EPA Guidelines

Regulatory monitoring and testing

Groundwater sampling

JUNE 2007

This document is currently under review and some information may be out of date. Please contact Tavis Kleinig on 820 48638 or epainfo@sa.gov.au for further information.

EPA South Australia

EPA Guidelines: Regulatory monitoring and testing
Groundwater sampling

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1 INTRODUCTION

1.1 Purpose

The purpose of this Environment Protection Authority (EPA) guideline is to provide for a consistent approach to sampling groundwater in South Australia.

There are a number of reasons for sampling groundwater, such as:

- meeting EPA conditions of authorisation or regulations
- gaining an understanding of hydrogeological processes
- assessing the extent of influence and significance of pollutants
- monitoring and assessing short and long-term trends in groundwater quality.

This guideline is a compilation of existing groundwater sampling documents and is intended to assist people who sample groundwater to be consistent, and to maintain quality and traceability in their monitoring program.

1.2 Scope

The guideline applies to the sampling of groundwater. It does not cover the sampling of surface water or wastewater. The *EPA Guideline—Regulatory monitoring and testing: Water and wastewater sampling* (EPA 2007) should be consulted for surface water sampling.

For additional information not provided in the above guidelines, the AS/NZS 5667 series of standards and the National Environment Protection (Assessment of Site Contamination) Measure 1999 (NEPC 1999) can be consulted for guidance on a range of hydrological environments.

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

1.3 Intended users

This guideline contains instructions and advice about information required by the EPA to show that groundwater samples collected for analysis are representative of the aquifer from which they were collected.

Those who collect samples for the following purposes should adhere to the approach detailed in this guideline:

- licensees sampling for compliance with regulatory monitoring and testing (RMT) requirements under the Environment Protection Act 1993 (EP Act)
- those collecting and/or analysing samples on behalf of the EPA
- any other monitoring results submitted to the EPA.

This guideline is also intended to provide guidance for sampling and analysing groundwater for any purpose other than the above.

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:

- Murray-Darling Basin groundwater quality sampling guidelines (MDBC 1997)
- Groundwater sampling guidelines (EPA Victoria 2000)
- AS/NZS 5667.11: Water quality—sampling—guidance on sampling of groundwater (Standards Australia 1998b).

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.

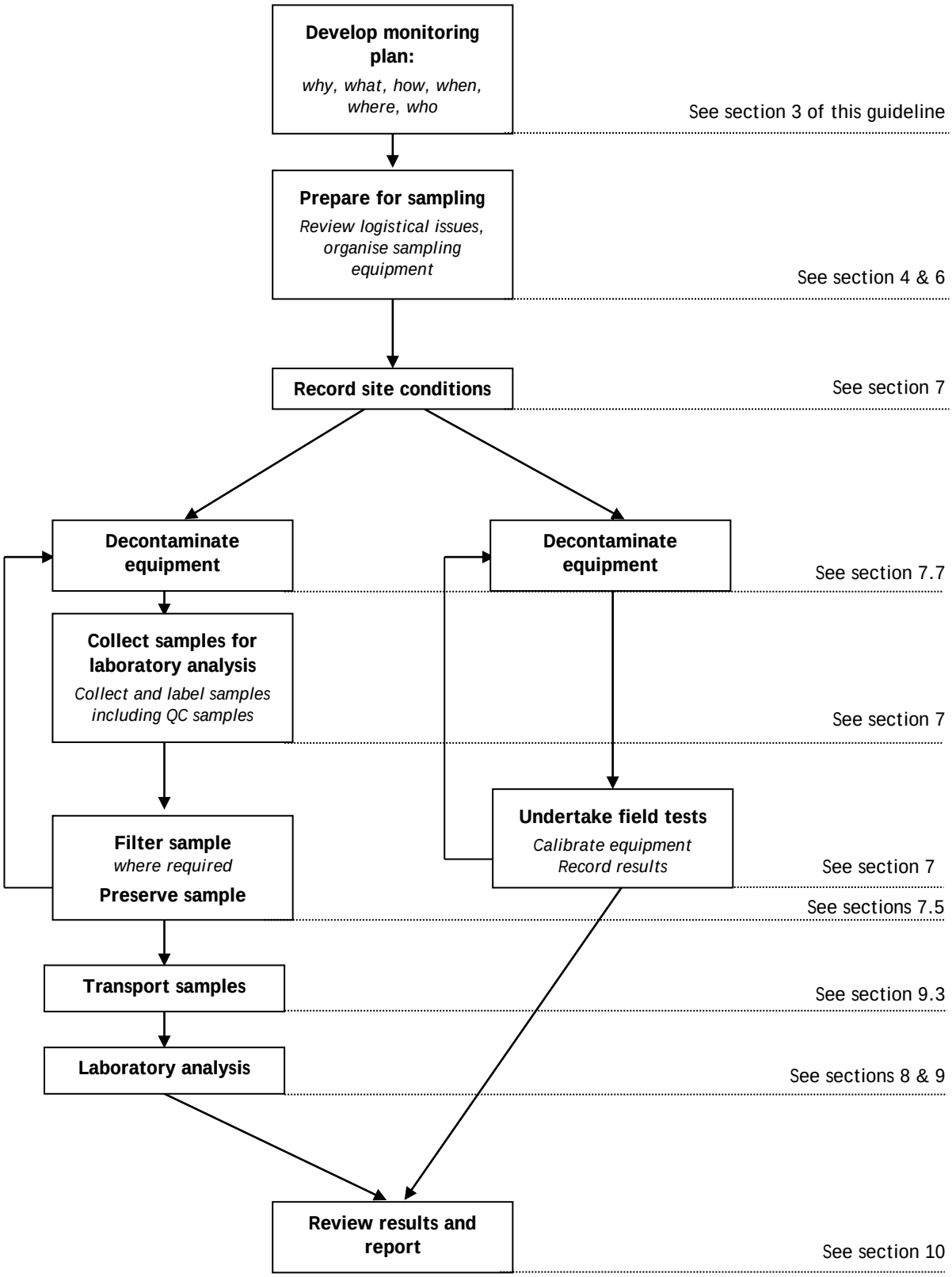

Figure 1 Stages of monitoring

Integrity of samples

To ensure that sampling is consistent, and of good quality, samples need to be representative of the body from which they were taken. If the sample integrity is poor, the information gained could be misleading and ultimately result in mismanagement or pollution of the water 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 losses 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, ie 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) – ie 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 multiple sample locations, duplicate samples, sampling times	Ensure sample collected is representative of aquifer 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 7 and Appendix 6	Yes
	Sample blanks—field, transport, equipment and container	Quantify contamination of samples during sampling process	Section 8 and Appendix 6	Equipment blanks only
	Decontamination of sampling equipment	Minimise contamination	Section 7.7	Yes
Sample filtration	Filtration procedures	Minimise physical and chemical changes to sample	Section 7.5	If field filtration performed
	Filtration blanks	Quantify physical changes and contamination during filtration	Section 8.2 (filtration blanks)	If field filtration performed
Field testing	Equipment calibration	Minimise and quantify bias and error in field equipment	Section 5	Yes
Transport and storage	Appropriate preservation techniques	Minimise physical and chemical changes to sample	Section 9 and Appendix 7	Yes
Analysis	NATA lab accredited for required analysis	Ensure laboratory undertakes appropriate QC including spikes, calibration of equipment	Section 8	Yes

Monitoring Step	QC protocols	Purpose	Refer to	Compulsory for RMT
	Duplicate samples—intra (within) lab	Check variability in lab analysis	Section 8.2	Yes
	Duplicate samples—inter (between) lab	Quantify differences between laboratories' analysis methods	Section 8.2	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

With increasing scarcity of good quality water it is important that the quality, as well as the quantity, of groundwater is managed properly. To protect groundwater resources we need reliable data on which to base management decisions.

The goal of sampling is to obtain a representative sample of groundwater and to maintain the sample's integrity from site to laboratory. The following discussion outlines the key considerations for developing a monitoring plan.

3.1 Monitoring objective

The first step in developing a monitoring plan is to work out the monitoring objectives, that is, what is to be monitored and why. This forms the basis of the design, execution, analysis and data assessment of the monitoring plan. The monitoring objective(s) should be clearly stated in the monitoring plan and when reporting results.

3.2 Preliminary assessment

Once clear about the objective(s), the next step is to make a preliminary assessment of the area where the investigation is to be made. This will help to develop an understanding of the hydrogeology of the area and work out what pollutants might be present. The preliminary assessment will guide decisions when planning monitoring and should be undertaken by a suitably qualified person.

The following information should be gathered as part of the preliminary assessment:

3.2.1 Site history

A site history should provide information that will assist with the effective design of the monitoring program. Information that should be included in the monitoring plan includes: a site plan, current and historical topography, current and historical activities conducted at the site and the potential for contamination from those activities.

3.2.2 Hydrogeological setting

An assessment of the hydrogeological setting to determine the geology of the area and of the aquifer(s) will help develop an understanding of the groundwater flow dynamics in the aquifer(s) and represent it in a conceptual model.

3.2.3 Existing field information

The construction details of the wells that could be sampled should be obtained, as should their geological logs and standing water levels. Information that will be useful includes well the identification number (unit number), well depth, casing diameter (internal) and type, production zone type, internal diameter, depths of production zone interval and well yield. Details of local groundwater use and potential use, ie potential receptors, such as groundwater dependant ecosystems or local groundwater extraction wells, should be investigated.

With this information and a clear understanding of monitoring plan objective(s) an appropriate plan can be developed.

3.3 Monitoring plan development

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. The development of a monitoring plan should undertake by a suitably qualified person.

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

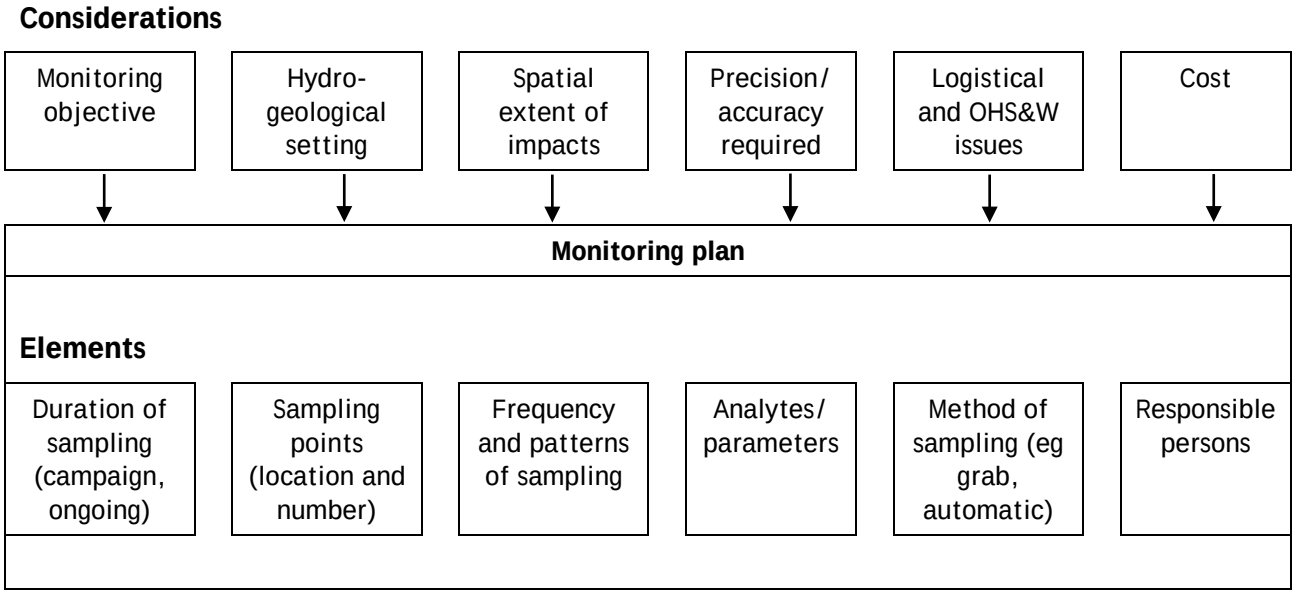

Figure 2 Designing a monitoring plan

The design of a groundwater monitoring plan will be dictated by the monitoring plan objective(s) and the preliminary assessment.

Specific factors will include complexity of subsurface lithology, variability in contaminant characteristics and/or geochemical conditions. For example:

- seasonal fluctuations of water table levels can influence sample timing and frequency of groundwater sampling. eg physical and chemical characteristics may change depending on the time of year
- local hydrological influences, such as large-volume extraction well(s), aquifer type, multiple aquifers, surface water and mounding from recharge or contamination points that may influence the flow dynamics of the aquifer
- the behaviour of potential contaminants, eg different well construction and sampling procedures will be required for light non-aqueous phase liquids (LNAPL) and dense non-aqueous phase liquids (DNAPL).

It should be noted that, regardless of the groundwater sampling approach, few sampling points (eg wells) have zones of influence in excess of a few metres (Puls and Barcelona 1996). Therefore, the spatial frequency of sampling points should be carefully selected and designed to take into account all the above factors.

Requirements for monitoring plans submitted to the EPA are contained within *EPA Guideline—Regulatory monitoring and testing: Monitoring plan requirements* (EPA 2006b). In particular, groundwater monitoring plans must contain the following elements:

- description of the monitoring objective(s)
- supporting information to enable an effective assessment of the adequacy of the monitoring plan. This will include sampling procedure descriptions and well location diagrams
- a sufficient number of wells to enable groundwater flow direction(s) to be determined with confidence. Wells are to be surveyed to a common datum and located in a manner that will allow groundwater flow direction to be determined. A minimum of three wells is required, but it is likely that at many sites more wells will be required
- the inclusion of an up-gradient, control or reference well(s) where there is no potential for effects on groundwater from the activity under investigation
- details of analytes to be sampled
- the frequency of sampling for each analyte
- quality control requirements such as sampling methods, QC sample, Chain of Custody documents, preservation, etc.

4 PLANNING A SAMPLING EVENT

Groundwater by its nature is difficult to access and sampling usually relies upon the use of constructed features (eg wells). Sampling groundwater presents unique challenges and needs careful planning and consideration. The cost of installing and sampling groundwater wells is high. Hence, careful planning can prevent unnecessary expense and can save time.

4.1 Logistics

Groundwater sampling requires the use of specialised equipment in order to have confidence in the data obtained. Careful planning and preparation of a groundwater sampling event is very important and can save time and reduce the number of difficulties that commonly occur during site work.

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 (ie 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, ie as much as practical, move from samples with lowest pollutant concentrations to highest concentrations. Be sure the diameter and depth of the monitoring wells to be sampled is known—the sampling equipment must be right for the job.

6 Check that you have all the equipment required for the sampling event. Select the appropriate sampling method and equipment (eg bailers, low flow pump) based on the potential contaminants and their likely distribution in the aquifer. 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 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
  - sampling area terrain
- 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 DRILLING AND WELL CONSTRUCTION

This section is provided as a general overview to assist those sampling em to identify issues that may directly affect the representativeness of the sample and the criteria to be addressed.

5.1 Permits

In South Australia a permit is required before a well is constructed. Under the *Natural Resources Management Act 2004* (NRM Act), only a licensed driller is permitted to drill a well. Applications for well permits are available from:

Resource Assessment Division
The Department of Water, Land and Biodiversity Conservation (DWLBC)
GPO Box 2834
Adelaide SA 5001
Telephone: 08 8463 6810

Wastewater or drilling fluids **must** be disposed of in accordance with the EPA guideline - *Pollutant management for water well drilling* (EPA, 2003).

5.2 Drilling methods

When selecting a drilling method or sampling an existing well, the potential effects of the drilling method should be considered. Contamination of the borehole and its surrounds needs to be avoided during drilling and construction of the well. Water contaminants, lubricants, oil, greases, solvents, coatings and corrodible materials may affect the suitability of the well for groundwater monitoring, especially when monitoring for contaminants.

To avoid cross-contamination all drilling and sampling equipment should be thoroughly cleaned before commencing drilling. Casing, drilling fluids and any materials used in the bore also needs to be free of contaminants. Casing and screens should be kept in their protective covers until required for installation.

There are many variations in methods used to drill monitoring wells. A driller experienced in the region being investigated can provide valuable advice on the best drilling method. The most common methods are described below with an overview of some of the issues that may affect the sampling of wells drilled using the technique. The selection of a drilling method for a monitoring well should take into account how it may influence analytes chosen for sampling.

When drilling a monitoring well, a geological record should be made by an experienced person able to identify the important features.

5.2.1 Auger drilling

Auger drilling works on the simple mechanical clearing of a hole as it is drilled. Auger drilling eliminates the need for a drilling fluid (liquid or air), and hence the potential influences from an introduced fluid. However, auger drilling has a high potential for smearing material such as clay or contaminants along the hole, thus affecting groundwater flow paths or increasing contaminant concentrations.

There are two major types of auger drilling:

- Solid-flight augers consisting of solid helical flights where extensions are added as the hole is drilled
- Hollow-flight augers consisting of augers that have a hollow centre.

Auger drilling is generally used in soils and soft rock for relatively shallow wells.

5.2.2 Rotary air drilling

Rotary air drilling uses a rotating drill bit combined with circulating air that clears the drill cuttings, blowing them to the surface. The major advantage of rotary air drilling is that groundwater-bearing formations tend to be easily identified when encountered. The disadvantage of rotary air drilling is the potential for oxidation, volatilisation and precipitation of substances of interest. The introduction of high pressure air may also disturb flow paths and hydrochemical profiles in some aquifers.

5.2.3 Rotary mud drilling

Rotary mud drilling works on the same principle as rotary air drilling except that liquid is used as a circulation medium. Rotary mud drilling is used to support an open hole in soft and unconsolidated formations. The use of liquid may influence the formation, and hence groundwater samples, in the following ways:

- drilling fluid may enter the aquifer and impact groundwater quality
- clay particles or other chemical products in the drilling mud may sorb or chemically alter the groundwater properties
- mud may restrict or block groundwater flow paths and hence rotary mud drilled wells may require a longer time to develop.

5.2.4 Cable tool drilling

Cable tool drilling involves lifting and dropping a string of drilling rods with a bit on the bottom that cuts the hole with each blow. The cuttings are retrieved by removing the drilling rods and collecting using a bailer. Cable tool drilling is slow and can compact aquifer material around the hole.

5.3 Well construction

Monitoring wells need to be constructed to a high standard to ensure ongoing and reliable data is obtained over the life of the well. A monitoring well should be constructed in accordance with the document *Minimum construction requirements for water bores in Australia* (National Minimum Bore Specifications Committee 2003) and the minimum construction requirements that are sent out by DWLBC with each well permit titled 'General Specifications for Well Construction Modification and Abandonment in South Australian Pursuant to the Natural Resource Management Act 2004'.

When constructing a well (see Figure 3), the casing material will be determined by the required well depth and monitoring requirements, including the type of contaminants to be monitored. The following materials should be considered, based on what is to be monitored:

- uPVC, stainless steel and fibreglass are suitable for monitoring most organic substances
- uPVC or fibreglass is suitable for monitoring most inorganic substances, particularly in corrosive waters.

The well casing for a monitoring well should have mechanical joints ie threaded coupling with an o-ring seal to avoid contamination by solvents such as uPVC solvent cleaner and cement. Organic-based lubricants (such as hydrocarbons) should not be used on casing joints, drilling rods or equipment when there is the intention to sample for organics.

A gravel pack should be used in screened wells, particularly to avoid siltation when fine-grained aquifers are encountered. The well annulus should be carefully and evenly filled to a level approximately one metre above the screened interval with a graded gravel pack.

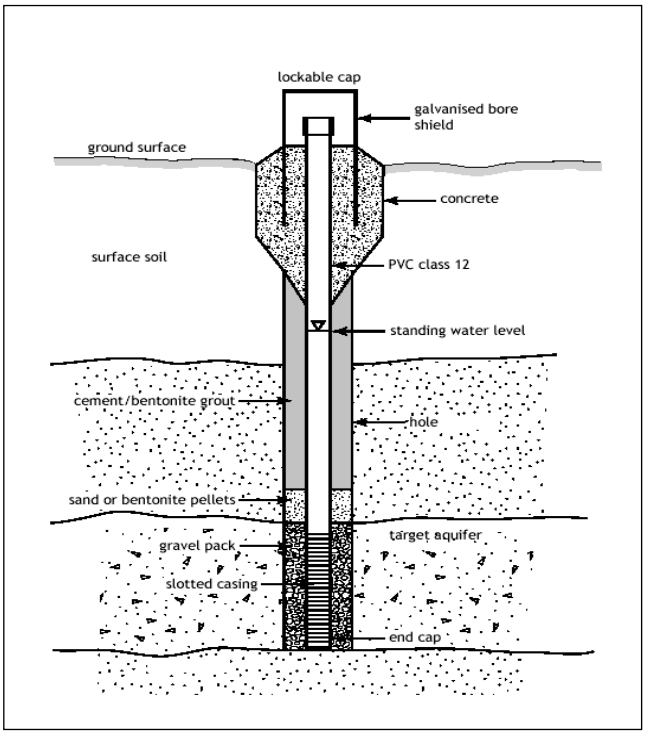

Figure 3 Typical groundwater monitoring well

A cement or bentonite seal at least one metre thick should be placed on top of the graded gravel pack to prevent water movement from the surface or between aquifers. A bentonite seal may be constructed using pellets inserted slowly down the annulus or a cement grout can be used. It should be noted that cement has the potential to cause changes in pH.

Where there is a possibility that contaminants are present in groundwater, or areas of significantly differing groundwater quality exists, extreme care must be taken to avoid contamination or degradation of other aquifers. Wells must be constructed to avoid cross-contamination of aquifers. Particular care needs to be taken when positioning the screen as it can provide a pathway between aquifers.

All wells should be capped with a lockable cap to prevent the ingress of surface water, dust or other foreign matter and to avoid tampering.

The well should be clearly labelled with the well name or ID number.

5.4 Development

Well development is the process used to improve the hydraulic connection between the well and its adjacent formation. The aim is to remove fine sand, silt and clay from the aquifer around the screen and to break down drilling mud (if present) on the borehole wall. By removing fines, the hydraulic connection between the well and the formation can be improved, as well as reducing the quantity of sediment that enters samples.

Well development should be undertaken for all new wells following construction. Following development the well sampling should be postponed for at least 24 hours and may need to be delayed for as long as week until it can be demonstrated that the well chemistry has stabilised. Development can involve the use of various mechanical agitation methods. Some of the more common methods for developing wells are discussed below.

5.4.1 Surging

Development by surging involves surging water in and out of the screen and into the surrounding aquifer by using a surging block or a bailer. If a surging block is used, the well will need to be bailed or pumped to remove the accumulated sediment from the bottom.

5.4.2 Compressed air

Development with compressed air involves jetting air into the screen and filter pack. Air development has the advantage of removing water and fines from the well, which helps the development. However, air development can affect the chemical and physical properties of the groundwater and wells needs to be left for a sufficient amount of time to re-equilibrate prior to

sampling. Also, when using compressed air, an in-line filter should be used to ensure hydrocarbon and metal contaminants do not enter the well from the air compressor.

5.4.3 Pumping

Monitoring wells in permeable formations can be developed by pumping water from the well at a high-flow rate. This method is generally not as effective as the above methods as the flow rates required to remove fines from the well walls are difficult to achieve.

When developing a well, techniques should be used that progress from gentle to vigorous agitation. Rapid dewatering of the well should be avoided in the early stages of development as it may collapse the screen or casing. During development, the well yield should be estimated by monitoring the rate of recovery of water level in the well after pumping. This information can then be used to select suitable methods for subsequent purging and sampling.

6 EQUIPMENT

6.1 Pumping and sampling equipment

The groundwater sampling method chosen will depend on the monitoring objective(s) and site-specific conditions. Site specific conditions that will affect the chosen sampling methods include the type of (suitable) sampling device, the position of the sampler intake, the purge criteria used, and the composition of the groundwater to be sampled (eg turbid, containing high levels of volatile organics, DNAPLs/LNAPLS). All sampling methods and equipment, including purge criteria and field readings, should be clearly documented.

The most important thing to consider when selecting a sampling device is whether it gives consistent results and disturbs the sample to the minimum extent possible. Table 2 details the different types of purging and sampling devices and their advantages and disadvantages. In some cases a different technique may be required for purging and sampling, eg when sampling for volatiles or semi-volatiles, an air-lift pump may be used for purging and a bailer used to sample so as to avoid vaporisation of volatile substances by the pump.

Table 2 Comparison of different purging and sampling devices

Purging and sampling equipment	Advantages	Disadvantages
Bailer	• can be constructed from a variety of materials compatible with substance to be monitored • size can be varied to suit the sampling point • no external power required • easy to clean, or disposable • inexpensive and readily available • low surface area to volume ratio • easy to transport • clear bailers can be useful for observing free water in wells	• time consuming, non-continuous flow • the person sampling the well is susceptible to exposure to any contaminants in the sample • it may be difficult to determine the point in the water column that the sample represents • can be impractical to remove casing storage (stagnant) water in a deep well with a bailer • sample may be aerated during collection in the bailer and transfer from bailer to sample bottle • when used in deep installations, more prolonged sample handling may affect air-sensitive chemical constituents • bailer check valves may fail to function properly • causes considerable disturbance to water column • swabbing effect of bailers that fit tightly in a well casing may allow fines from the formation to enter the well

Purging and sampling equipment	Advantages	Disadvantages
Syringe devices	• neither aeration nor outgassing of the sample is a problem as it does not come in contact with the atmosphere • can be made of inert or any material • inexpensive, highly portable and simple to operate • can be used in small diameter wells • sample can be collected at various depths • can be used as sample container	• inappropriate for collecting large samples • syringes cannot be used for evacuating stagnant water • syringes are relatively new for this application and may not be as readily available as other sampling devices • the use of syringes is limited to water with a low suspended solids content as some leakage may occur around the plunger
Air-lift samplers	• relatively portable • readily available • inexpensive • some are suitable for well development though this depends on yield rate of device	• causes changes in CO_2 concentration and thus is not suitable for pH-sensitive applications • because of degassing of sample it is not appropriate for detailed chemical analyses • oxygenation is impossible to avoid unless elaborate precautions are taken • needs a compressed air supply
Suction-lift pumps	• highly portable • easily available • flow rate can easily be controlled • inexpensive • can be constructed in small diameter • can purge deep wells with high SWL	• limited sampling depth (6–8 m) • loss of dissolved gases and volatiles due to vacuum effect • potential for hydrocarbon contamination of samples due to use of petrol or diesel for running the pump • use of centrifugal pumps results in aeration and turbulence
Gas-operated pump	• can be constructed in small diameter from a wide range of materials • portable • reasonable range of pumping rates • use of inert driving gas minimises chemical alteration	• if compressed air is used as the driving gas, then oxidation may occur causing the precipitation of metals • gas-stripping of volatiles may occur • CO_2 may be driven from the sample and alter pH

Purging and sampling equipment	Advantages	Disadvantages
Bladder pump	• portable, small diameter • non-contact, gas-driven pump that uses compressed air to expand and contract flexible bladder • minimal effect on water chemistry because of non contact • generally easily decontaminated with disposable bladders	• non-continuous flow • time consuming to purge large well volumes due to low-flow rate
Submersible pump	• constructed from various materials • wide range of diameters • readily available • high pumping rates are possible for evacuation of large volumes • provides a continuous sample over extended periods • 12V pumps are relatively portable	• conventional units cannot pump sediment-laden water without damaging the pump • small diameter pump is relatively expensive • some submersible pumps are too large for 50 mm diameter wells • may need to be able to pump at a low rate for sampling and a high rate for purging
Inertial pump (foot pump)	• simple construction, inexpensive • manual, gas or electric motor driven • good for sediment clogged wells • if dedicated, it avoids cross-contamination	• for use primarily in small diameter wells, as large wells increase the possibility of tubing sway • works optimally with deep installation of tubing • low flow capacity

Source: Modified from Murray-Darling Basin groundwater quality sampling guidelines (MDBC 1997), page 11

Purging and sampling equipment should be constructed from inert materials (eg stainless steel, Teflon®, glass) that will not contaminate the sample. The tendency for organics and metals to sorb into and out of many materials makes the selection of sample equipment critical when sampling trace concentrations.

Some sampling equipment is disposable, while other elements will need decontamination between samples. Decontamination is discussed further in Section 7.7. If choosing disposal equipment such as bailers and tubing, the equipment must be disposed of in accordance with the contamination risk.

It should be noted in instances where low-flow pumping and sampling are required, the pump should have a variable flow rate. Caution should be taken with some pumps that may heat up and affect the physical and chemical properties of the sample when run at low flow rates.

The following are important practical considerations that need to be taken into account when selecting a sampling pump:

- the depth of the standing water level (SWL) is important, as the deeper the SWL the more head the device must overcome to deliver the sample to the surface. Note also that the SWL may be increased due to draw down during pumping
- the well needs to be able to accommodate the sampling device; the smaller the diameter of the well, the more limited the options
- some pumps are easier to operate, clean and maintain than others
- being easy to service in the field is a distinct advantage
- reliability and durability is important as groundwater sampling devices are often operated for long periods, under heavy loads and in restricted spaces
- decontamination between sampling each well will need to be straightforward

6.2 Sampling containers

Containers used for collecting samples must not affect the integrity of the sample. As a result, specific container types are used for different analytes. Additionally, there are a number of treatments that are applied to containers to further reduce the chance of sample contamination. Appendix 2 provides guidance for container selection and treatments by analysis type. Sample containers are generally obtained from analytical laboratories.

7 SAMPLING METHODS

7.1 Groundwater levels

Standing water level (SWL) should be measured before purging and sampling. The SWL should be measured with a purpose-built tape or meter, and from a permanently marked reference point generally at the top of the casing.

Groundwater levels from different wells in the same aquifer may be used to determine the hydraulic gradient between the wells and allow the direction of lateral flow to be determined. The hydraulic gradient from wells in different aquifers should not be used to determine lateral flow. (However, this information may make it possible to calculate vertical flow.) With three or more wells, spaced roughly equally apart in a triangular arrangement groundwater flow direction can be estimated. This information is used, with other supporting information described in Section 3.2, to determine the hydrogeological setting.

When calculating flow direction, water levels should be taken on the same day or at shorter intervals if they are influenced by the tide. Groundwater flows may vary significantly over time. A groundwater contour map should be generated from several sampling events to find the direction of flow and variability across the site. Groundwater contours cannot be constructed unless all the wells used have been surveyed to a common datum.

Non-aqueous phase liquid (NAPL) levels can be measured with an interface probe, although there are other matters to be considered, which are discussed in Section 7.6.

The depth of the well is used to determine the volume of the well. If possible, depth of the well should be measured 24 hours before sampling, as a weight or tape hitting the bottom of the well may make the water turbid. Where the depth of the well is known from construction details or previous sampling this depth can be used and checked after the completion of sampling.

7.2 Measuring field parameters

Some parameters cannot be reliably measured in the laboratory as their characteristics change over a very short time scale. Temperature is the best example of this. Water temperature will begin to stabilise to the new ambient temperature as soon as the water is removed from the well. Thus, temperature must be measured in situ.

Parameters that should be measured in the field include temperature, dissolved oxygen, pH, conductivity, salinity, turbidity and redox potential. These can be reliably measured using a multi-parameter meter—usually with an electrode for each parameter. It is crucial to calibrate the meter accurately before using it, and regularly during use. Calibration procedures vary between meters and between manufacturers so it is important to follow the instructions supplied with the equipment.

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.

Ideally, parameters should be measured in situ, using down-hole water quality meters. However, this is often impractical. A flow-through cell should be used to prevent contact between the sample and the atmosphere. A flow-through cell will also provide for continuous measurement.

Where a flow-through cell is not available, the discharge tube should be placed at the base of the measuring container to minimise exposure to the atmosphere.

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.

7.3 Purging

Stagnant water that has been standing in the well casing can be different, both physically and chemically, from the aquifer water. Hence the well must first be purged before a representative sample can be obtained. Well purging introduces fresh groundwater into the well that is representative of the aquifer (or geological unit). The following sections detail purging methods. Each method has advantages and disadvantages and should be selected based on the monitoring objective(s) and the hydrological assessment.

7.3.1 Well-volumes method

The well-volume method is a simple reproducible sampling technique that aims to provide confidence that the sample collected is representative of water quality of the screened aquifer. The resulting sample is generally representative of a flow-weighted composite of the screened interval, and thus integrates small-scale vertical heterogeneities of groundwater chemistry (Yeskis and Zavala 2002). This sampling technique is useful for detecting subsurface contaminants. However, the detection of a contaminant at a low concentration in a thin, contaminated zone with long well screens may be difficult; vertical profiling techniques should be used here. This technique should not be used to purge aquifers contaminated by either LNAPLs or DNAPLs.

Pump placement

Where the standing water level (SWL) is above screen level, the purging pump should be above the screen. This will have the effect of vacuuming out the stagnant water and cause less stress on the screened section.

Where the SWL is within the screen, the pump should be placed at least one metre above the bottom of the well to avoid disturbing fine material on the bottom.

Purging method

To determine the volume of groundwater required to be purged the following calculation is used:

$$\text{Well Volume (kL)} = h \times \pi \times \frac{d^2}{4}$$

where h = height of the water column in the well (m)
d = inner diameter of the casing (m)

A minimum of four well volumes must be purged when using this method, although the actual number of well volumes removed will be based on the stabilisation of water quality parameters. It is best to use a flow-through cell when measuring the water quality parameters. Stabilisation is achieved when three successive measures of at least three parameters differ by less than the acceptable ranges listed in Table 3. Three successive measurements are defined as measurements taken at an interval corresponding with the purging of one half a well volume.

Table 3 Requirements for stabilisation

Parameter	EC	pH	Temp(°C)	DO	redox
Acceptable range	5%	± 0.1	0.2	10%	± 10 mv

Purging should be documented as discussed in Section 8.

At sites where the purged groundwater is known, or suspected, to contain contaminants, the water must be disposed of in a manner that does not allow it to enter the stormwater system or contaminate soil. The EPA guideline *Pollutant management for water well drilling* (EPA, 2003) can assist with the correct disposal of purge water.

7.3.2 Low-flow purging

Low-flow purging uses pumping at low-flow rates. This minimises drawdown of the static water table, and draws the water directly from the formation, thus avoiding the need to remove large volumes of stagnant water. Samples are collected directly from the pumping mechanism with minimum disturbance to the aquifer.

Low-flow purging can also significantly reduce the volume of purge water produced. This method has the advantage in that it can limit vertical mixing and vaporisation of volatile organic compounds in solution in the well casing, or borehole, as compared with high-flow purging and sampling. Low-flow purging generally reduces turbidity during purging, hence is suited to situations where the target parameters could sorb to particulate matter.

Low-flow purging is generally most effective with short screened intervals eg 1.5 to 9 m. This purging method is generally not suitable for:

- aquifers with very low hydraulic conductivities where minimal drawdown cannot be maintained
- long screened intervals (eg >9 m) or open-hole wells where the hydraulic flow pathways are unknown
- use were the aquifer is contaminated by either LNAPLs or DNAPLs.

Pump placement

Dedicated pumps are preferable for low-flow sampling as portable pumps will disturb the water column when lowered into the well; resulting in longer purge times to reach stabilisation. Care should be taken to minimise the disturbance of the water column when using a portable pump.

Generally the pump intake should be positioned in the mid-point of the screened or open zone. It should be noted that the flow within a well will be dominated by the hydraulic conductivity of the aquifer layers rather than the pump position resulting in a flow weighted sample.

If the substance(s) of interest are known to accumulate either near the top or bottom of the screen, it may be appropriate for the pump to be positioned closer to this zone.

Similarly, if there is a particular geological interval of interest then the pump should be positioned adjacent to that zone.

Purging method

The following method must be followed when low-flow purging:

- calibrate all equipment
- remove well cap and monitor head-space if volatile organic compounds (VOCs) are suspected
- measure the SWL from a surveyed reference point
- assemble the pump, ensuring that the pump and tubing do not come in contact with contaminated soil or other surfaces. It is preferable that the tubing length matches the

required depth of the pump. Excessive tubing may cause temperature changes and hence chemistry changes in the sample

- place pump in the screen, taking care to minimise disturbance to the water column
- connect the flow-through cell
- start the pump and adjust the flow so that there is minimal drawdown. The aim of flow purging is to establish a stabilised pumping rate while minimising the drawdown in the well. Water level needs to be measured continuously until an equilibrium between the flow rate and drawdown level is established. Flow rates are typically 0.1–0.5 L/min, with a drawdown generally less that 0.1m. (Puls & Barcelona 1996)
- once the flow rate is established and stabilised, stabilisation parameters can be measured to determine when purging is complete. Dissolved oxygen and electrical conductivity are the most reliable indicators used to decide when stabilisation has been achieved. Indicator parameters are considered stable when three consecutive readings fall within the ranges presented in Table 3. The three consecutive reading should be at least three minutes apart, or the time taken to evacuate the equivalent of one volume of the flow-through cell (whichever is greater).

When using low-flow purging, the following details should be recorded to support the method:

- construction details of the well
- depth of pump intake during purging and sampling
- flow rate
- draw-down distance required to achieve equilibrium
- purging time
- details of the stabilised parameters.

It is recommended that the Groundwater Sampling Record Sheet in Appendix 5 is used as a record for low-flow purging.

7.3.3 Purging low recharge wells

Low-yielding wells can be difficult to purge. Where possible, a low-flow purging method should be used or purging numerous times to avoid the exposure of the screen. However, it is recognised that in certain cases it is impractical to use the traditional purging methods.

Where stabilisation is not achievable, the well can be sampled without further purging. Ideally, the sample collection would entail acquisition of a sample with no or very little purging using a dedicated sampling system installed in the screened interval or a passive sample collection device (Puls & Barcelona 1996).

An alternative is to purge the well dry, however purging a well dry can affect the representativeness of the sample as a result of oxidation during exposure of the screened interval to the atmosphere. When a well is purged dry, the sampler (and the end-user of the data collected) needs to understand the limitations of the data collected, eg there is a potential for underestimation of contaminant concentrations for volatile organics and metals. The purging dry of a well should be documented on the Groundwater Sampling Record Sheet (see Appendix 5). It should be noted that rarely is a well purged completely dry therefore it is good practice to allow 75% recovery before sampling.

It is suggested that two sets of samples are collected, one of the stagnant well water and one of groundwater after recovery from purging and a comparison of both the samples is made. Hence a conservative approach can be used when interpreting the results on the basis of the monitoring objectives.

7.4 Collecting a sample

The sampling method used will depend on the goal of the monitoring plan and should take into account possible influences on the parameters being sampled. For consistency, the same sampling and purging methods should be used each time the wells is sampled, unless a different method would improve sample quality and data precision.

The following matters need to be considered and will directly affect the sample quality (these are also relevant to the choice of purging device):

- the sampling device should cause minimal physical or chemical alteration to the sample. It is important that the device does not cause degassing, aeration, volatilisation, oxidation, sorption or precipitation as a result of:
  - transporting the sample to the surface
  - the sample interacting with the materials from which the device is constructed
  - transferring the sample to its container.
- to gain the most representative data, it is recommended that sampling devices are constructed from inert materials such as stainless steel or Teflon®. Flexible components such as tubing should be PVC or polyethylene and ideally be Teflon® coated. However, the materials selected will depend on the sensitivity of the information required.
- when sampling with a pump, the flow rate should not be increased. If a flow-through cell is being used it should be disconnected or bypassed during sample collection as the water quality probe may alter the chemistry of the sample.

Table 2 provides information on the suitability of sampling devices for contaminants of concern and their potential effect on sample quality.

7.4.1 Passive samplers

In-situ or passive sampling devices are often used for monitoring subsurface gases such as VOCs. One type of passive sampler is a diffusion cell, which is generally a gas-filled, hollow-fibre membrane that is either connected directly to sensors in the probe or to sensors at the surface. The second main type of passive sampling is the grab sample method in which the sampling device is left in the well until suitable ambient conditions are achieved, at which time the device is deployed to capture the sample.

Passive samplers have the advantage of needing no pumping, therefore minimising disturbance of groundwater. They also provide the opportunity to measure the vertical stratification of water quality in a well. However, sampling for stratification can often be complicated by the vertical flow within the well.

The use of passive sampling devices requires confirmation that there is sufficient ambient flow through the screen interval. This can often be a time-consuming and expensive exercise.

7.4.2 Bacterial sampling

The following procedure should be used when sampling bacteria in groundwater:

- use only prepared sterile containers, preferably borosilicate glass. Do not rinse micro sample bottles
- use clean, sterile equipment
- do not remove the lid from the container until it is time to take the sample
- it is suggested that, as part of the decontamination process, the end of the discharge hose is sprayed with 70% ethanol or sodium hypochlorite, which is allowed to evaporate

- when taking a sample, take care not to touch the bottle tip or stopper with the delivery pipe or fingers. Samples can also be taken by lowering the bottle down the well, but take care not to touch the side of the well with the sample bottle
- record the ambient temperature of the aquifer that the sample was collected from (this will help with designing suitable laboratory culturing procedures)
- leave an air gap for any samples collected that require laboratory culturing and identification. Seal and store in the dark in a suitable container such as an esky that minimises the chances of the sample undergoing undue temperature fluctuations, but do not put on ice as that may cause too much of a temperature change
- it is advisable to take replicate samples as it is often found that bacteria are not detected in every sample from a well.

7.4.3 Biota (stygofauna) sampling

The science of groundwater biota, or stygofauna, is an emerging field and, as such, there is no standard method with which to sample.

It is advisable that when sampling for biota or stygofauna that the sampler attempt to preserve as many of the conditions in the sample container that were present in situ (for example temperature, darkness, pH, contact (or lack of contact) with air). For further information contact the EPA.

7.5 Filtration of samples

Whether samples need to be filtered depends on the monitoring objective(s). Ideally, the well construction, purging and sampling techniques used should minimise the turbidity of the groundwater sample so that there is no need to filter. However, there may be occasions when it is necessary to filter samples in the field to preserve certain parameters and prevent their alteration during the delay between sampling and analysis. Filtering may also be necessary to separate the soluble component for examples dissolved metals, from the rest of the sample.

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.)

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.

The procedure for filtering with a syringe is a follows. The sample should be drawn into the syringe directly from the sample container (and discharged to flush the syringe). A second sample is then drawn into the syringe and a 0.45 µm filter attached to the syringe. A pre-filter is recommended for turbid samples to avoid clogging the 0.45 µm filter. The sample can then be passed through the filters and the filtrate retained in a clean container. Care should be taken to ensure that the filters are changed as they have a tendency to clog. Excessive force may rupture filters or affect the properties of the sample.

Open sample containers are prone to contamination, particularly in dusty and dirty field environments. It is important when filtering samples in the field to take care to minimise the

chance of contamination by selecting a clean work environment and replacing caps on sample containers immediately.

7.6 NAPLs sampling

Non-aqueous phase liquids (NAPLs) are among the most common groundwater contaminants. They are typically found in areas where large volumes of hydrocarbons, solvents or other liquids of low solubility in water were used, handled, disposed of or stored. NAPL contamination occurs when these solvents or liquids are released below the surface. A typical scenario for this is when the metal skin of an underground storage tank containing solvent rusts and the contents of the tank leak into the ground.

There are two kinds of NAPLs: light non-aqueous phase liquid (LNAPL) and dense non-aqueous phase liquid (DNAPL). Due to their low solubility in water, NAPLs travel through the ground as a separate liquid phase, resulting in complex multi-phase clean-up problems. Sampling of NAPLs is a specialised subject and a detailed methodology is beyond the scope of this guideline. However, some of the issues that should be considered before sampling NAPLs are as follows:

- the well should be constructed to ensure that the target aquifer, normally the water table, is within the slotted interval of the well
- NAPLs may have a detrimental effect on plastic equipment such as PVC casings
- where a well has been installed to monitor NAPLs, prior to purging, the well should be monitored for the presence of separate phase product using equipment such as an oil—water interface probe
- a bailer is an effective means of collecting a sample of a LNAPL
- when purging a well that contains a NAPL, the purged water must be collected and disposed of by an appropriate method
- any equipment that is used when sampling NAPLs should be thoroughly decontaminated—the use of disposable equipment may be appropriate
- LNAPLs will be subject to smearing with rise and fall of the water table. Hence, the thickness of the LNAPL may not represent the quantity of LNAPL within the aquifer.

7.7 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 equipment particularly the purging system, for each well to reduce the risk of cross-contamination.

Any equipment that comes in contact with groundwater must be thoroughly decontaminated between sample collection and at the end of each sampling trip.

The following methods should be used when decontaminating sampling equipment:

- the equipment should be cleaned with decontamination solution and water, followed by multiple rinses with distilled water
- decontaminate the pump away from the sampling site
- place plastic sheets around the sample site to prevent contamination from ground material
- wear clean, sterile gloves and protective clothing when decontaminating
- prepare detergent solution in a large container or bucket. Put pump into container and pump until the pump hose is full of detergent solution
- specific cleaning solutions will depend on the contaminants being investigated, as follows:
  - for a general range of analyses phosphate-free detergent should be used
  - 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 solution of 10% nitric acid is recommended
- when sampling for microbiological parameters, bleach should be used to sterilise equipment between sample points (however, bleach is not to be used if sampling for chlorine). Subsequent to flushing with bleach, pump distilled water through the pump and line and rinse the external hose. Similarly, rinse the bailer. If distilled water is not available, then potable water may be used as a second choice
- if using a bailer, run several litres of detergent solution through the equipment
- collect an equipment blank sample, ie a sample of contaminant-free water after it has been pumped through the system. This is part of the QA/QC procedure to check on the effectiveness of the decontamination process (see Section 9.2)
- if contamination is suspected, the wastewater from the decontamination process may need to be contained and disposed of to a treatment facility. If this is the case, the water must not be disposed of to groundwater or surface local drainage.

8 SAMPLE IDENTIFICATION, TRANSPORT AND STORAGE

8.1 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 example in Appendix 5).

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 a sampling 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.

8.2 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.

8.3 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.

8.3.1 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.

8.3.2 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.

9 QUALITY

9.1 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 4 outlines a systematic approach to the development of a QA program for sampling.

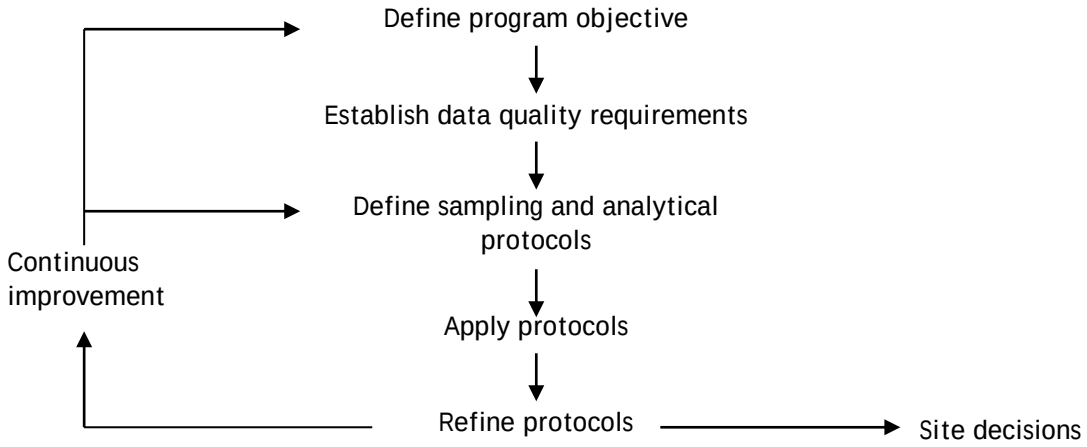

Figure 4 Quality assurance framework (Puls & Barcelona, 1996)

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.

9.2 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.

Appendix 6 states the minimum type and number of sample blanks and duplicates that must be taken for monitoring and testing required by the EPA (ie 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.

9.2.1 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.

9.2.2 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.

9.2.3 '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.

10 ANALYSIS, DOCUMENTATION AND REPORTING

10.1 Sampling documentation

The following minimum information must be recorded on a Groundwater Sampling Record sheet:

- location and well identification
- time and date of sampling
- weather conditions such as rain, sun, wind
- standing water level and well depth
- calculations of well volume (if applicable)
- purging and sampling method used
- field measurements and stabilisation criteria
- physical properties of the sample—turbidity, odour, colour
- flow rate of purging and volume purged, with the corresponding purging time
- well construction details
- sample code.

An example of a Groundwater Sampling Record sheet is provided in Appendix 5.

10.2 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 indicates 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.

10.3 Reporting

When submitting groundwater data to the EPA, the data **must** be accompanied by supporting information. When submitting a report, refer to the *EPA guideline—Regulatory monitoring and testing: Reporting requirements* (EPA 2006).

The supporting information must include:

- site identification, including site plan and survey data
- the monitoring objective
- reference to the monitoring plan
- sampling methodology (see Section 10.1)
- geological setting including local lithology (where available)
- groundwater level results including survey data (mAHD) and flow direction
- assessment criteria
- QA/QC evaluation
- interpretation and conclusions of results.

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GLOSSARY

AS	Australian Standard
Analyte	Refers to any chemical compound, element or other parameter as a subject for analysis
Aquifer	Permeable rock or sediment in a geological formation, or group of formations, or part of a formation that can transmit water
Biota	Plants, animals, including humans, fungi or bacteria
Casing	A tube used as temporary or permanent lining for a well□
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
EPA	South Australian Environment Protection Authority
Filtrate	The liquid portion of a sample after filtration
Heterogeneous	Made up of a variety of differing materials or having a number of different characteristics
Homogeneous	Having essentially uniform characteristics of composition, texture and appearance
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.
Hydraulic gradient	The change in the static head (of groundwater) per unit distance in a given direction

Hydrologeological assessment	The study of groundwater, especially the distribution of aquifers, groundwater flow and groundwater quality
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
NAPLs	Non aqueous phase liquids
NATA	National Association of Testing Authorities (of Australia) <www.nata.com.au>
NEPM	National Environment Protection Measure
Packer	A device placed in a well that plugs or seals the well
Permeability	The capacity of a porous medium to transmit water
Pollutant	Something that pollutes, such as sewage or mine waste, exhaust gases, etc
Purging	The act of evacuating (removing) stagnant water from a well. This includes water in the blank casing, screened casing, and filter pack
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)
Recovery	The measure of a well's return to its standing water level after purging
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
Screen	A special form of well liner used to stabilise the aquifer or gravel pack while allowing the flow of water through the well into the casing and permitting development of the screened formation
Screen interval	The area of an aquifer in which the screen has been positioned and hence from which groundwater may be drawn from.
Spike recovery value	A percentage indicating the detected concentration of a known volume of analyte over the known value
Stygofauna	Animals that live in aquifers
SWL	Standing water level - the depth to groundwater from the marked reference point, generally the top of casing.
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
Well (bore)	A hole drilled into an aquifer for the purpose of monitoring or extracting water. Another common term is 'bore'
Well development	The removal of fines (including drilling mud) from the aquifer immediately surrounding the well to create a filter zone around the well that prevents further movement of aquifer particles into the well

APPENDIX 1 SUMMARY OF QUALITY CONTROL 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.

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	

Analyte	Container type	Typical volume (mL)	Filling technique	Filtration and preservation	Holding time	Notes
inorganic (non-metallic)						
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

Analyte	Container type	Typical volume (mL)	Filling technique	Filtration and preservation	Holding time	Notes
nitrate	plastic or glass	250		field filter through 0.45µm cellulose acetate membrane and freeze	1 month	
				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)	

Analyte	Container type	Typical volume (mL)	Filling technique	Filtration and preservation	Holding time	Notes
nitrogen, total	plastic or glass	500		refrigerate or freeze	24 hours—1 month	
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	

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
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

Analyte	Container type	Typical volume (mL)	Filling technique	Filtration and preservation	Holding time	Notes
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						

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 SAMPLING PLANNING CHECKLIST (EXAMPLE)

Parameter	Reference	Preparation check	Execution check
Permissions to access land and wells for sampling or drilling			
Coordination with laboratories • sample containers • laboratories are prepared for samples • all paperwork required • QA/QC			
Equipment • see equipment checklist • ensure all sampling equipment is available and in working order • calibration of meters			
Site work • monitoring plan • safety plan • site plan, maps, diagrams • hydrological assessment • details of wells o construction details o SWL information • sampling o sample frequency o sample location o analytes			
Sample transportation • sample preservation • holding times • Chain of Custody • transport of samples (eg couriers, bus)			

APPENDIX 4 FIELD EQUIPMENT CHECKLIST (EXAMPLE)

Equipment list	Check	Equipment list	Check
Documentation		**Field filtration**	
Monitoring plan including site plan		Filtration apparatus, syringe etc	
Appropriate area maps		Filters	
Well records		**Kit bag/tool box**	
Field notebook/record sheets / Purge sheets		Tools—spanner/shifter/Stillson wrench/screw drivers	
Chain of Custody sheets		Spare pump motors	
Purging/Sampling equipment		Paper towel	
Water level probe and batteries		Disinfectant wipes	
Water quality meter		Ziplock bags for samples	
Standards to calibrate the water quality meter		**Safety equipment**	
Flow-through cell		First-aid kit	
Bailers & cord		Mobile phone/communication equipment	
Sample containers (including containers for duplicates and blanks)		PPE— wide brimmed hat wet weather gear disposable overalls	
Pump & Tubing		Sunscreen/sunglasses	
Labels for samples		**Sample storage and transport**	
Disposable gloves		Eskies and ice	
Quality control samples		Packing tape	
Field blanks		Address Labels (eskis)	
Transport/equipment blanks		Courier information	
Decontamination		**Other**	
Clean work area, eg plastic groundsheet		Other equipment for site specific or remote area requirements	
Buckets		Keys for gates/wells	
Demineralised/deionised water		GPS and batteries	
Detergent solution		Tools—spanner/shifter, etc	
Sponges, scrubbing brush		Digital camera and batteries/ charger	

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

APPENDIX 5 FIELD CALIBRATION RECORDS (EXAMPLE)

Calibration record sheets should be developed and maintained for each field meter. The example below is designed for a multi parameter meter measuring pH, DO, conductivity and temperature.

	Pre-calibration reading							Reading in check solution					DO membrane changed (2-monthly)
Date	**pH standard 1**	**pH reading**	**pH standard 2**	**pH reading**	**Cond. standard**	**Cond. reading**	**Temp °C**	**pH check solution**	**pH reading**	**Cond. Check solution**	**Cond. reading**	**Initials**	**Signature**

APPENDIX 6 GROUNDWATER SAMPLING RECORD SHEET (EXAMPLE)

Site details

Date: _____ Location: _____

Well ID: _____ Unit (DWLBC) Number _____

Well details:

SWL (Start): _____(m) Casing material: _____

Drill depth: _____(m) Screen length: _____(m)

Casing diameter: _____(m)

Purging:

Purge method: _____ Well volume: _____(L)

Time started: _____ Min purge Vol : _____(L)

Time stopped: _____ Pump depth set at: _____(m)

Flow rate: _____(L/min) Flow cell used: Y / N

Sampling:

Sampling method: _____ Date Sampled: _____

Time sampled: _____ Sampled By: _____

Field analyses:

Observations (colour, odour, etc)	Time (mins)	SWL (m)	Volume (L)	Cond (mS)	pH	Temp ^{o}C	DO (ppm)	Redox (mV)	Turbidity (NTU)

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					