottles that are free from organics
Collection technique	The sample can be collected in a clean sample container prior to filtration. Filtered sample is placed into a sample bottle, after rinsing. Ensure sample bottle is pre-rinsed three times with filtered sample water (3 × 20 mL) before final collection.
Filtration technique	Filter sample through 0.45 µm pore diameter cellulose acetate (membrane) filter <sup>B</sup>
Treatment to assist preservation	Refrigerate at 1–4°C, do not freeze Store in the dark
Filling technique	Pre-rinse sample bottle container with sample Fill container completely to the top to exclude air. The sample must be free of air bubbles.
Maximum sample holding time and storage conditions	Test should be carried out as soon as possible. Analyse within 7 days if acidified; kept refrigerated at 1–4°C and stored in dark. Do not freeze Alternative holding time is 3 days at 4°C (no acidification) <sup>D</sup>
Units of measurement	mg/L (mg carbon/L or µg non-purgeable organic carbon/L)
Analysis method	Total organic carbon by high temperature combustion and IR detection, method 5310 (APHA, 1998)
Comments	Inorganic carbon must be purged before analysis, hence volatile organic species will be lost. Report as non-purgeable organic carbon.

<sup>A</sup> Samples should be filtered as soon as possible after sample collection, preferably on site. Filter paper should be washed with sample first prior to filtration. Do not re-use filter paper.

<sup>B</sup> Optional: If the sample has high particulate matter content then it may be necessary to pre-filter using a glass fibre filter paper (GFC 1.2 µm).

<sup>D</sup> Guideline experimentally derived by Hosking Chemical Services for CSIRO and the Waters and Rivers Commission.

## 5.14 Soluble reactive silica (SiO<sub>2</sub>-Si)

Diatoms utilise silica in the construction of their cell walls and can become a nuisance if their numbers increase rapidly and cause a bloom. Therefore, it is important to quantify the amount of soluble reactive silica in estuaries and catchments.

**Table 18 Sampling procedures for soluble reactive silica**

Sample requirements	Filtered sample <sup>A</sup>
Volume	250 mL
Container	Plastic <sup>B</sup> or glass Use new pre-cleaned bottles
Collection technique	The sample can be collected in a clean sample container prior to filtration. Filtered sample is placed into a sample bottle, after rinsing. Ensure sample bottle is pre-rinsed three times with filtered sample water (3 × 20 mL) before final collection.
Filtration technique	Filter sample through 0.45 µm pore diameter cellulose acetate (membrane) filter <sup>C</sup>
Treatment to assist preservation	Refrigerate at 1–4°C, do not freeze
Filling technique	Fill to the shoulder of bottle
Maximum sample holding time and storage conditions	Analyse within 24 hours if sample is only kept refrigerated at 1–4°C. Analyse within 1 month of sample collection if sample was filtered and kept refrigerated at 1–4°C.
Units of measurement	mg/L (mg silica as silicon/L)
Analysis method	Automated method for molybdate-reactive silica method 4500-SiO <sub>2</sub> D, E (APHA, 1998)
Comments	SiO <sub>2</sub> -Si, NO <sub>x</sub> -N, NH <sub>4</sub> -N /NH <sub>3</sub> -N and soluble reactive phosphorus can be collected in the same 250 mL container.

<sup>A</sup> Samples should be filtered as soon as possible after sample collection, preferably on site. Filter paper should be washed with sample first prior to filtration. Do not re-use filter paper.

<sup>B</sup> Plastic sample bottles should not be made from low-density polyethylene (LDPE) as these tend to leak. Appropriate sample container plastics are high-density polyethylene (HDPE), polypropylene, polycarbonate or a fluoropolymer (e.g. teflon).

<sup>C</sup> Do not pre-filter with glass fibre filter paper (GFC 1.2 µm) as these contain silica and can contaminate the sample.

## 5.15 Biochemical oxygen demand (BOD)

Biochemical oxygen demand is a measure of the amount of biologically and/or chemically degradable organic material that is present in the water. It indicates the amount of oxygen that aerobic aquatic organisms could potentially consume in the process of metabolising all the organic matter available to them. The consequence of high BOD is low levels of dissolved oxygen in affected waterways resulting in aquatic organisms becoming stressed and in extreme cases, suffocating and dying.

**Table 19 Sampling procedures for biochemical oxygen demand**

Sample requirements	Unfiltered sample
Volume	1 L
Container	Plastic <sup>A</sup> or glass – brown (amber) <sup>B</sup> Use new pre-cleaned bottles only
Collection technique	Do not pre-rinse container with sample Direct collection into sample bottle or transfer into a sample bottle from collection vessel. Keep samples at or below 4°C during compositing. Limit compositing period to 24 hrs after sample collection.
Treatment to assist preservation	Refrigerate at 1–4°C and store in the dark Do not freeze
Filling technique	Do not pre-rinse container with sample Fill container completely to the top to exclude air The sample must be free of air bubbles
Maximum sample holding time and storage conditions	Analyse directly as soon as possible after sample is collected, but within 24 hours if the sample is refrigerated at 1–4°C in the dark. Do not freeze
Units of measurement	mg/L
Analysis method	5-day BOD test method 5210 B (APHA, 1998)
Comments	Need a separate sample container for BOD Sample must be free of air bubbles Dark (or amber) glass bottles are preferable for samples that are low in BOD (<5 mg L <sup>-1</sup> ).

<sup>A</sup> Plastic sample bottles should not be made from low-density polyethylene (LDPE) as these tend to leak. Appropriate sample container plastics are high-density polyethylene (HDPE), polypropylene, polycarbonate or a fluoropolymer (e.g. teflon).

<sup>B</sup> Amber glass bottles are preferable for samples that are low in BOD (< 5 mg L<sup>-1</sup>).

## 5.16 Metals – total and dissolved metals and metalloids

Many metals are toxic to aquatic animals. They can also bioaccumulate through food chains and this has implications for human health as well as environmental health.

- Metals commonly determined include: aluminium (Al), silver (Ag), arsenic (As), boron (B), barium (Ba), beryllium (Be), calcium (Ca), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), mercury (Hg), potassium (K), lithium (Li), magnesium (Mg), manganese (Mn), molybdenum (Mo), sodium (Na), nickel (Ni), lead (Pb), antimony (Sb), selenium (Se), tin (Sn), titanium (Ti), uranium (U), vanadium (V) and zinc (Zn).
- Total metals can be analysed by digesting the sample using a concentrated nitric/hydrochloric acid added to an unfiltered water sample prior to analysis (see 3010 A (APHA, 1998)).
- Dissolved metals are determined by analysing those metals in a filtered sample that passes through a 0.45 µm membrane filter [see 3010 A (APHA, 1998)]. Before analysis of a field-filtered, field-acidified sample, some extra dilute acid is added to the filtered sample, to ensure dissolution of any precipitates formed after filtration.
- The sample must not be filtered when determining total metals (which include those metals bound to the particulate matter in the sample); otherwise, the same collection procedure is followed.
- The specific metals that are required to be determined must be stated on the chain of custody form (COC).
- Mercury should be analysed by the more sensitive technique described in a separate table at the end of this section. The normal mercury analysis will not meet detection limits that are required for comparison to the mercury toxicant 99% ANZECC & ARMCANZ (2000) guideline trigger value, for the protection of slightly-to-moderately disturbed freshwater ecosystems. The determination of mercury to lower detection limits must be requested specifically on the COC (in the remarks section of the COC, or by means of an attached sheet specifying variables and limits of reporting). For more accurate mercury analysis, a separate sample should be collected.
- Slightly different analysis techniques are also required if speciation is necessary to determine concentrations of ferrous iron [Fe (II)] and hexavalent chromium [Cr (VI)].

**Table 20 Sampling procedures for heavy metals**

Dissolved (soluble) Metals	Al, Ag, As (total, III, V), B, Ba, Be, Ca, Cd, Co, Cr (total, III), Cu, Fe (total), Hg, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se (total, IV, VI), Sn (not including tributyl tin as Sn), Ti, U, V & Zn
Sample requirements	Filtered sample <sup>A</sup>
Volume	250 mL, unless speciation of As (total, trivalent, pentavalent) and/or Cr (total, trivalent) is required, in which case 500 mL is required.
Container	Plastic <sup>B</sup> Bottle cap must have a teflon liner Use new pre-cleaned acid rinsed bottles
Collection technique	Decant from collection vessel and filter immediately. Filtered sample is placed directly in sample bottle.
Filtration technique	Filter sample through 0.45 µm pore diameter cellulose acetate (membrane) filter <sup>C</sup> .
Treatment to assist preservation	After filtration, add 10% nitric acid (concentrated HNO <sub>3</sub> ) to pH <2 <sup>D</sup> (if bottle from laboratory does NOT already have 2 mL present in pre-prepared bottles). Do not pre-rinse these sample bottles. Refrigerate at 1–4°C or freeze
Filling technique	If the sample bottles contain acid do not pre rinse them, otherwise, pre-rinse bottle with filtered sample three times, then add filtered sample and add acid preservative. Fill to the shoulder of bottle.
Maximum sample holding time and storage conditions	1 month if at 1–4°C, and pH < 2 6 months if frozen
Units of measurement	mg/L or µg/L (mg metal/L or µg metal/L)
Analysis method	Measured by a range of methods: ion chromatography, colorimetry, ICP-MS, ICP-AES, flame ASS, graphite furnace ASS, or cold vapour generation AAS methods.
Comments	Samples for total metal concentrations are not filtered. Generally, all metals/metalloids can be analysed from the same sample bottle, except for when the special Hg analysis or speciation analysis is required. Safety note: Use the appropriate personal protective equipment (e.g. safety glasses and gloves) when filling the sample bottles for dissolved metal analysis. Avoid contact or accidental splashing with the concentrated nitric acid preservative present in the bottles. Concentrated nitric acid is corrosive and care should be taken to avoid any eye or skin contact, or inhalation of fumes. If eyes or skin are exposed to the acid, wash thoroughly and with copious amounts of water and seek medical attention.

<sup>A</sup> Samples should be filtered as soon as possible after sample collection, preferably on site. Filter paper should be washed with sample first prior to filtration. Do not re-use filter paper.

<sup>B</sup> Plastic sample bottles should not be made from low density polyethylene (LDPE) as these tend to leak. Appropriate sample container plastics are high-density polyethylene (HDPE), polypropylene, polycarbonate or fluoropolymer (e.g. nalgene, teflon (polytetrafluoroethylene, PTFE)). NMI now use 125 mL nalgene bottles for heavy metals, as the previously used HDPE bottles were found to leach trace quantities of Zn over time.

<sup>C</sup> Optional FOR SOLUBLE METALS ANALYSIS ONLY: If the sample has high particulate matter content then it may be necessary to pre-filter using a glass fibre filter paper (GFC 1.2 µm).

<sup>D</sup> For the analysis of Li, K, and Na in samples, acidification is not required. These metals in solution are stable for 1 month without acidification (but acidification allows analysis of other metals).

### **Dissolved hexavalent chromium [Cr (VI)]**

- A minimum volume of 100 mL of sample is required. The same sample treatment as above applies, except the sample should not be acidified. Rather, after filtration, the pH of the sample should be adjusted to  $> 8$  with 1 M (4%) sodium hydroxide solution, and refrigerated at  $1-4^{\circ}\text{C}$  (do not freeze). Samples should be analysed within 24 hours of collection.

### **Dissolved ferrous iron [Fe (II)]**

- A minimum volume of 100 mL of sample is required. The same sample treatment as above applies, except that the sample is acidified with concentrated hydrochloric acid to  $\text{pH} < 2$ , and refrigerated at  $1-4^{\circ}\text{C}$  (do not freeze). Additionally, the sample container must be filled completely to exclude air from the container thus preventing conversion to ferric iron [Fe (III)] and further hydrolysis to form insoluble hydrated ferric oxide. Samples should be analysed within 24 hours of collection.

## Dissolved total mercury (Hg), to detection limits below 99% ANZECC & ARMCANZ (2000) guideline trigger value

**Table 21 Sampling procedures for dissolved mercury (to very low limits of detection)**

Sample requirements	Filtered sample <sup>A</sup>
Volume	500 mL
Container	Glass Bottle cap must have a teflon liner Use new pre-cleaned acid rinsed bottles
Collection technique	Decant from collection vessel and filter immediately. Filtered sample is placed directly in sample bottle.
Filtration technique	Filter sample through 0.45 µm pore diameter cellulose acetate (membrane) filter <sup>B</sup>
Treatment to assist preservation	After filtration add 2 mL of a 20% solution of potassium dichromate in approximately 4M nitric acid per litre of sample water. Refrigerate at 1–4°C or freeze
Filling technique	If the sample bottles contain acid do not pre rinse them, otherwise, pre-rinse bottle with filtered sample three times, then add filtered sample and add acid preservative. Fill to the shoulder of bottle
Maximum sample holding time and storage conditions	1 month if at 1–4°C, and pH < 2 6 months if frozen
Units of measurement	mg/L or µg/L (mg mercury/L or µg mercury/L)
Comments	Particular care is needed to ensure that the samples containers are free from contamination.

<sup>A</sup> Samples should be filtered as soon as possible after sample collection, preferably on site. Filter paper should be washed with sample first prior to filtration. Do not re-use filter paper.

<sup>B</sup> Optional: If the sample has high particulate matter content then it may be necessary to pre-filter using a glass fibre filter paper (GFC 1.2 µm).

<sup>C</sup> A separate sample is required for the determination of mercury I this way as the addition of potassium dichromate would compromise the determination of potassium and chromium. Potassium dichromate is added to the sample when only mercury is being analysed, or if the client specifically asks for it, or there is a large organic concentration in the sample expected, or if low detection limits are required, or if the samples will be held for more than one week before analysis.



## 5.17 Total water hardness (as CaCO<sub>3</sub>)

Historically water hardness was a measure of the capacity of water to precipitate soap, chiefly due to the presence of calcium and magnesium ions in the water. More recently other species such as polyvalent cations have been implicated in the precipitation of soap. Total hardness is therefore now defined as the sum of calcium and magnesium concentrations in water, expressed as calcium carbonate equivalents in milligrams per litre according to the following formula (APHA, 1998).

Hardness equivalent CaCO<sub>3</sub>/L = 2.497 [Ca, mg/L] + 4.118 Mg, mg/L].

**Table 22 Sampling procedures for total water hardness**

Sample requirements	Unfiltered sample
Volume	125 mL
Container	Plastic <sup>A</sup> Bottle cap must have a teflon liner Use new pre-cleaned acid rinsed bottles
Collection technique	Decant from collection vessel, ensuring sample bottle is pre-rinsed three times with sample water (3 × 20 mL) before final collection.
Filling technique	Pre-rinse bottle with sample water three times, then add sample water. Fill to the shoulder of bottle
Maximum sample holding time and storage conditions	7 days
Units of measurement	mg/L (mg CaCO <sub>3</sub> /L)

<sup>A</sup> Plastic sample bottles should not be made from low-density polyethylene (LDPE) as these tend to leak. Appropriate sample container plastics are high-density polyethylene (HDPE), polypropylene, polycarbonate or fluoropolymer (e.g. nalgene, teflon).

## 5.18 Total acidity and total alkalinity (as CaCO<sub>3</sub>)

The total *alkalinity* of water is a measure of its acid-neutralising capacity to a designated pH. It is the sum of all titratable bases, including carbonates, bicarbonates, and hydroxides, and also borates, phosphates, silicates and other bases if they are present.

Total *acidity* is a quantitative measure of the capacity of water to react with a strong base to a designated pH.

For analysis of total alkalinity APHA, 1998 requires titration with a standard hydrochloric acid solution to an end-point pH of 3.7 (i.e. the methyl orange end-point). To determine total acidity APHA, 1998 requires titration with a standard sodium hydroxide solution to an end-point pH 8.3 (i.e. the phenolphthalein end-point).

**Table 23 Sampling procedures for total acidity and total alkalinity**

Sample requirements	Unfiltered sample
Volume	125 mL
Container	Plastic <sup>A</sup> Use new pre-cleaned bottles
Collection technique	Direct collection into sample bottle or transfer into a sample bottle from collection vessel. Ensure sample bottle is pre-rinsed three times with sample water (3 × 20 mL) before final collection.
Treatment to assist preservation	Refrigerate at 1–4°C Do not freeze
Filling technique	Fill container completely to the top to exclude air. The sample must be free of air bubbles. Cap tightly.
Maximum sample holding time and storage conditions	Analyse within 1 day if sample is kept refrigerated at 1–4°C. Do not freeze
Units of measurement	Both total acidity and alkalinity are expressed as mg/L (mg CaCO <sub>3</sub> /L
Analysis method	Acidity and alkalinity method 2310 B. and 2320 B. (APHA, 1998) Also in accordance with AS 3550.3:1992
Comments	Both total alkalinity and total acidity require separate bottles for analysis.

<sup>A</sup> Plastic sample bottles should not be made from low-density polyethylene (LDPE) as these tend to leak. Appropriate sample container plastics are high-density polyethylene (HDPE), polypropylene, polycarbonate or a fluoropolymer (e.g. teflon).

## 5.19 Total petroleum hydrocarbons (TPHs)

The C<sub>6</sub> to C<sub>9</sub> petroleum hydrocarbon fraction will predominantly consist of the BTEX compounds, so the same method described for BTEX (see section 5.21) is applied to the sample for this hydrocarbon fraction.

The other molecular weight range fractions namely C<sub>10</sub> to C<sub>14</sub>, C<sub>15</sub> to C<sub>28</sub>, and C<sub>29</sub> to C<sub>36</sub> are estimates of the total petroleum hydrocarbons since:

1. the solvent extraction techniques also extracts non-petroleum (biological) hydrocarbons from the sample
2. the cut off points for each fraction is based on gas chromatographic retention time rather than molecular structure.

**Table 24 Sampling procedures for total petroleum hydrocarbons**

Sample requirements	Unfiltered sample
Volume	1 L
Container	Glass – brown (amber) container Cap must have teflon-lined insert Use new pre-cleaned bottles that are free from volatile organics
Collection technique	Do not pre-rinse container with sample Bottle must be used to collect sample directly No decanting
Treatment to assist preservation	Refrigerate at 1–4°C, do not freeze and store in the dark.
Filling technique	Do not pre-rinse container with sample Do not completely fill sample container
Maximum sample holding time and storage conditions	Analyse within 14 days if refrigerated at 1–4°C and stored in the dark. Do not freeze
Units of measurement	µg/L.

## 5.20 Polycyclic aromatic hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons (PAHs) have multiple aromatic rings in their chemical structure. They are also referred to as polynuclear aromatic hydrocarbons. PAHs are found in coal tar, crude oil, creosote, and roofing tar, but a few are used in medicines or to make dyes, plastics, and pesticides. They can be formed during the incomplete burning of coal, oil and gas, garbage, or other organic substances like tobacco or char-broiled meat, and are typical components of asphalts, fuels, oils, and greases. Some PAHs are manufactured as colourless, white, or pale yellow-green solids.

A suite of 16 individual PAHs, identified as priority pollutants by the US EPA, are usually determined in environmental samples. This suite comprises:

**Table 25 Suite of 16 PAHs, identified as priority pollutants by the US EPA**

naphthalene, acenaphthylene, acenaphthene, anthracene, benzo[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[ghi]perylene, benzo[a]pyrene, chrysene, dibenz[a,h]anthracene, fluoranthene, fluorene, indeno[1,2,3-cd]pyrene, phenanthrene & pyrene

Other alkylated PAHs, commonly found in petroleum, may also be targeted for example 1-methylnaphthalene and 2-methylnaphthalene.

**Table 26 Sampling procedures for polycyclic aromatic hydrocarbons**

Sample requirements	Unfiltered sample
Volume	1 L
Container	Glass – brown (amber) container Cap must have teflon-lined insert Use new pre-cleaned bottles that are free from volatile organics
Collection technique	Do not pre-rinse container with sample. Bottle must be used to collect sample directly No decanting
Treatment to assist preservation	Refrigerate at 1–4°C and store in the dark Do not freeze
Filling technique	Do not pre-rinse container with sample Do not completely fill sample container
Maximum sample holding time and storage conditions	Extract within 7 days and analyse within 40 days, if refrigerated at 1–4°C and stored in the dark. Do not freeze
Units of measurement	µg/L
Comments	Detection limits and limits of reporting may be decreased for trace level analysis by increasing the volume of water to 1 litre. Decreasing the volume of water to 500mL increases the detection limits and limits of reporting.

## 5.21 Volatile organic compounds (VOCs)

A suite of volatile organic compounds including benzene, toluene, ethyl benzene and xylene isomers (BTEX), other C<sub>6</sub> to C<sub>9</sub> petroleum hydrocarbons, other monocyclic aromatic compounds and halogenated compounds may be determined in water samples to investigate anthropogenic contamination.

This suite might include some of the following compounds. Please note that these lists are not exhaustive:

**Table 27 Examples of monocyclic aromatic hydrocarbons**

acrylamide, benzene, tert-butylbenzene, sec-butylbenzene, n-butylbenzene, dimethylamine, EDTA (ethylenediaminetetraacetic acid), epichlorohydrin, ethylacrylate, ethyl benzene, isopropylbenzene [cumene], p-isopropyltoluene, n-propylbenzene, styrene (vinyl benzene), toluene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, m-xylene, o-xylene, p-xylene & a-methylstyrene

**Table 28 Examples of chlorinated VOCs**

Bromobenzene, bromochloromethane, bromoform, carbon tetrachloride, chlorobenzene, chloroform, 2-chlorotoluene, 4-chlorotoluene, bromodichloromethane, dibromochloromethane, 1,2-dibromo-3-chloropropane, 1,2-dibromoethane, dibromomethane, o-dichlorobenzene, 1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, 1,1-dichloroethane, 1,2-dichloroethane, 1,1-dichloroethene, trans-1,2-dichloroethene, cis-1,2-dichloroethene, dichloromethane, 1,2-dichloropropane, 1,3-dichloropropane, 2,2-dichloropropane, 1,1-dichloropropene, cis-1,3-dichloropropene, trans-1,3-dichloropropene, hexachlorobutadiene, tetrachloroethene, 1,2,3-trichlorobenzene, 1,2,4-trichlorobenzene, trichlorobenzenes (total), 1,1,1,2-tetrachloroethane, 1,1,2,2-tetrachloroethane, 1,1,1-trichloroethane, 1,1,2-trichloroethane, 1,2,3-trichloropropane, trichloroethene, trichlorofluoromethane, vinyl chloride, chloroacetic acid, cyanogen chloride (as cyanide), dichloroacetic acid, trichloroacetaldehyde (chloral hydrate), trichloroacetic acid & trihalomethanes (THMs) (total)

**Table 29 Sampling procedures for volatile organic compounds**

Sample requirements	Unfiltered sample
Volume	40 mL × 2 (1 for BTEX & 1 for VOCs – can be sampled individually)
Container	Glass vial Cap must have teflon-lined septum Use new pre-cleaned bottles that are free from volatile organics
Collection technique	Do not pre-rinse container with sample Bottle must be used to directly collect sample. No decanting. However, if acid preservative is present in bottle prior to collection (as with pre-prepared laboratory bottles), decant sample from another collection vessel into sample vial. Sample should be collected such that there is minimum exposure of sample (in either the collection or sample container) to the atmosphere.
Treatment to assist preservation	Bottles may come including a fixative, from the laboratory. Do not rinse these pre-prepared bottles. Refrigerate at 1–4°C but do not freeze
Filling technique	Do not pre-rinse container with sample Completely fill sample container to capacity with a ‘bulging meniscus’ but not overflowing. Cap sample so that there are no air spaces or bubbles. Tightly seal sample bottles and store with the teflon-lined septum cap face down.
Maximum sample holding time and storage conditions	7 days if refrigerated at 1–4°C and acidified, extract within 7 days, analyse within 40 days. Do not freeze
Units of measurement	µg/L
Analysis method	Analysis of volatile organic compounds by the purge and trap technique 6040 C, 6200 (APHA, 1998)
Comments	Sample should be collected such that there is minimum exposure of sample (in either the collection or sample container) to the atmosphere. Sample must be free of air bubbles For chlorinated VOC determination, for each 40 mL of sample add either: (a) 3 mg of sodium thiosulphate (Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> ); or (b) 25 mg ascorbic acid (vitamin C, C <sub>6</sub> H <sub>8</sub> O <sub>6</sub> ); or (c) 3 mg sodium sulphite (Na <sub>2</sub> SO <sub>3</sub> ); to container prior to sample collection for preservation <sup>BC</sup> . <b>Safety note:</b> Take care and use the appropriate personal protective equipment (e.g. safety glasses and gloves) when filling the sample bottles for BTEX analysis, as there is a need to avoid contact or accidental splashing with the concentrated hydrochloric acid preservative if present in the bottles.

<sup>B</sup> The laboratory can add these substances if required (need to indicate on COC).

<sup>C</sup> For *a*-methylstyrene and vinyl chloride analysis add only the 25 mg ascorbic acid (vitamin C, C<sub>6</sub>H<sub>8</sub>O<sub>6</sub>) for each 40 mL of sample.

## 5.22 Surfactants

A surfactant molecule contains a strongly hydrophobic portion, usually a hydrocarbon chain containing about 10 to 20 carbon atoms, and a hydrophilic portion. The hydrophilic part of the molecule is usually either ionic or uncharged. Ionic surfactants (i.e. the hydrophilic portion of the molecule is ionic) may be further categorised as cationic, where the ion retains a positive charge, and anionic where the charge is negative.

Surfactants often enter waters and waterways through the discharge of aqueous wastes from household and industrial laundering and other cleansing operations.

### Anionic surfactants

These include linear alkylbenzene sulphonates (LAS), alkylsulphonates and alkylsulphates.

**Table 30 Sampling procedures for anionic surfactants**

Sample requirements	Unfiltered sample
Volume	1 L
Container	Glass Cap must have teflon-lined insert Use new pre-cleaned bottles that are free from detergent Do not wash glass sample bottle with detergent Bottle should be solvent washed with methanol (according to ISO 7875-1, 1996)
Collection technique	Bottle must be used to directly collect sample No decanting
Treatment to assist preservation	Add 10% sulphuric acid ( $\text{H}_2\text{SO}_4$ ) to pH < 2 (this is not necessary if analysing MBAS) Refrigerate at 1–4°C Do not freeze
Filling technique	Fill container completely to exclude air
Maximum sample holding time and storage conditions	Immediate analysis is preferable Analyse within 2 days if sample is kept refrigerated at 1–4°C Do not freeze.
Units of measurement	µg/L
Comments	For the analysis of methylene blue active substances (MBAS), do not acidify

## Cationic surfactants

These include polyethoxylated tallow amine, commonly used as a wetting agent in herbicide formulations and alkylquaternary ammonium salts, common ingredients in hair shampoos and conditioners.

**Table 31 Sampling procedures for cationic surfactants**

Sample requirements	Unfiltered sample
Volume	1 L
Container	Glass Cap must have teflon-lined insert Use new pre-cleaned bottles that are free from detergent Do not wash glass sample bottle with detergent Bottle should be solvent washed with methanol (according to ISO 7875-1, 1996)
Collection technique	Bottle must be used to directly collect sample No decanting
Treatment to assist preservation	To prevent adsorption on container wall, add (on-site) 5 mg/L linear alkylethoxylated non-ionic detergent. Add 10% sulphuric acid (H <sub>2</sub> SO <sub>4</sub> ) to pH < 2 (this is not necessary if analysing MBAS). Refrigerate at 1–4°C, do not freeze
Filling technique	Fill container completely to exclude air
Maximum sample holding time and storage conditions	Immediate analysis is preferable Analyse within 2 days if sample is kept refrigerated at 1–4°C Do not freeze
Units of measurement	µg/L
Comments	For the analysis of methylene blue active substances (MBAS) do not acidify



## Non-ionic surfactants (NIS)

These include alkyl poly (ethylene oxides), commonly used in oil spill dispersants

**Table 32 Sampling procedures for non-ionic surfactants**

Sample requirements	Unfiltered sample
Volume	1 L
Container	Glass Cap must have teflon-lined insert Use new pre-cleaned bottles that are free from detergent DO NOT wash glass sample bottle with detergent Bottle should be solvent washed with methanol (according to ISO 7875-1 and ISO 7875-2, 1996)
Collection technique	Bottle must be used to directly collect sample No decanting
Treatment to assist preservation	Add 40% (v/v) formaldehyde solution to give a 1% (v/v) final concentration Refrigerate at 1–4°C Do not freeze
Filling technique	Fill container completely to exclude ai
Maximum sample holding time and storage conditions	Analyse within 1 month if sample is kept refrigerated at 1–4°C Do not freeze
Units of measurement	µg/L

## 5.23 Oil and grease

In the determination of oil and grease specific substances are not quantified. Rather, groups of substances with similar physical characteristics are determined qualitatively on the basis of their common solubility in an organic extracting solvent. 'Oil and grease' is defined as any material recovered as a substance soluble in a particular solvent. It includes petroleum based fuels such as gasoline, diesel, and kerosene, emulsifiable oil, and petroleum hydrocarbons ( $C_6$ – $C_9$ ,  $C_{10}$ – $C_{14}$ ,  $C_{15}$ – $C_{28}$ , and  $C_{29}$ – $C_{36}$ ). The organic solvent currently prescribed by standard methods is a mixture of 80% *n*-hexane and 20% methyl-*tert*-butyl ether (MTBE). Because the extraction is not specific for these petroleum products, other non petrogenic compounds are also determined. These include biological hydrocarbons and well as photosynthetic pigments. Volatile organic compounds are not recovered from this analysis.

**Table 33 Sampling procedures for oil and grease**

Sample requirements	Unfiltered sample
Volume	1 L
Container	Glass – brown (amber) container Cap must have teflon-lined insert Use new pre-cleaned bottles that are free from volatile organics Bottle should be solvent washed (with acetone/hexane/methanol) and free of organics
Collection technique	Do not pre-rinse container with sample Bottle must be used to directly collect sample No decanting
Treatment to assist preservation	Add either hydrochloric acid (concentrated HCl) or 10% sulphuric acid ( $H_2SO_4$ ) until sample is at pH <2 Refrigerate at 1–4°C and store in the dark Do not freeze
Filling technique	Do not pre-rinse container with sample Do not completely fill sample container
Maximum sample holding time and storage conditions	Analyse within 28 days if acidified, refrigerated at 1–4°C and stored in the dark. Analyse within 1 day if refrigerated at 1–4°C and stored in the dark, but not acidified. Do not freeze.
Units of measurement	mg/L (mg extractable material/L)
Comments	Extract on site where practical Extract sample container as part of the sample extraction procedure

## 5.24 Pesticides and herbicides - organochlorine and organophosphate pesticides (OC and OP pesticides), carbamate pesticides, triazine herbicides and others

Pesticides and herbicides are, by definition, toxic and this provides a potential risk to the ecosystem if natural waterways are polluted. The toxic action can be either direct; by killing similar organisms to that which they were designed to kill, or by bioaccumulation; rendering normal food sources for potential predators and consumers (e.g. fish, mussels and humans) unsafe for consumption. Pesticides and herbicides can be determined in water samples according to the requirements of the sampling program. These commonly include:

- *Organochlorine pesticides*:  $\alpha$ -BHC;  $\beta$ -BHC;  $\delta$ -BHC, lindane, heptachlor, aldrin, oxychlordane,  $\alpha$ -endosulphan, pp'-DDD; pp'-DDE; pp'-DDT, dieldrin, endrin, endrin aldehyde, endrin ketone,  $\beta$ -endosulphan, methoxychlor,  $\gamma$ -chlordane, endosulphan sulphate,  $\alpha$ -chlordane, heptachlor epoxide, hexachlorobenzene, hexachlorobutadiene; hexachlorocyclopentadiene; mirex; pentachlorobenzene; 1,2,3,4-tetrachlorobenzene; 1,2,3,5-tetrachlorobenzene; 1,2,4,5-tetrachlorobenzene.
- *Organophosphate pesticides*: azinphos-ethyl, azinphos-methyl (guthion), bromophos ethyl, carbofenthion, chlorfenvinphos E, chlorfenvinphos Z, chlorpyrifos, chlorpyrifos methyl, demeton-s-methyl, diazinon, dichlorvos, dimethoate, ethion, fenthion, fenamiphos, fenitrothion, malathion, methidathion, monocrotophos, parathion methyl, parathion ethyl, pirimiphos ethyl, prothiofos., co-ral; dicofol; fenchlorophos; methamidophos; naled; profenofos; phosdrindi-syston; phosmet; prophos; temephos; zolone.
- *Carbamate pesticides*: aldicarb, carbaryl, carbendazim, carbofuran, carbophenothion, carboxin, methiocarb, methomyl, molinate, pirimicarb, promecarb, thiobencarb, thiram
- *Triazine herbicides*: atrazine, simazine, propazine, hexazinone.
- *Others*: acetophenone; acrylonitrile; amitrole; diquat; glyphosate; paraquat; acephate; ametryn; benomyl; bentazone; bioresmethrin; bromazil; bromophos-ethyl; n-butylmercaptan; chlorothalonil; chloroxuron; chlorphenvinphos; clopyralid; dichlobenil; dichlorvos; diclofop-methyl; difenzoquat; diphenamid; disulfoton; Diuron; EDB; endosulfan; endothal; EPTC; ethoprophos; etridiazole; fenarimol; fenchlorophos; fenoprop; fensulphothion; flamprop-methyl; fluometuron; formothion; fosamine; hexaflurate; maldison; metolachlor; metribuzin; metsulfuron; metsulfuron-methyl; mevinphos; napropamide; nitralin; norflurazon; oryzalin; oxamyl; parathion; pebulate; pendimethalin; piperonyl butoxide; pirimiphos-methyl; propachlor; propanil; propargite; propiconazole; propyzamide; pyrazophos; quintozone; sulprofos; terbacil; terbufos; terbutryn; tetrachlorvinphos; thiometon; thiophanate; triadimefon; trichlorofon; triclopyr; trifluralin; vernolate.

**Table 34 Sampling procedures for pesticides and herbicides**

Sample requirements	Unfiltered sample
Volume	1 L
Container	Glass – brown (amber) container <sup>A</sup> Cap must have teflon-lined insert Use new pre-cleaned bottles that are free from volatile organics
Collection technique	Do not pre-rinse container with sample Bottle must be used to directly collect sample No decanting
Treatment to assist preservation	Refrigerate at 1–4°C and store in the dark Do not freeze
Filling technique	Do not pre-rinse container with sample Do not completely fill sample container
Maximum sample holding time and storage conditions	Extract within 7 days and analyse within 40 days, if refrigerated at 1–4°C and stored in the dark Do not freeze
Units of measurement	µg/L
Comments	Pesticides/herbicides can be collected in same container but consult with analytical laboratory regarding sample volume requirements.

<sup>A</sup> *Soft glass type bottles should not be used to determine trace levels of some pesticide, as they may sorb to the walls of the container. It may be necessary to check if the particular trace pesticide compound required to be determine has the tendency to sorb to glass.*

## 5.25 True colour

Colour in water samples can result from the presence of natural metallic ions (iron and manganese), humus and peat materials, plankton, weeds, and industrial wastes. Colour or true colour refers to the colour of water upon removal of suspended solids (i.e. once the sample has been filtered).

**Table 35 Sampling procedures for true colour**

Sample requirements	Filtered sample <sup>A</sup>
Volume	500 mL
Container	Plastic <sup>B</sup> or glass Use new pre-cleaned bottles If necessary, bottles should be washed in phosphate-free detergent and rinsed three times with tap water and three times with deionised water.
Collection technique	The sample can be collected in a clean sample container prior to filtration. Filtered sample is placed into a sample bottle, after rinsing. Ensure sample bottle is pre-rinsed three times with filtered sample water (3 × 20 mL) before final collection.
Filtration technique	Filter sample through 0.45µm pore diameter cellulose acetate (membrane) filter <sup>C</sup>
Treatment to assist preservation	Refrigerate at 1–4°C and store/transport in the dark. Do not freeze
Filling technique	Fill to just below shoulder of the bottle; do not completely fill
Maximum sample holding time and storage conditions	Analyse within 2 days if sample is kept refrigerated at 1–4°C in the dark.
Units of measurement	Colour units or platinum-cobalt units (PCU, Pt/Co or Pt-Co units)
Comments	Requires a separate bottle

<sup>A</sup> Samples should be filtered as soon as possible after sample collection, preferably on site. Filter paper should be washed with sample first prior to filtration. Do not re-use filter paper.

<sup>B</sup> Plastic sample bottles should not be made from low-density polyethylene (LDPE) as these tend to leak. Appropriate sample container plastics are high-density polyethylene (HDPE), polypropylene, polycarbonate or a fluoropolymer (e.g. teflon).

<sup>C</sup> Optional: If the sample contains a lot of particulate matter then it may be necessary to pre-filter sample using a glass fibre (GF/C) filter paper (GFC 1.2 µm).

## 5.26 Gilvin – colour

Gilvin is the name given to the natural dissolved organic carbon compounds that give water a brown colouration (i.e. absorb light in the 400–440 nm wavelength and reduce the blue region of the spectrum). Gilvin, or soluble humic colour, is often the major single component absorbing light in inland waters. There are many compounds and compound classes that make up gilvin, and tannin is just one of these.

Gilvin is also used as a descriptor for 'colour' in water.

The amount of light transmitted through the water (the light climate) is an important indicator of the potential for primary production within a wetland system. Highly coloured systems will contain different assemblages of plants and animals to clear or weakly coloured systems. They will also have lower primary productivity due to lower levels of photosynthesis. Measurement of colour (gilvin) will provide information on the light climate of a wetland and thus its capacity for primary productivity.

**Table 36 Sampling procedures for gilvin colour**

Sample requirements	Filtered sample
Volume	500 mL
Container	Plastic <sup>A</sup> or glass Use new pre-cleaned bottles
Collection technique	Direct collection into sample bottle preferred (or transfer into a sample bottle from collection vessel) Ensure sample bottle is pre-rinsed three times with sample water (3 × 20 mL) before final collection.
Filtration technique	Filter sample through 0.45µm pore diameter cellulose acetate (membrane) filter <sup>B</sup>
Treatment to assist preservation	Refrigerate at 1–4°C and store/transport in the dark Do not freeze
Filling technique	Fill container completely to the top to exclude air The sample must be free of air bubbles Cap tightly
Maximum sample holding time and storage conditions	Analyse within 2 days of collection if sample is kept refrigerated at 1–4°C and in the dark. Do not freeze Alternative holding time is 2 days at 4°C, or 7 days at 4°C and also in the dark <sup>D</sup>
Units of measurement	Gilvin <sub>440</sub> /m
Comments	Freezing of samples should be avoided as irreversible changes in gilvin may occur if the sample is frozen. Requires a separate bottle

<sup>A</sup> Plastic sample bottles should not be made from low-density polyethylene (LDPE) as these tend to leak. Appropriate sample container plastics are high-density polyethylene (HDPE), polypropylene, polycarbonate or a fluoropolymer (e.g. teflon).

<sup>B</sup> Optional: If the sample has high particulate matter content then it may be necessary to pre-filter using a glass fibre filter paper (GFC 1.2 µm).

<sup>D</sup> Guideline experimentally derived by Hosking Chemical Services for CSIRO and the Waters and Rivers Commission.

## 5.27 Bromide (Br<sup>-</sup>)

**Table 37 Sampling procedures for bromide**

Sample requirements	Filtered sample <sup>A</sup>
Volume	500 mL
Container	Plastic <sup>B</sup> or glass Use new pre-cleaned bottles If necessary, bottles should be washed in phosphate-free detergent and rinsed three times with tap water and three times with deionised water.
Collection technique	The sample can be collected in a clean sample container prior to filtration. Filtered sample is placed into a sample bottle, after rinsing. Ensure sample bottle is pre-rinsed three times with filtered sample water (3 × 20 mL) before final collection.
Filtration technique	Filter sample through 0.45 µm pore diameter cellulose acetate (membrane) filter <sup>C</sup>
Treatment to assist preservation	Refrigerate at 1–4°C and store in the dark or freeze
Filling technique	Fill to below shoulder of bottle if freezing
Maximum sample holding time and storage conditions	Analyse within 1 month if sample is kept refrigerated at 1–4°C and stored in the dark.
Units of measurement	mg/L (mg Br/L)

<sup>A</sup> Samples should be filtered as soon as possible after sample collection, preferably on site. Filter paper should be washed with sample first prior to filtration. Do not re-use filter paper.

<sup>B</sup> Plastic sample bottles should not be made from low-density polyethylene (LDPE) as these tend to leak. Appropriate sample container plastics are high-density polyethylene (HDPE), polypropylene, polycarbonate or a fluoropolymer (e.g. teflon).

<sup>C</sup> Optional: If the sample contains a lot of particulate matter then it may be necessary to pre-filter sample using a glass fibre (GF/C) filter paper (GFC 1.2 µm).

## 5.28 Chloride (Cl<sup>-</sup>)

**Table 38 Sampling procedures for chloride**

Sample requirements	Filtered sample <sup>A</sup>
Volume	500 mL
Container	Plastic <sup>B</sup> or glass Use new pre-cleaned bottles If necessary, bottles should be washed in phosphate-free detergent and rinsed three times with tap water and three times with deionised water.
Collection technique	The sample can be collected in a clean sample container prior to filtration. Filtered sample is placed into a sample bottle, after rinsing. Ensure sample bottle is pre-rinsed three times with filtered sample water (3 × 20 mL) before final collection.
Filtration technique	Filter sample through 0.45 µm pore diameter cellulose acetate (membrane) filter <sup>C</sup>
Treatment to assist preservation	Refrigerate at 1–4°C or freeze
Filling technique	Fill to below shoulder of bottle if freezing
Maximum sample holding time and storage conditions	Analyse within 1 month if sample is kept refrigerated at 1–4°C.
Units of measurement	mg/L (mg Cl/L)

<sup>A</sup> Samples should be filtered as soon as possible after sample collection, preferably on site. Filter paper should be washed with sample first prior to filtration. Do not re-use filter paper.

<sup>B</sup> Plastic sample bottles should not be made from low-density polyethylene (LDPE) as these tend to leak. Appropriate sample container plastics are high-density polyethylene (HDPE), polypropylene, polycarbonate or a fluoropolymer (e.g. teflon).

<sup>C</sup> Optional: If the sample contains a lot of particulate matter then it may be necessary to pre-filter sample using a glass fibre (GF/C) filter paper (GFC 1.2 µm).



## 5.29 Fluoride (F<sup>-</sup>)

**Table 39 Sampling procedures for fluoride**

Sample requirements	Filtered sample <sup>A</sup>
Volume	500 mL
Container	Plastic (either high-density polyethylene (HDPE), polypropylene, PET or equivalent) <sup>B</sup> Do not use glass (it sorbs), or PTFE (polytetrafluoroethylene) plastic containers Use new pre-cleaned bottles If necessary, bottles should be washed in phosphate-free detergent and rinsed three times with tap water and three times with deionised water.
Collection technique	The sample can be collected in a clean sample container prior to filtration. Filtered sample is placed into a sample bottle, after rinsing. Ensure sample bottle is pre-rinsed three times with filtered sample water (3 × 20 mL) before final collection.
Filtration technique	Filter sample through 0.45 µm pore diameter cellulose acetate (membrane) filter <sup>C</sup>
Treatment to assist preservation	Refrigerate at 1–4°C or freeze
Filling technique	Fill to below shoulder of bottle if freezing.
Maximum sample holding time and storage conditions	Analyse within 1 month if sample is kept refrigerated at 1–4°C.
Units of measurement	mg/L (mg F/L)
Comments	Do not use glass or PTFE sample containers

<sup>A</sup> Samples should be filtered as soon as possible after sample collection, preferably on site. Filter paper should be washed with sample first prior to filtration. Do not re-use filter paper.

<sup>B</sup> Plastic sample bottles should not be made from low-density polyethylene (LDPE) as these tend to leak.

<sup>C</sup> Optional: If the sample contains a lot of particulate matter then it may be necessary to pre-filter sample using a glass fibre (GF/C) filter paper (GFC 1.2 µm).

## 5.30 Iodide ( $I^-$ )

**Table 40 Sampling procedures for iodide**

Sample requirements	Filtered sample <sup>A</sup>
Volume	500 mL
Container	Plastic <sup>B</sup> or glass Use new pre-cleaned bottles If necessary, bottles should be washed in phosphate-free detergent and rinsed three times with tap water and three times with deionised water.
Collection technique	The sample can be collected in a clean sample container prior to filtration. Filtered sample is placed into a sample bottle, after rinsing. Ensure sample bottle is pre-rinsed three times with filtered sample water (3 × 20 mL) before final collection.
Filtration technique	Filter sample through 0.45 µm pore diameter cellulose acetate (membrane) filter <sup>C</sup>
Treatment to assist preservation	Refrigerate at 1–4°C or freeze
Filling technique	Fill to below shoulder of bottle if freezing
Maximum sample holding time and storage conditions	Analyse within 1 month if sample is kept refrigerated at 1–4°C.
Units of measurement	mg/L (mg I/L)

<sup>A</sup> Samples should be filtered as soon as possible after sample collection, preferably on site. Filter paper should be washed with sample first prior to filtration. Do not re-use filter paper.

<sup>B</sup> Plastic sample bottles should not be made from low-density polyethylene (LDPE) as these tend to leak. Appropriate sample container plastics are high-density polyethylene (HDPE), polypropylene, polycarbonate or a fluoropolymer (e.g. teflon).

<sup>C</sup> Optional: If the sample contains a lot of particulate matter then it may be necessary to pre-filter sample using a glass fibre (GF/C) filter paper (GFC 1.2 µm).

## 5.31 Sulphide ( $\text{S}^{2-}$ -S)

Includes all dissolved sulphide species (e.g.  $\text{HS}^-$  and  $\text{H}_2\text{S}$  etc), plus any acid-volatile metallic sulphides present in particulate matter.

Sulphide is often present in groundwater and sediment. It is produced by the decomposition of organic matter and bacterial reduction of sulphate.

**Table 41 Sampling procedures for sulphide**

Sample requirements	Unfiltered sample
Volume	500 mL
Container	Plastic <sup>A</sup> or glass Cap must have teflon-lined insert Use new pre-cleaned bottles If necessary, bottles should be washed in phosphate-free detergent and rinsed three times with tap water and three times with deionised water.
Collection technique	Do not pre-rinse container with sample Bottle must be used to directly collect sample No decanting. However, if acid preservative is present in bottle prior to collection decant sample from another collection vessel into sample vial. Sample should be collected such that there is minimum exposure of sample (in either the collection or sample container) to the atmosphere.
Treatment to assist preservation	Add 2 mL of 10% (m/v) zinc acetate solution per 500 mL of sample, and add sodium hydroxide (concentrated NaOH solution) to a pH > 9. Some bottles already have the required zinc acetate and sodium hydroxide preservative present in their pre-prepared bottles; do not pre-rinse these sample bottles. Refrigerate at 1–4°C, do not freeze
Filling technique	Fill container completely to exclude air Close cap tightly
Maximum sample holding time and storage conditions	Analyse within 1 week if sample is kept refrigerated at 1–4°C and not exposed to the atmosphere.
Units of measurement	mg/L (mg S/L)
Comments	Do not filter sample as this can cause losses of $\text{H}_2\text{S}$ (gas)

<sup>A</sup> Plastic sample bottles should not be made from low-density polyethylene (LDPE) as these tend to leak. Appropriate sample container plastics are high-density polyethylene (HDPE), polypropylene, polycarbonate or a fluoropolymer (e.g. teflon).

## 5.32 Sulphate ( $\text{SO}_4^{2-}$ -S)

**Table 42 Sampling procedures for sulphate**

Sample requirements	Filtered sample <sup>A</sup>
Volume	200 mL
Container	Plastic <sup>B</sup> or glass Use new pre-cleaned bottles If necessary, bottles should be washed in phosphate-free detergent and rinsed three times with tap water and three times with deionised water.
Collection technique	The sample can be collected in a clean sample container prior to filtration. Filtered sample is placed into a sample bottle, after rinsing. Ensure sample bottle is pre-rinsed three times with filtered sample water (3 × 20 mL) before final collection.
Filtration technique	Filter sample through 0.45 µm pore diameter cellulose acetate (membrane) filter <sup>C</sup>
Treatment to assist preservation	Refrigerate at 1–4°C or freeze
Filling technique	Fill to below shoulder of bottle if freezing
Maximum sample holding time and storage conditions	Analyse within 1 week if sample is kept refrigerated at 1–4°C.
Units of measurement	mg/L (mg S/L or mg $\text{SO}_4^{2-}$ /L)

<sup>A</sup> Samples should be filtered as soon as possible after sample collection, preferably on site. Filter paper should be washed with sample first prior to filtration. Do not re-use filter paper.

<sup>B</sup> Plastic sample bottles should not be made from low-density polyethylene (LDPE) as these tend to leak. Appropriate sample container plastics are high-density polyethylene (HDPE), polypropylene, polycarbonate or a fluoropolymer (e.g. teflon).

<sup>C</sup> Optional: If the sample contains a lot of particulate matter then it may be necessary to pre-filter sample using a glass fibre (GF/C) filter paper (GFC 1.2 µm).

## 5.33 Boron

Boron commonly exists as  $\text{H}_3\text{BO}_3$  in natural waters.

**Table 43 Sampling procedures for boron**

Sample requirements	Unfiltered sample
Volume	250 mL
Container	Plastic <sup>A</sup> Use new pre-cleaned bottles If necessary, bottles should be washed in phosphate-free detergent and rinsed three times with tap water and three times with deionised water.
Collection technique	Direct collection into sample bottle or transfer into a sample bottle from collection vessel. Ensure sample bottle is pre-rinsed three times with sample water (3 × 20 mL) before final collection.
Treatment to assist preservation	Refrigerate at 1–4°C Do not freeze
Filling technique	Fill container completely to exclude air Close cap tightly
Maximum sample holding time and storage conditions	Analyse within 1 month if sample is kept refrigerated at 1–4°C and not exposed to the atmosphere.
Units of measurement	mg/L (mg B/L)
Comments	Use alkali resistant sample containers

<sup>A</sup> Plastic sample bottles should not be made from low-density polyethylene (LDPE) as these tend to leak. Appropriate sample container plastics are high-density polyethylene (HDPE), polypropylene or polycarbonate.

## 5.34 Microbiological analyses

For example, total plate count, total coliforms, faecal coliforms (or thermotolerant coliforms), *E. coli*. (*Escherichia coli*), Enterococci).

Microbiological analyses are performed by Path West WA (see section 3 'Laboratories' for details).

**Table 44 Sampling procedures for microbiological analysis**

Sample requirements	Unfiltered sample
Volume	For each parameter tested, at least 100 mL of sample is required (this does not include plate count); e.g. 200 mL is required for the AS method for coliforms and <i>E. coli</i> , and total plate count; and an additional 100 mL is required if sulphite reducing spore formers are also requested.
Container	Sterilised <sup>A</sup> plastic <sup>B</sup> or glass Use new pre-cleaned sterilised bottles If necessary, bottles should be washed in phosphate-free detergent and rinsed three times with tap water and three times with deionised water, prior to sterilisation.
Collection technique	Keep sterilised sample bottle closed until it is ready to be filled Carefully remove container cap & do not contaminate inner surface of bottle and cap Do not rinse sample container with sample Direct collection into sample bottle or transfer into a sample bottle from collection vessel Replace cap immediately
Treatment to assist preservation	Store in the dark Refrigerate at 1–4°C Do not freeze
Filling technique	Fill to below shoulder of bottle to facilitate mixing by shaking. If composite samples are prepared, care must be to ensure that the samples remain homogeneous during transfer.
Maximum sample holding time and storage conditions	Immediate analysis is preferable. Analyse within 24 hours if sample is kept refrigerated at 1–4°C
Units of measurement	Coliform density is reported as counts per 100 mL water sample

<sup>A</sup> Sterilisation by autoclaving is preferable. Sterilise glass containers for no less than 1 hour at a temperature of 170°C, and plastic containers at 121°C for no less than 15 minutes. For plastic bottles, loosen caps before autoclaving to prevent distortion.

<sup>B</sup> Plastic sample bottles should not be made from low-density polyethylene (LDPE) as these tend to leak. Appropriate sample container plastics are high-density polyethylene (HDPE), polypropylene, polycarbonate or a fluoropolymer (e.g. teflon).

## 5.35 Bacteria

Indicator bacteria analysis could include thermotolerant (faecal) coliforms (presumptive or confirmed), and Enterococci (confirmed). Cell counts can be of presumptive or confirmed numbers.

**Table 45 Sampling procedures for bacteria**

Sample requirements	Unfiltered sample
Volume	250 mL
Container	Plastic <sup>A</sup> Use new pre-cleaned bottles from Path Centre
Collection technique	Direct collection into sample bottle or, only if flow is excessive, transfer into a sample bottle from a collection vessel Bottle only to be uncapped during sample collection and at no other time Do not rinse
Treatment to assist preservation	Refrigerate at 1–4°C and store/transport in the dark Do not freeze
Filling technique	Fill container to the shoulder of the bottle
Maximum sample holding time and storage conditions	Samples must arrive at the Path Centre on the same day of collection, or within 24 hours if sample is kept refrigerated at 1–4°C in the dark.
Units of measurement	e.g. Presumptive thermotolerant coliforms CFU/100 mL Confirmed Enterococci MPN/100 mL
Comments	Sample analysis conducted at the Path West WA. Water examination laboratory request forms are provided by Path West WA. Requires separate bottle (can't be combined with other parameters)

<sup>A</sup> Plastic sample bottles should not be made from low-density polyethylene (LDPE) as these tend to leak. Appropriate sample container plastics are high-density polyethylene (HDPE), polypropylene, polycarbonate or a fluoropolymer (e.g. teflon).

## 6 Useful contacts

If you have any questions on the information provided in this document, please contact any of the Department of Water staff members listed below:

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Trish Bunting, QA officer, (08) 6364 7449

John Patten, WIN database manager, (08) 6364 7455

If you have any questions relevant to relevant to surface water sampling, monitoring program design, chemical or physicochemical analysis or quality assurance and control please contact the Department of Water, Water Science Branch.



## 7 Glossary

<b>ANZECC</b>	Australian and New Zealand Environment and Conservation Council
<b>APHA</b>	American Public Health Association
<b>AS/NZS</b>	Australian/New Zealand Standard
<b>WIN</b>	Water INformation database

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