EPA Guidelines

Regulatory monitoring and testing

Water and wastewater sampling

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EPA South Australia

EPA Guidelines: Regulatory monitoring and testing
Water and wastewater sampling

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1 INTRODUCTION

1.1 Purpose

The purpose of this guideline is to set minimum standards and to provide practical guidance on water and wastewater sampling for regulatory purposes in South Australia.

1.2 Scope

This guideline applies to the sampling of waters and wastewaters including:

- receiving waters such as oceans, rivers, creeks and estuaries
- end-of-pipe or channel effluents and industrial process waters, cooling waters or wastewaters.

This guideline does not cover sampling of groundwaters. The *EPA guidelines: Groundwater sampling* (2006a) should be consulted for advice on groundwater sampling.

For additional information not provided in the above guideline, we recommend that the AS/NZS 5667 series of standards be consulted.

This guideline does not provide detailed guidance on analysis methods or interpretation of data.

1.3 Intended users

This guideline is primarily aimed at:

- sampling to determine compliance with environmental regulatory requirements, including authorisations under the *Environment Protection Act 1993* (EP Act)
- collecting and/or analysing samples for comparison with the *Environment Protection (Water Quality) Policy 2003* (Water Quality Policy) criteria.

However, given suitable justification, alternative methods may be approved for unique circumstances upon written application to the Environment Protection Authority (EPA)**.**

This guideline may also provide guidance for water sampling for non-regulatory reasons such as collecting samples for ambient or hot spot monitoring. Any monitoring submitted to the EPA for these purposes should also meet the requirements of this guideline.

1.4 Legal framework

The principal legislation dealing with pollution in South Australia is the EP Act. The EPA may impose conditions on person(s) required to hold a licence or authorisation. In particular, under Section 52 of the Act, the EPA can require holders of an authorisation to carry out

> … specified tests and environmental monitoring relating to the activity undertaken pursuant to the authorisation, or activities previously undertaken at the place to which the authorisation relates, and to make specified reports to the Authority on the results of such tests and monitoring … (in Section 52).

The requirement to undertake monitoring and testing can also be imposed under clause 44 of the Water Quality Policy on any person granted an exemption under the Policy.

Monitoring and testing that is required under these powers is termed ‘regulatory monitoring and testing’ (RMT).

1.5 Further guidance

The principles in this guideline are based on the following standards:

- AS/NZS 5667.1: 1998: Water quality—sampling—guidance on the design of sampling programs, sampling techniques and the preservation and handling of samples (Standards Australia 1998a)
- AS/NZS 5667.6: 1998: Water quality—sampling—guidance on sampling of rivers and streams (Standards Australia 1998c)
- AS/NZS 5667.10: 1998: Water quality—sampling—guidance on sampling of waste waters (Standards Australia 1998d)
- Australian guidelines for water quality monitoring and reporting (ANZECC 2000).

If this guideline does not provide enough direction or detail, the above references should be consulted for further guidance.

The methods in this guideline were consistent with the requirements of the AS/NZS 5667 series at the time of writing. These standards are reviewed and updated regularly and it is possible that there will be discrepancies between future standards and this guideline. For the purposes of regulatory monitoring and testing, this guideline takes precedence to the extent of the inconsistency.

2 AN OVERVIEW OF MONITORING

2.1 Steps in the monitoring process

The main steps associated with monitoring are presented in Figure 1 below.

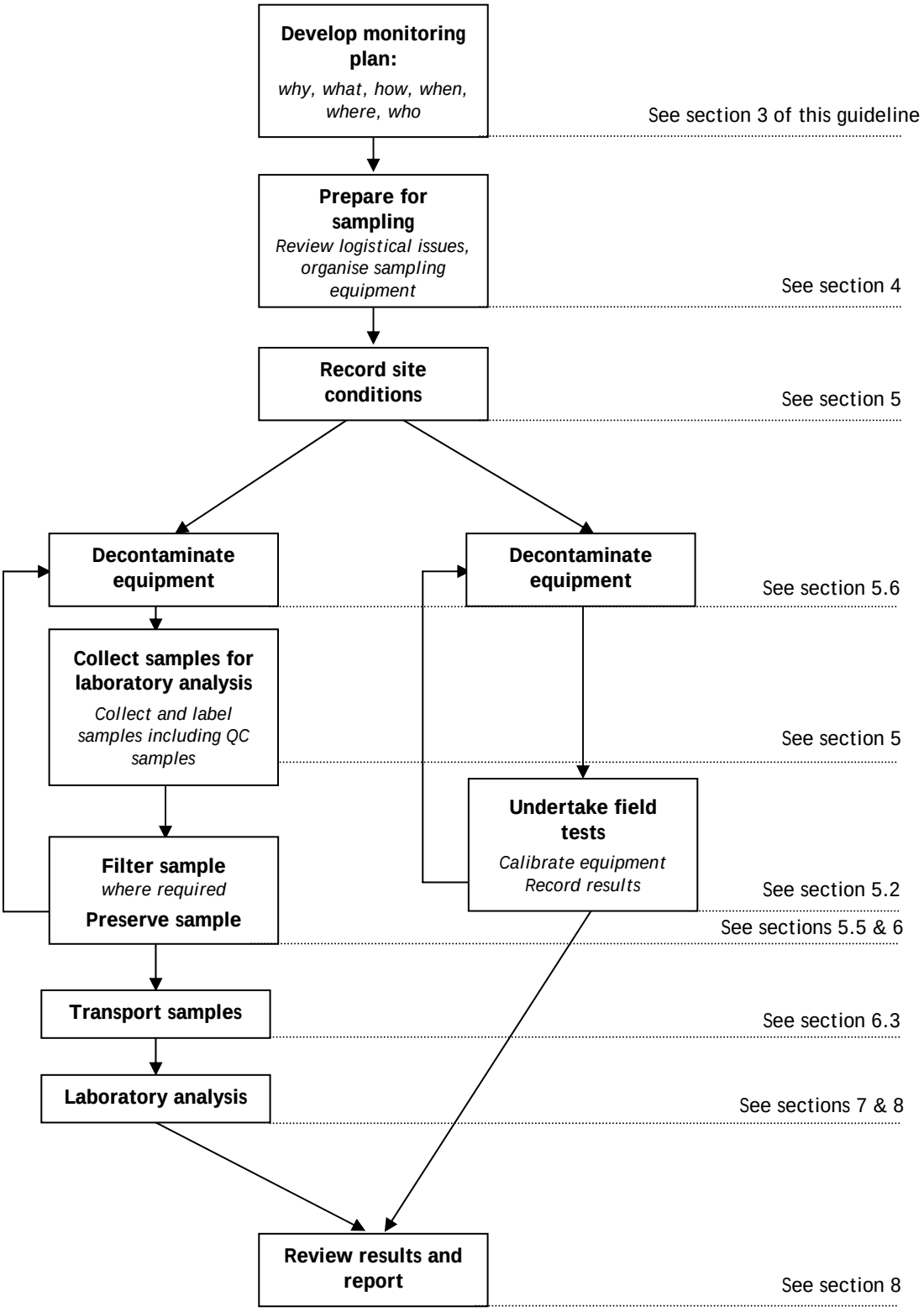

Figure 1 Stages of monitoring

2.2 Integrity of samples

To ensure that sampling is consistent, and of good quality and traceability, samples need to be representative of the body from which they were taken. If the sample integrity is altered, the information gained from analysis could be misleading and ultimately result in mismanagement of water resources and/or polluting of the resource.

The main processes that have the potential to affect the integrity of a sample are listed below. These processes are interlinked and a change in one thing may have a flow-on effect that will influence another, eg a change in temperature can cause chemical changes.

Contamination

Contamination of a sample occurs when foreign substances are introduced into it. This will lead to the sample having characteristics that are not representative of the in situ conditions. Contamination of a sample can occur at any stage of the sampling process from the collection of samples through to the final analysis, and will have a direct effect on the integrity of the sample. As many results are reported in fractions of grams, even extremely small volumes of contaminants can significantly affect results. Contamination can be very costly, especially if decisions are based on unrepresentative data.

Physical changes

Any process that changes the physical nature of a sample may affect the integrity of that sample. Examples of physical changes are listed below:

Temperature of water varies throughout the day and year. A change in temperature can alter the chemical properties of a wide range of many parameters.

Volatilisation is the loss of dissolved compounds by evaporation. It is controlled by the vapour pressure of the solute or solvent. Compounds most susceptible to volatilisation include volatile organic compounds such as chlorinated hydrocarbons (eg TCE) and monocyclic aromatic hydrocarbons (eg benzene).

Sorption is the attraction of dissolved substances to the surface of solid particles, sampling equipment and sampling bottles. Any process or activity that increases suspended solids in samples can change the measured concentrations of dissolved major ions, heavy metals and hydrophobic organic compounds (eg organochlorinated pesticides).

Degassing is the loss of dissolved gas from a solution and can result from either an increase in temperature, or a decrease in pressure. Parameters potentially affected by degassing are pH (likely to increase through loss of carbon dioxide) and pH-sensitive parameters such as dissolved heavy metals, alkalinity and ammonium. Total dissolved solids (TDS) and total organic carbon (TOC) are also affected and are likely to decrease in concentration due to degassing.

Chemical changes

Precipitation is the formation of solids from dissolved constituents. It can be caused by a change in conditions, such as temperature, pH, chemical concentration, or the presence of seed particles to begin the process. For example, where a groundwater sample experiences loss of carbon dioxide a rapid change in pH can occur, causing precipitation of metals such as iron.

Oxidation is caused by the introduction of oxygen (in air) to the sample. Oxidation results in increased dissolved oxygen, pH and redox. These changes can lead to decreases in concentrations of calcium ions, magnesium ions, heavy metals (particularly iron and manganese), hydrogen sulphide and ammonium. Oxidation could also lower the concentrations of bulk organic parameters, chemical oxygen demand (COD), biological oxygen demand (BOD) and TOC, due to

accelerating oxidation of organic constituents such as volatile fatty acids and semi-volatile organic carbon.

Biological processes

Biological activity in a sample may affect both its physical and chemical characteristics. Parameters such as nitrite and nitrate can be affected by bacterial activity, i.e. denitrification. Biological activity may change the amount of dissolved oxygen, the pH and/or redox. Factors influencing the biological activity of a sample may in turn be influenced by temperature, available oxygen, pH and exposure to UV light.

The collection, equipment and preservation methods used for sampling should be chosen to minimise the impacts of the above-mentioned factors. To minimise and to quantify the impact of these processes on sample integrity, quality control protocols and procedures must be developed and implemented at all stages of monitoring.

Quality control (QC) protocols that are typically used in monitoring are shown in Table 1. This table also states the minimum quality control that is required for licensees undertaking regulatory monitoring and testing (RMT) – i.e. monitoring required as a condition of authorisation.

Table 1 Quality control in monitoring

Monitoring Step	QC protocols	Purpose	Refer to	Compulsory for RMT
Develop monitoring plan	Various, including control sites, multiple sample locations, duplicate samples, sampling times	Ensure sample collected is representative of body from which it was taken	Section 3 of this guideline	If specified
	Review of monitoring plan by EPA	To ensure that monitoring plan is in compliance with authorisation and meets monitoring objective	Monitoring plan requirements (EPA, 2006)	Yes
Sample collection	Appropriate containers, filling and preservation techniques	Minimise changes to sample (physical and chemical)	Section 5 and Appendix 3	Yes
	Sample blanks—field, transport, equipment and container	Quantify contamination of samples during sampling process	Section 7.2	Equipment blanks only
	Decontamination of sampling equipment	Minimise contamination	Section 5.6	Yes
Sample filtration	Filtration procedures	Minimise physical and chemical changes to sample	Section 5.5	If field filtration performed
	Filtration blanks	Quantify physical changes and contamination during filtration	Section 7.2.1 (filtration blanks)	If field filtration performed
Field testing	Equipment calibration	Minimise and quantify bias and error in field equipment	Section 5.2	Yes
Transport and storage	Appropriate preservation techniques	Minimise physical and chemical changes to sample	Section 6.3 and Appendix 2	Yes

Monitoring Step	QC protocols	Purpose	Refer to	Compulsory for RMT
Analysis	NATA lab accredited for required analysis	Ensure laboratory undertakes appropriate QC including spikes, calibration of equipment	Section 8	Yes
	Duplicate samples—intra (within) lab	Check variability in lab analysis	Section 7.2.2	Yes
	Duplicate samples—inter (between) lab	Quantify differences between laboratories' analysis methods	Section 7.2.2	Yes
Reporting	Peer review validation	Validate that sampling is undertaken as per monitoring plan and in accordance with sampling guidelines	Independent verification requirements (EPA, 2006)	When stated in licence

3 DEVELOPING A MONITORING PLAN

To ensure that monitoring is specific, targeted and cost effective, a monitoring plan should be developed. A monitoring plan is the document that details the actions, responsibilities and timeframes that will deliver monitoring that meets monitoring objectives.

When developing a monitoring plan in response to a condition of authorisation the *EPA guidelines —Regulatory monitoring and testing: Monitoring plan requirements* (EPA 2006b) sets out what should be included in a monitoring plan (i.e. the elements). The monitoring plan guideline does not, however, provide guidance on **how** to design an effective monitoring plan (i.e. the considerations)

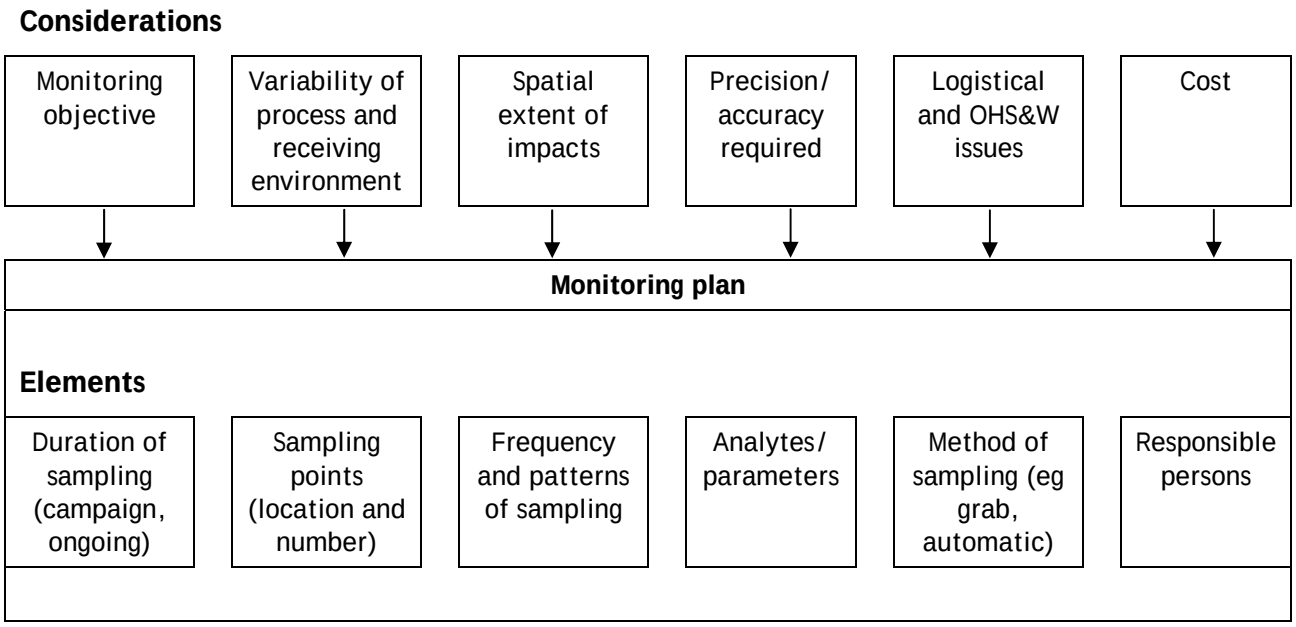

Figure 2 Designing a monitoring plan

Issues that should be considered in designing monitoring for water and wastewater include:

- the objective of monitoring
- variability of process and receiving environment
- the spatial extent of impacts
- precision and accuracy required
- logistical and OHS&W issues
- costs compared with benefits.

These considerations are discussed in Appendix 1.

Further guidance on how to design water or wastewater monitoring plan is available within the *Australian guidelines for water quality monitoring and reporting* (ANZECC 2000).

The EPA has also developed industry-specific guidelines such as *Guidelines for wineries and distilleries* (EPA 2004). These industry specific guidelines primarily provide guidance on what specific industries may be required to monitor and why. In the event of any inconsistency your licence, and the *Monitoring plan requirements* guideline take precedent.

4 PLANNING A SAMPLING EVENT

Careful planning and preparation of a sampling event is important and will save time and reduce the number of difficulties that commonly occur during sampling.

4.1 Logistics

The basic steps for planning a sampling event are as follows:

1 Review the monitoring plan, including monitoring locations, number of samples required, sampling methods, and Occupational Health, Safety and Welfare (OHS&W) issues.

2 Inform the client or property owner of your intended schedule and be aware of any liabilities that you may incur.

3 Co-ordinate with the analytical laboratory. Obtain appropriate sample containers (i.e. containers of suitable material and volume that contain preservatives as listed in Appendix 2). Discuss any problems you foresee, for example, with procedures, containers or limitations of reporting.

4 Schedule the monitoring event, including planning how and when you will transport the samples back to the laboratory. The aim is to have all samples preserved and delivered to the laboratory as quickly as possible and within recommended holding times. This is especially relevant for samples with holding times of 24 hours or less. (Holding times are listed in Appendix 2).

5 Organise and review site maps and locations to determine logistics of sampling including sampling order. Sampling order should be designed to avoid cross-contamination, i.e. as much as practical, move from samples with lowest pollutant concentrations to highest concentrations.

6 Check that you have all the equipment required for the sampling event. Test that the equipment is operational and calibrated. Ensure you are able to decontaminate equipment that is to be reused between samples.

7 Fill out as much paperwork as practical before sampling such as preparation of labels.

4.2 Communication

It is strongly recommended that the analytical laboratory be consulted before implementing a sampling plan. Each laboratory may use different analytical techniques that require specific sampling techniques, preservatives or field treatments (such as filtering and freezing).

It is important to inform the laboratory of any analytes that may be in particularly high or low concentrations. Some analytical methods need to be modified for the extremes in concentration ranges and prior knowledge of the expected range can speed up the turnaround. Some instruments may be affected if exceptionally high concentrations of certain analytes are introduced without prior dilution. Factors such as salinity of a sample can also influence the choice of analytical methods, and some sample characteristics can cause interference with procedures for other analytes.

During the implementation of a monitoring program it is useful to stay in communication with the laboratory so they know when to expect the samples and whether there are any problems with sample collection. This is especially important with microbiological samples.

4.3 Equipment

An example of an equipment checklist is included in Appendix 3. Major items of equipment likely to be needed are discussed as follows:

Paper work and record keeping: Good planning and record keeping is imperative. The sampling plan, or concise sampling schedule and map should provide all the required information such as location of monitoring points, the number and type of samples that need to be collected and container types. Records of observations and actions can be critical for future reference. A sampling data sheet similar to that in Appendix 4 is recommended to ensure that a complete record of each sampling site and event is kept. Other required paperwork includes Chain of Custody forms (see Section 6.2 and Appendix 5) and labels.

Navigational aids: It is important to be able to accurately locate the sampling site for future reference. A modern Global Positioning System (GPS) can be a useful aid in accurately locating a sampling site. Before attempting to navigate using GPS the sampler should be trained and competent in the use of these systems. The sampling locations should also be recorded on site maps.

Field testing meters: Some analytes are most reliably determined at the point of sampling. See Section 5.2 for further information.

Sampling containers: As the wrong sampling equipment can affect the integrity of the sample, it is important to use appropriate sample containers for each of the various parameters. Additionally, treatments are applied to the sampling containers for some parameters to ensure sample integrity. Appropriate sample containers and preservation methods are listed in Appendix 2. Your analytical laboratory should be able to provide appropriate containers with required treatments.

Other sampling equipment: Other forms of sampling equipment may include sampling rods, bucket and rope (refer to Section 5.3), depth equipment (Section 5.3) or filtration equipment (Section 5.5).

Decontamination of sampling equipment: All sampling equipment presents a risk of cross-contamination and should be thoroughly cleaned between samples. Further information on decontamination is outlined in Section 5.6. Decontamination equipment may include detergents, ethanol, scrubbing brushes, tap water, distilled water and a receptacle for collecting waste rinse. A burner or 10% sodium hypochlorite solution may be required for microbiological samples.

Esky or refrigerator: Most types of sample require chilling as a means of preservation. Samples can be stored on ice in an esky or in a car refrigerator, and the temperature should be maintained between 1°C and 4°C.

Camera: Photographs can show where the sample was taken and illustrate observations recorded on the field datasheet. It is good practice to take photographs on the first visit to a sampling location and when there are any unusual conditions at the site that may affect the sample.

4.4 Occupational health, safety and welfare

There are many hazards to be aware of when working in any field environment. It is recommended that a specific safety plan be developed for each monitoring plan. The safety plan should be developed to address risks and may include such things as:

- hazard identification, risk assessment and hazard control measures. Typical hazards in sampling include:
  - vehicle breakdown or accident, bogging in wet conditions
  - exposure to hazardous substances eg decontamination chemicals, analytes, toxic products formed from sample preparation or stabilisation (eg acidification) and toxic gases such as hydrogen sulphide, bacteria in wellhead or groundwater
  - temperature hazards, typically sunburn and heatstroke
  - working in, over or adjacent to water
  - poisonous animals (spiders, snakes) and plants
- actions to be undertaken to remove, reduce or control risk
- emergency procedures and information such as location of nearest medical facility.

When conducting a sampling event, the right safety equipment will make the task safer. This equipment can be preventative or provide assistance in the case of an incident. The sampling checklist (see Appendix 3) provides an example list of the type of personal protective equipment (PPE) that may be required for sampling in the field. Additional protective equipment may be necessary as required by the specialist nature of a particular sampling task or the OHS&W policy of your employer.

5 SAMPLE COLLECTION AND FIELD TESTING PROCEDURES

Samples should only be collected by personnel who have proper training and adequate experience.

5.1 Field observations

During every sampling event, observations of field conditions that could assist in the interpretation of monitoring data are to be recorded. This can provide useful information about the water being sampled, which can help diagnose the source and potential impact of pollutants found by chemical analysis.

Examples of such field conditions are as follows:

- recent rain can wash potential pollutants from surrounding land into waterways
- winds may drive some constituents toward one side of the waterbody or create mixing which might help dissipate them more quickly
- shading from cloud and vegetation can influence the level of dissolved oxygen.

Any abnormalities that may indicate pollution or affect water quality, such as absence of flow, presence of surface scum, water colour or odours, excessive algal or plant growth, dead fish or invertebrates should also be noted.

5.2 Field measurements

Analytes that quickly degrade after they are sampled must be tested in the field. Field testing may also be used for other samples that can be reliably and cheaply measured in the field. Where possible, field measurements should be undertaken in situ. AS/NZS 5667.1 recommends the following analytes be measured in the field as concentrations of these analytes can be significantly changed during transport and storage:

- dissolved oxygen (DO)
- temperature
- pH
- conductivity
- redox (reduction/oxidation potential)
- turbidity
- chlorine.

Many of these analytes can be reliably measured using multi-parameter meters—usually with an electrode for each analyte (Figure 3). Field meters will not provide accurate results unless they are calibrated before use. In particular, dissolved oxygen, pH and turbidity often drift from day to day. Calibration requirements will vary between meters and manufacturers so it is important to follow the instructions supplied with the equipment. It is recommended that meters be calibrated prior to every sampling event as a minimum.

Most electrodes are calibrated using standard solutions of known properties. These can be purchased from various laboratory supply companies or sourced from a National Association of Testing Authorities (NATA) accredited analytical laboratory. Standard solutions have a limited shelf life and can deteriorate if not stored correctly (away from light at 20°C for most solutions is acceptable). The quality of standard solutions will directly influence the performance of the meter so it is important that if there is any doubt, fresh standard solutions be obtained. Calibration of all meters should be routinely recorded on a standard sheet including dates,

temperatures and calibration readings. This will provide a record of the performance of each meter and provide evidence that quality procedures are being employed.

Figure 3 Examples of the various types of field meters available. From left to right: a dissolved oxygen meter, a multi-parameter meter and a redox meter.

Some manufacturers are producing ion-specific probes that measure analytes such as nitrite, calcium, sulphide, bromide, fluoride, ammonium and chloride in the field. They may be suitable for situations where parameters are present in high concentrations, but may be subject to interference from other substances. Therefore, the results produced by these field meters may not be comparable to those produced in the laboratory. Additionally, some colorimetric methods are becoming available, particularly for online applications. To apply these methods in a regulatory monitoring plan the EPA must be consulted prior to field testing.

5.2.1 Dissolved oxygen

Dissolved oxygen (DO) is a measure of the amount of oxygen available within a waterbody and is measured on a scale of 0 mg/L–20 mg/L or as percentage saturation. It can be determined using portable electronic meters (Figure 3) or by titration. Electronic meters are by far the most convenient method and should be used wherever possible. In waterbodies DO usually varies due to depth and time of day. Photosynthesis by plants and algae adds oxygen to the water. This means as the day proceeds DO often increases, reaching a peak in late afternoon. As night falls photosynthesis stops and respiration decreases DO. The solubility of oxygen also decreases at higher temperatures and salinities.

DO is highly unstable and should always be measured in situ as the process of taking a sample can influence the amount of dissolved oxygen in the sample. A DO measurement of a sample taken in a bucket is not ideal. An electronic meter should be immersed directly in the water column at a depth appropriate to the sample being taken. For measurements in the surface layer, as is most common when grab sampling, the DO electrode should be placed within the top 30 cm of the water column. For depth stratification, the electrode should be lowered to the depth of interest.

It is important to know the specific procedures for the meter being used. For example:

- If using traditional membrane-type DO meters the electrode needs to be placed in an area with flow, or continually moved through the water to obtain an accurate reading.

The reason for this is that membrane-type DO electrodes consume oxygen at the water/membrane interface causing the DO reading to drift downwards. Care should be taken to ensure that the movement is not rigorous enough to introduce more oxygen into the water. However, some DO meters have mechanisms such as an inbuilt stirrer, a vibrating probe or take short pulsed readings rather than continuous. These can deliver a correct reading without the need to have water moving over the probe.

- Salinity and atmospheric pressure (and therefore altitude) can affect oxygen readings. Many modern meters automatically correct for these variables and, therefore, the manual should be checked to ensure this is the case. Meters without automatic correction may require manual entry of this information.

5.2.2 Temperature

Temperature of a waterbody will vary throughout the day and at different depths. Water temperature will move towards ambient temperature as soon as a sample is removed from the waterbody. Thus, temperature should be measured in situ. Temperature can be measured using a liquid-in-glass thermometer or a digital meter. However, multimeters, pH meters, conductivity meters and DO meters will also often measure temperature, so it is unlikely you will need a separate device. The probe or thermometer needs to be left fully immersed until a stable reading is obtained. The time required for the thermometer to stabilise will vary according to the temperature of the water and the individual thermometer or probe. Insufficient time can lead to inaccurate readings.

5.2.3 pH

Field testing of pH can be achieved using a calibrated electronic meter or pH test strips. If pH strips are available with the range and resolution required for sampling they can give a robust and reliable measurement. Meters have a higher resolution but require careful calibration and maintenance. Traditional pH meters have potassium chloride (KCl) solutions that need to be topped up. The newer electrodes (including non-glass (ISFET), gel or liquid filled) are more robust and reliable for field use.

As pH is temperature dependent, newer pH meters have been designed to automatically measure temperature and adjust to give a correct pH reading. The user manual should be checked to determine if this is the case. When calibrating a pH meter the temperature of standard solution should be as close as possible to the sample solution to minimise the possibility of temperature causing erroneous readings. Electrodes used for measuring pH are usually calibrated using a two or three-point calibration with standard buffers of known pH. The buffers are commonly of around pH 4 and 9, while the third would fall between the two to represent a neutral reading. Buffer solutions for calibration should be either side of the range anticipated in the sampled waters. This means that if it is anticipated that the sample will be strongly acidic or basic, calibration standards that match the pH range to be worked within should be used.

5.2.4 Conductivity

Conductivity is easily measured in the field using a portable meter and electrode. This provides a measure of the total ionic concentration of the sample solution in units of electrical conductivity (EC), which can then be converted into total dissolved solids (TDS) by calculation.

EC can be converted to TDS using the equation:

$$TDS = (0.548 \times EC) + (2.2 \times 10^{-6} \times EC^2)$$

where TDS = Total Dissolved Solids (mg/L)
EC = Electrical conductivity (µS/cm)

Many conductivity meters will automatically calculate TDS from EC. However, the equation above was developed for a wide range of South Australian waters and is applicable for samples within the conductivity range from 20 μS/cm to 60 000 μS/cm. This range covers the majority of waters except for hypersaline environments. Any TDS calculated from conductivity measurements outside this range should be treated with caution.

The conductivity of waters increases with temperature. Most modern portable conductivity meters automatically compensate for small temperature variations from the calibration temperature. However, if there is a large difference between the temperature of standard solutions at the time of calibration and the sample solution at the time of measurement, a new calibration may be required. For example, if a conductivity meter is calibrated early in the morning and the temperature rises significantly through the course of the day, it is preferable to recalibrate during the day. Similarly, standard solutions that have been refrigerated overnight should be returned to room temperature before calibration.

5.2.5 Redox

Direct redox potential (or oxidation reduction potential) measurements determine the oxidising or reducing capacity of waters. Redox must be measured in situ and it often varies substantially in a waterbody, especially with depth. Redox potential can be measured using an electronic meter or multimeter.

5.2.6 Turbidity

Turbidity meters are generally based on light attenuation principles. There is a large variation in the reliability and accuracy of turbidity meters. It is therefore essential that turbidity meters are regularly calibrated. When a reliable turbidity meter is not available, a representative sample may be collected and turbidity measurement undertaken in a laboratory.

5.2.7 Chlorine

Chlorine dissipates quickly in solution and should be tested in the field.

It is important to determine what form of chlorine is required to be reported. Total chlorine consists of free chlorine (chlorine gas, hypochlorite ion and hypochlorous acid) and combined chlorine (eg chloramines). The most common forms required are total chlorine or free residual chlorine. Free residual refers to the residual chlorine remaining at a certain location (eg outlet of settling tank).

Chlorine can be tested in the field using a meter, a field titration or a pre-prepared chlorine kit. Most of these methods are based upon colorimetry, where the reagent diethyl-*p*-phenylene diamine (DPD) changes colour upon reaction with chlorine. Where tablets are provided it is important that the tablets are current (not expired) and that contamination of the tablets prior to use is avoided.

Where total chlorine is required to be measured chlorine meters or chlorine kits are recommended, rather than field titrations. Field titrations can provide an accurate result and differentiate between the different species of chlorine. However, they require specialised equipment, are more easily contaminated and often impractical.

5.3 Collection of samples for analysis

5.3.1 Sampling equipment

It is important when undertaking sampling, particularly for trace analytes, that the sampling equipment is inert, that is, it does not cause contamination or interference with the sample.

For example:

- Organics have a tendency to adsorb to plastic (including polyethylene, polypropylene and polycarbonate). Therefore, stainless steel equipment such as buckets and sampling rods should be used. Glass sample containers are preferred.
- When sampling for metal analytes the use of metal equipment, and some glasses such as soda glass should be avoided. Rubber can also cause contamination when sampling for trace concentrations. Plastic equipment should be used when possible when analysing for metals.
- When sampling for analytes that are the major constituents of glass (eg sodium, potassium, boron and silicon), glass equipment and containers should be avoided.

Appendix 2 provides information on the type of sampling container (eg glass, plastic), typical required volume, filling technique and preservation requirements for common analytes. The container type, as listed in Appendix 2, is a useful guide to the most appropriate material for sample equipment. Where uncertainty exists as to whether the sampling equipment may cause contamination or other effects, an equipment blank (as detailed in Section 7) should be collected and analysed.

5.3.2 Surface samples—grab sampling

When the waterbody is shallow and well mixed, sub-surface water sampling is generally adequate. Sub-surface samples should be taken from approximately 30 cm depth, with care taken to ensure no floating films or organic material are collected unless they are of specific interest. Stirring up and collection of bottom sediments will also compromise sample integrity. Try and collect the sample a reasonable distance from the edge, unless specifically trying to determine the water quality at the edge, as edge water quality is generally not typical of the majority of the waterbody. When practical, collect the sample directly into the sample container. Where this is not practical (such as when a sample cannot be collected without loss of preservative) an intermediate container may be used.

When sampling by hand, surface films can be avoided by removing the cap, inserting the container into the water vertically with the neck facing down. Once at the required depth, the container can then be inverted, allowing the sample to flow in. The mouth of the container should be faced into the current while keeping the hands, sampler and any other equipment (eg boat) downstream to minimise the chance of contamination (Figure 4). When sampling still water move the container slowly forward to obtain a continuous uncontaminated sample. Refer to Appendix 2 to determine whether the sample container should be filled to the top (to exclude air) or whether an air gap (1–2 cm at top of container) should be left.

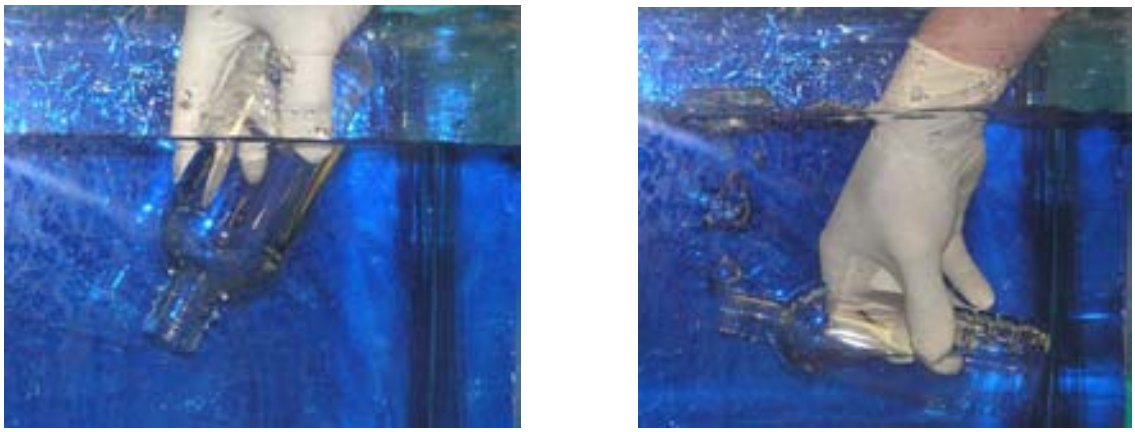

Figure 4 Sampling by hand

Where it is impractical or unsafe to sample by hand, a sampling rod can be used (Figure 5). Sampling rods are polycarbonate or stainless steel poles with a large clamp or cage on one end designed to securely hold various sizes of sample container. Containers are placed in the cage while sampling to provide extra reach or to prevent the hands from contaminating the sample or contacting wastes. The container should be gently but quickly lowered into the water to minimise the contribution of surface films to the sample.

Figure 5 Using sampling rod

The sample may also be collected using a bucket and rope in situations where access to the water is limited (eg when the sampling point is a high bridge). In this case, a sub-sample is immediately taken from the bucket using the techniques above for sampling directly from the watercourse.

5.3.3 Sampling at depths

When samples are required from particular depths, such as for depth profiling, specific equipment is required. The equipment falls into three general categories as follows:

Pumping systems

These can be used for depths up to 10 m. Water is sucked to the surface through PVC or PTFE tubing around 10-mm diameter. The inlet of the tube should face the direction of water flow. At least one volume of water should be pumped through the tubing before collecting a sample to minimise the effects of pumping including entrainment of suspended solids by dissolved gases.

Issues with pumping include the large surface area to volume of tubing that increases the chance of absorption of analytes and increases the risk of contamination between samples taken at different places or times. The pumping rate may also affect the sample. Ideally the velocity of the water in the inlet should be at the same velocity as the water being sampled (i.e. isokinetic sampling conditions). Where this is impractical the velocity of pumping should not be lower than 0.5 m/s (as this may reduce suspended solids within the sample) or greater than 3 m/s (as high velocities may cause blockages by debris). For dissolved gases and organics, sealed immersion devices or open tube devices are preferred over pumping systems.

Sealed immersion devices

These devices, also called 'closed pipe' or 'air displacement' devices, consist of sealed containers filled with air that are lowered to the correct depth. A trigger mechanism then releases the end caps and the device is filled with water.

Open tube or cylinder devices

Such devices are similar to sealed immersion devices, with the exception that the ends are left open during the lowering of the device to the required depth. A trigger mechanism such as weight, water pressure or electromagnetic signal seals both ends of the device capturing the sample inside. Van Dorn samplers, shown in Figure 6, are an example of this type of device. When sampling in fast-flowing waters, sampling devices that can be placed horizontally (such as the Zukovsky) are preferred over vertical devices, as isokinetic sampling is more closely obtained.

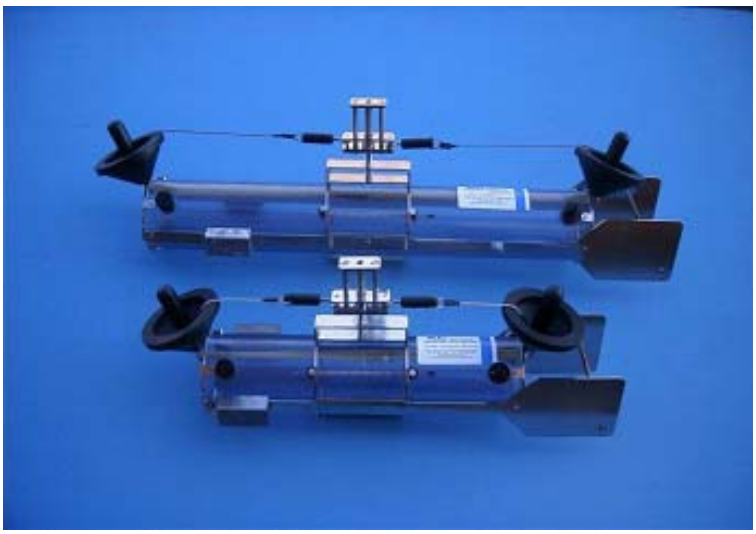

Figure 6 Van Dorn samplers with cup ends set open (Photo courtesy of AWQC)

5.3.4 Automatic samplers

Automatic samplers can be used to take discrete, continuous or composite samples.

Issues that need to be considered when using automatic samplers include:

- where discrete samples are taken, the sampling lines should be decontaminated or purged between samples.
- preservation, filling technique and holding times (Appendix 2) must be observed. It may be necessary for the sampler to be able to keep samples cooled (to 4°C), to store the samples in the dark and/or to add or maintain preservative in the sample containers.
- the inlet velocity of the sampler may affect the sample. Ideal sampling conditions are isokinetic (the velocity of the water in the inlet should be the same velocity as the water

being sampled). The inlet velocity should be a minimum of 0.5 m/s and maximum of 3 m/s.

- the materials of an automatic sampler may affect the sample, eg organics can adhere to plastic inlet tubing.

5.3.5 Composite samples

A composite sample is a sample consisting of two or more sub-samples mixed together in known proportions. Composite samples may be collected manually (by combining grab samples), or by an automatic sampler.

Composite samples are not appropriate for analytes that degrade during sampling or transport (eg dissolved oxygen, chlorine) or for easily contaminated samples such as microbiological sampling.

There are two basic types of composite samples in water sampling:

- time-weighted samples
- flow-weighted samples.

Time-weighted samples are sub-samples of equal volume taken at constant intervals during the sampling period. For example, four samples are taken six hours apart to create a 24-hour composite sample.

In flow-weighted sampling, the sub-samples are proportional to the effluent flow or volume during the sampling period. A flow-weighted sample can be created by taking samples at constant intervals but with varying sample volumes that are proportional to the flow at the sampling time; or by taking samples of equal volume that are taken at the time when fixed amounts of effluent have passed the sampling point.

For both types of composites, the volume of the sub-samples should be able to be accurately measured to ±5%, and the smallest sub-sample should be at least 50 mL in volume.

When undertaking composite samples it is important that holding times and preservation requirements (refer Appendix 2) are adhered to. The holding time should be measured from the collection of the first sub-sample. The composite sample needs to be appropriately preserved between additions of the sub-samples.

5.4 Specific considerations

This section provides further guidance on issues associated with the sampling of different types of analytes.

5.4.1 Sampling for physical characteristics

Many physical properties are best determined in situ by field measurements. If unable to determine in this way, ensure that a representative sample is taken and that recommended filling, preservation and holding times (as listed in Appendix 2) are met.

5.4.2 Sampling for dissolved gases

When collecting samples for dissolved gases, care should be taken to minimise aeration and retain the gases within the sample. Gases are maintained within the sample by displacing water rather than air when collecting the sample, eg by using open tube devices when sampling depths. If sampling from a tap, insert a flexible inert tube from the tap to the bottom of the sample container with water exiting within the container rather than to air.

5.4.3 Sampling for nutrients

When sampling for nutrients it is important to determine the nutrient form that is required and to determine how that form is to be reported.

Forms of nitrogen (in order of decreasing oxidation state) include nitrate, nitrite, ammonia and organic nitrogen. Oxidised nitrogen, or total oxidised nitrogen, includes nitrate and nitrite. Kjeldahl nitrogen is a term that refers to ammonia and organic nitrogen, and a specific analytical method that is used to determine the concentrations. All forms are generally reported as 'nitrogen'.

There are also many forms of phosphorus and classifications of phosphorus according to how they naturally occur in waterbodies (eg dissolved or suspended, organically bound, condensed or orthophosphates). Phosphorus is further classified according to the analysis method used. 'Reactive phosphorus' relates to phosphates that respond to a particular colorimetric test and mainly consist of orthophosphate but also may contain a fraction of condensed phosphate. Reactive phosphate occurs in both dissolved and suspended forms. Criteria may be set as either total phosphorus or soluble phosphorus.

If monitoring to compare results against a set of criteria, make sure that the sampling technique, in particular the filter size and the nutrient form is the same as the criteria.

5.4.4 Sampling for metals

When sampling for metals care must be taken not to cause contamination during sampling. Avoid metal (including stainless steel) sampling equipment, using plastic wherever possible. If analysing for trace metals deionised water is recommended for decontamination rather than distilled. Distilled water may contain trace metals such as mercury.

When sampling for metals it is important to determine prior to collection whether total or just the soluble phase is required. This will determine the preservation and filtration requirements. When soluble metals are required, samples may either be field filtered or sent to a laboratory for filtering. If sending to the laboratory for filtering, samples must not be acidified, but be cooled to 4°C, and filtered in the laboratory as soon as possible. Laboratory filtering is not appropriate where there is a risk of increased precipitation or mobilisation of metals prior to analysis. Field filtering procedures are discussed in Section 5.5. Both vacuum and pressure filtration are suitable for metals.

5.4.5 Sampling for organics

Organics have a tendency to adsorb to plastic (polyethylene, polypropylene and polycarbonate). Therefore, stainless steel buckets and sampling rods, and glass containers are recommended. One of the most critical elements for organic analysis is the holding times, and some analyses (eg BOD) having holding times of only 24 hours.

5.4.6 Sampling for microbiological analytes

Obtaining representative microbiological samples can take considerable care and timing. Microbiological samples can often require large sample volumes and are easily contaminated, as bacteria are present on most surfaces and in the air. They also have short holding times (preferably less than six hours).

Communication with the laboratory is necessary to confirm the sample volumes and to ensure that samples can be received and processed efficiently. A laboratory may have to arrange staffing to meet processing needs, as the processing capacity of a laboratory may be set by

NATA. In particular laboratories should be warned of incoming samples that must be performed within 24 hours.

Specific precautions need to be taken to minimise the possibility of sample contamination. Prior to and between collection of samples, hands should be washed then disinfected with an alcohol-based hand disinfectant, eg 70% ethanol or hexifoam. Wearing latex gloves will help avoid contamination of samples during collection. Gloves should be changed between samples.

Whenever possible collect the sample directly into the sample container, ensuring that the inside of the cap and the neck of the container are not touched or exposed to the air for longer than necessary. For samples of chlorinated or chloraminated water, the container should contain sufficient sodium thiosulphate to neutralise the disinfectant. Care should be taken not to overdose excessively, as this may cause changes in dissolved oxygen and pH. Analytical laboratories should be able to supply suitably treated bottles.

The hierarchy with regard to sampling equipment for microbiological analytes is:

- minimise usage of sampling equipment where possible, thus avoiding risk of contamination.
- use disposable pre-sterilised equipment (as per AS/NZS 2031:2001) for each sample.
- use metal sampling equipment (eg stainless steel bucket, sterilised stainless steel jug as intermediary container, metal sampling rod). Equipment should be sterilised prior to and between samples by flaming with a gas burner. All sections of the sampling equipment that may come in contact with the container and the waterbody should be flamed. The burner should be fuelled by propane or butane. Methylated spirit burners do not produce a flame hot enough for sterilisation (as per AS/NZS 5667.1).
- for plastic and glass or when unsafe to use a flame, a solution of 10% sodium hypochlorite should be used. (Household bleach can range from 2% to 15% sodium hypochlorite, and will degrade over time). Flood the surface with the solution and wait approximately two minutes. For pump lines and hoses, trap bleach solution within the hose or equipment. The hose doesn't need to be totally full as the gas from the solution does the work. Wait for a minimum of 15 minutes.
- in an emergency, scalding with boiling water for 10 minutes may disinfect a suitable glass or plastic container and equipment.

5.4.7 Sampling for biological analytes

'Biological sampling' can cover a broad spectrum of sampling of aquatic organisms from plankton to macroinvertebrates, fish and other vertebrate aquatic animals. If undertaking biological sampling it is recommended that other specific texts be referenced. Wherever practical, sampling should be undertaken by a trained biologist who will be better able to recognise signs of environmental changes through observations of conditions in the field. This guideline only touches on sampling of phytoplankton.

Sample size depends on the concentration of plankton in the water being sampled, the type of determination to be made (eg phytoplankton count, algal identification or chlorophyll concentration) and the analysis method. In general, there is not a great contamination risk from the actions of the sampler. However, preservation methods, storage and transportation can affect the results and cross-contamination between samples can occur. In most cases, follow the general sampling techniques described in Section 5.3 for surface or depth samples as required.

When collecting samples for live analysis leave an air gap in the container. Marine samples should be kept at close to ambient temperature because marine flagellates will burst if subjected to temperature shocks. Freshwater phytoplankton is more robust and samples can be refrigerated for transport. Both marine and freshwater samples for phytoplankton analysis should

be protected from exposure to direct sunlight. Samples should be examined as soon as possible after collection (within 48 hours). If phytoplankton samples are to be counted much later, fill the container completely, preserve samples and transport and store in the dark. The most suitable preservative for phytoplankton is Lugol's solution. Formalin, merthiolate and glutaraldehyde are not recommended preservatives because of their toxicity to humans.

Recommendations for preservation and holding times of samples for chlorophyll determination are included in Appendix 2. Sample containers can be wrapped in aluminium foil for protection from light. Filter samples as soon as possible after collection. Guidance on field filtration, including for chlorophylls is given in Section 5.5. Once filtered, opaque bottles are recommended for storage of pigment extracts as even brief exposure to light can alter chlorophyll concentrations. Labelling should identify the sampling technique to allow laboratory staff to better interpret results.

5.4.8 Sampling for radiochemical analytes

For background radioactivity in surface waters, the procedures and techniques for sampling for radiochemical analysis are the same as for general sampling. Sample storage, transport and pre-treatment requirements vary depending on the type of radioactivity of interest although most require acidification with nitric acid to pH 1–2. See Appendix 2 for details regarding sample holding times, minimum volumes and other requirements of sampling for radiochemical analysis.

Radioactivity at background levels does not normally present a hazard to the sampler. There are no additional decontamination procedures or personal protective equipment required when sampling surface waters for radiochemical analyses at low levels. While it is unlikely that high levels of radioactivity will be encountered in current or foreseeable situations in South Australia, if the sampler has concerns, advice should be sought from a suitably qualified person with experience in dealing with radioactive substances.

5.5 Field filtration

Field filtration can be undertaken for a number of purposes:

- to maximise a sample's integrity during transport from the sampling site to the laboratory—nutrients such as ammonia, nitrate and nitrite can have a short retention period in a sample and filtering can extend this significantly
- to separate the total and the soluble portions of analytes (eg dissolved metals)—the soluble portion of an analyte is generally more bio-available, and therefore can have greater impact upon the ecosystem
- to extract filtered material for biological analytes such as chlorophyll and algae
- to separate biomass when undertaking wastewater analysis.

There are various methods and equipment available for field filtration from simple gravity or syringe pressure systems to more complex pump operated pressure or vacuum systems. The best method to use will depend upon the analysis to be performed.

Pressure filtration is preferable over vacuum filtration where the drawing off of volatiles may compromise results. This is likely to be the case when analysing for nutrients and volatile organics.

Vacuum filtration is recommended for chlorophyll samples. The pressure difference across the filter should not exceed 40 mmHg to prevent rupture of cells. Vacuum filtration can be easier than pressure filtration when large sample volumes are required.

Always follow the operating instructions of your filtering equipment. Factors to consider when filtering include:

- filters may need to be decontaminated or preconditioned through washing or soaking prior to use. Check the requirements during planning of the sampling event as some decontamination/soaking procedures can take up to 24 hours.
- the type and pore size of the filter will affect the results. Select the right type and size of filter for the job. A 0.45µm filter should be used, except where otherwise specified by criteria (eg Water Quality Policy).
- be careful not to contaminate samples during the filtration process. When filtering samples in the field minimise the chance of contamination with a clean work environment and by replacing caps on sample containers immediately. A plastic sheet on the ground is a good method of defining and maintaining a clean work area.
- samples with lots of suspended material can be difficult to filter in the field. Pre-filters may be needed for pressure filtration. For vacuum filtration it may be necessary to change the filters as they become clogged with sediment. Excessive force may rupture clogged filters requiring recommencement of the sampling.

It is acknowledged that field filtering of very turbid samples may be problematic and it may be more practical for filtering to occur in the laboratory. If samples are laboratory filtered this should be annotated on your results appropriately. Contact your laboratory for instructions on collecting samples for laboratory filtration (eg if sampling for dissolved metals analysis should not be acidified as required in Appendix 2.)

For analysis of parameters such as chlorophyll and suspended solids retain the filter paper, not the filtrate. Record the volume of sample filtered, as this will be used later to calculate the concentration of the sample. When retaining the filter papers, fold the filters so the residue surfaces are against themselves and place them in a sample tube or opaque bottle. Appropriate preservation techniques must also be followed for filter paper such as dark storage or refrigeration.

5.6 Decontamination

Decontamination is the cleaning of sampling equipment to remove trace analytes and avoid cross-contamination of samples. Reliance should not be placed solely on decontamination procedures. Minimise the chance and consequence of contamination with good sampling design and equipment. When planning sampling consider:

- eliminating the need of multiple-use equipment eg collect sample directly into container rather than using a bucket to collect and then transfer
- using disposable equipment instead of multiple-use equipment eg disposable syringes for field filtration
- undertaking tasks within a sterile laboratory rather than in the field eg requesting that a laboratory undertake filtration rather than attempt field filtration
- reducing the risk of contamination by, as much as practical, sampling from locations with lowest concentration of analyte to highest concentrations
- dedicating a set of sampling equipment to different uses eg equipment used for wastewater sampling should not be used for receiving environment sampling.

Multiple-use equipment must be decontaminated prior to sampling and between collection of samples. Equipment should also be decontaminated at the end of each sampling trip (optional in terms of sample integrity, but good practice to ensure contamination is not transported off-site).

Refer to operating manuals for specific decontamination instructions for equipment such as field meters and automatic samplers. The following methods should be used when decontaminating sampling equipment:

- Decontaminate equipment away from sampling site. Use plastic sheets to prevent contamination from ground material.
- It is advisable to wear clean, sterile gloves and protective clothing when performing the decontamination process.
- Prepare detergent solution[1] in large container or bucket, place equipment into container and scrub clean. Detergents should be phosphate free. To clean hoses/pumps, pump decontamination solution through lines.
- Rinse equipment thoroughly (preferably triple rinse). Distilled or deionised water should be used for rinsing.
- Clean equipment with further decontamination solutions if required. The cleaning solution will depend on the contaminants being investigated, as follows:
  - for oil and grease, hydrocarbons, pesticides, PCBs or PAHs a solvent should be used. Rinse equipment with acetone then solvent such as methylated spirits.
  - for metal analysis acid washing is recommended. Rinse equipment with 10% nitric acid, followed by distilled or deionised water rinse.
  - microbiological samples should be further sterilised as per Section 5.4.6
- If contamination is suspected, the wastewater resulting from the decontamination process may require containment and disposal to a treatment facility. If this is the case, the water must not be disposed to groundwater or local drainage.

The effectiveness of the decontamination procedure should be checked following determination of the protocol and when concern or uncertainty about the effectiveness exists. Section 7.2 provides guidance on collection of an 'equipment blank' to check the decontamination process.

[1] Except for determination of silicon, boron and surfactants where detergent should not be used

6 SAMPLE IDENTIFICATION, TRANSPORT AND STORAGE

6.1 Labelling and identification

Samples need to be labelled so they can be readily identified at all times. Sample containers should be marked in such a way that they can be clearly identified and distinguished from other samples in the laboratory. Without appropriate labelling, all samples may look alike. Labels will need to be durable. Most samples will be preserved in ice so labels which will not come off when wet need to be used and the ink used will need to be insoluble in water. It is important to take care when packing samples, as samples are often subject to vibration during transport causing identification to rub off or become illegible.

It should be noted that xylene in permanent markers can contaminate samples intended for organic analysis. Biro or pencil should be used for organic samples.

Labelling on samples should contain as much information as practical. Sample labels **must** specify a clear and unique identifying code that can be cross-referenced to the monitoring location and time of sampling (eg via sampling record sheet – see Appendix 4).

Labels may also contain:

- date of sampling
- time of sampling
- location and name of sampling site (include GPS coordinates if available)
- job or project number
- name of sampler
- container pre-treatment and preservations added
- other observations that may affect the method or results of the analysis.

The information above should be recorded on the Field Record Sheet and retained as a permanent record.

Hazardous or potentially hazardous samples (such as solvents) should be clearly marked as such. Similarly, any samples that could reasonably be expected to have particularly high concentrations of a particular analyte should be brought to the attention of the laboratory, as this may affect the analytical technique.

6.2 Chain of Custody

Chain of Custody procedures and documentation demonstrate sample control. This gives confidence that the sample integrity has not been compromised and imperative if the samples are to be used in legal proceedings or if there is any suspicion that the samples might be tampered with at any stage of the process. The Chain of Custody documentation is a record used to trace possession and handling of a sample from the time of collection through analysis, reporting and disposal.

The basis of Chain of Custody control is that a sample is always in someone's custody and as such they are responsible for it. It is important to realise that couriers will often not recognise the contents of a sample container, but only take responsibility for the container itself. As such, the item (eg esky) should be secured with tape so that it would be obvious if the items had been tampered with.

The sampler should complete the Chain of Custody forms prior to packing the samples. The original Chain of Custody form must remain with the sample at all times to enable the completion of custody details at each stage of progression through transportation, analysis and reporting (see Appendix 5 for an example Chain of Custody form).

A copy of the final completed Chain of Custody form should be sought from the laboratory to confirm receipt and appropriate transfer and handling. The analytical laboratory should also include a copy of the completed chain of custody form as part of the analytical report.

6.3 Transport and storage

During sample transport and storage it is vital that all procedures are followed to ensure that samples are not significantly altered in condition and are in a state fit for analysis at the laboratory. Contamination of samples can easily occur during transport due to container cross-contamination, packaging material or chilling products. During sample storage, degradation can occur due to lack of appropriate preservation, inappropriate storage conditions, excessive storage times and sample cross-contamination.

The key aspects of effective transport and storage are to:

- ensure samples are appropriately packed to avoid breakage and cross-contamination
- reduce sample degradation through appropriate preservation
- ensure time between sampling and analysing does not exceed holding time
- sample containers should be sealed, carefully packed with an appropriate packing material, chilled or frozen (as required) and transported in an appropriate cooler (esky) or fridge. It is sometimes necessary to take further action to prevent cross-contamination, either between samples or from ice, during transport. This could include placing sample containers in snap-lock bags or airtight, plastic tubes with screw caps before transport.

If a courier is to be employed, sample security, Chain of Custody and refrigeration issues need to be considered prior to transporting the samples. If a courier is not able to meet all the requirements an alternative form of transport should be found.

A basic list of equipment required for sample transport and storage is listed in the Sampling Checklist (see Appendix 3) and includes labels for sample containers (if not already on containers), snap-lock bags or tubes if required, esky or fridge, ice bricks or crushed ice, packing material (eg foam packing), packing tape, consignment note for external courier and Chain of Custody forms.

6.3.1 Preservation techniques

Preservation techniques are vital to minimise changes to the sample following sampling. Changes that may occur if poor or incorrect preservation occurs are summarised in Section 2.2. Required preservation techniques for specific analytes are detailed in Appendix 2. Some common preservatives are described below.

Refrigeration: Keeping samples between 1°C and 4°C will preserve the majority of physical, chemical and biological characteristics in the short term (< 24 hours) and as such is recommended for all samples between collection and delivery to the laboratory. It is recommended that microbiological samples be refrigerated between 2°C and 10°C (as per AS/NZS 2031:2001). Ice can be used to rapidly cool samples to 4°C before transport. Ice bricks are preferred over loose ice or dry ice.

Freezing: In general, freezing at <–20°C will prolong the storage period. However, the freezing process significantly alters some nutrients and biological analytes such as chlorophyll, and the laboratory should be consulted before samples are frozen. Filtering samples in the field before freezing may be required. This is usually done for soluble nutrients, particularly when same-day delivery to the laboratory is not possible.

Chemical addition: The appropriate chemical preservative and dose rate can vary between analytes and according to container size. The analytical laboratory should always be consulted to establish which chemical preservative is appropriate for the analytical technique employed by that laboratory. Preservatives include acidic and basic solutions, and biocides. It is important these are used in the form of concentrated solutions so that the volume of preservatives required is minimised. This will minimise the dilution effect the preservative has on the sample. Chemical additives are normally added by the laboratory and supplied pre-prepared. When sampling with pre-prepared additives, it is important that the bottle is not flushed during sampling. It is also important to minimise the amount of spillage from the bottle during collection.

All preservation procedures employed should be recorded such as on the field sheet or chain of custody form. Some preservatives need to be removed or negated before analysis (eg pH corrections) and are required to be considered by the laboratory before analysis. It is crucial that a clear record of any sample treatments is available to the laboratory.

6.3.2 Holding times

While preservation techniques can reduce degradation rates they may not completely halt such changes. All analytes therefore have a holding time, which is the maximum time that can elapse between sampling and analysis, and where the sample is unlikely to be significantly modified under the recommended preservation conditions. Holding times for each analyte are included in Appendix 2. Samples must be delivered to the laboratory within the required holding times.

7 QUALITY

7.1 Quality assurance

Quality assurance (QA) is the policies, procedures and actions established to provide and maintain a degree of confidence in data integrity and accuracy.

For a monitoring program to successfully meet its objectives, a rigorous and thorough program of checks, comparisons and communication must be implemented. In order to achieve consistent data collection, a QA system must be followed.

Figure 7 outlines a systematic approach to the development of a QA program for sampling.

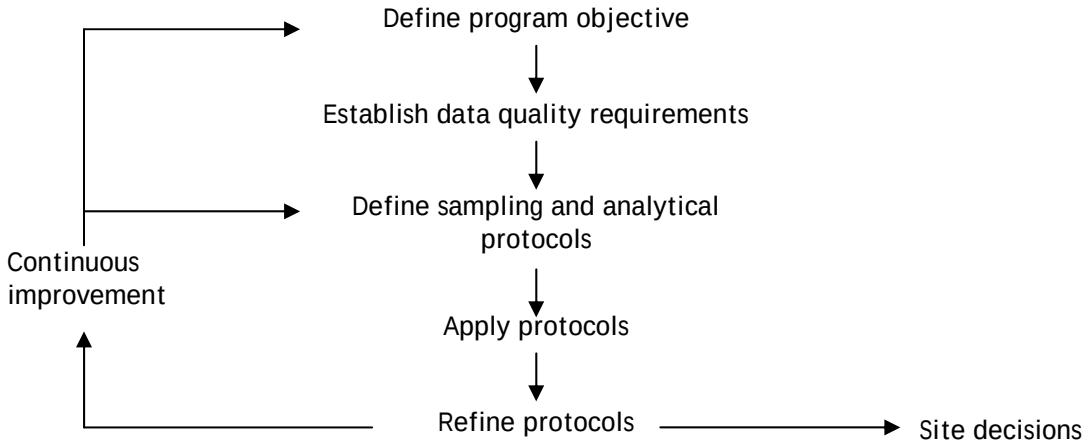

Figure 7 Quality assurance framework (Puls & Barcelona, 1996)

To control errors in field sampling to a level acceptable to the data user, various aspects of a QA program should be implemented from the monitoring program design stage through to delivery at the laboratory. Table 1 outlines typical quality assurance protocols for monitoring.

7.2 Quality control

Quality control (QC) is a sample or procedure intended to verify performance characteristics of a system. Water sampling quality control ensures that the monitoring data sufficiently represents the condition of the target waters when the sample was collected. That is, that any significant change in, or contamination to, the sample due to containers, handling and transportation is identified through the incorporation of QC samples.

The type and number of QC samples collected should be based on data quality objectives. The required confidence in results will be reflected in the quantity of QC samples. The greater the number of QC samples the greater the degree of confidence in the reliability of results. The most common types of QC samples are blanks, spikes and duplicates, which are described in the following section.

Table 2 states the minimum type and number of sample blanks and duplicates that must be taken for monitoring and testing required by the EPA (i.e. regulatory monitoring and testing; RMT). When stricter or less stringent requirements are appropriate, the requirements may be modified through licence conditions (EPA) or by approval of monitoring plan. Discussions must be held with your licence coordinator prior to developing a monitoring plan with QC that does not conform to the requirements within this guideline.

7.2.1 Blanks

QC blank samples are typically made from high purity water. The extremely low level of all analytes in high purity water enables identification of any contamination. If an elevated result of a particular analyte is found in a blank, it is reasonable to assume that similar contamination may have occurred in other samples.

Each type of blank is designed to assess the contamination from a particular part of the process and together a system of blanks isolates contamination from the sampling, transport and analytical process.

If elevated concentrations of target analytes are detected during the analysis of a blank sample, a thorough review of the areas of the sampling plan that may be introducing the contamination must be undertaken to determine the effect on the results and corresponding conclusions.

Field and transport blanks

Field blanks are designed to illustrate the effect of handling on sample integrity. They detect contamination from sources such as dust and atmospheric fallout. To collect field and transport blanks, high purity water is poured into three sample containers prior to going on site. If the water to be sampled is known to be saline the blanks should be of corresponding salinity. Two of the sample containers are taken to the site and one is sent to the laboratory. At the site, the cap of the field blanks should be removed and replaced at the end of sampling. During transport and storage the containers should be treated as if they hold a real sample. The transport blank need not be opened but should be carried with the rest of the samples.

Container blanks

Container blanks show if there has been any contamination of the sample from the container itself, the washing process or any preservation techniques. Containers are selected randomly, filled with distilled water in the laboratory and the appropriate preservation applied. These blanks should be held in the laboratory for the same time as the samples before analysis. They are particularly important when the holding time is in the order of several days or weeks.

Equipment (rinsate) blanks

Contamination introduced into the sample through contact with sampling equipment is measured using an equipment blank. Ideally, an equipment blank is prepared before sampling to show contaminants have not been introduced and at the conclusion of sampling to show the effectiveness of the decontamination procedure. The equipment should be decontaminated in the usual manner. The final rinse with distilled water (or similar) in the decontamination process has completed preparation of the equipment blank. If the washing process is cleaning the equipment sufficiently, the equipment blanks should show no change in composition from the rinse water.

Filtration blanks

Some parameters require a sample to be filtered in the field. A filtration blank allows determination of contamination from the filtering process. This can be from dust and atmospheric fallout during the filtration process or from the filter and filtration equipment. After the filtration equipment has been decontaminated in the usual manner, process a blank of high purity water through the filtration apparatus in the same way that the sample would be. The filtrate should then be collected in a normal sample container, preserved as appropriate and transported to the laboratory with the other samples.

7.2.2 Duplicates

Field duplicate samples are obtained by dividing a sample collected from a sampling point. They can be used to measure the precision or repeatability of the analytical process in the laboratory. Duplicate samples should be blind-coded so that the laboratory cannot tell which primary samples they correspond to. Remember the corresponding sample to the duplicate needs to be recorded on the field sheet. Note that duplicate analysis is generally targeted at the contaminants of concern and will not necessarily consist of a full set of analytes.

There are two types of duplicate samples:

- intra-lab duplicates, where the duplicate sample is transported to the same laboratory (primary laboratory) as the bulk of the samples—these duplicates measure the precision/variation of the primary laboratory's analytical methods
- inter-lab duplicates, where samples are sent to a different laboratory (often called secondary or QA laboratory)—these duplicates give an indication of the variability between laboratories which can provide a degree of confidence in the accuracy of the laboratories.

The duplicate samples should produce identical results within the specific tolerances of the analytical procedure.

7.2.3 'Spikes' or sample spiking

Spiked samples have a known amount of a particular analyte added to a sub-sample. This is generally done in the laboratory but can be undertaken in the field. Spikes are used to determine the effectiveness of the overall sampling and analysis program including all of the QC samples described earlier (as per AS/NZS 5667.1). As the final concentration of that analyte is known, spiked samples can be used to check the analytical process. It is important that the person analysing the spiked samples is not aware of the spiked value to ensure they are treated in the same way as regular samples. They are usually prepared in the analytical laboratory by trained personnel but can be prepared in the field if required.

If used, the concentration of the spiked samples should be within the general range of the contaminant expected in the real water samples.

Table 2 Summary of blank and duplicate samples

QC sample type	Quantifies contamination from:	Action in the laboratory	Action in field	Number	
				Recommended by AS5667.1 and ANZECC/ARMCANZ 2000	Minimum requirement if monitoring as condition of authorisation
Field and transport blanks	Contamination due to the field conditions	Select three identical sample containers. Fill all with distilled water (or water of corresponding salinity to sample). One sample is left in the laboratory as a control sample. Two samples are taken to the field—one as a field blank and one as a transport blank. The actions in the field are then carried out.	Field blank—open container in the field for a similar period of time as is required to take sample. Re-cap container and transport to laboratory for analysis.	1 set (of 3 containers) per sampling trip[a] 1 blank per 10 samples[b]	Nil
	Contamination during transport		Transport blank—Carry a sealed sample container in the cooler with other samples. No other action necessary in the field. Return to laboratory for analysis.		Nil
Container blanks	Contamination due to the container, washing process and preservatives	Fill a sample container with distilled water—do not rinse. Apply the preservation appropriate to samples taken in that container type. The sample is to be held in the laboratory for a similar period of time as the majority of samples are held before analysis.	None	1 per batch of containers[a] 1 per 10 samples[b]	Nil
Equipment blanks	Residue on sampling equipment	Nil	Wash sampling equipment as required. Collect final rinse water as the blank.	No specific recommendation	1 per sampling event if equipment is used

QC sample type	Quantifies contamination from:	Action in the laboratory	Action in field	Number	
				Recommended by AS5667.1 and ANZECC/ARMCANZ 2000	Minimum requirement if monitoring as condition of authorisation
Filtration blanks	Contamination or changes during field filtration	Nil	After washing the filtration equipment as required filter distilled water using filtration apparatus as for a normal sample. Collect filtrate for analysis.	No specific recommendation	1 per sampling event (if sample is field filtered)
Duplicate samples—to primary laboratory	Variability of analysis within laboratory	Nil	Split a sample into two sub-samples and preserve as required. Ensure samples are labelled uniquely. Transport to laboratory as required.	1 per 20 samples (5% of samples)[b]	1 per year or 1 per 20 samples (whichever is greater)[C]
Duplicate samples—to secondary (QA) laboratory	Variability of analysis between laboratories	Nil	Split a sample into two sub-samples and preserve as required. Transport one sample to primary laboratory and one sample to secondary laboratory.	No specific recommendation	1 per year or 1 per 20 samples (whichever is greater)[C]

Recommendations sourced from:
[a] AS/NZS 5667.1:1998
[b] ANZECCARMCANZ 2000
[c] Note that duplicate analyses should be targeted at the contaminants of concern and will not necessarily consist of a full set of analytes.

8 ANALYSIS AND REPORTING

This guideline is intended primarily to provide guidance on the sampling process. However, some simple tips on analysis and reporting are provided in this section.

8.1 Data review

It is important that the data obtained is reviewed prior to assessment and interpretation. Simple reviews can be undertaken that will highlight major issues in the quality of sampling or analysis and provide useful information on accuracy and precision of sampling and analytical methods. The reviews should:

Compare duplicate samples results

As duplicate samples are a sub-sample of the same initial sample the variation between samples should be within the tolerances for the analytical procedure. Differences between duplicates are often quantified as relative percentage difference (RPD).
The relative percentage difference (RPD) of each field duplicate set can be calculated to assess the overall sample precision by using the formula:

$$RPD = \left[(R_1 - R_2) \div \frac{(R_1 + R_2)}{2} \right] \times 100$$

where R_1 = result of sample, R_2 = result of duplicate sample

If an RPD is >20%, or if the RPD of intra-laboratory duplicates is much greater than the RPD of inter-laboratory duplicates, an investigation as to the cause should be investigated and documented.

Review spike recovery values

Spiked samples have a known amount of an analyte added to them. This is generally done in the laboratory. Laboratories should report the results of spiked samples. As the actual concentration of the analyte is known, spiked samples are used to check the analytical process. Spike recovery values should be within the 80–120% range. Consistently high or low spike recovery values indicate that there may be bias in the analytical process.

Review blank samples results

Blank samples should have low or zero concentrations of the analytes of concern. Should high concentrations of analytes be detected, the monitoring should be thoroughly reviewed to determine whether there is a problem with contamination.

8.2 Reporting

When submitting a monitoring report to the EPA as a requirement of an authorisation, the data must be reviewed and accompanied by appropriate supporting information.

Licensees are referred to the *EPA guidelines—Regulatory monitoring and testing: Reporting requirements:* (EPA 2006c) with regard to the type and presentation of information.

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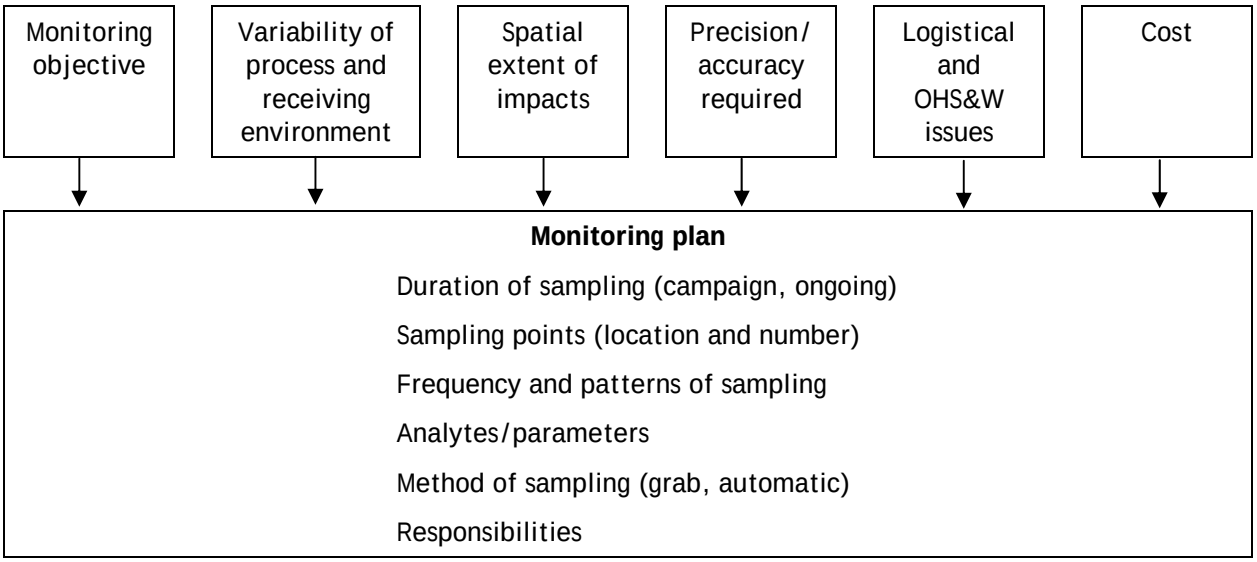
GLOSSARY

AS	Australian Standard
Analyte	Refers to any chemical compound, element or other parameter as a subject for analysis
ANZECC	Australian and New Zealand Environment Conservation Council
BOD	Biochemical or biological oxygen demand. A measure of the decrease in oxygen content in a sample of water—usually over five days (BOD-5)
COD	Chemical oxygen demand. The oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant
Criteria	A value (numerical or relational) set through a condition of licence that imposes a requirement on the licensee (eg that the licensee must meet or that requires the licensee to report or take other action if exceeded)
Distilled water	Distilled water has been used throughout this guideline for decontamination and other purposes, where water that will not impact upon the results of analysis is required. The water should have no detectable concentration of the element to be analysed, and be free of substances that interfere with the analytical method The most common types used for this purpose are distilled, demineralised or deionised water. Distilled or demineralised water is the most appropriate type of water except where dissolved ionised gases are under investigation. Deionised water may not be suitable when investigating dissolved organics, particulates or bacteria 'Spring' water should not be used during sampling as in most cases no contaminants have been removed and high levels of some analytes (such as metals and inorganic non-metallics) will be present Where uncertainty exists as to the suitability and impacts of the water used, quality control blanks (as described in Section 7.2) should be employed
DO	Dissolved oxygen
EC	Electrical conductivity. The ability of water to conduct an electrical current; commonly used as a measure of salinity or total dissolved salts
Entrainment	Of a current or fluid, incorporating and sweeping along in its flow
Environmental values	Particular values or uses of the environment that are important, such as ecosystem, health or amenity that merit protection from the effects of contaminants, waste discharges and deposits. Several environmental values may be designated for a specific waterbody
EPA	South Australian Environment Protection Authority
Filtrate	The liquid portion of a sample after filtration
Holding time	After taking a sample, the time by which the sample should be analysed. Exceeding the recommended holding time is likely to cause deterioration of the sample.
Isokinetic	Same velocity; eg isokinetic sampling conditions occur when velocity of water at sample inlet is the same velocity as the water being sampled
LOR	The laboratory limit of reporting, also often referred to as limits of detection
Monitoring plan	A documented plan detailing the actions, responsibilities and timeframes that will deliver monitoring that meets the defined objectives

Monitoring program	A system developed to achieve the monitoring objectives
NATA	National Association of Testing Authorities (of Australia) <www.nata.com.au>
NEPM	National Environment Protection Measure
Orthophosphate	Form of phosphorus that is immediately accessible for plants and animals to use
Plankton	Microscopic plants (phytoplankton) or animals (zooplankton) found in the water column of aquatic ecosystems
Protected environmental value	In relation to waters or a particular body of water, means the beneficial aspects or uses of water as are designated by the *Environment Protection (Water Quality) Policy 2003* in respect of those waters or that body of water for protection from pollution
Pollutant	Something that pollutes, such as sewage or mine waste, exhaust gases, etc
QA	Quality assurance. The implementation of checks on the success of quality control
QC	Quality control. The implementation of procedures to maximise the integrity of samples and data (eg cleaning procedures, contamination avoidance, sample preservation methods)
RMT	Regulatory monitoring and testing. Monitoring undertaken as a condition of authorisation or in order to enable an environmental risk to be assessed, or to assess the effectiveness of risk controls and management within the scope of the EP Act.
RPD	Relative percentage difference. Refer to Section 8 for equation and description
Spike recovery value	A percentage indicating the detected concentration of a known volume of analyte over the known value
Titration	A measured amount of a solution of unknown concentration is added to a known volume of a second solution until the reaction between them is just complete; the concentration of the unknown solution (the titer) can then be calculated
Water quality criteria	In relation to protecting a particular protected environmental value, means the maximum concentrations of certain substances permitted by the *Environment Protection (Water Quality) Policy 2003* to be in water or the minimum or maximum levels permitted for certain characteristics of water

APPENDIX 1 GUIDANCE ON DEVELOPING AN EFFECTIVE MONITORING PLAN

The following appendix provides general guidance on issues to be considered when developing a monitoring plan for water or wastewater sampling. Consideration of these issues will assist in designing a monitoring plan that is specific, targeted and cost-effective.



A1 Key considerations

A1.1 Monitoring objective

The first step in developing a monitoring plan is to clearly identify the objectives of the monitoring. For licensees required to undertake regulatory monitoring and testing (RMT) the EPA intends to specify objectives of the monitoring as a condition of authorisation or order. Where monitoring is being undertaken for purposes other than, or in addition to, a requirement of an authorisation or order, the *Australian guidelines for water quality monitoring and reporting* (ANZECC 2000) can provide further advice and assistance in setting monitoring plan objectives.

Water and wastewater monitoring can be undertaken to meet many objectives from gaining an understanding of an aquatic ecosystem and the physical, chemical and biological processes that operate within it, to the review of water quality within a specified criteria.

A1.2 Variability considerations

Variability, in time and space, is probably the most significant aspect to be considered in the design of sampling plans. Variability will determine the number of sites, number of replicates and the frequency of sample collection. High variability in the environment or the industrial discharge combined with poor sampling design or too few samples can result in data that is too variable to reveal an impact, disturbance or trend.

Industrial process variability

Examples of variation in wastewater due to process variability include:

- daily and weekly variation—particular processes such as scheduled cleaning might always occur on the same day of the week leading to a consistent pattern of variation in the quality of the discharge
- seasonal variation, such as that experienced in the wine industry, as shown in the case study presented later in this section [2]
- event variation—the influent (and effluent) from sewage treatment plants varies after a rainfall event due to the infiltration and inflow into the sewage system diluting the concentration but increasing the volume of wastewater.

How process variability considerations are taken into account in the design of a monitoring plan will depend upon the objective of monitoring, eg to determine the maximum concentrations of a pollutant, the variability of discharge or the average concentration.

Receiving environment variability

Variation in water quality can occur at different frequencies for varying reasons, including but not limited to:

- diurnal variation—changes in dissolved oxygen and pH throughout the day due to respiration and photosynthesis, changes in water temperature
- depth variation—stratification effects can occur in lagoons and lakes as well as in rivers, creeks, marine water and estuaries
- seasonal and event variation—variations in flow and salinity due to rainfall and temperature
- tidal variations—variation in flow direction and volume due to tide (in rivers and estuaries as well as marine environment)
- spatial variation—occurs in the receiving environment due to a range of factors from natural biological variability, wave action and turbulence through to flow and concentration modifications around structures such as jetties and weirs.

Knowledge of the variations likely to affect monitoring results are important in selecting the frequency and pattern of sampling as well as sampling points.

A1.3 Precision required

It is important when developing a monitoring plan that the amount and frequency of sampling is sufficient to provide confidence in the interpretation of results. Most of the sampling undertaken for regulatory purposes is a form of hypothesis testing—i.e. testing the hypothesis that environmental harm has not occurred. In hypothesis testing there are two types of errors to aim at avoiding: falsely detecting environmental harm when it has not occurred and not detecting environmental harm when it has occurred. The probability of a false positive is called the level of significance. The probability of a false negative (Type II error) is related to the power of the test. Further information on determining the probabilities is provided in texts such as *Australian guidelines for water quality monitoring and reporting* (ANZECC 2000). For regulatory purposes it is important to minimise both of these probabilities.

[2] This information has been taken from the EPA Winery and Distillery guideline that outlines the monitoring requirements for the winery industry

Case Study: Excerpt from *EPA guidelines for wineries and distilleries (January 2004)*

Wastewater quality

Winery wastewater comes from a number of sources that include:

- cleaning of tanks
- ion exchange columns
- hosing down of floors and equipment
- rinsing of transfer lines
- stormwater diverted into or captured in the wastewater management system
- spent wine and product losses
- bottling facilities
- filtration units
- laboratory wastewater.

Wine production is seasonal, and the characteristics of wastewater vary with the production period. Up to six production periods can be defined; these are summarised in the table below.

Description of winery wastewater production periods at wineries

Period	Typical months of the year	Description
Pre-vintage	January–February	Bottling, caustic washing of tanks, non-caustic washing of equipment in readiness for vintage
Early vintage	February–March	Wastewater production is rapidly rising to peak vintage flows and has reached 40% of the maximum weekly flow; vintage operations dominated by white wine production
Peak vintage	March–May	Wastewater generation is at its peak; vintage-only operations are at a maximum
Late vintage	April–June	Wastewater production has decreased to 40% of the maximum weekly flow; vintage operations dominated by production of red wines; distillation of ethanol spirit may coincide with this period
Post-vintage	May–September	Pre-fermentation operations have ceased; effect of caustic cleaning, ion exchange etc. is at its greatest, and wastewater quality may be poor
Non-vintage	June–December	Wastewater generation is at its lowest—generally less than 30% of maximum weekly flows during vintage; wastewater quality is highly dependent on day-by-day activities

To accurately determine the pollutant load that is discharged to the environment, sampling must reflect wastewater quality during the production period. It must be performed at a suitable location before it is disposed of to land or re-used for irrigation. Monitoring plans submitted to the EPA to comply with licence requirements must be accompanied by a schematic diagram. This must indicate the sequence of wastewater treatment processes employed and where the wastewater sampling is to be performed, to enable the EPA to advise on the suitability of the monitoring point.

The table below shows the EPA monitoring frequency requirements for differing volumes of wastewater generated by wineries. For facilities that do not have distinct production periods, a suitable frequency must be discussed with the EPA.

Wastewater produced per year, ML	Frequency
> 10	Once per production period
10–20	Twice per production period
> 20	Three times per production period

Case Study cont: Excerpt from *EPA guidelines for wineries and distilleries (2004)*

For a winery that generates more than 10 ML of wastewater per year the EPA may permit a reduction in wastewater monitoring frequency if: an adequate treatment system approved by the EPA to treat wastewater before application to land has been installed; the facility fully implements an irrigation management plan (IMP) approved by the EPA; or the wastewater management system is equipped with in-line monitoring devices for dissolved oxygen (DO) and pH or EC to indicate irregularities that may indicate a need for further testing.

The parameters to be monitored in wastewater are listed in Table 5 (in EPA Guideline for wineries and distilleries, January 2004). The winery may need to consult its EPA licence coordinator to confirm whether the optional parameters listed in the table need to be monitored. If a winery generates less than 1 ML of wastewater per year, the EPA may permit the omission of some minor wastewater parameters from the monitoring regime if it can be demonstrated that the risk to the environment is low, and the wastewater management system has been working effectively for the past two years.

The EPA recommends that winery effluent not be combined with wastewater generated from cellar door and food preparation activities. This is due to health concerns. If separation is not possible, the winery must seek advice from the Department of Human Services.

A2 Elements of a monitoring plan

A2.1 Duration of sampling

For regulatory monitoring, sampling will generally be ongoing to show continued compliance with criteria, or to monitor the ongoing influence of discharges on the receiving environment.

Campaign monitoring or pilot studies should be considered when the variability of a wastewater stream or receiving environment is uncertain. A pilot study of high frequency discrete and/or composite sampling will provide information regarding the variability in the wastewater stream due to random and systematic influences. Based on an understanding of the results of the pilot study, a more targeted, cost-effective ongoing monitoring plan that will adequately characterise the water can be developed.

A2.2 Sampling locations

The design of a sampling plan to monitor water or wastewater composition should ensure samples are collected at sites and times that provide a representative sample, thus providing an accurate description of the overall quality of the wastewater stream. Additionally, sampling sites should be located in areas that are safe to access, accessible under all conditions of flow and discharge, be well mixed to ensure a homogenous sample is collected and be easily identifiable for later sampling. Permanent sampling locations should be established in any sampling environment to ensure that representative samples can be compared over time.

Determine impacts on receiving waters

In the case of examining the effect of a point source discharge, sites should be arranged in such a way that the end-of-pipe, and upstream and downstream of the discharge water is sampled. The degree of mixing within the waterbody will determine the proximity of sites to each other—where mixing is strong (the water is homogenous) sites may be spread further apart.

As a minimum, sampling the effects of a point source discharge should include the following sample locations:

- end-of-pipe samples to characterise the discharge
- in the receiving water upstream of the point of entry
- in the waterbody at the point of entry
- multiple samples at progressive distances downstream from the point of entry.

Wastewater sampling

The number of samples required to determine the composition of wastewater will depend upon the accuracy/precision required from the study and the variability of the stream. Generally, grab samples can be used where the analyte of interest is not expected to vary greatly over time.

Sampling of wastewater may be undertaken in tanks, drums, pipes, lagoons, drains, open channels and from taps or valves. Wastewater in pipes will often exhibit laminar flow and samples taken from taps can be strongly influenced by boundary effects, which may not produce a representative sample. In the case of in-pipe laminar flow, the sampling location should be situated downstream of a restriction or obstacle which creates turbulence and mixing in the wastewater stream.

Profiling depth

It is often sufficient to take discrete samples just below the surface at a given site, particularly in shallow and well-mixed environments, such as adequately sized and designed lagoons. In deeper or poorly mixed waters, a 'surface sample' may not accurately describe the characteristics of the entire water column and other sampling techniques should be employed. These can include integrated vertical column samples or discrete samples at given depths.

A2.3 Sampling frequency and patterns of sampling

There are no strict rules regarding how frequently sampling should occur, but the sampling frequency will be dictated by the variability of the discharge and the objectives of the plan. During the planning stages, consider the aims of the study and choose a sampling frequency that has the best chance of providing the information required to meet the objectives of the plan. It is important to consider the frequency carefully. If samples are not taken frequently enough, the characteristics of the waters or wastewaters might not be adequately described resulting in a poor understanding of the system and potentially inaccurate reporting of compliance or non-compliance. Alternatively, overly frequent sampling may be a waste of time and resources.

In general, if a measurement parameter has a predictable pattern which has been shown statistically or through a pilot study (eg discharge at a certain time of day) the sampling plan can be tailored to sample at regular intervals. Alternatively, if the system or processes are highly variable or unpredictable, the sampling should be undertaken more regularly over several time scales.

Sampling to determine loads

Determination of loads should be undertaken using a flow meter (mechanical or magnetic) in combination with sampling. If the flow rate of the wastewater is variable, flow-weighted composite sampling is most appropriate. This can be done either discretely with knowledge of flow, or using an automatic sampler where sampling is triggered after a predetermined volume of flow has passed a given point.

A2.4 Analytes

Choice of analytes will depend on the contaminants from the process under consideration and the criteria against which the monitoring is to be evaluated. The environmental values of the waters must be considered and the relevant criteria that are common to the discharge and the values should be considered. Environmental values and criteria to be considered in South Australia are set out in the *Environment Protection (Water Quality) Policy 2003*.

Key considerations when choosing analytes include the form of analyte (eg total metals, dissolved metals, chemical speciation) and the confounding factors (eg faecal coliforms are often used to indicate contamination from human faeces, however in lagoons faecal coliforms may be the result of the presence of birds).

A2.5 Sampling procedures

Various types of samples can be taken according to the requirements of the specific monitoring plan. Thorough consideration of the objectives of the sampling plan should occur before deciding on the types of samples to be taken. If an inappropriate type of sample is collected the water quality data gained may not provide the information desired.

Grab samples

Grab samples are discrete samples that are taken at a location to provide a 'snapshot' of the water quality characteristics at that time. For the purposes of quantifying water or wastewater constituents, grab samples will show the concentrations at that location and time of sampling. They will not provide any information about the concentrations outside that point in time. As such, if grab samples are employed, a high number of samples (high sampling frequency) may be required to show the nature of change over time. A sampling plan using grab samples could show the dispersal of discharge constituents in the receiving environment at the time of day when the discharge is present. They can also be used to show worst-case scenario situations, eg in the case of surface scums of algae or oil and greases. However, taking manual grab samples is labour intensive and often impractical for long, intensive sampling plans.

Composite samples

Composite samples are those collected through mixing multiple grab samples to obtain a single mixed sample. Compositing samples can increase the temporal and spatial extent of sampling, without increasing the number of samples or sampling and analysis costs. These types of samples are used when the average water quality characteristics are of interest over a given period of time or volume of flow. They may be more appropriate than grab samples when the distribution of constituents within the waste stream is random or when the variability within that stream is low. Composite samples are also useful when the determination of loads of constituents is required. However, compositing does have its limitations. Prior knowledge of the stream is required to determine if composite samples are appropriate (i.e. random distribution of contaminants and low variability). This may require a pilot study of discrete grab samples. Additionally, compositing may mask variability within the waste stream by hiding peak and trough concentrations.

APPENDIX 2 CONTAINERS, PRESERVATION METHODS AND HOLDING TIMES

The information in this appendix is sourced from the *AS/NZS 5667.1:1998*, unless otherwise noted. **This table is not comprehensive but provides an overview of the most common analytes sampled**. Where analytes are not listed in this table please refer to Australian Standards, International Standards, ASTM or APHA. This information is reproduced with the permission of Australian Standards.

Analyte	Container type	Typical volume (mL)	Filling technique	Filtration and preservation	Holding time	Notes
physical and aggregate samples						
acidity and alkalinity	plastic or glass	500	fill container completely to exclude air	refrigerate	24 hours	preferable to analyse sample in field
colour—true	plastic or glass	500	fill container completely to exclude air	refrigerate and store in the dark	2 days	
conductivity (at 25 °C)	plastic or glass	100	fill container completely to exclude air	none required	24 hours	preferably carried out in field for samples of low conductivity (<20 µS/cm)
oxygen, dissolved	glass			fix oxygen in the field and store in the dark (as per method of analysis used)	24 hours	preferably determined in the field
pH	plastic or glass	100		refrigerate	6 hours	carry out test as soon as possible and preferably in situ
solids (dissolved or suspended)	plastic or glass	500	dissolved: fill container completely to exclude air	refrigerate	24 hours	
turbidity	plastic or glass	100	fill container completely to exclude air	none required	24 hours	preferable to analyse sample in field or in situ

Analyte	Container type	Typical volume (mL)	Filling technique	Filtration and preservation	Holding time	Notes
metals						
aluminium barium beryllium cadmium chromium cobalt copper lead manganese molybdenum nickel silver tin vanadium zinc	acid washed, plastic or glass	100		acidify with nitric acid to pH 1 to 2	1 month	
antimony	acid washed, plastic or glass	100		acidify with nitric acid or hydrochloric acid to pH 1 to 2	1 month	hydrochloric acid should be used if hydride technique is used for analysis—consult laboratory
arsenic	acid washed, plastic or glass	500	fill container completely to exclude air	acidify with nitric acid or hydrochloric acid to pH 1 to 2	1 month	hydrochloric acid should be used if hydride technique is used for analysis—consult laboratory
boron	plastic	100	fill container completely to exclude air	none required	1 month	
chromium (VI)	acid washed, plastic or glass	100	fill container completely to exclude air	refrigerate	1 day	sample container should be rinsed thoroughly

Analyte	Container type	Typical volume (mL)	Filling technique	Filtration and preservation	Holding time	Notes
iron (II)	acid washed, plastic or glass	500	fill container completely to exclude air	acidify with hydrochloric acid to pH 1 to 2	24 hours	
iron, total	acid washed, plastic or glass	500		acidify with nitric acid to pH 1 to 2	1 month	
lithium	plastic	100		none required, but may acidify with nitric acid to pH 1 to 2 and refrigerate	1 month	acidification allows the sample to be analysed for lithium as well as other metals
magnesium	acid washed, plastic or glass	100	fill container completely to exclude air	none required	1 week	samples with pH > 8 or high carbonate content to be analysed solely for calcium, magnesium or hardness should be acidified
				acidify with nitric acid to pH 1 to 2	1 month	acidification permits determination of other metals from same sample
mercury	acid washed, glass	500		acidify with nitric acid to pH 1 to 2 and add potassium dichromate to give a 0.05% (m/v) final concentration	1 month	particular care is needed to ensure that the sample containers are free from contamination
potassium	acid washed, plastic or glass	100		none required/acidify with nitric acid to pH 1 to 2	1 month	acidification allows the sample to be analysed for potassium as well as other metals
selenium	acid washed, plastic or glass	500		acidify with nitric or hydrochloric acid to pH 1 to 2	1 month	
uranium	acid washed, plastic or glass	200		acidify with nitric acid to pH 1 to 2	1 month	
inorganic (non-metallic)						

Analyte	Container type	Typical volume (mL)	Filling technique	Filtration and preservation	Holding time	Notes
ammonia	plastic or glass	500		refrigerate	6 hours	strict protocol required to reduce effects of contamination store in area free of contamination (ammonia vapour may permeate the walls of even high density polyethylene containers) pressure filtering is preferred
				field filter through 0.45 µm cellulose acetate membrane and refrigerate	24 hours	
				field filter and freeze	1 month	
chlorine	plastic or glass	500		keep out of direct sunlight, analyse immediately	5 minutes	this analysis should be carried out in the field within 5 minutes of sample collection
cyanide, total	plastic or glass	500		if no interfering compounds are present, then add sodium hydroxide to pH >12, refrigerate and store in the dark	24 hours	the preservation technique will depend on the interfering compounds present sulfides and oxidising agents potentially cause large errors in the determination of different cyanide forms refer to the analytical method for suitable preservation techniques
iodide	plastic or glass	500		refrigerate	1 month	
fluoride	plastic	200		none required	1 month	PTFE containers are not suitable
nitrate	plastic or glass	250		field filter through 0.45µm cellulose acetate membrane and freeze	1 month	

Analyte	Container type	Typical volume (mL)	Filling technique	Filtration and preservation	Holding time	Notes
				refrigerate	24 hours	unfiltered sample
nitrite	plastic or glass	200		immediate analysis		analyse as soon as possible after collection
				freeze	2 days	
				field filter through 0.45µm cellulose acetate membrane and freeze	1 month	
phosphorus, total	plastic or glass	500		refrigerate	24 hours	acidification not recommended for persulfate oxidation method
				freeze	1 month	
				acidify with sulfuric acid or hydrochloric acid to pH 1 to 2, refrigerate and store in dark	1 month	
phosphorus, dissolved	plastic or glass	50		field filter through cellulose acetate membrane and refrigerate or field filter and freeze	24 hours—1 month	
sulfate	plastic or glass	200		refrigerate	1 week	
sulfide, total	plastic or glass	500	fill container completely to exclude air	none required for field measurement. Preserve with zinc acetate for laboratory analysis	1 week (preserved)	
nitrogen, total	plastic or glass	500		refrigerate or freeze	24 hours—1 month	

Analyte	Container type	Typical volume (mL)	Filling technique	Filtration and preservation	Holding time	Notes
TKN: total Kjeldahl nitrogen	plastic or glass	500		acidify with sulfuric acid or hydrochloric acid to pH 1 to 2, refrigerate	24 hours	
				refrigerate	24 hours	
				freeze	1 month	
Organics						
biochemical oxygen demand (BOD)	plastic or glass	1000	do not pre-rinse container with sample fill container completely to exclude air	refrigerate and store in the dark	1 day	glass containers are preferable for samples with low BOD (<5 mg/L)
chemical oxygen demand (COD)	plastic or glass	100	fill container completely to exclude air	acidify with sulfuric acid to pH 1 to 2, refrigerate and store in dark	1 week	glass containers are preferable for samples with low COD (<5 mg/L)
	plastic	100		freeze	1 month	
Hydrocarbons, oil and grease	glass, solvent washed	1000	do not pre-rinse container with sample do not completely fill container[a]	refrigerate	1 day	extract on site where practical extract sample container as part of the sample extraction procedure
				acidify with sulfuric acid or hydrochloric acid to pH 1 to 2 and refrigerate	1 month	

Analyte	Container type	Typical volume (mL)	Filling technique	Filtration and preservation	Holding time	Notes
MAH: monocyclic aromatic hydrocarbons	glass, vials with PFTE lined septum	500	fill container completely to exclude air.	Acidify with hydrochloric acid to pH 1 to 2 and refrigerate. If residual chlorine is present, for each 40ml of sample add a) 25 mg of ascorbic acid; b) 3 mg of sodium thiosulfate; or c) 3 mg of sodium sulfite	1 week	2 x 40mL vials are recommended for purge and trap analysis
PAH: polycyclic aromatic hydrocarbons	glass, solvent washed	500	do not completely fill container do not pre-rinse	refrigerate and store in the dark if sample is chlorinated, add 80 mg of sodium thiosulfate for every 1000 mL of sample to container prior to sampling	1 week	extract on site where practical extract sample container as part of the sample extraction procedure
PCBs: polychlorinated biphenyls	glass, solvent washed with PTFE cap liner	1000–3000	do not completely fill container do not pre-rinse	if sample is chlorinated, add 80 mg of sodium thiosulfate for every 1000 mL of sample to container prior to sampling	1 week	extract on site where practical extract sample container as part of the sample extraction procedure a 40 mL vial with PTFE-lined septum is recommended for micro extraction

Analyte	Container type	Typical volume (mL)	Filling technique	Filtration and preservation	Holding time	Notes
pesticides (organochlorine, organophosphorus and nitrogen-containing)	glass, solvent washed with PTFE cap liner	1000–3000	do not pre-rinse container with sample do not completely fill sample container with air	refrigerate if sample is chlorinated, add 80 mg of sodium thiosulfate for every 1000 mL of sample to container prior to sampling	7 days	extract on site where practical extract sample container as part of the sample extraction procedure
phenolic compounds (including chlorinated phenols)	amber glass, solvent washed with PTFE cap liner	1000	do not pre-rinse container sample do not completely fill container	refrigerate and store in the dark	24 hours	
				acidify to pH 1 to 2 refrigerate and store in dark if sample is chlorinated, add sodium thiosulfate to container prior to sample collection	3 weeks	
TOC: total organic carbon	amber glass with PTFE cap liner	100		acidify with sulfuric acid to pH 1-2, refrigerate and store in the dark	1 week	analyse as soon as possible phosphoric acid can be used instead of sulfuric if necessary inorganic carbon needs to be purged before analysis so volatile organic compounds will be lost
	plastic			freeze	1 month	
Microbiological / biological						

Analyte	Container type	Typical volume (mL)	Filling technique	Filtration and preservation	Holding time	Notes
faecal coliforms or *E.coli*, etc	glass or plastic, sterilised.	Confirm with laboratory	do not completely fill container	for chlorinated/ chloraminated water add sodium thiosulfate to concentration 100 mg/L for samples with high heavy metals add EDTA refrigerate	24 hrs (preferably < 6 hrs)	from AS/NZS 2031:2001
chlorophylls	plastic or glass	1000		refrigerate filter and freeze residue	24 hours 1 month	refrigerate in dark
radiochemical analysis						
alpha and beta activity (gross)	plastic or glass	1000	no air gap	acidify with nitric acid to pH 1 to 2	1 month	
alpha and beta activity except radio-iodine	plastic	as required	no air gap	filter for soluble analysis immediately add 20 ±1 ml of 50% (v/v) nitric acid per litre of sample the pH should be <1 refrigerate and store in the dark	analyse as soon as possible	safety precautions and shielding are dependent on the activity of this sample it is imperative that radioactive dust is not inhaled or left on clothing
gamma activity	plastic	consult laboratory		see endnote b	depends on the half-life of the radionuclide	safety precautions and shielding are dependent on the activity of this sample it is imperative that radioactive dust is not inhaled or left on clothing

Endnotes:

a	Samples for oil and grease analysis should be collected in glass containers with teflon-coated equipment as these analytes will stick to the rubber tubing of automated sampling equipment resulting in an unrepresentative sample.
b	If there is suspended matter and a separate measurement is required, or the solids are not readily dissolved, filter the sample and treat as two separate samples. Add quantitatively to the sample a known amount of solution containing non-radioactive isotopes of interest. For samples containing metals, the solution is usually acidified to a pH of less than 2; the acid used should not precipitate or volatilise the elements of interest. Refrigerate and store in the dark.
Notes from AS/NZS 5667.1:1998	Plastic = plastic containers, eg polyethylene, PTFE, polypropylene, PET and similar. Glass = borosilicate glass container. Vials are flat-bottomed borosilicate glass vials, typically 30-50 mL capacity with screw caps. The caps should have PTFE faced septa, or liner. The preservation technique will depend on the method of analysis to be used. Other methods of preservation may be suitable and prior liaison with the analytical laboratory is required. Refrigerate = cool to between 1^{o}C and 4^{o}C (see clause 11.2.2 of AS). Freeze = freeze to -20^{o}C (see clause 11.2.3 of AS)

APPENDIX 3 FIELD EQUIPMENT CHECKLIST (EXAMPLE)

Equipment list	Check	Equipment list	Check
Documentation		**Quality control samples**	
Monitoring plan including site plan		Field blanks	
Appropriate area maps		Transport/equipment blanks	
Field notebook/record sheets		**Sample storage and transport**	
Chain of Custody		Eskies and ice	
Pens and textas		Packing material	
Sampling equipment		Ice packs/blocks	
Sampling rod		Packing tape	
Depth sampler		Address Labels	
Field meters		Courier information	
Disposable gloves		**Safety equipment**	
Sample containers (including containers for duplicates and blanks)		First-aid kit	
Labels for samples		Sunscreen/sunglasses	
Decontamination		Drinking water	
Clean work area, eg plastic groundsheet		Mobile phone/communication equipment	
Buckets		PPE— wide brimmed hat wet weather gear waders/rubber boots disposable overalls	
Demineralised/deionised water		Antiseptic hand wash	
Detergent solution		Lifejackets/EPIRB	
Ethanol (in wash bottle)		**Other**	
Sponges, scrubbing brush		Tools—spanner/shifter, etc	
Gas burner/sodium hypochlorite (for microbiological)		Digital camera and batteries/ charger	
Field filtration		GPS and batteries	
Filtration pump		Keys for gates	
Filtration apparatus, syringe etc		Other equipment for site specific or remote area requirements	
Filters			

Note: No claim is made that this list is comprehensive. It is a suggestion for consideration and requires tailoring to individual needs.

APPENDIX 4 FIELD RECORD SHEET (EXAMPLE)

Sampling summary

Sampler		Project number	
Date		Time (begin and end)	

Site information

Site ID		GPS	
Location		Photo numbers	

Field observations

Weather	Temperature		
	Wind and direction Cloud cover/rain		
Water	Tide/depth		
	Flow Choppy/mixed/calm		
Observations examples	Surface film?		
	Algae/phytoplankton? Debris? Odour?		
Other/additional			

Field measurements

Analyte	Result/s		Instrument
Temperature			
Dissolved oxygen			
Turbidity			
Conductivity			
pH			
Chlorine			

Sample collection

Sample No. *	**Notes** (eg collection method, filter method, duplicate, decontamination method)

***** Record in the order taken including duplicates and blanks

APPENDIX 5 CHAIN OF CUSTODY FORM (EXAMPLE)

Customer	SA EPA	**Laboratory**	ABC Labs
Project Name	Clean lake	**Contact Name**	Sam Linard
Reference Number	05112/36	**Address**	524 Magill Road, Tranmere
Contact	P Bond	**Phone**	8234 5678
Phone	8123 4567		

Sample I.D.	**Sample**	**Matrix**	**Sampling**		**Container**			**Analysis required**						**Notes**
								0.05 Ammonia	5 BOD 5	0.02 Phos				←Max LOR
	Location	**(Water, soil)**	**Date**	**Time**	**Type**	**Size (mL)**	**Preserv.**							
W1-1	W1	Water	1/11/05	2.00pm	G	1000	4°C	x	x					Ammonia—total as N
W1-2	W1	Water	1/11/05	2.00pm	G	250	4°C			x				Phosphorus—total as P
W1-3	W1	Filter	1/11/05	2:30pm	Filter paper									2 Litres filtrate

Sample relinquished by:				**Sample received by:**					**Agreed condition (temp, intact, etc)**
Name/organisation	**Initials**	**Date**	**Time**	**Name/organisation**	**Signature**	**Date**	**Time**	**Sample Condition**	
Sampler				Courier					
Courier				Laboratory					