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Baskaran Sundaram, Andrew J. Feitz, Patrice de Caritat, Aleksandra Plazinska, Ross S. Brodie, Jane Coram and Tim Ransley

Record
2009/27
GeoCat # 68901

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GEOSCIENCE AUSTRALIA
RECORD 2009/27

by

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Australian Government
Geoscience Australia

Department of Resources, Energy and Tourism
Minister for Resources and Energy: The Hon. Martin Ferguson, AM MP
Secretary: Mr John Pierce

Geoscience Australia
Chief Executive Officer: Dr Neil Williams PSM

ISSN 1448-2177
ISBN 978-1-821672-08-8 (Hardcopy)
ISBN 978-1-921672-07-1 (Web)

GeoCat # 68901

Bibliographic reference: Sundaram, B., Feitz, A., Caritat, P. de, Plazinska, A., Brodie, R., Coram, J. and Ransley, T., 2009. Groundwater Sampling and Analysis – A Field Guide. Geoscience Australia, Record 2009/27 95 pp.

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1. Introduction

Groundwater resources support many urban, rural and remote communities around Australia. Aquifers are a source of water for drinking, irrigation, stock supply, bottling and many other uses, accounting for over 30% of Australia's total water consumption (NWC, 2008). As industrial and agricultural development of Australia increases, the demand for water also steadily grows. In some parts of the country, the current rate of groundwater extraction is depleting the resource faster than it is being recharged. Therefore understanding the basic processes about groundwater as well as the factors that can affect its quantity and quality is of vital importance in managing this significant resource. Monitoring provides data on groundwater quantity and quality and is an integral aspect of groundwater management. Sampling of groundwater for analysis of its chemical constituents is part of this strategy. Ideally, such sampling and analysis should be carried out on a regular basis where groundwater is being extracted for a variety of uses. Depending on the purpose of monitoring, different parameters can be tested.

Surface water quality sampling procedures have been developed over the past 50 years and are very well documented. Groundwater sampling requirements and goals are often quite different to those of surface water sampling and there has been less emphasis in the past to define a set of standards applicable to groundwater. The objective of groundwater sampling is to obtain a sample with minimum disturbance to the in situ geochemical and hydrogeological conditions.

There exist publications by the State agencies on groundwater sampling (Jiwan and Gates, 1992; Rayment and Poplawski, 1992; Vic EPA, 2000; SA EPA, 2007), groundwater quality sampling in the Murray-Darling Basin (MDBC, 1997), groundwater monitoring for community groups (Waterwatch, 2005) and sampling for contaminated sites (AWRC, 1991). Although these documents are very relevant to the specific issues they address, there is a need to provide a comprehensive set of sampling guidelines that can be used as a standard generic guide across a range of geoscientific disciplines. This recognises that groundwater sampling and analysis is an activity within projects dealing with carbon capture and storage, mineral exploration, geothermal and energy resources, as well as for groundwater resource assessment and management.

The purpose of this field guide is to present a set of standard groundwater sampling protocols that focus on a range of groundwater quantity and quality issues throughout Australia. A uniform, accurate and reliable set of sampling procedures will foster the collection of comparable data of a known standard. Ultimately, this allows for greater confidence in the interpretation of any field based data. This guide does not cover the aspects of core sampling, geological grain size analysis, pore fluid extraction and analysis.

1.1 WHY GROUNDWATER SAMPLING?

Groundwater sampling can be undertaken for a variety of reasons. For example, the information derived from groundwater sampling, and the ensuing analyses and interpretations of the hydrochemical and isotopic results could significantly assist in the:

- identification of the aquifers intercepted by water bores
- determination of leakage and hydraulic connection between aquifers
- assessment of groundwater movement and flow patterns
- understanding of recharge-discharge mechanisms
- determination of the nature of surface water and groundwater interconnectivity
- identification of the magnitude, sources and transport of salt, nutrients, pesticides and other contaminants
- delineation of natural discharge and environmental use (such as base-flow)
- identification and evaluation of groundwater-dependent ecosystems
- evaluation of baseline groundwater quality and the relevant beneficial uses of the groundwater resource
- understanding of the evolution of the groundwater chemistry and flow patterns, and possible causes for groundwater quality changes
- assessment of the impact of land use changes, irrigation and groundwater extraction on the regional groundwater quantity and quality
- developing groundwater as an effective sampling medium for mineral exploration
- assisting in the characterisation of geothermal resources and technical issues associated with their development, and
- assisting with site selection and monitoring of geologically stored CO_2.

1.2 SCOPE OF THIS GUIDE

This guide has been developed to provide sufficient information to plan and carry out field groundwater sampling of a high standard, ensuring that only representative, high integrity samples are collected and submitted for laboratory analysis. The main aims of the guide are to:

- provide a comprehensive practical overview covering the basic elements of effective groundwater sampling
- provide simple and efficient methods for monitoring groundwater systems, and
- outline procedures for sampling from the bore site to delivery to the laboratory.

2. Groundwater Hydrogeochemistry and National Water Quality Guidelines

2.1 GROUNDWATER HYDROGEOCHEMISTRY

Groundwater contains a variety of chemical constituents at different concentrations. The greater part of the soluble constituents in groundwater comes from soluble minerals in soils and sedimentary rocks (Waterwatch, 2005). A much smaller part has its origin in the atmosphere and surface water bodies. For most groundwaters, 95% of the ions are represented by only a few major ionic species: the positively charged cations sodium (Na^+), potassium (K^+), calcium (Ca^{2+}) and magnesium (Mg^{2+}), and the negatively charged anions chloride (Cl^-), sulfate (SO_4^{2-}), bicarbonate (HCO_3^-) and nitrate (NO_3^-). These ionic species when added together account for most of the salinity that is commonly referred to as total mineralisation or total dissolved solids (TDS).

Chemical signatures of groundwater, in terms of concentrations and isotopic ratios, can be used to understand groundwater processes. Isotopic methods have received a great share of attention as tracers in hydrogeology, but it is important to validate any interpretation with other chemical, hydraulic, geophysical or geological approaches. Since most hydrogeological situations are complex, a multi-parameter approach is often advantageous. In many instances, the hydrogeochemistry may be used effectively to derive parameters such as recharge, discharge and mixing rates. For example, changes in the groundwater chemistry can be used to track the movement of water, yielding information such as water residence time in the saturated zone, identifying recharge processes and the source of recharge water. The unsaturated zone is a special case where major ion composition, particularly chloride concentrations, can play a major role in recharge studies, providing quantitative estimates that are difficult or costly to measure using other methods.

The potential applications of inorganic chemical tracers are shown conceptually in Figure 1. Fluxes of solutes from rainfall and runoff are shown (natural and anthropogenic) as well as reactions within the soil and in the saturated zone. Note the distinction between open system and closed system with respect to the gas phases (principally carbon dioxide, CO_2, and oxygen, O_2) in the unsaturated and saturated zones respectively.

2.2 MICROBIOLOGICAL QUALITY OF GROUNDWATER

Groundwater also contains a broad spectrum of microbial types similar to those found in surface soils and waters. These microbes encompass bacteria, fungi and protozoa, and are representative of most physiological types. On occasion pathogenic viruses, bacteria and protozoans of gastrointestinal origin from domestic, agricultural and other anthropogenic activities, may infiltrate through soils, sediments and rocks to the underlying groundwater (Plazinska, 2000). Measurement of microbiological

quality of groundwater is difficult and costly. However, to allow quick and relatively inexpensive detection of faecal contamination in drinking water, faecal indicator bacteria (FIB) are used as surrogates in a number of studies (Plazinska, 2000). The National Health and Medical Research Council (NHMRC, 2003) recommend the use of *E.Coli* as a primary indicator of faecal contamination of drinking water.

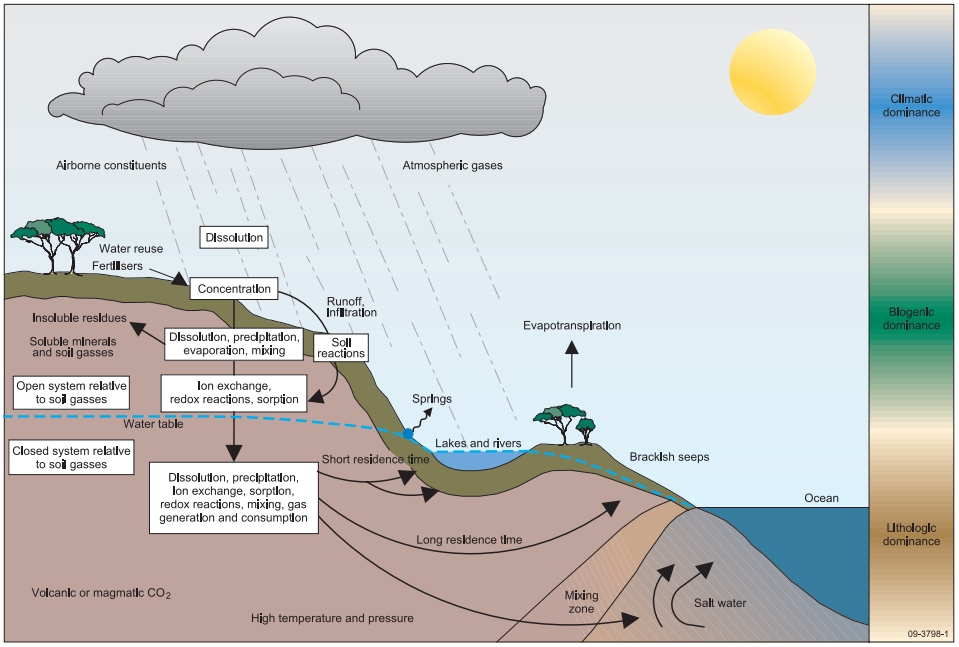

Figure 1: *Conceptual diagram of the hydrogeochemical cycle incorporating the processes affecting the transport and reactions involving major ions (adapted from Back et al. 1993)*

2.3 NATIONAL WATER QUALITY GUIDELINES

The current national water quality guidelines for drinking water (ADWG, 2004) and irrigation, livestock watering and aquatic ecosystems (ANZECC/ARMCANZ, 2000) provide a critical framework for regulators, managers, researchers and the community. The national guidelines are summarised in Table 1. The guidelines place specific thresholds on the quality of water that is intended for specific uses. The goal of groundwater protection is to protect the groundwater resources of the nation so that these resources can support their identified beneficial uses and values in an economically, socially, and environmentally sustainable and acceptable manner.

Guideline values have been determined for those chemical components that are considered to have significant potential to harm human health at concentrations above the specified limits. Guideline values should not be exceeded in public water supplies. It should also be noted that exceeding the guideline values may not always be a matter for immediate concern, but rather a trigger for follow-up action.

In many regions groundwater is used mostly for agriculture. The quality of groundwater is then assessed relative to guidelines established for livestock and irrigation. Since different crops and livestock vary considerably in their ability to tolerate salts in water, the major characteristic to be considered for water intended for use in agriculture is salinity and sodicity. Water quality guidelines for aquatic ecosystems also apply to groundwater. Guideline trigger values have been established for selected indicators. For some indicators, trigger values are based on alternative levels of species protection.

Table 1: Australian Guidelines for Drinking Water[a], Livestock[b] and Irrigation Water[b]

PARAMETER	DRINKING WATER (mg/L)		LIVESTOCK WATERING	IRRIGATION LTV[d]	IRRIGATION STV[e]
	HEALTH	AESTHETIC	(mg/L)	(mg/L)	(mg/L)
Thermotolerant coliforms	0 CFU/100 mL	-	100 CFU/100 mL	<10-10000 CFU/100 mL	
Aluminium	NAD	0.2	5	5	20
Antimony	0.003	-	-	-	-
Arsenic	0.007	-	0.5-5[c]	0.1	2
Barium	0.7	-	-	-	-
Beryllium	NAD	NAD	-	0.1	0.5
Boron	4	-	5	0.5	Crop dependent
Calcium	-	-	1000	-	-
Cadmium	0.002	-	0.01	0.01	0.05
Chloride	-	250	-	Crop dependent	Crop dependent
Chromium (as VI)	0.05	-	1	0.1	1
Cobalt	-	-	1	0.05	0.1
Copper	2	1	0.4 (sheep) 1 (cattle) 5 (pigs/ poultry)	0.2	5
Fluoride	1.5	-	2.0	1.0	2.0
Iodide	0.1	-	-	-	-
Iron	-	0.3	-	0.2	10
Lead	0.01	-	0.1	2	5
Lithium	-	-	-	2.5 (0.075 on citrus)	
Magnesium	-	-	-	-	-
Manganese	0.5	0.1	-	0.2	10
Mercury	0.001	-	0.002	0.002	0.002
Molybdenum	0.05	-	0.15	0.01	0.05

PARAMETER	DRINKING WATER (mg/L)		LIVESTOCK WATERING	IRRIGATION LTV[d]	IRRIGATION STV[e]
	HEALTH	AESTHETIC	(mg/L)	(mg/L)	(mg/L)
Nickel	0.02	-	1	0.2	2
Selenium	0.01	-	0.02	0.02	0.05
Silver	0.1	-	-	-	-
Sodium	-	180	-	Crop dependent	Crop dependent
Uranium	0.02	-	0.2	0.01	0.1
Vanadium	-	-	-	0.1	0.5
Zinc	-	3	20	2	5
Ammonia (as N)	-	0.41	-	-	-
Nitrite (as N)	0.9	-	9.12	-	-
Nitrate (as N)	11.3	-	90.3	-	-
pH	-	6.5-8.5	-	6-8.5	
Sulfate	500	250	1000	-	-
TDS	-	500	Stock dependent	Site specific	Site specific

[a] From *Australian Drinking Water Guidelines*, National Water Quality Management Strategy, NHMRC/NRMMC, 2004.
[b] From *Australian and New Zealand Guidelines for Fresh and Marine Water Quality*, ANZECC/ARMCANZ, 2000.
[c] May be tolerated if not provided as a food additive and natural levels in the diet are low.
[d] LTV denotes long-term trigger value, the maximum concentration of contaminant in the irrigation water that can be tolerated assuming 100 years of irrigation, based on irrigation loading assumptions.
[e] STV denotes short-term trigger value, the maximum concentration of contaminant in the irrigation water which can be tolerated for a shorter period of time (20 years), assuming the same maximum annual irrigation loading to soil as for the LTV.
NAD denotes No Available Data.

3. Designing a Groundwater Sampling Plan

3.1 SAMPLING PLAN

It is important to prepare a good sampling plan. The plan will describe where, what, why, how and when you will be sampling, and who will be doing it. The sampling plan should be prepared in consultation with stakeholders and field and laboratory technicians. The main steps associated with groundwater sampling are presented in Figure 2, and such planning is the first step in this workflow.

When designing a monitoring or sampling plan, issues of possible hazards as well as standard behaviour at the sampling site should be considered. By observing basic safety rules you will minimise the risk of accidents and ensure safety of the members of your sampling group.

Build your groundwater sampling plan around the following questions (modified from Waterwatch (2005)).

- Why are you field sampling?
- Who will use your data?
- How will the data be used?
- How will the data be achieved?
- What will you sample?
- What data quality do you require?
- What methods will you use?
- Where will you sample?
- How will the sample be preserved?
- When and how often will you sample?
- Who will be involved and how?
- How will the data be managed and reported?
- How will you ensure your data are credible?
- What potential hazards are there associated with the sampling?
- How can these hazards be mitigated?

3.2 CRITERIA FOR SAMPLING

Existing bores in a study area largely define the potential sites for groundwater sampling, however natural features (such as springs) or artificial features (such as mine shafts or pits) can also be used for groundwater access. It is a common practice to sample surface water bodies and rainfall to integrate with the groundwater chemistry. Different criteria can determine which bores are to be sampled, including the:

- spatial and depth distribution allowing reasonable representation across and within the target aquifer(s)
- spatial distribution to allow development of cross sections parallel and perpendicular to regional groundwater flow paths
- depth to water level ranging from shallow to deep groundwater systems (including perched and multiple aquifers). Some nested or multi-stemmed piezometers may need to be sampled to investigate chemical variations with depth (from the shallow watertable aquifer to deeper confined systems) at a site
- representation of the various land uses covering broad acre agriculture, various crops types, irrigation practices, industrial or urban areas. Sampling needs to be carried out to address the groundwater contamination potential with particular reference to nutrients, pathogens and pesticides
- representation of sampling to describe the recharge and nature and extent of groundwater/surface water interaction. Hence, bores may be selected on the basis of being close to surface water sites (such as streams, lakes, wetlands and estuaries)
- representation of the diversity of groundwater use in the area, including irrigation, stock, domestic and town water supply, and
- logistical issues that define bore accessibility, such as bore ownership, operating condition, road access and the existence and nature of bore equipment (such as an installed pump).

3.3 FREQUENCY AND DURATION OF SAMPLING

The frequency and duration of groundwater sampling (Table 2) is an important issue that should be considered when designing a sampling plan. For example, if the monitoring is for a basic groundwater resource assessment it is recommended quarterly sampling for groundwater levels, annual sampling for basic quality indicators (e.g., electrical conductivity (EC) and temperature (T)) and as-need basis for other quality parameters (Table 2). Collection of long-term (one or more decades) water level data is recommended for better understating issues associated with groundwater availability and sustainability (USGS, 2001).

Table 2: Indicative monitoring frequency for various groundwater monitoring purposes (adapted from Timms et al., 2009).

PURPOSE FOR MONITORING	GROUNDWATER LEVEL	GROUNDWATER QUALITY INDICATOR (e.g., EC, T)	GROUNDWATER QUALITY PARAMETERS**
Basic Resource Monitoring	Quarterly	Annual	As required
Resource Monitoring at Sensitive Sites (*eg. Significant Drawdown, Well Head Protection Zone, Risk of Groundwater Quality Impacts*)	Daily	Monthly	Quarterly
Recharge Processes & Rainfall Response	Daily or Hourly	Monthly or Hourly	As required
Measure Aquifer Confinement and Specific Storage	Hourly or 15 minute*	-	-
Point Source Contamination – Potential Impacts^	Quarterly	Quarterly	Half-yearly
Diffuse Source Contamination – Potential Impacts	Half-yearly	Half-yearly	Annual

* Including barometric pressure measurement at the bore site, # NSW Groundwater Quality Protection Policy,
^ Depending on Groundwater Quality Protection Level.
** Selection of appropriate water quality parameters for testing depends on the purpose of monitoring, possible contaminants and constraints on the cost of analyses.

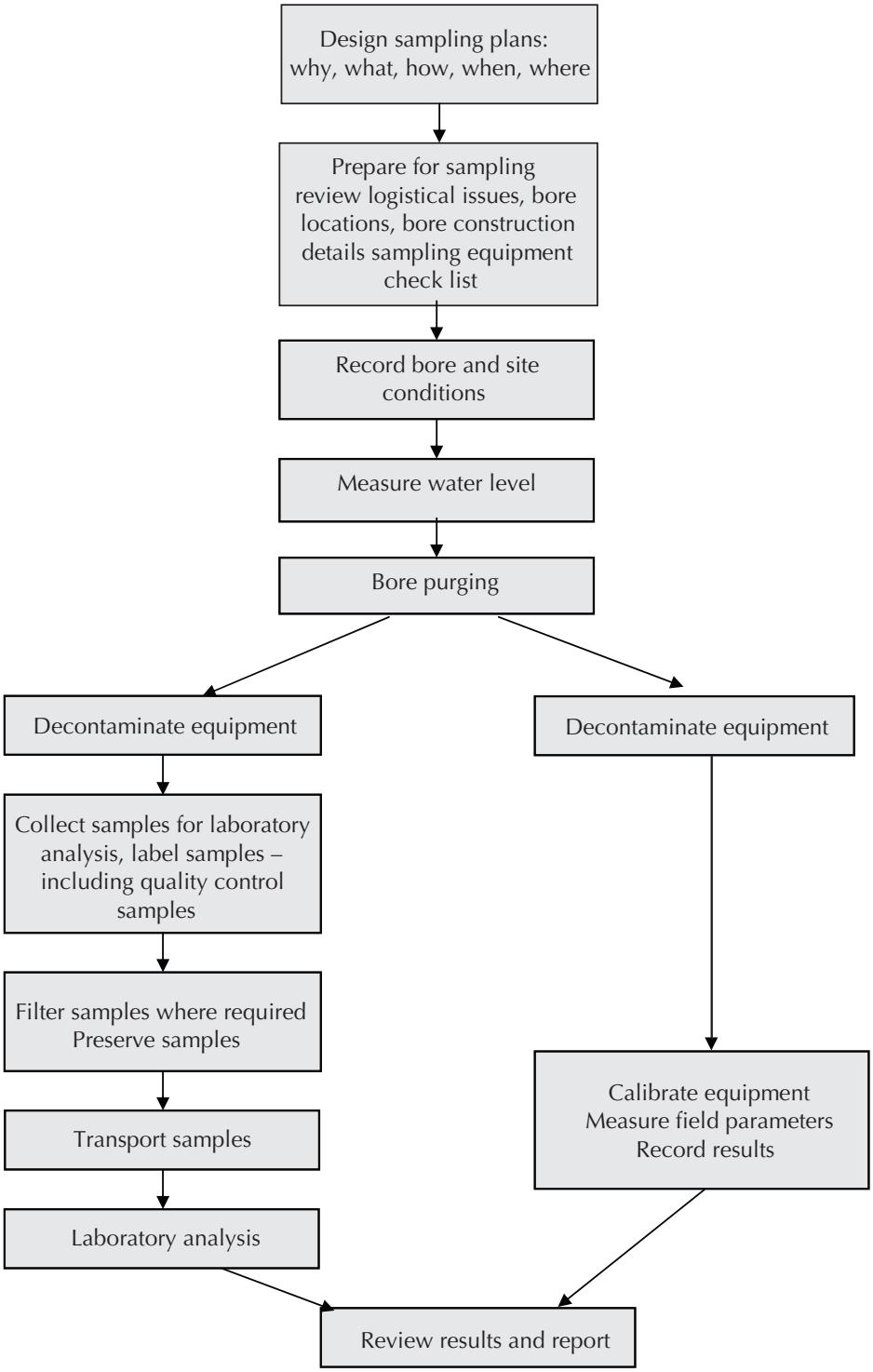

Figure 2: *Steps in groundwater sampling*

4. Drilling and Bore Construction

The simplest way to access groundwater is to dig a well. Wells can be dug manually to reach the shallow water table within the unconfined aquifer. However, if an aquifer is deeper than a few meters, a proper borehole needs to be drilled. Choosing a site, drilling method and bore construction are complex tasks requiring hydrogeological knowledge, a skilled driller and specialised equipment.

Many issues need careful consideration before a bore can be constructed. Some of the questions that need to be answered include (modified from Waterwatch, 2005):

- What is the geology and geomorphology of the area?
- How many aquifers exist, and which is the most appropriate one for the study purpose?
- How deep is the targeted aquifer?
- What is the purpose of the bore (monitoring, production, injection etc)?
- If it is a production bore, how much water is needed and how much water can reasonably be extracted?
- What are the licensing requirements and conditions operating within the State or Territory?
- Is there a groundwater management plan for the area?
- Are there any other bores in close proximity?
- Is the proposed location far enough from potential contamination sites like irrigation, septic tanks, drainage lines, animal feedlots, etc.?
- If it is a monitoring bore, is it in a suitable position to monitor the impacts of potential contamination sites?
- Is the bore sited in an area where is could be prone to damage (such as by flooding, erosion, vandalism etc)?
- Is the bore sited to minimise any disturbance or inconvenience to the land holder?
- Is the bore sited where there is infrastructure that is underground (such as water pipes, electrical cables, optical fibre networks) or overhead (such as power lines)?

All groundwater bores should be drilled, cased and equipped according to national construction standards defined in *Minimum Construction Requirements for Water Bores in Australia* (ARMCANZ, 2003). This document deals with a broad scope of issues pertaining to water bore construction from licensing to construction, development and decommissioning for shallow small-diameter and low-yielding bores, through to high-yielding, deep and large-diameter bores.

4.1 DRILLING METHODS

Drilling methods are many and varied, ranging from simple digging with hand tools to high speed drilling with sophisticated equipment. Each of the drilling methods

has its advantages and disadvantages. The choice of drilling method employed should be made on the basis of geological and hydrogeological conditions and the type of facility to be constructed. The most commonly used drilling methods are described briefly below.

When selecting a drilling method or sampling an existing bore, 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 bore. Water contaminants, lubricants, oil, grease, solvents, coatings and corrodible materials may affect the suitability of the bore for groundwater monitoring, especially when monitoring for contaminants.

All drilling and sampling equipment should be thoroughly cleaned before commencing drilling. Casing, drilling fluids and any materials used in the bore also need 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 bores. 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 bores drilled using the technique. The selection of a drilling method and construction materials for a monitoring bore should take into account how these may influence analytes chosen for monitoring.

When drilling a monitoring bore, a lithological log (and preferably a stratigraphic interpretation) should be made by an experienced person able to identify the important features.

4.1.1 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 reduces 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 bores. It is possible to insert the casing into the hollow centre of a hollow flight auger before it is removed from the hole. This does require a large diameter borehole, but can be particularly useful in sandy ground.

4.1.2 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.

4.1.3 Rotary mud drilling

Rotary mud drilling works on the same principle as rotary air drilling except that liquid is used as a circulation medium. Mud additives are 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 fluids may enter the aquifer and mix with groundwater
- 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.

4.1.4 Cable tool drilling

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

4.1.5 Direct push technology

Direct push (DP) technologies are an alternative method to conventional drilling techniques for sampling groundwater and installing monitoring bores in unconsolidated materials such as clay, silt, sand, and gravel. They are appropriate for sampling in the saturated zone and to depths of around 20m. Typically, a truck mounted mechanical hammer or hydraulic rig is used to push a string of steel hollow rods or a drive casing to the desired depth with a sacrificial tip. The rod assembly is disengaged from the tip and the sampling screen exposed. By directly pushing the sampler, the soil is displaced and helps to form an annular seal above the sampling zone. Direct push technologies are generally faster to install and more economical for high density sampling. They produce little or no cuttings during installation. DP installed groundwater bores are not appropriate for high volume sampling, are not recommended when telescoped bores are required to prevent migration of contaminants below confining layers, and may not penetrate hard bands, bedrock and some unconfined layers (US EPA, 2005; ASTM, 2005).

4.1.6 Sonic drilling

Sonic drilling is a relatively new technique, where a high frequency vibration is

combined with rotation to advance the drill stem. The core barrel is retrieved and the sample vibrated into a plastic sleeve or core trays. The advantage of this technique is relatively continuous and undisturbed geological samples, without the use of drilling fluids or other potential contaminants.

4.1.7 Vibro coring

Vibro coring method is used wherever soil conditions are unsuited to gravity corers or where greater penetration of the seabed is necessary. Standard size vibro coring equipment will produce 86 mm diameter core samples to a maximum depth of 6 m. In coarse aggregates larger diameters up to 150 mm can be obtained. This method is used widely throughout the geotechnical investigation industry and ca be deployed in water depths up to 1000 m.

4.2 BORE CONSTRUCTION

Monitoring bores need to be constructed to a high standard to ensure ongoing and reliable data is obtained over the life of the bore. A bore should be constructed in accordance to national construction standards defined in *Minimum Construction Requirements for Water Bores in Australia* (ARMCANZ, 2003).

When constructing a bore (see Figure 3), the casing material will be determined by the required bore 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:

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

Consideration should also be given to the selection of an appropriate casing diameter that will allow pumping and monitoring equipment to be easily installed.

The bore casing for a monitoring bore should have mechanical joints to avoid contamination by solvents such as PVC solvent cleaner and cement. Organic-based lubricants (such as hydrocarbons) should not be used on casing joints, drilling rods or equipment if sampling for organics is required.

A gravel pack may be used to avoid siltation when fine-grained aquifers are encountered. The bore annulus should be carefully and evenly filled to a level approximately one metre above the screened interval with a graded gravel pack. Screen and gravel pack intervals should not be installed across different geological units or water-bearing zones.

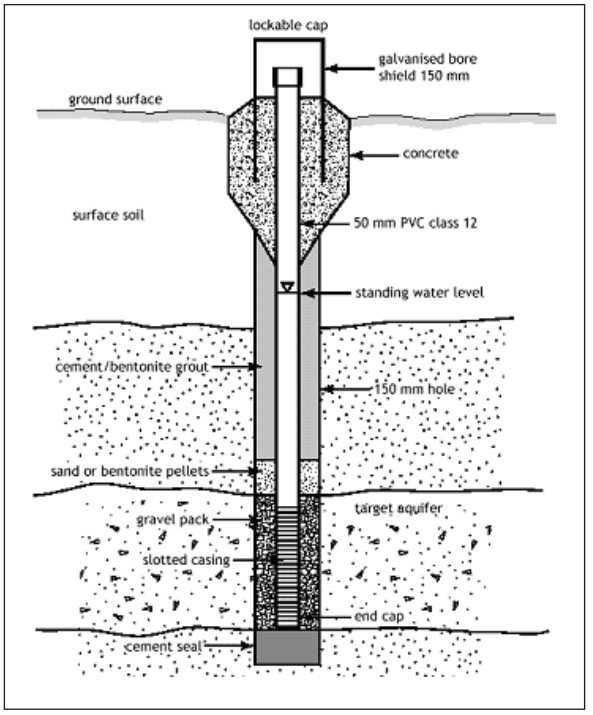

Figure 3: *A typical water monitoring bore (adapted from ARMCANZ, 2003)*

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.

Where there is a possibility that contaminants are present at high levels, or are known to exist, extreme care **must** be taken to avoid contamination of deeper aquifers. Bores 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 bores should be capped with a lockable cap to prevent ingress of surface water, dust or other foreign matter and to avoid tampering.

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

Additional information on bore construction requirements and standards can be obtained from the document *Minimum construction requirements for water bores in Australia* (ARMCANZ, 2003).

4.3 SHALLOW PIEZOMETER CONSTRUCTION AND INSTALLATION

Piezometers are shallow pipes used to monitor characteristics of an unconfined aquifer, generally within 5 m of the ground surface. Piezometers can be made easily from PVC pipe (Figure 4) and installed using an auger. The national minimum construction requirements for water bores (ARMCANZ, 2003) also provides information concerning small-diameter shallow piezometers. An example of a simple construction method is outlined below.

Figure 4: *Nested piezometer construction*

4.3.1 Shallow piezometer construction

4.3.1.1 Equipment

The equipment you will need to construct a piezometer includes:

- 2–3 m of 50 or 80 mm diameter PVC pipe
- two 80 mm PVC caps
- saw

4.3.1.2 Procedure

1. Dig test hole to determine the depth to groundwater, the piezometer should be 500 mm longer than the depth to the water table.
2. Using the saw, cut small slots along the bottom 500 mm of the piezometer to allow the groundwater to enter (see Figure 5).
3. Place a PVC cap over the bottom of the piezometer.

4.3.2 Shallow piezometer installation

4.3.2.1 Equipment

The equipment you will need to install a piezometer includes:

- auger (extendable to 5 m) with a 100 mm tip
- bucket of gravel or sand, with the typical grainsize dependent on the aquifer lithology
- bentonite pellets (pre-soaked)
- premixed concrete
- a capped galvanised or clay pipe (large enough to case the piezometer above the ground)
- extra PVC pipe and extension joint
- hacksaw

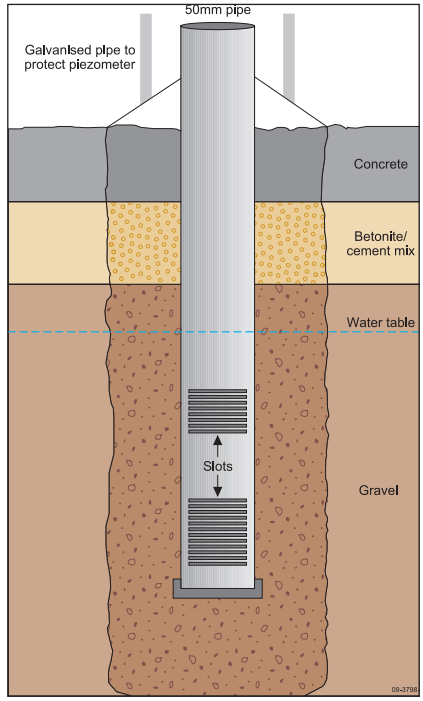

Figure 5: *Cross section of a piezometer*

4.3.2.2 Procedure

1. Use the auger to dig a hole to the length of the prepared piezometer. The depth should be at least equal to, but preferably greater than, the depth to the water table.
2. Put a small amount of gravel pack at the bottom of the hole. Place the piezometer in the centre of the hole, ensuring that it extends at least 100 mm above the ground.

3. Fill around the pipe with the remaining gravel pack, to within 400 mm of the surface.
4. Fill the next 300 mm with a concrete/bentonite slurry, and the remainder with a concrete mix. Slope the concrete so surface water flows away, reducing the likelihood of contamination of the piezometer with surface water.
5. Place a larger diameter casing (typically PVC or galvanised iron) over the top of the piezometer to reduce the likelihood of damage.
6. Quite often when drilling or augering holes, particularly in clay formations, the bore wall can become smeared. To ensure the through-flow of groundwater it is recommended that the fully constructed bore is pumped or bailed for a period immediately after construction and before it is used for monitoring. This will remove debris and fine material from the annulus.

4.4 BUNDLED MINI-PIEZOMETERS

Bundled mini-piezometers are used for discrete vertical sampling of water quality and hydraulic head measurements in unconsolidated sands (Acworth, 2007). This method is particularly useful for sampling at 0.25 or 1 m intervals through the saline-fresh interface in coastal sands. These mini-piezometers can also be used with a manometer board for density head corrections in coastal aquifers at the fresh/saline interface.

Several designs are possible with this method; however, bundles consisting of a number of flexible plastic tubes—8 mm outer diameter (OD), 5 mm inner diameter (ID)—attached to the outside of a stem made from 25-mm-plastic pipe (electrical conduit) have been successfully used (Acworth, 2007).

When connected to a vacuum and manometer, the advantage of this method is that it can be used to derive a vertical profile of water quality and hydraulic head measurements. Purging and sampling volumes can be minimised with very small tubing and this can be constructed using readily available and cheap PVC tubing. However, this method is suitable only for shallow unconfined and sandy aquifers. It requires an experienced person to construct and install and is time consuming.

Additional information on the bundled mini-piezometers construction and installation can be obtained from Acworth (2007).

5. Groundwater Sampling Equipment

5.1 PUMPING AND SAMPLING EQUIPMENT

Groundwater sampling methods should take into account the monitoring objective(s) and the site-specific conditions. Groundwater sampling methods will vary, depending on the type of extraction device used, the position of the sampler intake, the purge criteria used, and the composition of the groundwater to be sampled (e.g. turbid, containing high levels of volatile organics, DNAPLs/LNAPLS, etc). The sampling methods and equipment, including purge criteria and field readings, should be clearly documented.

The most important thing to consider when selecting sampling equipment is whether it gives consistent results that adequately reflect the in-situ groundwater in the aquifer. Table 3 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, e.g., 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 3: Groundwater sampling equipments: advantages and disadvantages (modified from Murray-Darling Basin groundwater quality guidelines (MDBC, 1997)).

PURGING AND SAMPLING EQUIPMENTS	ADVANTAGES	DISADVANTAGES
Bailer 	• can be constructed from a variety of materials compatible with various substances to be sampled • size can be varied to suit the sampling point • easy to clean and no external power required • inexpensive and readily available • low surface area to volume ratio • easy to transport	• Time consuming, non-continuous flow • the person sampling the bore 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 bore with a bailer • sample may be aerated during collection in the bailer and transfer from bailer to sample bottle

PURGING AND SAMPLING EQUIPMENTS	ADVANTAGES	DISADVANTAGES
		• 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 bore casing may allow fines from the formation to enter the water columns
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 bores • 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 pump	• relatively portable • readily available • inexpensive • some are suitable for well development though this depends on yield rate of device	• causes changes in carbon dioxide 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 an inert gas (e.g., N_2) is used instead of air
Suction-lift pump 	• highly portable • easily available • flow rate can easily be controlled • inexpensive • can be constructed in small diameter	• 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

PURGING AND SAMPLING EQUIPMENTS	ADVANTAGES	DISADVANTAGES
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 air or oxygen is used as the driving gas, then oxidation may occur causing the precipitation of metals • gas-stripping of volatiles may occur • carbon dioxide may be driven from the sample and alter pH
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	• non-continuous flow • low-flow rate • time consuming to purge bore volumes • lift capacity ~60m
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 • may overheat if not submerged
Inertial pump (foot valve)	• simple construction, inexpensive manual, gas or electric motor driven • good for sediment clogged bores • if dedicated, it avoids cross-contamination	• for use primarily in small diameter bores, as large bores increase the possibility of tubing sway • works optimally with deep installation of tubing—this may result in the bore not being properly purged • low flow capacity
Submersible piston pump 	• portable, small diameter • non-contact, gas-driven pump that uses compressed air to activate a piston • minimal effect on water chemistry because of non contact • does not overheat even if not in water • capacity to pump from large depths - lifts up to 300m	• non-continuous flow (though reciprocating pistons models are near-continuous) • relatively low flow (time consuming to purge bore) • relatively expensive

PURGING AND SAMPLING EQUIPMENTS	ADVANTAGES	DISADVANTAGES
	• capacity to sample very deep bores using extension drop tubing • simple robust mechanical operation	
Flow meter water sampler 	• capable of retrieving both gas and liquid samples at downhole pressure conditions • minimum contamination from atmospheric gases and reduce fill-up time • capable of sampling for CFCs • EC/temperature sonde can be run simultaneously to log water quality changes at 1 cm vertical increments	• relatively expensive

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 from which the sample is collected is important, as the deeper the sample the more head the device must overcome to deliver the sample to the surface
- the bore needs to be able to accommodate the sampling device; the smaller the diameter of the bore, 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 bore will need to be straightforward.

5.2 SAMPLING EQUIPMENT

Sampling equipment should be constructed from relatively inert materials (e.g., Teflon®, glass, stainless steel) that will not contaminate the sample. Sampling equipment includes anything that will come into contact with the samples, including the pump, pump tubing, bailer and sample container.

The tendency for organics and trace metals to sorb into and out of many materials makes the selection of sample equipment critical when sampling trace concentrations.

5.3 SAMPLING CONTAINERS

Containers used for collecting groundwater samples must not affect the integrity of the sample. As a result, certain sample containers are specified for common sample types. Additionally, there are a number of treatments that are applied to containers to further reduce the chance of sample contamination. Section 6.9 provides guidance for container selection by analysis type. Sample containers can be obtained from specialised providers or analytical laboratories.

6. Groundwater Sampling Methods

This section provides information about how to obtain a representative groundwater sample from bores and the procedures that have to be followed before sampling can begin. Groundwater sampling should be undertaken by, or in consultation with, hydrogeologists. This is especially critical in situations where a site is underlain by complex hydrogeology. Some of the field sampling methods described in this section has been adapted from Waterwatch (2005).

6.1 GROUNDWATER LEVEL MEASUREMENTS

The total depth and depth to the water level should be measured within the bore before any purging and sampling. Groundwater level measurements can provide information on lateral and vertical head distribution and hydraulic gradients within individual aquifers and between aquifers in layered aquifer systems. Long-term groundwater level measurement provides information on the temporal trends in groundwater levels (and therefore flow direction and rates) due to the effects of drought, high rainfall events and groundwater pumping.

6.1.1 Measuring total depth of the bore

When monitoring unequipped bores the first parameter to be measured is total depth (TD) of the bore. When monitoring a bore that has pumping equipment permanently installed and does not provide access to the bore casing, the TD cannot be measured. Total depth should be obtained from the owner or custodian of the bore and noted on the Bore Information Sheet (Appendix 2). Note that all depth measurements are conventionally taken from the top of the casing or bore shield (at a marked point, such as the padlocking point). Hence, the height above the ground surface of this reference point should also be measured.

Over time, the base of the monitoring bores can silt up, and this can occur to the top of the slotted/screened interval. Comparing the measured total depth reading with the depth documented at the time of construction can be useful to determine the status of the bore.

6.1.1.1 Equipment

Total bore depth can be measured using a weight attached to a tape measure. Use a tape measure that is at least as long as the deepest bore to be measured. To avoid mistakes in depth measurements use quite a heavy weight that can easily reach the bottom of the bore.

6.1.1.2 Procedure

1. Lower the weight into the casing until it reaches the bottom of the hole – as this happens the tape will become slack.
2. Lift and drop the tape several times to 'feel' the bottom of the bore.
3. Remember to add the length of the weight onto the tape measurement (if this has not been accounted for).

4. Subtract the height of the casing above the ground level from the measurement.
5. Record the result as total depth (in metres) of the bore on the Bore Information Sheet.
6. Clean the tape before using it again.

6.1.2 Measuring depth to water table

The depth to the water level in the bore is also called depth to groundwater or the standing water level (SWL). Methods and instruments used to collect and record groundwater levels can vary substantially. The more common instruments are fox whistle, plopper and tape measure, electrical tape, pressure transducer and pressure gauge.

Depth to water table should be measured and recorded before every sampling event. Water level cannot be measured in production bores that have permanently installed pumping equipment as there is no direct access to the bore casing. These bores cannot be used for water level monitoring. Some production bores may, however, have additional casing of small diameter that was installed specifically for the purpose of water level monitoring. This casing will run alongside the main bore casing used for water extraction.

6.1.2.1 Water level measurement using a plopper and tape measure

Depth to the standing water level in the bore can be measured using a tape measure with an attachment that is designed to make noise or some other signal when it touches the water surface. The simplest version is the plopper/sampler made from a 15 to 20 cm stainless steel tube and a tape measure (Figure 6).

Figure 6: *Plopper/sampler and tape measure*

The metal tube is sealed at the end at which it is attached to the tape with a loop wire. The other end that touches the water should be left open. When the tube is lowered into the bore and touches the water surface it makes a distinctive plopping sound.

6.1.2.2 Procedure

1. Lower the plopper into the bore until it hits the water.
2. Lift and drop the plopper several times to find the exact water level, this should give a reading accurate to within 1 cm.
3. Remember to add the length of the plopper onto the tape measurement (if this has not been accounted for).
4. Subtract the height of the casing above the ground level from the measurement.
5. Record the result as water level (in metres) with the date of the measurement on the Bore Information Sheet.
6. To record the water level relative to the ground surface, the measured distance between the measuring point (eg top of casing) and the ground surface is subtracted. If the water level in the bore is below ground, record the result as negative (–) and positive (+) if it is above ground (water standing in the casing above ground).
7. Wash the tape and the plopper thoroughly with tap water before using it again to prevent contamination of the next bore. Dry and roll the tape.

6.1.2.3 Water level measurement using a water level meter

There is wide range of water level meters and interface meters are available on the market. The water level meter uses a probe attached to a permanently marked polyethylene tape, fitted on a reel (Figure 7). The probe detects the presence of a conductive liquid between its two electrodes and is powered by a standard 9 volt battery. When contact is made with water, the circuit is closed, sending a signal back to the reel. This activates a buzzer and a light. The water level is then determined by taking a reading directly from the tape, at the top of the bore casing or borehole. Use of a tape guide gives extra accuracy and protects the tape.

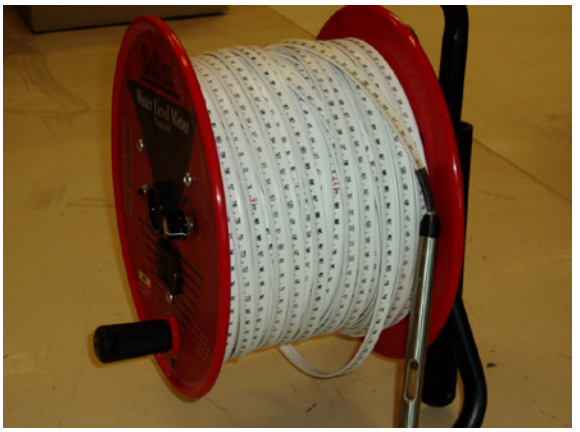

Figure 7: *Water level meter*

6.2 COLLECTING A REPRESENTATIVE WATER SAMPLE

There are two main methods of sampling that can be employed to obtain a representative groundwater sample. These are the bore purging method and the low flow sampling method. The type of method to be used is determined by the pump design. Generally the bore purge method results in a representative sample by making sure stagnant water within the bore is removed, whereas the low flow method is designed to leave the stagnant water within the bore undisturbed, whilst obtaining a representative sample directly from the aquifer through the screened interval at the depth of the pump.

6.3 BORE PURGING METHOD

The purpose of groundwater sampling is to retrieve a water sample that represents the characteristics of water below the ground surface. To obtain a representative sample it is necessary to remove the stagnant water from the bore casing before a sample is taken. This is called purging. It is recommended that at least three casing volumes of water should be removed before sampling. Usually pumping of the bore is continued even after three casing volumes have been removed until such time as the pH, EC and temperature of the discharge water are observed to stabilise. Only then is the obtained sample considered to be representative of groundwater residing in the aquifer surrounding the bore screen.

Important: Bore has to be purged before each sampling event.

The volume of the water in the bore casing is calculated using the following formulae:

$V = \pi r^2 \times L \times 1000$

where:

V – volume (in litres)
r – radius of the casing in metres, that is, half the inner diameter
L – length of the water column in metres (TD minus standing water level, or SWL, measured to the same datum)
π – constant (3.14)

Hence, the steps to calculate the casing water volume are:

- Measure the inner diameter of the bore casing in metres and halve it to obtain the radius.
- Measure TD – the total depth of the bore (refer section 6.1.1), or obtain this from the relevant bore database or the bore owner.
- Measure water level – the depth to the water table or water level (refer section 6.1.2).
- Calculate the length of the water column (total depth – water level).
- Calculate the volume of water using the formula above.
- Multiply by three to calculate three casing volumes.
- Approximate values of common casing widths are shown in Table 4.

It is often useful to know the time it will take to purge the bore. This is obtained by dividing the water volume (in L) by the average pumping or flow rate achieved (in L/sec or L/min). The later can be simply measured using a bucket and watch.

Table 4: Example of casing diameter and volumes of water to purge from the bore

CASING DIAMETER	VOLUME OF 1 METRE OF WATER COLUMN (L)	VOLUME OF WATER TO PURGE PER METER (L)
25 mm	0.5	1.5
50 mm	2	6
75 mm	5	15
100 mm	8	24
125 mm	12.5	37.5
150 mm	17.7	53
200 mm	31.5	95

6.3.1 Purging using a bailer

A bore can be purged using a bailer only when a reasonably small volume of water is to be removed. It will take a considerable length of time to purge even a very shallow bore. When using a bailer it is difficult to ensure that all stagnant water has been removed from the bore and consequently the sample may represent a mixture of fresh and stagnant water.

6.3.1.1 Equipment

A bailer is a simple mechanical device that can be used to draw water from the bore (Figure 8). It consists of some form of tubing with a one-way check valve at the bottom. When the bailer is lowered into the bore casing below the water level, it fills with water. The check valve closes once the bailer containing the water sample is lifted to the surface.

Figure 8: *Bailer*

Bailers come in various types (polyethylene, Teflon®, stainless steel, acrylic), lengths (from 30 cm to 180 cm), widths (19 mm to 90 mm) and with numerous features

like weighted, unweighted, single check-valve, double check valve, controlled flow bottom, etc.

6.3.1.2 Procedure

1. Lower the bailer to the level of the slotted part of the casing (screened interval).
2. Lower and withdraw the bailer slowly and try not to disturb the water column by splashing.
3. Use a bucket of known volume to record the volume of water being discharged.
4. Remove the calculated volume of water.
5. Continue purging until pH, EC and temperature readings stabilise.

6.3.1.3 Advantages

- simple construction and reliable operation
- do not require electric or pneumatic power
- easy for one person to operate
- extremely portable
- relatively easy to clean and maintain
- inexpensive

6.3.2 Purging using a pump

Truly effective purging that can guarantee the integrity of the sample can be done using a pump.

6.3.2.1 Equipment

There is a wide range of groundwater pumps employing different operating methods, available on the market. There are pneumatic pumps that require a compressed air/gas source, electric pumps that require 240 volt AC or 12–24 volt DC, and mechanical pumps, which use linkages to provide the lift mechanism.

Choice of pump will depend on the:

- cost of the equipment
- depth of the bore
- diameter of the bore casing
- amount of water that has to be lifted

Small inexpensive electric pumps in plastic housings that operate from a 12-volt battery are the most convenient pumps to use for groundwater sampling of shallow, small diameter monitoring bores (Figure 9). The advantage over other pumping equipment is that they are simple and safe to operate, require only a 12-volt battery and can be used in small diameter (50 mm) monitoring bores.

There are several types of submersible, battery operated, pumps available, which have slightly different parameters such as maximum flow rate and ability to pump to a certain depth. Before deciding which pump to use make sure you know the depth

of the bores you are going to monitor and the depth to the water table.

Note: *Turbidity* can affect submersible electric pumps. Suspended solids can reduce the pumping rate or even cause pump failure, by restricting the rotation of the pump. Use a bailer to check turbidity of water before using submersible pumps to purge the bore.

Using DC electrical powered pumps you will need:

- 12 volt submersible pumps
- 40 m of 2- or 3-core electrical cable
- 40 m of clear plastic hose, 12 mm inside diameter
- battery clips
- a 12-volt lead-acid battery
- a battery charger

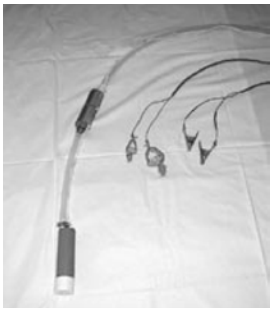

Figure 9: *Submersible 12 volt pump*

6.3.2.2 Procedure

1. Lower the pump to about 1 m above the screens (if known) or to about 1–2 m from the bottom of the bore if the screen depth is not known; beware of the risk of drawing silt into the pump which can occur if it is set too close to the screens.
2. After starting the pump, establish the highest flow rate possible without causing the bore to stop yielding.
3. Calculate the flow rate (refer section 6.3.2.3 below).
4. Once a constant flow rate is established, the bore can be 'vacuumed'. This is done by slowly lifting the pump to near the top of the water column while pumping, then slowly lowering it to the previous depth. This way the column of stagnant water sitting in the casing above the slotted level is evacuated.
5. Pump for calculated length of time needed to remove the three casing volumes of water or until pH, EC and temperature measurements stabilise.

Note: If there is silt in the bore, operators can unknowingly lower the 12 volt pump into silt and thus block the pump. Also if there is a large volume of water to purge or water contains suspended sediment, there is a risk of pump failure. A large air-

compressor setup should be considered to properly develop and purge the bore prior to the first sampling.

Usually pumping of the bore is continued even after three casing volumes have been removed until such time as the pH, EC and temperature of the discharge water are seen to stabilise. Only then is the obtained sample truly representative of groundwater residing in the aquifer surrounding the borehole.

6.3.2.3 How to calculate flow rate:

Measure the time needed to fill a 10 L bucket with discharge water.

Calculate flow rate (FR) in litres per minute (L/min) using the formula:
FR (L/min) = (60 divided by time in seconds taken to fill 10 L container) x 10

See Appendix 3 for flow rate conversion for different times.

Knowing the volume of water standing in the casing (V) and the flow rate (FR), calculate how much time (T) it will take to pump out three casing volumes using the formulae:

T = (V/FR) x 3

6.3.3 Purging a production bore

6.3.3.1 Equipment

No special equipment is needed.

6.3.3.2 Procedure

1. If the bore is pumped only occasionally, turn on the pump and run it for the amount of time you calculate is necessary to remove three casing volumes or until pH, EC and temperature readings stabilise.
2. If bore is used for continuous pumping at certain times of the day (e.g., irrigation, town water supply) there is no need to purge – simply be prepared to sample when the bore is used.

6.4 LOW FLOW METHOD

The low flow method employs specifically designed sample pumps. The principle behind this method is to extract formation water through the bore screen (or slotted interval) at approximately the same rate it flows out of the formation, without disturbing the stagnant water column above. This is achieved by pumping at a rate which results in minimal drawdown of the water level within the bore. The method also has the added advantage of minimising the entrainment of sediment within the water that is to be sampled. Further, the time required for sampling is much less than traditional bore purging methods that require a minimum of three casing volumes to be pumped, before a representative sample can be obtained. Typical flow rates for low flow sampling are in the order of 1 to 2L/min.

Low flow sampling pumps usually incorporate a piston or bladder that is operated by compressed air or gas. Piston operated pumps can lift up to 300 m head and obtain sample from depths as great as 800 m or more.

6.4.1 Procedure

1. Lower pump to the middle or slightly above the middle of the slotted interval.
2. Set pumping rate to a level that will not induce or drawdown minimum – check water level before and during pumping.
3. Monitor field parameters to ensure stabilisation before taking sample.

6.4.2 Advantages

- reduced time required for sampling
- reduced turbidity
- reduced volume of water required to be pumped and disposed of

6.5 SAMPLING MONITORING BORES

To draw water from a monitoring or unequipped bore (typically with no pump installed), a bailer or a pump has to be used. Sampling using existing monitoring bores will be the most convenient and cost effective way to obtain groundwater samples. However in areas where such bores are not available and water table levels are known to be very close to the ground surface (2 m), installation of a very simple monitoring bore or piezometer may be considered (refer section 4.3). Piezometers should be sampled using the same procedures as described for monitoring bores.

6.5.1 Bailing

6.5.1.1 Equipment

- A bailer (refer section 6.3.1)
- A length of graduated cable (with marks every metre for instance)

6.5.1.2 Procedure

1. Lower the bailer slowly and gently into the water column of the bore until it is submerged, do not allow the bailer to come into contact with the bottom of the bore.
2. Before collecting the sample, purge the bore by removing the calculated volume of water. A bore can be purged using a bailer only when a reasonably small volume of water is to be removed (shallow and narrow bores).
3. Carefully remove the water sample and empty it from the bottom of the bailer into a prepared sample container.
4. If using a conventional bailer, the equipment should be cleaned after each use to avoid contamination of the next sample. Wash the bailer thoroughly, using tap water and detergent.

6.5.2 Pumping

Using a pump is a much more efficient way of sampling a bore (Figure 10). When using a pump, you can be more confident of efficient bore purging and that the obtained sample is representative of aquifer water.

6.5.2.1 Equipment

See description of 12 volt submersible pumps (Figure 9) and their use under purging using a pump (refer section 6.3.2).

6.5.2.2 Procedure

1. Assemble a single pump system, keeping in mind how much water your particular pump can lift, and that any extension of the casing above ground level will reduce this capacity.
2. Purge the bore by pumping out the appropriate volume of water (refer section 6.3.2).
3. Continue pumping water until pH, EC and temperature readings are stable before taking a sample, with the pump in the same position as for purging.
4. If the position of screened section is not known, lower the pump almost to the bottom of the bore (be careful not to hit the bottom) and lift up 2–3 m, pump from this position.
5. The pump should be cleaned after each use to avoid contamination of the next sample. Cleaning is done by submerging the pump in a container of pure (tap) water and pumping continuously for several minutes to ensure the pump and plastic hose are rinsed thoroughly.
6. Using a pump for purging and sampling a bore ensures that representative sample of water residing in the aquifer will be obtained. Make sure your pumping technique is consistent and every sample is obtained following the same procedure.

Figure 10: *Groundwater sampling in a monitoring bore using a pump*

6.6 SAMPLING DEEP BORES

In some instances it may be desirable or necessary to sample groundwater from a greater depth than the typically less than 100 m depth achieved by most common setups. The reasons for this may be that the aquifer is very deep and we always strive to sample as close as possible to the bore's slotted interval (especially when only limited pumping rates can be achieved), or simply that the standing groundwater level in the bore is beyond the reach of most pump hoses.

Some pump manufacturers have designed pumps that can be connected to a synthetic, e.g., low density polyethylene (LDPE), extension tubing attached below the pump. Some of these pumps can even function completely above the water level without risk of overheating.

6.6.1 Equipment

- pump capable of being connected to an extension or drop tubing
- required length of tubing
- weights
- inlet screen

6.6.2 Procedure

The principle for deep groundwater sampling is that a rod-like intake screen unit and weights are attached at the bottom part of a length of tubing and lowered down the bore. The weights are necessary to counter the buoyancy created by the LDPE tubing, and their total mass will be dependent on the length of tubing used. At the other (upper) end, the tubing is connected to the bottom of the pump, which is itself lowered down the bore as deep as required. Caution has to taken not to kink the tubing, so as to not weaken it.

Groundwater is lifted inside the tubing mainly by the pressure differential between the deeper end (higher hydrostatic pressure) and the shallower end (lower hydrostatic pressure) of the tubing under only a minimal drive from the pump's sucking action. Once the water is inside the pump it is pushed up the pump hose as per normal. Pumping rates are expected to be quite slow, and even with the intake screen positioned right at the casing's slotted interval, it will still take a long time to ensure that native groundwater is being pumped up. Continued monitoring of field parameters, as discussed elsewhere in the document, is of paramount importance here.

The experience in GA has been to successfully sample groundwater from depths up to 850 m below ground level using a Bennett™ double piston, compressed air pump connected to lengths of either 700 or 800 m of 3/8 x 0.250 Esdan™ food grade LDPE tubing rated for up to 120 psi pressure (Figure 11a). The tubing is made up from two lengths of 300 m and two lengths of 100 m joined together with Swagelok™ stainless steel connectors (Figure 11b). This combination allows the flexibility of incrementally increasing the length of tubing by 100 m up to 800 m, by varying the combination

of these four lengths of tubing. The intake screen unit is a QED™ stainless steel unit (Figure 11c). Weights are cut lengths of stainless steel rod, approximately 34 cm in length and 2.2 kg in weight (Figure 11c). Three weights have been successfully used for either 700 or 800 m of tubing. The tubing is connected to the intake of the Bennett pump (Figure 11d). At about 850 m depth (right within the slotted interval), pumping rates of ~1-2 L/min are achieved with this setup, and it is recommended that pumping continues for at least 3 to 4 hours (while monitoring for field parameters pH, temperature, EC, Eh and DO, see section 'Measuring field parameters') before sampling for geochemical analysis. Note that some water/environmental agencies may ban rapid pumping (purging) to remove the theoretical three bore volumes of water, especially for old bores whose casing may collapse if the contained water is removed. This leaves low-flow pumping within (or as near as possible to) the slotted interval as the only viable alternative for obtaining a proper groundwater sample. At the bore site, it is useful to have a tripod and swivelling block to lower and retrieve the tubing (Figure 11e). Once the tubing is inside the bore, the pump can be lowered from its standard swinging arm. To retrieve the apparatus, the pump hose is first wound onto its reel via the swinging arm, and then the LDPE tubing is manually pulled up via the block and tripod. The tubing is immediately wound onto a dedicated reel mounted on a stand.

Figure 11: *Deep groundwater sampling equipment: a) reel of LDPE tubing; b) connection between lengths of tubing; c) intake screen with weights in background; d) connecting the tubing to the pump; and e) tripod and swivelling block used to lower and retrieve tubing*

6.7 SAMPLING PRODUCTION (EQUIPPED) BORES

The use of existing production bores for sampling is the most convenient method available. Generally production bores have high yields and are often used for extended periods every day.

6.7.1 Equipment

No special equipment is needed.

6.7.2 Procedure

1. If the bore is pumped only occasionally, turn on the pump and run it for the length of time estimated to purge the bore (i.e. remove three casing volumes).
2. Collect water sample after purging is completed.
3. If the bore is used for continuous pumping at certain times of the day (irrigation, town water supply), there is no need for purging; correlate time of sampling with times when bore is used, or has just been used.

6.8 MEASURING FIELD PARAMETERS

Some physicochemical parameters cannot be reliably measured in the laboratory as their characteristics change over a very short time scale. Parameters that should thus be measured in the field include pH, electrical conductivity (EC), temperature, dissolved oxygen (DO), redox potential (Eh) and alkalinity. It is recommended that field parameters be measured in a flow cell (Figure 12) to avoid contact between the groundwater and the atmosphere. The field parameters can be reliably measured using a multiparameter meter—usually with an electrode for each parameter (Figure 13). It is crucial to calibrate the meter accurately before using it, and regularly during use against known standards and according to standard operating procedures. Calibration procedures vary between meters and between manufacturers so it is important to follow the instructions supplied with the equipment.

Figure 12: *Flow cell used to monitor field parameters during pumping*

Most electrodes are calibrated using standard solutions. These can be purchased from laboratory supply companies or sourced from a National Association of Testing Laboratories (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 the standard solutions will influence the performance of the meter, so it is important to obtain new solutions if there is any doubt.

When calibrating a meter, record on a standard sheet the date, temperature and calibration readings. This will keep a record of the performance of each meter and provide evidence that quality procedures are being used. Appendix 5 provides an example of a field calibration record sheet.

Some manufacturers produce ion specific probes that measure analytes such as nitrite, calcium, sulfide, bromide, fluoride, ammonium and chloride in the field. The results obtained from these field meters are rarely comparable to those produced in the laboratory, as they require a carefully managed environment in order to work correctly. However, they can have value when only relative indicative values are required. Some field colorimetric methods are becoming available, particularly for some applications.

Figure 13: *Testing of field measurements using multiparameter meters*

6.9 TESTING FIELD PARAMETERS

6.9.1 pH

A pH meter measures pH and temperature, and adjusts the reading according to the temperature of the sample (as pH varies with temperature).

Groundwater pH is a fundamental property that describes the acidity and alkalinity and largely controls the amount and chemical form of many organic and inorganic substances dissolved in groundwater. Many important properties of water are determined by pH; for example, both the suitability of groundwater for domestic

and commercial uses and the ability of water to transport potentially harmful chemicals are controlled by pH.

pH meters usually display results in pH units. A wide variety of meters are available, but the most important part is the electrode. Buy a good, reliable electrode and follow the manufacturer's instructions for proper maintenance. Infrequently used or improperly maintained electrodes are subject to corrosion, which renders them highly inaccurate. The electrode tends to last only 1 or 2 years, so you may consider purchasing a meter with a replaceable electrode. Repeated measurements at elevated temperatures or at very high alkaline pH can quickly reduce the lifetime of the probe.

6.9.1.1 Equipment

The equipment you will need for this method includes:

- pH meter
- flow cell
- sample bottle
- deionised water
- calibration solutions and containers

6.9.1.2 Calibration

A good quality pH meter can detect minimum variations (sensitivity) of 0.01 pH units in water and can be calibrated at two or three pH levels. This type of instrument will give more accurate readings over a wider pH range than one-point calibration meters.

Meters must be calibrated with buffer solutions before each sampling trip and periodically during sampling, e.g., every tenth sample, to check if the meter has drifted off calibration. Your check on the calibration standard should be within ±0.1 pH units of the buffer used. If you are using a two-point calibration meter, use buffer solutions at 4.01 and 7.00 for instance. If you are using a three-point calibration meter, use buffer solutions at 4.01, 7.00 and 10.01 for instance. Buffer tablets or powder pillows can be purchased from test kit supply companies and must be used within their expiry date. A buffer solution of pH 4.01 will last three months, but a solution of pH 7.00 will last six months if stored in a cool dark place.

6.9.1.3 Procedure

1. Rinse the electrode well with deionised water.
2. Place the electrode in the sample. Wait 2–3 minutes for the reading to stabilise but be aware that some change will occur as pH reacts with carbon dioxide dissolving from the air.
3. Record the result on the Bore Information and Field Analyses Sheet (refer Appendix 2).
4. Within the laboratory, periodically measure the pH of the calibration solution to test accuracy. If it has drifted, recalibrate the electrode using a new buffer solution.

6.9.1.4 Maintenance

Always follow manufacturer's recommendations. If not available, rinse the electrode well with deionised water, replace cap with 3M KCl solution when finished. After field work is completed or at any sign of electrode sluggishness or poor performance, clean the electrode with the manufacturer's recommended cleaning solution. A storage solution may also be recommended for medium term electrode storage.

6.9.2 Electrical Conductivity

Electrical conductivity (EC) is an indirect measure of water salinity, and one of the most common and convenient methods used to test water. Electrical conductivity is significantly affected by the temperature, so all results should be normalised to a standard temperature of 25°C. The EC is also strongly dependent upon the ionic composition of water. Chloride (Cl^-) and sodium (Na^+) are most commonly the main ions influencing groundwater EC. Other ions that contribute to salinity are carbonates, sulfates, magnesium, calcium and potassium.

6.9.2.1 Equipment

The equipment you will need for this method includes:

- electrical conductivity meter
- flow cell
- operating manual for the meter and probe
- calibration solution
- deionised water

A good conductivity meter should have, apart from the EC electrode, a temperature probe that enables measurement of temperature and automatic compensation for temperature in the conductivity reading. If you have a non-compensating meter, you must measure the water temperature at the same time as the electrical conductivity and use compensation tables to be able to standardise your EC reading and report it as electrical conductivity at 25°C. Be aware that meters with different EC ranges are available, e.g., 0–1990 µS/cm (approx 0–1275 mg/L TDS) and 0–19 900 µS/cm (approx 0–12 800 mg/L TDS), so select one that matches the expected conductivity range for the groundwater you will be monitoring. Also make sure you write down the units, as some meters will automatically swap between µS/cm and mS/cm, depending on the EC range.

6.9.2.2 Calibration

Use a conductivity calibration solution (usually potassium chloride) to calibrate the meter to the range you will need. For example, a 0.01 molar KCl solution has a conductivity of 1413 µS/cm, and a 0.001 molar KCl solution has a conductivity of 147 µS/cm.

To prepare a 0.01 molar conductivity solution, dissolve 0.7456 g of KCl (that has been dried overnight at 105°C) in deionised water and dilute to 1 L (this can be stored

for six months). To prepare a 0.001 molar solution, use 0.0746 g of KCl (this can be stored for three months). Store solutions in a dry, dark and cool room.

If your EC meter does not have an inbuilt temperature probe (i.e., no automatic temperature compensation) make sure your calibration solution is brought to a temperature of 25°C before calibration, otherwise significant errors can result. For example, if the meter is calibrated using a solution at 15°C, it will give erroneous sample readings that are 20% too high.

Tip a small volume of calibration solution into a small clean container for use when calibrating the meter. Discard used solution (do not return it to the bottle). Do not immerse the EC probe in the stock solution container. Rinse the electrodes with deionised water.

6.9.2.3 Procedure

1. Before going to the site, calibrate your meter.
2. On site, rinse the electrode in deionised water.
3. Dip the electrode into the sample and, if necessary, select the appropriate conductivity range.
4. Do not immerse the probe too far (some probes/meters are not waterproof above a certain point).
5. Move the electrode slowly in a circle for one minute until the digital readout stabilises or continually jumps between two numbers.
6. Record the results in a Bore Information and Field Analyses Sheet (refer Appendix 2).
7. Rinse the electrode with deionised water.

6.9.2.4 Maintenance

Rinse the electrode with deionised water from a squeeze bottle. Dry the electrode by carefully dabbing (not rubbing or wiping) it with a paper towel; replace the cap and place the meter back in your kit. The electrode needs to be kept clean and dry.

To ensure accurate readings, you should periodically clean the electrode with methylated spirits. Put it into a beaker with enough methylated spirits to just cover it, and leave it to stand for 15–20 minutes. Remove the electrode and dab it with a soft tissue soaked in methylated spirits. Finally rinse it thoroughly with distilled water.

6.9.3 Temperature

The temperature of water directly affects many of its physical and chemical characteristics. Because groundwater is stored underground it has a relatively constant temperature throughout the year. In the upper 100 metres below surface, the temperature of groundwater is normally 1–2°C higher than the average annual air temperature. Penetration of the seasonal surface temperature fluctuation is determined by geological factors, like the distance from the surface to the groundwater, the heat transferability of the rocks, the groundwater formation,

and by anthropogenic factors. Temperatures of shallow aquifers reflect annual surface temperatures and differ according to the climatic zones. Temperatures of groundwater from deep *artesian aquifers* can reach very high values, often above 80°C.

6.9.3.1 Equipment

The equipment you will need for this method is a glass thermometer or a digital meter. Before using a glass thermometer, check the glass for cracks and check the alcohol or mercury column for breaks.

6.9.3.2 Procedure

1. Place the thermometer a few centimetres into the water sample as soon as it has been collected.
2. Wait one minute, until the reading is stable.
3. Read the temperature to the nearest 0.5°C while the thermometer bulb, or temperature probe, is still immersed in the water; make sure you take the reading as close as possible to eye level.
4. Record your results on a Bore Information and Field Analyses Sheet (Appendix 2).

6.9.3.3 Maintenance

After use, rinse the thermometer or meter probe with clean water, dry it and return it to its protective container. Keep the thermometer free from dirt and other contaminants. Make sure the glass does not get scratched or cracked.

6.9.4 Dissolved oxygen

Dissolved oxygen (DO) is a measure of the quantity of oxygen present in water. Groundwater, in general, will have low dissolved oxygen content where there is a lack of direct contact with air or where the existing oxygen has been utilised in chemical and microbiological processes. Oxygen is supplied to groundwater by recharge of oxygenated water or by movement of air through the unsaturated material above the watertable. Depletion of DO can encourage microbial reduction of nitrate to nitrite, sulfate to sulfide and increase the amount of ferrous iron in solution (Hem, 1989).

A dissolved oxygen meter is an electronic device in which oxygen diffuses across a membrane in a submerged probe, to complete an electrical circuit. It records the dissolved oxygen concentration in milligrams per litre or percentage saturation. The advantage of this type of meter is that you can measure directly in the groundwater samples.

6.9.4.1 Equipment

The equipment you will need for this method includes:

- dissolved oxygen meter and probe (electrode)
- flow cell
- operating manual for the meter and probe

- spare membranes and electrolyte solution for the probe
- spare batteries for the meter

6.9.4.2 Calibration

The DO probe is generally calibrated in a special sleeve containing a water-saturated songe before each sampling trip and periodically during sampling, e.g., every tenth sample or every day, to check if the meter has drifted off calibration.

6.9.4.3 Procedure

1. Turn the meter on and allow 15 minutes for the meter to reach equilibrium before calibrating.
2. Calibrate the meter before each use, according to the manufacturer's instructions.
3. Place the probe in the flow cell.
4. Set the meter to measure temperature and allow the temperature reading to stabilise. Record temperature reading on a water quality results sheet.
5. Switch the meter to read 'dissolved oxygen'. Record your results on a Bore Information and Field Analyses Sheet (refer Appendix 2).
6. Re-test water to obtain a field replicate result.

6.9.5 Redox Potential (Eh)

Redox potential (Eh) is a measure of the oxidising/reducing conditions of the groundwater system. This information can be useful in interpreting metal species in solutions and the possible corrosive effects of groundwater on metal pipes (Lloyd and Heathcote, 1995). Redox is measured in units of millivolts (mV) and is usually reported as relative to the standard hydrogen electrode (SHE). High Eh (>400 mV) indicates a strong oxidising tendency of groundwater whereas low Eh (<400 mV) indicates a strong reducing tendency of groundwater. Characteristically, recharge waters will exhibit high, positive redox potentials indicating oxidising conditions.

The redox sensor is a two-electrode system used to make a potentiometric measurement. The redox electrode serves as an electron donor or electron acceptor depending upon the test solution. A reference electrode is used to supply a constant stable output for comparison. Electrical contact is made with the solution using a saturated potassium chloride (KCl) solution. The electrode behaviour is described by the Nernst equation:

$$E_m = E_o - (RT/nF) \ln \{[ox] / [red]\}$$

Where

E_m is the potential from the ORP electrode,
E_o is related to the potential of the reference electrode,
R is the Gas Law constant,
F is Faraday's constant,
T is the temperature in Kelvin,

n is the number of electrons,
[ox] is the oxidant concentration in moles/L, and
[red] is the reductant concentration in moles/L.

6.9.5.1 Equipment

The equipment you will need for this method includes:

- redox meter and probe (electrode)
- flow cell
- operating manual for the meter and probe
- extra batteries for the meter

6.9.5.2 Calibration

Be sure to calibrate the meter according to the manufacturer's instructions, before each use.

6.9.5.3 Procedure

1. Turn the meter on and allow 15 minutes for the meter to reach equilibrium before calibrating.
2. Calibrate the meter before each use, according to the manufacturer's instructions.
3. Place the probe in the sample container.
4. Switch the meter to read 'redox' in relative mV (SHE). Record your results on a Bore Information and Field Analyses Sheet (refer Appendix 2). Note that some redox probes will not report redox in SHE and the measured ORP needs to be added to the voltage of the reference system (typically ~200 mV), which is also dependent on temperature. Refer to operators manual.
5. Re-test water to obtain a field replicate result.

6.9.6 Alkalinity using burette titration

Alkalinity is the measure of the concentration of bicarbonate and carbonate ions in groundwaters, in proportions determined by the pH of the sample. The principal sources of bicarbonate in groundwater are presumed to be atmospheric, biologically derived carbon dioxide moving through the soil and unsaturated zone to the water table, and dissolution of minerals such as calcite. Alkalinity determination should be completed as soon as possible after sample collection. Although not as strongly affected by air contact as a DO would be, alkalinity should be measured in the field to minimise the period of exposure to air before titration. Alkalinity is normally measured by potentiometric titration using a potentiometer. While field analysis of alkalinity is recommended, a laboratory measurement will generally provide a representative measure of the alkalinity provided good field sampling and laboratory analysis procedures have been followed.

6.9.6.1 Equipment and reagents

The equipment and reagents you will need for this method includes:

- potentiometer
- pH meter
- operating manual for the meter and probe
- HCl
- magnetic stirring plate
- dispenser
- spare batteries for the meter

6.9.6.2 Procedure

1. Filter the alkalinity samples with 0.45µm filter paper and allow 2-3 volumes of overflow to flush away sample water that has contacted air.
2. Set up a beaker, magnetic stirring plate, titrant dispenser, and the calibrated pH meter for a titration.
3. Pipette 25 mL of sample into 100 mL beaker (containing stirring magnet), lower the pH electrode into sample and wait for equilibration.
4. Start the magnetic stirrer at a slow but constant rate. Use a titrator to deliver the acid to the titration sample and continue the titration to pH 3.0.
5. Record the volume of acid used to achieve point (s) of inflection in the titration curve (the number of cm from starting point to the line on which inflection point is found, divided by 4); if the pH of the sample is greater than 8.3 there will be two inflection points at about pH 8.3 and pH 4.5; if pH is lower than 8.3 there will be only one inflection point.

Calculate alkalinity (expressed as mg/L $CaCO_3$) using the formula:

$$\text{Alkalinity} = V_a \times C \times 50000 / V_s$$

Where

V_a = volume of acid added
C = concentration of acid
V_s = volume of sample added in ml

For the samples with pH greater than 8.3 phenolphthalein alkalinity is present (resulting in two inflection points). The volume of acid used (V1) is the total amount of acid used for the entire titration (from the starting line to second inflection point).

Freshly made up Na_2CO_3 of known concentrations should be titrated with HCl used in the analysis to determine exact HCl concentration; this concentration should then be used in all calculations (A.Plazinska, personal communication). Sea water should be titrated as a control before each batch of samples (alkalinity of seawater equals 119 mg of $CaCO_3$).

Note: An alternative method is to use a digital titrator and methyl orange indicator.

6.9.7 Alkalinity using alkalinity titrator

Digital Titrator is a precision dispensing device fitted with compact cartridges that contain concentrated titrants (Figure 14). Accurate titrations are made without the bulk and fragility of conventional burettes. A main drive screw in the digital titrator controls a plunger which forces the concentrated titrant from a titration cartridge in a carefully regulated flow through the delivery tube. The titrator body is constructed of precision-molded, heavy-duty, chemical- and impact-resistant acetal plastic. Accuracy of this method is rated at ± 1%.

Figure 14: *Digital titrator for measuring alkalinity*

The alkalinity titrator is preferable to a standard burette dispenser for several reasons:

- smaller, faster unit to use in the field. No glass parts.
- accurate to ±1%
- virtually no exposure to acid, with small volumes of concentrated acid released directly into the sample via a sealed delivery tube.
- digital unit 'automatically' accounts for acid delivered with a simple factor to convert to alkalinity in mg/L.
- interchangeable sealed acid cartridges and multiple titration methods available.

6.9.7.1 Equipment and reagents

The equipment and reagents you will need for this method includes:

- digital titrator
- titration catridge
- alkalinity reagent set
- erlenmeyer flask 250 ml
- graduated cylinder
- pipette

6.9.7.2 Procedure

1. Select the sample volume and Sulfuric Acid (H_2SO_4) Titration Cartridge corresponding to the expected alkalinity concentration as mg/L calcium carbonate ($CaCO_3$).

2. Insert a clean delivery tube into the titration cartridge. Attach the cartridge to the titrator body.
3. Turn the delivery knob to eject a few drops of titrant. Reset the counter to zero and wipe the tip.
4. Use a graduated cylinder or pipet to measure the sample volume.
5. Transfer the sample into a clean 250-mL Erlenmeyer flask. Dilute if necessary.
6. Add the contents of one Phenolphthalein Indicator Powder Pillow and swirl to mix. If the solution turns pink, titrate to a colourless end point.
7. Place the delivery tube tip into the solution and swirl the flask while titrating with sulfuric acid. Record the number of digits required.
8. Calculate: Digits Required x Digit Multiplier = mg/L $CaCO_3$ Phenolphthalein Alkalinity.
9. Add the contents of one Bromcresol Green-Methyl Red Indicator Powder Pillow to the flask and swirl to mix.
10. Continue the titration with sulfuric acid to a light greenish blue-gray (pH 5.1), a light violet-gray (pH 4.8), or a light pink (pH 4.5) colour, as required by the sample composition.
11. Calculate:Total Digits Required x Digit Multiplier = mg/L as $CaCO_3$ Total Alkalinity.

Further details on the alkalinity measurement using digital titrator can be obtained from http://www.hach.com/fmmimghach?/CODE%3A1690008_24ED-210509%7C1

6.10 HYDROCHEMICAL SAMPLING

When collecting the actual samples for analysis (as opposed to monitoring the pumped water on site), the flow cell containing the electrodes described above must be by-passed. Samples can thus be taken upstream of the flow cell by diverting the water flow into a clean sampling beaker.

6.10.1 Filtration of groundwater samples

Whether samples need to be filtered depends on the monitoring objective(s). Ideally, the bore construction, purging and sampling techniques used should minimise the turbidity of the groundwater sample so that there is no need to filter for certain applications. However, it is often necessary to filter samples in the field to preserve certain parameters (cation, anion, and some isotopes) during the delay between sampling and analysis. Filtering is necessary to separate the operationally defined and conventional soluble component from the rest of the sample.

There are various methods and equipment available for field filtration, from simple syringe systems to more automated pump operated (positive) pressure or vacuum (negative pressure) systems. For nutrients, pressure filtration is preferable to vacuum filtration systems as the latter can draw off the more volatile nutrients and compromise results. Conventionally, 0.45 µm filters have been used in the industry and research communities. In the last 10 years or so, some groups have been using

finer filters (e.g., 0.1 µm). These may present some advantages and disadvantages under certain circumstances, but on the whole, 0.45 µm is still the most common fitlter size used. Note that filter membrane types (e.g., nitrocellulose, cellulose acetate, coated Teflon®, etc.) and filtering protocols can affect the composition of the filtered water (e.g., Horowitz et al., 1996).

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.

6.10.2 Syringe filters

There are range of disposable filters and syringes available on the market that can be readily be used for filtering ground water samples in the field (Figure 15). They come individually packed, minimising the contamination of samples.

Figure 15: *Syringe filter*

The sample should be drawn into the syringe directly from the sampling beaker. The syringe should be rinsed with the sample three times with the rinses discarded. A volume of water is then drawn into the syringe before a 0.45-µm filter is attached to the syringe. A pre-filter is recommended for turbid samples to avoid quickly clogging the 0.45-µm filter. The sample can then be pushed through the filter and the filtrate retained in a clean container, itself rinsed three times with the filtered sample. Care should be taken to ensure that the filters are changed as they have a tendency to clog. Excessive force may rupture filter or affect the properties of the sample.

6.10.2.1 Advantages

- Simple to use
- No field decontamination required
- Inexpensive

6.10.3 Hand operated vacuum pumps with filtration unit

The hand operated vacuum pumps easily and quickly attains and holds a vacuum of 635mm Hg and can be used in the field for filtration (Figure 16). Vacuum trigger

releases require only one hand to operate and releases the vacuum with the touch of an index finger. An adjustable vacuum release rate can be controlled by a lever on the pump. These units are vacuum-driven filtration and storage devices for larger volumes than the syringe filters (e.g., 150 mL to 1 L). The vacuum pump is used to draw water from the top vessel, through the filter paper and down into the bottom vessel. The filtered sample is then transferred into sample bottles, which should be rinsed with filtered sample. Care should be taken to clean the filtration unit after each sample to avoid cross contamination. The filter media has a pore size of 0.45µm. When transferring liquids, use an air trap to prevent liquid from entering pump. The vacuum pump filtration unit described in this section has been developed through the Australian groundwater quality assessment project (Please et al., 1996; Ivkovic et al., 1998; Watkins et al., 1998; Watkins et al., 1999).

Figure 16: *Hand operated vacuum pump filtration unit*

6.10.3.1 Advantages

- Ideal for larger volume of sample
- Suitable for both field or lab use
- Easy to use
- Relatively inexpensive

The drawback of this system is that the negative pressure exerted to draw the water through the filter may promote degassing of any gasses dissolved in the water (e.g., carbon dioxide), which can negatively impact the quality of the water analysis as a whole (e.g., by increasing the pH).

6.10.4 Filter capsules and hand operated pressure pumps

As an alternative to using filter syringes and filter paper, sophisticated, single-use filter capsules have recently become widely available. Providing up to 600 cm^2 of surface area (at 0.45 µm pore size) in a compact and sealed design, they are very practical (Figure 17a). Positive pressure necessary to push water through the capsule can

generally be provided by the pump. Alternatively, a pressure flask (Figure 17b) and hand pump can be used (Figure 17c). The filter capsule are individually wrapped in plastic pouches, decreasing the risk of contamination.

6.10.4.1 Advantages

- Ideal for larger volume of sample, or turbid water due to huge surface area
- Suitable for both field or lab use
- Positive pressure prevents degassing
- Low contamination risk (single use, sealed bags)
- Can generally be directly connected to a pump hose outlet
- Easy to use

6.10.4.2 Disadvantages

- Cost

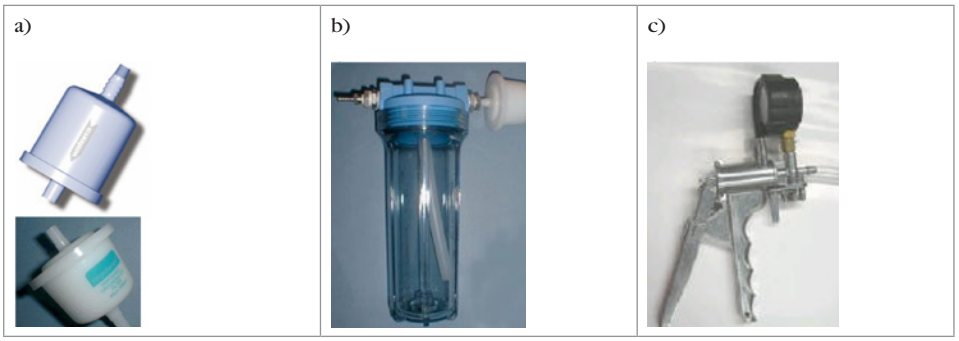

Figure 17: *a) Filter capsules; b) pressure flask; and c) hand operated pump*

6.11 SAMPLING PROCEDURE AND SAMPLE PREPARATION

Collect and prepare samples for major chemistry, trace elements, nutrients and isotopes according to Table 5 below. Some of the sample preparation steps described below for various analytes has been developed through the Australian groundwater quality assessment project (Please et al., 1996; Ivkovic et al., 1998; Watkins et al., 1999; Radke et al., 2000).

6.11.1 Anions

Most anions in groundwater (Cl^-, SO_4^{2-}, F^-, Br^-, NO_3^- and PO_4^{3-}) can be analysed using ion chromatography. Some anions (F^-, I^-) can be analysed by ion specific electrode (ISE) techniques. Bicarbonate (HCO_3^-) is determined by alkalinity titration in the field.

6.11.2 Major and minor cations

Major (Na, K, Ca and Mg) and minor (Fe, Si, B, Ba, Li, Sr, Al, Cu, Mn and Zn) cations in groundwater can be analysed by either inductively coupled plasma-atomic emission spectrometry (ICP-AES), or inductively coupled plasma-mass spectrometry (ICP-MS) or ICP-optical emission spectrometry (ICP-OES). Analyse U, Pb and V using ICP-MS.

Table 5: Summary of sample preparation for major and minor chemistry, nutrients and isotope analyses.

ANALYTE	CONTAINER	PREPARATION	PRESERVATION
Anions	125+ mL HDPE new bottle	Filter through 0.45 µm membrane filter	Store in a cool place.
Cations	50+ mL HDPE new or acid-rinsed bottle	Filter through 0.45 µm membrane filter	Acidify to pH <2 with ultrapure nitric acid. Store in a cool place.
Trace As, Se, Hg	125 mL brown glass bottle	Filter through 0.45 µm membrane filter	Add a drop of 5% potassium dichromate in 5% ultra pure nitric acid. Store in a cool place.
Dissolved Organic Carbon (DOC)	125 mL PE bottle	Filter through 0.45 µm membrane filter	Refrigerate at 4 *C.
Nutrients	125 mL PE bottle	Filter through 0.45 µm HVLP membrane filter	Freeze.
Trace Metals	125+ mL PE bottle	Filter through 0.45 µm HVLP membrane filter	Acidify to < pH 2 with 0.5 mL ultra pure nitric acid. Store in a cool place.
Fluoride & Iodide	125 mL brown glass bottle	Filter through 0.45 µm membrane filter	Refrigerate at 4 *C.
Stable Isotopes-Deuterium, Oxygen in water	28 mL glass McCartney Bottle or 15 mL Vacutainers®	None. No air bubbles.	Store in a cool place.
Stable Isotopes-Sulfur, Oxygen in Sulfate	500+ mL HDPE bottle	Filter through 0.45 µm membrane filter	Add 1-2 mL of acid (HNO_3, HCl), shake and let react, then add 10 g barium chloride to precipitate barium sulfate.
Carbon-14	Brown glass Winchester bottle	None	Add 50 mL NaOH, shake and let react, then add 600 mL saturated strontium chloride to precipitate strontium carbonate.
Dissolved gasses	250 mL glass bottle with perforated screw cap and thick synthetic wad	None	Fill to brim then remove 10 mL, seal tightly. Store in a cool place.
Radioactive Isotope-Tritium	2.5 L glass Winchester bottle	None	Fill bottle directly from pump discharge hose. Leave 1 cm air-gap for expansion. Store in a cool place.

ANALYTE	CONTAINER	PREPARATION	PRESERVATION
Chlorine-36	125 mL brown glass bottle	Filter through Whatman GF/C filter	Store in the dark.
Gold	1L HDPE bottle	Filter through 0.45 µm membrane filter	Fill bottle almost to top, add 30 g sodium chloride, 2-3 mL nitric acid and then one carbon sachet.

HDPE: High Density polyethylene; PE: Polyethylene; GF/C: Glass Fibre Filters

6.11.3 Trace elements

A large number of trace elements in groundwater (including Al, Au, As, Be, Sc, Cd, Co, Cu, Cr, Fe, Mo, Pb, Rb, Sr, Th, Ti, U, V, W, Zr and rare earth elements) can be analysed by inductively coupled plasma-mass spectrometry (ICP-MS) or inductively coupled plasma-optical emission spectroscopy (ICP-OES) or inductively coupled plasma-atomic emission spectrometry (ICP-AES) . In some cases a preliminary treatment is necessary to enhance sensitivity (e.g., hydride generation for As, Sb, Se; resin exchange for Pb; collision/reaction cell for Se). Atomic adsorption spectrometry (AAS) is an alternative technique for many trace elements. Although it is slower, it can provide information on speciation.

6.11.4 Chlorine-36

Chlorine-36 is naturally produced in the atmosphere, mostly from cosmic ray interactions with argon. It is dissolved in water vapour and falls out with rainfall, together with sea-spray or terrestrially-derived salt. ^{36}Chlorine has a half-life of 301 000 ± 4000 years (Bentley et al., 1986) and can be used to date groundwater with subsurface ages exceeding one million years, and also has a myriad of uses for tracing subsurface water at shorter time scales.

6.11.4.1 Procedure

1. Fill a 2.5 L Winchester bottle with water from the discharge hose.
2. Filter through GF/C membrane filters and pour into a 2.5 L Winchester bottle that has been pre-rinsed with filtered sample.
3. Acidify the sample by adding 2 mL of nitric acid followed by two grams of silver nitrate or 10 ml of silver nitrate solution.
4. Allow a precipitate to form and settle overnight.
5. Decant the water off, saving some for topping up the sample bottle, then pour the precipitate into a 125 mL brown glass bottle. Top up the bottle with saved sample, replace the lid, avoiding entrapment of air bubbles and store the bottles in the dark.
6. Analyse ^{36}Cl concentration on the accelerator mass spectrometer.

Note: Gloves must be worn during this process to prevent sample contamination.

6.11.5 Radon-222

Radon-222, a noble gas with a half-life of 3.82 days, is frequently used in the hydrological and environmental studies. These include tracing groundwater input to streams (Ellins et al., 1990; Cook et al., 2003), lakes (Corbett et al., 1997; Tuccimei et al., 2005), and coastal zones (Cable et al., 1996; Corbett et al., 2000; Schwartz, 2003), as well as rates of river water infiltration to banks (Hoehn and von Gunten, 1989). ^{222}Rn in natural waters can be extracted and measured through liquid scintillation counting (Leaney and Herczeg, 2006).

6.11.5.1 Equipment

The equipment you will need for this method includes:

- 1.3 L plastic soft drink bottle
- glass nozzle
- syringe
- vials with mineral oil

6.11.5.2 Procedure

1. Fill a 1.3-L soft drink plastic water bottle with water from the discharge hose, ensuring minimal agitation of the sample during collection.
2. Use a syringe to remove ~50 mL of sample water from the water bottle.
3. Add a mineral oil (20 mL) into the water bottle, replace the lid, and shake the bottle for 4 min, during which time the ^{222}Rn is preferentially transferred to the mineral oil.
4. Allow the bottle to stand for 1 min as the mineral oil and water separate.
5. Remove the lid of the plastic bottle and insert a glass nozzle in the bottle. The nozzle consists of 1 mm ID capillary glass tubing blown onto a B24 ground-glass cone that fits tightly into the bottle opening (see Figure 18).
6. Displace the mineral oil into the vial by squeezing the plastic bottle, carefully ensuring that no water is displaced into the vial. Recap the vial tightly and seal with insulation tape
7. Take duplicate samples.
8. Record date and time of sampling.
9. Post immediately to laboratory, as ideally samples should be counted within few days of collection.
10. Analyse water samples for Rn concentration by measuring alpha decays for the 20 ml.
11. Vials using a Qantulus liquid scintillation counter (Leaney and Herczeg, 2006). Report the results as Becquerels per litre (BqL-1).

Figure 18: *Photo of the glass nozzle fitted to the PET bottle as used when displacing mineral oil to the scintillation vial (adapted from Leaney and Herczeg, 2006)*

6.11.6 Carbon -14

^{14}C is a radioactive isotope of carbon with a half-life of ~5730 years. The mean residence time of groundwater is determined primarily by the radioactive decay of ^{14}C which is calculated by comparing the measured ^{14}C concentration of the dissolved inorganic carbon (DIC) in groundwater with the estimated ^{14}C concentration of the carbon as it enters the saturated zone. A water sample to be analysed for ^{14}C is firstly treated to form a carbonate precipitate which is then converted to carbon dioxide for analysis.

6.11.6.1 Equipment

- 20 L white plastic jerry cans
- brown-glass winchester bottle
- conc. NaOH solution
- saturated $SrCl_2$ solution
- magnafloc solution
- 0-14 pH test strips

6.11.6.2 Procedure

1. Acid-wash plastic containers in approx. 5 % HCl and distilled water. Avoid sample contamination by minimising contact with air as much as possible. 20 L of sample is usually enough to yield at least 6 g of CO_2, although alkalinities less than 400 mg/L will require more sample (up to 100 L).
2. To each clean 20 L plastic jerry can, rinse and fill with sample directly from the pump discharge hose. Any sediment must be removed by settling overnight and decanting into another container before processing.
3. Add 50 mL NaOH solution and mix by shaking. Check that pH is >9 and add more NaOH if necessary.
4. Add 600 mL saturated strontium chloride ($SrCl_2$) solution and mix by shaking.

5. Add 5 mL of Magnafloc solution, shake well and allow precipitate to settle out (overnight if possible).
6. Again check that the pH is =>9.0
7. Siphon clear water from top of precipitate then decant the precipitate into a Winchester bottle (by funnel). Fill head space in the winchester with nitrogen gas if available, then seal with a plastic insert and cap tightly.
8. Record the date and time of sampling.
9. Transport sample to the laboratory for analysis of ^{14}C.
10. ^{14}C concentrations in water samples can be measured using the direct absorption method (Leaney et al., 1994; Vita-Finzi and Leaney, 2006).

Note: An alternate method using Accelerator Mass Spectrometry (AMS) is available to measure ^{14}C concentration in water. Five litre of water is usually sufficient for AMS ^{14}C analysis, although as little as 2L may be required. Water samples are directly submitted to the laboratory, where the dissolved inorganic carbon is extracted from the sample and prepared for the AMS analysis. This method of analysis is more expensive than the direct absorption method.

6.11.7 Pesticides

Pesticides in groundwater samples can be extracted based on USEPA Method 525.2 (Eichelberger et al., 1994) as described below. Briefly, samples can be filtered and extracted on conditioned C_{18} solid phase extraction cartridges at the bore site to minimise analyte degradation. Pesticides in the samples can be eluted with solvent in the laboratory and analysed by gas chromatography-mass spectrometry (GC-MS) in full scan and selected ion monitoring modes. The pesticide extraction procedure described in this section has been adopted from the Australian groundwater quality assessment project (Watkins et al., 1998; Watkins et al., 1999).

6.11.7.1 Equipment

- FMI QB1 Pump (or equivalent) and Teflon tubing
- RHB Pump and Teflon filter holder
- C_{18} cartridges (pre-cleaned)
- desiccator cabinet
- HPLC grade water and methanol
- acetone
- 4 x 1 L Teflon bottles
- 47 mm diameter GF/F filters
- micropipettor
- glass dispenser (methanol)
- 200g capacity rechargeable battery powered top-pan balance and charger
- stopwatch
- 3 x rechargeable sealed 12 V batteries and charger
- marking pens
- cartridge taps (Luer lock fitting)

- wash bottle - HPLC water
- wash bottle - pH 2.2 HPLC water
- supelco Visi-1 sample processor, P/N 5-7080
- cartridge holder and clamp

6.11.7.2 Extraction procedure

1. Rinse two Teflon 1 L bottles three times in the sample supply end then collect 1 L of the sample.
2. Prepare the 47 mm diameter Teflon in-line filter unit by placing a GF/F glass fibre filters in the unit and seal tightly.
3. Pump the sample through the unit using the RHB pump, collecting the sample in other rinsed Teflon bottles.
4. Weigh 400 mL of filtered sample into a tared 1 L teflon bottle and add 3 g of methanol to the water sample and record the total weight of the sample.
5. Add surrogate mixture (100 µL of ~5 µg/mL solution) with a glass-tipped micropipette.
6. Pre-clean the C-18 cartridge by conditioning with 2 mL of methanol, followed by 2 mL of HPLC-grade water.
7. Pump the filtered sample through the conditioned cartridge at 20-25 mL/min using a FMI-QB1 pump, or equivalent, and collect the spent water into the pre-weighted beaker and reweigh after collecting the processed water.
8. Remove all residual water from the cartridge with a Visi-1 (Supelco) syringe. Store the dried cartridges in a labelled vial at ambient temperature until laboratory analysis.

6.11.7.3 Analysis

Gravity-elute the cartridges in the laboratory with 2x2 mL of hexane:isopropanol (3:1) and then concentrate the aliquot to 500 µL and finally add an internal standard (phenanthrene-d_{10}). Analyse the concentrated extracts by GC-MS in full scan electron impact (EI) mode to screen for the bulk of pesticides. Finally reanalyse the samples by GC-MS in selected ion monitoring mode (SIM) to quantify identified compounds.

Note: Prevent the cartridge from running dry; if this occurred the conditioning phase needs to be repeated (Watkins et al., 1998; Watkins et al., 1999).

6.11.8 Microbiology

Groundwater, like any natural habitat, has been found to contain a broad spectrum of microorganisms similar to those found in surface soils and waters. Microbial groups found in groundwater encompass bacteria, fungi, and protozoa and are representative of most physiological types. Occasionally pathogenic bacteria, viruses and protozoa of gastrointestinal origin from domestic, agricultural and other anthropogenic activities, may infiltrate through soils, sediments and rocks to underlying groundwaters. They can survive for sufficient time to be ingested by humans and livestock drinking extracted groundwater.

Faecal Indicator Bacteria

There are many known waterborne pathogens capable of causing infections when digested even in very small numbers. Most are present in large numbers in human and animal excreta. It is recognised that monitoring for presence of specific pathogens in water (drinking water supplies) is impractical. An indirect approach has been universally adopted where water is examined for indicator bacteria whose presence implies some degree of faecal contamination (NHMRC, 2003).

Total coliforms

Several organisms have been suggested as potential indicator organisms, but the coliform group has been universally accepted. According to historical definition developed on the basis of the methods of detection, the coliforms are:

"..all aerobic and facultatively anaerobic, Gram negative, non-sporeforming and rod shaped bacteria that ferment lactose with acid and gas production at 35-37°C within 48 hours."
(APHA, 1995).

In more recent research it has been accepted that definition of coliforms must be based on:

possession of the beta-galactosidase gene coding for betagalactosidase enzyme which catalyses the breakdown of lactose into galactose and glucose (fundamental characteristic of family Enterobacteriaceae) (Gleeson and Gray, 1997).

The coliform group also includes the *thermotolerant faecal coliforms* which are defined as being able to ferment lactose at 44ºC.

Coliforms are largely of faecal origin but also include species which are non-pathogenic – commonly found in unpolluted soils and on vegetation, and therefore do not present a public health problem. In addition, microorganisms from the coliform group are capable of regrowth in aquatic environments. The coliform presence is therefore interpreted as a **presumptive result** and samples found to contain total coliforms should be re-examined for the presence of thermotolerant (faecal) coliforms. The presence of coliforms (total and thermotolerant) is still widely used as the reliable indicator of faecal pollution for potable water. According to Australian Drinking Water Guidelines no sample should contain coliforms (minimum sample volume 100mL) (NHMRC/NRMMC, 2004).

Thermotolerant (faecal) coliforms

The thermotolerant coliform group (Entrobacteriaceae that are able to ferment lactose at 44°C) include several species of genera *Klebsiella*, *Enterobacter* and *Citrobacter* as well as *Escherichia coli.* ***E.coli*** **is considered the only true faecal coliform**, representing up to 95% of the Enterobacteriaceae found in faeces (Waite 1985). Other thermotolerant coliforms are able to multiply and colonise natural environments and can be derived from non-faecally contaminated waters.

The presence of thermotolerant coliforms generally indicates that faecal contamination has occurred, but their presence in water does not always imply a health hazard. It is now widely accepted that the use of E.coli may be more appropriate for routine surveillance of drinking waters. According to Australian Drinking Water Guidelines no sample should contain thermotolerant coliforms (minimum sample volume 100mL) (NHMRC/NRMMC, 2004).

6.11.8.1 Method of detection: membrane filtration

This method enables enumeration of microorganisms present in samples of water. A measured volume of samples is filtered through a membrane. The pore size of the membrane is such that the microorganisms are retained on the surface of the membrane. The membrane is then aseptically transferred to a medium (solid or a pad saturated with liquid medium). After incubation at a specific temperature for a specific length of time growth will occur. Colonies of characteristic morphology and colour are counted and number of organisms per 100 mL calculated. The results are expressed in colony forming units per 100 mL (CFU/100 mL).

Membrane filtration method can be used for enumeration of different groups of microorganisms in water such as faecal indicator organisms (total and thermotolerant coliforms) as well as non-pathogenic hetrotrophic bacteria naturally occurring in waters (APHA, 1995).

This method:

- Has to be used in laboratory conditions, in clean, preferably sterile environment, sterile growth media, plates, filtration sets, sample bottles are necessary.
- Sample processing has to be conducted by trained personnel
- Collected water samples have to be processed within 4 hours from collection.

Testing groundwater samples for presence of faecal indicator bacteria using membrane filtration method requires setting up field laboratory. At least 3-4 meters of bench space that can be easily cleaned and disinfected, preferably in the clean room not used by others, is required. Prepacked sterile media and Petri plates are available commercially but access to autoclave is necessary for sterilisation of filtration equipment and sample bottles.

6.11.8.2 Equipment and laboratory consumables

- sterile sample bottles or disposable sterile Whril-pak bags for sample collection
- portable Bunsen burner
- portable field incubators
- fridge (for media storage)
- low power (20 x) magnification, binocular, wide-field microscope (Millipore) used for scoring colonies on the plates
- vacuum pump
- filtration flask holder or manifold, 1L collection flask

- sterile filtration sets consisting of a funnel and base (1 per sample)
- microbiological media (Millipore)
- petri dishes with absorbent pads (available from Millipore)
- sterile 5 mL pipette tips
- 5 mL automatic pipette
- tweezers
- 0.45 µm acetate-cellulose sterile filters packed in single envelopes (available from Millipore)
- alcohol

Prepacked sterile liquid media are available from Millipore. These are:

- M-Endo Broth in 2 mL ampoules for enumeration of total coliforms
- m-FC Coliform Broth in 2 mL plastic ampoules for enumeration of thermotolerant (faecal) coliforms

6.11.8.3 Field procedures – sampling

- Use pre-sterilised plastic bottles for sample collection from bores or surface water.
- Bottles can be substituted by disposable sterile plastic Whril-pak bags (500 mL volume).
- Samples should be stored at 4°C and processed within maximum three hours after collection.

6.11.8.4 Filtration

- Pre-sterilised filtration set should used for sample processing.
- Filter three volumes of the sample for each test (faecal or total coliforms): 10, 50 and 100 mL.
- Use 5 mL automatic pipette and a 5 mL sterile plastic tip for the 10 mL volume, and 50 and 100 mL volumes can be carefully poured straight into the graduated filtration funnel.
- Use 0.45 µm grided Millipore filters packed in individual sterile envelopes.
- Place the filters in sterile Petri dishes on top of absorbent pads saturated with appropriate medium (M-Endo or m-FC).

6.11.8.5 Incubation and scoring

- Incubate plates for enumeration of total coliforms (with M-Endo medium) at 35°C for 24 hours.
- Typical coliform colony is pink to dark red with a metallic surface sheen – only such colonies should be scored.
- Incubate plates for enumeration of faecal coliforms (with M-FC medium) at 44.5°C for 24 hours.
- Typical thermotolerant (faecal) coliform colonies are various shades of blue.
- Score the plates using the Millipore microscope after 24 hours of incubation and record results in the scoring sheet.

6.11.8.6 Results

- Calculate the results from the plates with the ideal range of 20 – 60 colonies.
- If only one plate is having a count in the ideal range then: CFU/n mL = count/ volume filtered x n, where n denotes volume of sample.
- If two or more plates have counts in the ideal range then: CFU/n mL = (count1+count2)/(volume1+volume2) x n.
- Express the results in colony forming units per 1 mL (CFU/1mL).

Additional information on the membrane filtration method can be obtained from Plazinska (2000, 2003).

6.11.8.7 Method of detection: presence and absence tests

Presence/absence tests (P-A) provide qualitative information on the presence or absence of microorganisms in the test sample. When compared with other detection techniques, the P-A test for coliforms has been found a more sensitive method and requiring significantly less effort and expense.

This method:

- Can be used in field conditions
- Can be performed by personnel with minimal training.
- Can be performed with minimal preparation time

The Colilert test for detection of coliforms and E.coli uses the principle of '*defined substrate technology*': substrates (chromogenes and fluorogenes) that produce colour and fluorescence upon cleavage by specific enzyme. It is based on detection of the beta-galactosidase enzyme which caltalyses the breakdown of lactose to galactose and glucose (characteristic of family Enterobacteriaceae). The assay is based on biochemical reaction in which beta-galactosidase cleaves the substrate (ONPG) to produce yellow nitrophenol (Manafi et al., 1991).

The detection of E.coli is based on detection of beta-glucoronidase activity (the substrate is hydrolysed by beta-glucoronidase to produce an end-product which fluoresces when irradiated with long-wave UV light).

Colilert is US EPA approved and is included in Standard Methods for Examination of Water and Wastewater. It is used in over 90% of all US State laboratories (APHA, 1995).

6.11.8.8 Equipment and laboratory consumables

- sterile sample bottles or disposable sterile Whril-pak bags for sample collection
- when sterile equipment for sample collection is not available, sample can be collected directly to the 100 mL incubation vessel
- portable field incubator
- hand-held UV lamp
- sterile 100 mL sample vessels
- pre-packed dehydrated media with appropriate substrates

6.11.8.9 Field procedures: sampling and incubation

- Collect water samples into sterile bottles or bags (as described above); if sterile bottles are not available collect directly into incubation vessel.
- Collect only one 100 mL sample and incubate the sample.
- Sample vessels have 100 mL volume mark on the side of the bottle, so there is no need for additional sterile measuring equipment.
- Add dehydrated Colilert reagent in pre-measured satchet to the sample.
- Incubate sample at 35°C for 24 hours.

6.11.8.10 Results

- Examine samples after 24 hours - development of yellow colour indicates presence of coliforms.
- Examine samples under long-wave UV light using a small hand-held lamp - fluorescence of the sample indicates a positive test for *E.coli*.

7. Gas Sampling at Water Bores

7.1 INTRODUCTION

Sampling of gases from water bores has a number of applications, from hydrocarbon prospectivity, monitoring potential CO_2 migration from carbon capture and storage reservoirs (e.g., detection of associated tracers, CO_2, etc) to gaining a better understanding of hydrologic processes. In this section, information is provided on different sampling techniques for analysis of commonly sampled groundwater gases.

7.1.1 Dissolved versus entrained/evolving gas samples

There are two approaches for sampling gas from water bores: 1) analysis of dissolved gases from a collected water sample; or 2) collection of gases at the bore and analysis of the gases directly either in the field or at a laboratory. Both techniques have their advantages and disadvantages.

The sampling protocols for analysis of dissolved gases are well established (USGS, 2006) and quantitative concentrations of the dissolved gas per volume of water can be obtained. The primary disadvantage is that accurate measurement requires exemplarily sampling to ensure that there are no bubbles and a very good seal. A poor seal will results in equilibration of the dissolved gases with the atmosphere during storage and transportation and a lower estimate of the true dissolved gas content. Samples must also be kept at 4°C at all times to lower the rate of microbial degradation and minimise sample loss. Samples cannot be frozen and should be shipped within several days of collection. Preparation of the sample at the analytical laboratory requires creating a headspace in the sample bottle (typically with helium) and allowing for partitioning between the gas and liquid phases. An aquilot of the headspace is withdrawn and analysed using gas chromatography.

Analysis of evolving gases is not a widely used monitoring practice but has been used with some success for hydrocarbon prospectivity in Australia (Moffitt and Weatherall, 2003). It typically involves passing bore water through a separator and analysing the evolving gases in the headspace of the separator. The gases can be either analysed in the field or collected and sent to a laboratory for analysis. The technique is particularly suitable for semi-quantitative field analysis of gases, particularly methane and carbon dioxide. While the degree of quantification is less than for dissolved gas analysis, the samples do not require refrigeration, and, if field analysis is conducted, there is less chance of contamination (i.e., gas loss) during transportation and storage.

Another approach between the strict analysis of dissolved gases and the capture of gas samples in the field is the collection of gas-water sample. This semi-quantitative technique involves collecting a water sample and flowing gassy water into an inverted water sample bottle (kept underwater in a bucket) until a sufficient headspace has been created. The bottle is sealed with a septa cap or plug and sent to a laboratory for gas analysis (Radke et al., 2000). In some cases, a water sample is

simply collected in a 1L Duran glass bottle equipped with a silicon rubber septa cap, leaving a headspace of approximately 150mL (Pallasser, 1996). These samples are contaminated with air but if collected in a similar manner, can provide a qualitative comparison between bores. While later analysis of the sample is simplified (i.e. inject an aliquot of headspace directly into a gas chromatograph), the chance of contamination with air during storage and transportation is greatly increased. In addition, samples must also be kept at 4°C at all times to prevent sample degradation and should be analysed shortly after collection. Sometimes $HgCl_2$ is added to the sample as a preservative (Radke et al., 2000).

7.2 SAMPLING OF DISSOLVED GASES

To ensure accurate dissolved gas analysis of groundwaters, field samples need to be collected without headspace and with a good seal. The sampling procedures outlined below are an adaptation guidelines published by the USGS Reston Chlorofluorcarbon Laboratory (USGS, 2006) and US EPA National Risk Management Research Laboratory (Kampbell and Vandegrift, 1998). Please refer to these publications for further details and for a discussion on reproducibility of the sampling methods.

7.2.1 N_2, Ar, CH_4, O_2, CO_2 and ^4He

7.2.1.1 Equipment

- 150mL serum bottle
- Needle
- 20mm grey butyl rubber stopper
- Bucket or 2L beaker
- (Optional: 20mm aluminium crimp caps, Crimper)

7.2.1.2 Procedure

1. Insert a needle into the rubber stopper until the tip just exists through the stopper.
2. Fill bucket or beaker with the groundwater.
3. Place water discharge tube from the bore into the bottom of a serum bottle and fill.
4. Once water starts to overflow from the serum bottle, place in filled bucket or 2L beaker.
5. Continue to fill, making sure no bubbles have adhered to the sides of the bottle. Remove tube and insert the stopper in the bottle while it is submerged.
6. Remove the needle from the stopper while it is still submerged.
7. Remove filled serum bottle from bucket or beaker and check that there are no gas bubbles, otherwise empty and resample (use new stopper).
8. As an additional precaution, crimp-seal with aluminium crimp caps.
9. Label each bottle with the bore name, date, and time of sampling and the sequence number of each bottle as it was collected.
10. Keep samples cold during transit.
11. Analyse samples within a few days of collection.

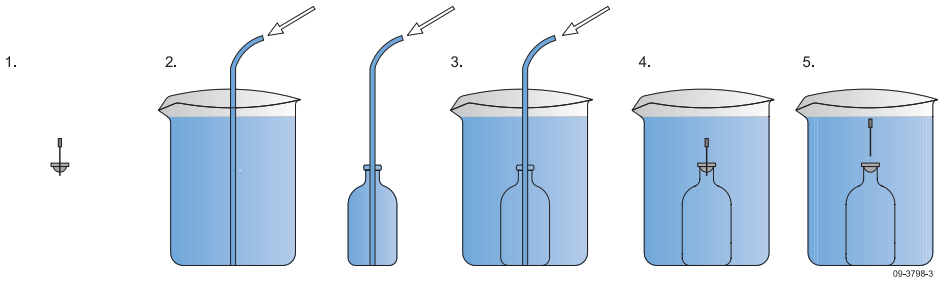

Figure 19: *Collection and analysis of groundwater samples for dissolved gas analysis by Gas Chromatography*

7.2.2 Dissolved hydrocarbons

A modified procedure from that outlined above is recommended for hydrocarbons. Sulfuric acid is added as a preservative.

7.2.2.1 Equipment

- 60mL serum bottle
- 20mm butyl rubber stopper with Teflon septa
- 20mm aluminium crimp cap
- Crimper
- 50% sulfuric acid
- Pipette

7.2.2.2 Procedure

1. Gently add water down the side of a serum bottle, avoiding agitation or the creation of bubbles.
2. Once bottle is full, add several drops of 50% sulfuric acid as a preservative.
3. Cap and seal bottle with a 20mm butyl rubber stopper with Teflon faced seal and aluminium crimp seal.
4. Check that there are no gas bubbles, otherwise empty and resample (use new cap)
5. Label each bottle with the bore name, date, and time of sampling and the sequence number of each bottle as it was collected
6. Keep samples cold during transit
7. Analyse within 14 days of collection

7.2.3 SF_6

SF_6 is used for dating of modern groundwater age and sometimes as a tracer for geological storage of CO_2. Care must be taken to avoid gas bubbles, otherwise the SF_6 in the sample is likely to be lost with the bubble and the groundwater age will be biased as old.

7.2.3.1 Equipment

- Refrigeration grade copper tubing or nylon tubing (SF_6 sticks to most other tubing materials)
- Bucket or 2L beaker
- 1L amber glass bottle (plastic safety coated preferred) with a polyseal cone lined cap (e.g., amber Wheaton narrow mouth bottles with Poly-Seal® cone liner caps)
- Electrical tape

7.2.3.2 Procedure

Purge the bore.

1. Thoroughly rinse caps and bottle with groundwater to be sampled.
2. Place 1L bottle in 2L beaker or bucket.
3. Place tubing from pump in the bottom of 1L bottle.
4. Fill bottle and allow it to overflow from the neck (about 2.5L).
5. Slowly remove tubing from the bottle while water is still flowing. The bottle should be completely submerged at this stage.
6. Cap bottle (do not leave any headspace) underwater, remove and wipe dry.
7. Retighten cap and tape cap in a clockwise direction with electrical or similar tape. The tighter the cap the better.
8. Check that there are no gas bubbles, otherwise empty and resample (use new cap).
9. Label each bottle with the bore name, date, and time of sampling and the sequence number of each bottle as it was collected.
10. Collect at least two bottles per site.
11. Keep bottles in the cooler (but not on ice) and not in the sun. Prevent exposure to excessive heat/cold.
12. Samples should not be refrigerated or stored upside down.
13. Analyse samples within three months of collection.

7.2.4 CFC and other halogenated volatile organic compounds (VOCs)

The sampling procedure is identical to the procedure for SF_6 but different sized sample bottles and aluminium lined caps are used. Use only aluminum lined caps – this is the key to the success of the analytical method.

7.2.4.1 Equipment

- Refrigeration grade copper tubing or nylon tubing (CFC adheres to most other tubing materials)
- Bucket or 2L beaker
- 125mL clear glass bottle with aluminium foil lined caps (e.g., Wheaton narrow mouth bottle)
- Electrical tape

7.2.4.2 Procedure

1. Refer to sampling procedure for SF_6 (steps 1-12, but with 125mL bottles and aluminium foil lined caps).
2. Samples should not be refrigerated.
3. Store upside down until shipment. A small bubble may form in the sample bottle during storage. This is normal.
4. Analyse samples within 6 months of collection.

7.2.5 Noble gases

Sampling of noble gases requires filling a special copper sample tube (typically ¼ inch x 30-100cm) and sealing using pinch-off clamps. A full description of the procedure can be found at the USGS Reston Chlorofluorocarbon Laboratory (http://water.usgs.gov/lab/3h3he/sampling/).

7.3 SAMPLING OF ENTRAINED/EVOLVING GASES

Field sampling of entrained/evolving gases can provide an immediate semi-quantitative measurement of common gases at a bore or provide a secure method to capture gases on site without the need for refrigeration/eskies and the use of hazardous preserving agents (e.g., $HgCl_2$ or 50% sulfuric acid). The risk of biological degradation of the sample is negligible and the technique can be used for sampling groundwaters at elevated temperatures, where collection of dissolved gas samples is either too hazardous or where a high proportion of the dissolved gases may have volatilised. The primary risk factors for this technique are non-reproducibility of sampling and the risk of air contamination but these can be minimised by following the procedures outlined below.

7.3.1 Field analysis of CH_4, O_2, CO_2, CO and H_2S

These gases are suitable for semi-quantitative measurements on site. A hardy, self-priming marine diaphragm pump with pressure cut-out and dry run capability is recommended.

7.3.1.1 Equipment

- Two inch diversion T-piece with gate valve (for flowing bores)
- approximately 10L gas separator equipped with gas outlet valve and pressure gauge
- 12V diaphragm pump (e.g., through car cigarette lighter or battery)
- Calibrated field gas analyser with in-built vacuum pump (e.g. Geoscientific Instruments GA2000)
- $^1/_2$ inch Nylon hose for water
- $^1/_8$ inch hose for gas sample line
- Reduction fittings and ball valves

7.3.1.2 Procedure

1. Connect diversion T-piece between gate valve to bore/pump headworks and outlet piping/tubing (Figure 20).
2. Attach additional gate valve to T-piece and use a nylon hose to connect to the gas separator liquid inlet valve (see Figure 21).
3. Connect pump to gas separator outlet and additional nylon hose to bucket (for measuring flowrate) or direct away from the sampling area. Close gas separator liquid outlet valve.
4. Open top gas outlet valve.
5. Once stabilised flow conditions from the main bore outlet has been established, open gate value at diversion T-piece, open gas separator liquid inlet valve, and slowly fill gas separator until overflowing through top gas outlet valve.
6. Close liquid inlet valve.
7. Close top gas outlet valve, turn on pump and immediately open liquid outlet valve.
8. Draw down the liquid level inside the gas chamber and create vacuum, (e.g., -800 mbar).
9. Once the water level has decreased to approximately 3cm below the surface of the lid, gradually turn on the water inlet valve and adjust the outlet water valve so that the water level in the chamber is lowered to halfway in the chamber. Maintain this water level and a vacuum for the duration of the measurement. A water flow rate of approximately 2 L/min is recommended.
10. To take a field gas measurement, the vacuum within the chamber needs to be reduced to be less than the vacuum rating of the field gas analyser pump (e.g. -400 mbar). This can be achieved by reducing the outlet flow from the vacuum pump. Once the pressure in the chamber equilibrates at a suitable negative pressure, connect the portable gas analyser to the top gas sampling valve. Make sure there is a protective Nylon or Teflon filter between the gas analyser instrument and the gas sample line to prevent water entering the gas analyser.
11. Open top gas valve.
12. Continuously monitor concentration of gases until readings equilibrate.

Figure 20: *Install diversion T-piece between bore headworks and outlet*

Figure 21: *Creating a vacuum and stripping out dissolved gases*

Figure 22: *Setup of gas separator and field gas analyser*

7.3.2 Collection of gas samples from a gas separator/stripper

Gas samples can be collected from a gas separator, preferably before taking field measurements. Such samples can be used to check the measurements of the field gas analyser back in the laboratory and to analyse for analytes that cannot be measured in the field.

7.3.2.1 Procedure

1. Follow the procedure for field analysis of gases above (steps 1 – 9) to create an equilibrated headspace within a gas separator.
2. The volume of headspace gas accumulated within the chamber can be checked by closing the gas chamber outlet valve and slowly filling the chamber until just below zero pressure is obtained. After running the separator for 30 – 60 mins, a slightly gassy bore will typically generate 3cm of headspace below the top lid of the chamber (~2000 cm^3 for 30cm diameter separator). Do not let the chamber

go into positive pressure at this stage and pop the top seal, otherwise the sample will be contaminated with air when it is returned to vacuum. Note the volume of headspace and re-open the gas chamber liquid outlet valve to return to vacuum and normal sampling conditions.

3. To sample, close liquid outlet valve.
4. Reduce liquid inlet flowrate and continue to flow groundwater into gas separator, increasing the water level, and building up slight positive pressure within chamber. Be sure not to pop the top seal of the chamber.
5. Slowly open gas outlet valve to flush out any water/contaminated air that has accumulated in the gas sampling line (still maintain positive pressure in chamber) and then connect to sample vessel (e.g., sample bag, syringe, septum port gas sampling tube, etc.).
6. Continue to fill gas separator with groundwater, maintaining positive pressure, until the desired amount of headspace has been collected in sample vessel.
7. Close gas outlet value and close liquid inlet valve.

Notes

The success of this technique relies on maintaining a positive pressure to push gas out of the gas separator into the sample vessel. If a positive pressure is not maintained, the chamber will be contaminated with atmospheric air. The use of evacuated stainless steel flasks (e.g., Summa canisters) for sampling is not recommended because the pressures generated in the separator are too low and there is a high risk of atmospheric contamination.

7.3.3 Transfer of gas sample from a syringe to a glass bottle

This sample transfer procedure is based on recommendations by the USGS Reston Chlorofluorocarbon Laboratory (USGS, 2007).

7.3.3.1 Materials

- 125mL Wheaton bottle
- Grey butyl rubber stopper
- Gas tight syringe with luer lock and valve
- Thin Teflon tubing with luer lock fitting
- 2L beaker or bucket
- 20mm aluminium crimp caps
- Crimper

Table 6: Various sample containers for gas sampling of water bores.

SAMPLE CONTAINERS	IMAGE	COMMENTS
Septum port sampling gas tube[a]		For short term storage (e.g., less than 24 hours)
Gas tight syringe (e.g. 60mL)[b]		For initial capture of gas sample only. Sample must be transferred to a gas bag or in the headspace of a water bottle (see Figure 23) for longer term storage (e.g., a couple days).
Cali-5-bond bag		Ideally suited for low pressure inflation (requires only 1.7 kPa). These bags appear to be the most suitable for longer term sample storage
Teldar Sampling bag[c]		Recommended for soil gas sampling by US EPA (US EPA, 1999). For short term storage (e.g., 24-48 hrs).

[a] image from www.amglassware.com/gassamplingproducts.htm
[b] image from www.restek.com/restek/prod/1642.asp
[c] image from http://www.celscientific.com/files/Tedlar_Bag_1.jpg

7.3.3.2 Procedure

1. remove gas from separator using a gas tight syringe (e.g., 60mL). Close gas tight valve (Figure 23).
2. Attach Teflon tubing to syringe.
3. Fill 125mL bottle with groundwater and place in beaker also filled with the same groundwater.
4. Place rubber stopper in beaker.

5. Place teflon tubing in beaker, release valve on gas tight syringe, flush a small amount of sample gas through telfon tubing to flush out any atmospheric gases in tubing.
6. Place teflon tubing at the bottom of the filled sample bottle and invert in the filled beaker. Slowly transfer gas to sample bottle.
7. Attach stopper underwater, remove bottle, dry, and immediately crimp-seal.
8. Keep samples cold during transit and store upside down.
9. Analyse samples within a few days of collection.

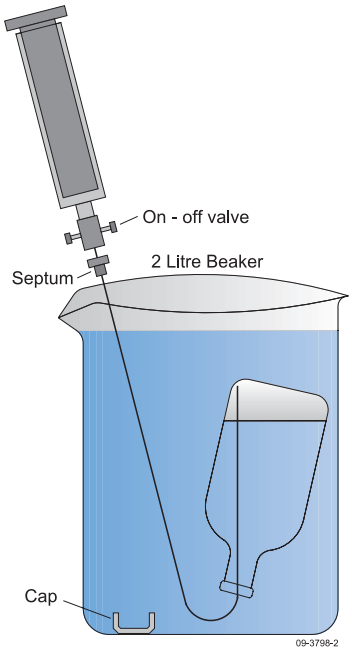

Figure 23: *USGS recommended transfer technique of gas samples taken using a syringe into a Wheaton bottle. Use cap/stopper appropriate for analysis (e.g. aluminium foil lined cap for CFC and grey rubber stopper for standard gas analysis) (USGS, 2007)*

8. Decontamination

Decontamination of pumping and sampling equipment is recommended for all sampling work although it is not routine for major ion analyses. It is necessary if the sampling is for microbiological, pesticide and organic parameters. Decontamination prevents cross contamination from the previous sample and should be completed before each bore sampling. Any equipment introduced into the bore should be decontaminated. The decontamination procedures described in this section has been developed through the Australian groundwater quality assessment project (Please et al., 1996; Ivkovic et al., 1998; Watkins et al., 1999).

8.1 GENERAL PROCEDURE

1. Prepare bleach wash solution by adding 200 mL of bleach concentrate to 20 L of tap water, and allow to stand for 45 minutes before use. Volume of bleach required depends on bleach strength used (see Table 7 for details).
2. Prepare 5 % HCl acid rinse by adding 125 mL concentrated HCl to a 2.5 L Winchester bottle of de-ionised water (Caution: add acid to water).
3. Spray the depth-measuring tape with 70 % ethanol and leave to dry on a cleaned surface before measuring the water depth.
4. Record bore information on Bore Record Sheet (refer Appendix 2) as required.
5. Set up the sprayer platform, spray unit and spray pumps, with the distilled water spray closest to the bore and the bleach spray furthest from the bore.
6. Clean the hoses from the spray pumps with 70 % ethanol before they are placed in their respective containers. Keep lids from bleach and water containers in labelled plastic bags to prevent contamination.
7. Place the generator downwind of the sampling site.
8. Sterile gloves should be worn by anyone handling the pumping equipment.

Table 7: Volume of bleach required for 100 mg/L chlorine concentration in 100L of water.

BLEACH STRENGTH (% SODIUM HYPOCHLORITE)	VOLUME OF BLEACH REQUIRED (ML)
3	330
5	200
10	100
12.5	80

8.2 PUMP-INTERNAL WASH

8.2.1 Procedure

1. Unscrew the pump from the pump hose.
2. Use a syringe or dispenser to inject about 10 mL of detergent into the pump hose. Screw the pump back onto the hose and keep the pump vertical until it is

placed in the cleaning tank. Turn on the pump as soon as it is placed in the tank to avoid detergent flowing out of the pump and into the tank.

3. Wash the "bleach only" tank with about 5 L of bleach solution to decontaminate, then tip out bleach and rinse with about the same quantity of distilled water. Discard water also. Spray the pump and first 50 cm of hose with 70% ethanol and allow to dry. Fill the tank with the remaining distilled water.
4. Ensure that the discharge hose is connected so it is subjected to the same amount of cleaning as the pump line. Take care with all end plugs and stainless fittings and make sure these are regularly cleaned with ethanol and placed in a plastic bag when not in use.
5. Place pump in water and pump through hose at a rate of approximately 100 Hz.
6. After all the water has been pumped through the system disconnect the discharge hose extension and the power cable. Once again take apart the fitting in the top of the pump and pour about 200 mL of methanol into the hose and over the pump. Leave the screw-in plug out of the end of the pump hose to allow the methanol slug to move through the hose as the pump is lowered down the hole. Keep the pump high to keep methanol in the line.

8.3 PUMP-EXTERNAL WASH

The pump, a small part of the hose and the rollers on the sprayer platform do not get fully spayed by the washing machine. It is important to spray by hand these areas with 70% ethanol.

Start the bleach and polished water spray pumps. While lowering it down the hole pass the pump and hose through the spray chamber, maintaining a negative loop in the hose to keep the methanol in the line. Once a constant flow rate is established the water column should be evacuated by 'vacuuming' to remove all the stagnant water from the bore. This is done by slowly lifting the pump to the top of the water column while pumping, then slowly lowering it to the pump depth again.

Figure 24: *Soaking pump and sample tubing in bleach (container on right), with rinse container on left (photo courtesy of UNSW Water Research Laboratory)*

9. Quality Assurance/Quality Control

Quality Assurance/Quality Control (QA/QC) is a set of operating principles that is adopted to help produce data that is of known, consistent and defensible quality. The QA/QC process is used to check the accuracy and precision of field sampling procedures and laboratory analyses and is done by taking duplicate, spike and equipment blank samples. The QA/QC procedures described in this section has been developed through the Australian groundwater quality assessment project (Please et al., 1996; Ivkovic et al., 1998;Watkins et al., 1998; Watkins et al., 1999).

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 sampling 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 25 provides a systematic approach to developing a QA program for sampling. The model emphasises recognition of the causes of variability (eg use of inappropriate equipment to purge wells, imprecise or operator-dependent methods) and the need to control avoidable errors.

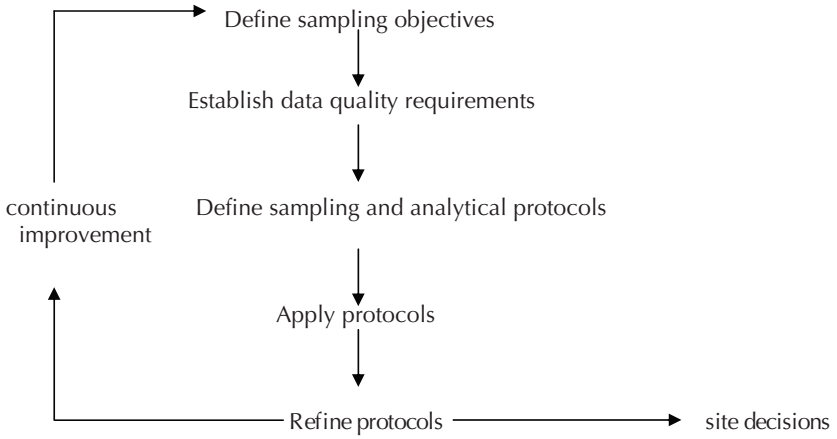

Figure 25: *Quality assurance framework (adapted from Puls and Barcelona, 1996)*

To keep errors in field sampling to a level acceptable to the data user, a QA program should be implemented from the sampling program design stage through to delivery at the laboratory. During these stages, QA should include peer review, training, standardised field procedures, submission of quality control (blank) samples, sample container and field equipment checks, sample transport processes and traceability, and continuous review and improvement of the field sampling plan.

9.2 QUALITY CONTROL

Quality control (QC) is a sample or procedure intended to verify performance characteristics of a system. Water sampling QC should focus on ensuring that the results obtained by analysing samples represent the groundwater as it was when the sample was collected. That is, if there is any significant change in, or contamination of, the sample due to containers, handling and transportation, it will be picked up by QC.

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 number of QC samples; more QC samples will provide a greater degree of confidence in the results. The most common types of QC samples are blanks, spikes and duplicates; their purpose and the minimum requirements are summarised below.

9.2.1 Blanks

A blank is a portion of deionised water that is carried through all or part of the sampling and analytical process and is designed to provide an indication of contamination. It is important that the volume used for blanks be the same as the samples. The various types of blanks include:

Method blanks: A sample of deionised water is carried through the entire sampling and analytical process.

Trip blanks: These blanks are used to monitor potential contamination during shipping and storage. These blanks are sent from the laboratory with empty bottles and remain with other samples throughout the sampling trip but are not opened in the field.

Field and equipment blanks: These blanks are taken under field conditions and include filtration and addition of preservatives, as appropriate.

Decontamination/pump blanks (a subset of field/equipment blanks):The purpose of these blanks is to check on the decontamination process of the pump system. Two blanks are taken - one BEFORE decontamination water is pumped through pump system and one AFTER decontamination water is pumped through the system. They should be collected, treated and stored as per normal. These blanks should be taken at the beginning and end of each trip and anytime that pumping equipment is changed.

9.2.2 Duplicate Samples

These are taken to test for analytical precision in the laboratory and put through the same filtering, storage and analysis processes.

One in every 10 – 15 sites should be sampled in triplicate to provide the following set of samples:

- Original
- Duplicate
- Spiked Duplicate

One sample is split, or three samples bottled in immediate succession and each is given its own identification number.

Duplicate samples, prepared about every ten samples, can be used to monitor reproducibility of sampling and analysis. Calculate the relative percentage differences (RPDs) to observe the variation in duplicates, as follows (Nielsen, 1991):

$$\text{Relative Percentage Difference (\%)} = \frac{\text{concentration } S_A - \text{concentration } S_B}{\text{average concentration of } S_A + S_B} \times 100$$

where S_A denotes Sample A; S_B denotes the duplicate, sample B; units will be consistent within a calculation.

9.2.3 Spiked Duplicate Samples

These are taken to test the accuracy of the analytical process and to detect any degradation or chemical alteration of the sample from the point of collection to analysis. Known amounts of a number of elements of interest can be added to a sample. The spiking solutions are taken into the field and added during the sampling process, usually when a duplicate sample is taken.

The sample to be spiked should be filtered in the same way as the original and duplicate. 5 L of filtered sample will be sufficient for the spiked samples. This should be kept cool until required. Keep all spiking solutions refrigerated until required.

Rinse all glassware in 5 % HCl + 3 rinses in de-ionised water after each spiking procedure.

Note that in some cases the volume of spiked sample submitted for analysis is less than the usual sample volume. This is necessary to minimise the use of expensive spiking solutions. Sampling personnel should ensure that adequate supplies of these sample bottles are stocked.

Spiked triplicates, sampled at the time of the duplicate samples, should have a known concentration of analytes added. Examples of major analytes and the normal spiking concentrations are presented in Table 8 below:

Table 8: Sample analytes and spiking concentrations.

ANALYTES	SPIKING SOLUTION CONCENTRATIONS (MG/L)
Major chemistry (Ca, Mg, Na, K, Br, Cl and SO_4)	4 -100
Minor chemistry and trace elements (Al, Fe, Mn, Cu, Zn, Ba, Ag, As, Be, Co, Cr, Ni, Pb, V, Hg)	0.005-0.5
Fluoride and iodide	2.0
Nitrate-N and total oxidised nitrogen-N	5
Ammonia-N and orthophosphate-P	1

Recovery levels of spiked triplicates can be calculated as follows:

$$\text{Recovery (\%)} = \frac{\text{concentration ST - concentration AD}}{\text{concentration SS}} \times 100$$

where ST denotes spiked triplicate, AD denotes average of duplicates and SS denotes spike solution. Units are consistent within a calculation.

$$\text{Relative standard deviation (\%)} = \frac{\text{standard deviation}}{\text{mean}} \times 100$$

9.2.4 Anion-Cation Balance

The accuracy of the laboratory analysis can be readily checked by looking at the anion-cation balance. Since water is neutrally charged, the sum of anions should equal the sum of cations. The anion-cation balance is normally expressed as percentage.

$$\text{Ion balance} = (\sum C - \sum A)/(\sum C + \sum A)/100$$

Where, $\sum C$ is the sum of cations and $\sum A$ is the sum of anions

If the anion-cation balance is >5% that indicate an error in analysis and the results should not be relied on for subsequent interpretation.

9.3 GOVERNANCE AND DATA REPORTING

Water agencies in each of the State and Territories have responsibility for the management of groundwater resources. The owner or legal occupier of the land on which a bore is to be constructed must obtain the appropriate licence or permit from the licensing authority in the relevant State or Territory. After the bore has been constructed, the driller must provide the drilling logs, construction details of the bore and decommissioning report to the State and Territory water agencies.

Field and laboratory analytical data can be exported into an Excel spreadsheet for editing and verification. Carry out auditing and verification of data using range of quality procedures, including matching results with sample description sheets and manual checking for outliers. All laboratory results less than limit of detection can be halved prior to calculation of medians and prepare graphs for the purposes of presentation. The results of water quality data can be presented in a multitude of ways, including bar graphs of hydrochemical parameters against bore number, spatial distribution of key parameters on schematic maps, X-Y scatter plots, correlation coefficients between parameters, box plots and Piper diagrams.

10. Sample Identification, Transport and Storage

10.1 LABELLING AND SAMPLE IDENTIFICATION

Samples need to be labelled so they can be identified. Sample containers should be marked so that they can be distinguished from other samples in the laboratory. Without good labelling, all samples may look alike. Labels need to be durable. Most samples will be preserved in ice, so waterproof labels and ink must be used. Careful packing of samples is important as they are often subjected to vibration during transport and labels can rub off or become illegible.

Note that the xylene used in permanent markers can contaminate samples intended for organic analysis. All permanent markers should be avoided for this type of sample. Stick-on labels marked with ink pen or biro is preferable.

Labels should contain as much information as practical and must have:

- a clear and unique identifying code that can be cross-referenced to a Bore Information Sheet (Appendix 5), ie bore name or ID
- date of sampling
- time of sampling

They may also contain:

- location and name of sampling site (include GPS coordinates if available)
- field measurements (temperature, DO, redox, etc)
- name of sampler
- container pre-treatment and preservations added
- other observations that may affect the results of the analysis

The information above should be recorded on a Bore Information Sheet and retained as a permanent record. Hazardous, or potentially hazardous samples such as solvents should be clearly marked. Similarly, samples that could reasonably be expected to have particularly high concentrations of an analyte should be brought to the attention of the laboratory, as this may affect the analysis.

10.2 CHAIN OF CUSTODY

Chain of Custody procedures and documentation demonstrate sample control. This gives confidence that the samples are representative of the sampled water, and are an imperative if the samples are to be used in legal proceedings, or if there is any suspicion that they might be tampered with at any stage of the process. Chain of Custody documentation is used to trace possession and handling of a sample from collection through to analysis, reporting and disposal.

The basis of Chain of Custody control measures is that a sample is always in someone's custody and they are responsible for it at that time. A sample is considered to be in someone's custody if it is in that person's physical possession, in their sight, secured in a tamper-proof way by that person or secured in an area restricted by them to authorised personnel.

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, sample containers should be secured with tamper-proof tape, an official seal or locked. This will quickly show if a sample or sample container has been tampered with.

The sampler should complete Chain of Custody forms before packing the samples in the field. The original Chain of Custody form shall remain with the sample at all times so that custody details can be completed at each stage, from transportation to analysis and reporting. See Appendix 7 for a sample Chain of Custody form.

A copy of the final completed Chain of Custody Record sheet should be sought from the laboratory to confirm receipt and appropriate transfer and handling.

10.3 TRANSPORT AND STORAGE

During transport and storage, it is vital that all procedures and rules are followed thoroughly to ensure that samples are not significantly altered and arrive at the laboratory in a state fit for analysis. Samples can easily be contaminated during transport due to container cross-contamination, packaging material or chilling. During storage, samples can degrade due to lack of preservation, inappropriate storage conditions, excessive storage time and sample cross-contamination.

To ensure degradation and contamination of samples does not occur, it is imperative to maintain the preservation conditions prescribed in Table 3. It may be necessary to pack samples with different preservation requirements into separate transport containers. Containers should be sealed with packing tape and a tamper-proof seal, carefully packed with appropriate packing material, chilled and transported in a cooler or fridge. It is sometimes necessary to take further care to prevent cross-contamination between samples or from ice during transport. This could include placing sample containers in snap-lock bags or air-tight, plastic tubes with screw caps, before transport.

If a courier is to be used, sample security, Chain of Custody and refrigeration issues need to be considered. If a courier is not able to meet all requirements, find an alternative form of transport.

A basic list of equipment required for sample transport and storage should include:

- tamper-proof seals
- snap-lock bags or tubes
- cooler or fridge

- ice bricks or crushed ice if a cooler is to be used
- packing tape
- packing material (eg foam)
- consignment note for courier
- labels for sample containers, if not already on containers.

Samples should be delivered to the laboratory within the specified holding times.

11. Occupational Health and Safety

It is recommended that a general safety plan be developed for each sampling trip. The plan should be designed 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 sulfide
  - temperature hazards, typically sunburn and heatstroke
- actions to be undertaken to remove, reduce or control risk
- emergency procedures and information such as location of nearest medical facility.

When working on-site, the right equipment can make the task safer. This could be preventative or for attracting assistance in the case of an incident. Items to consider when sampling include, but are not limited to:

- comprehensive first aid kit
- mobile or satellite phone
- EPIRB (emergency position and identification radio beacon)
- fire extinguisher
- PPE (personal protective equipment)
- MSDS (material safety data sheet) for every chemical.

Field safety procedures should be followed to reduce the frequency and severity of accidents, injuries, or incidents. Standard occupational health and safety protocols should be established and implemented for any staff involved in fieldwork. Ensure that proper attention is given to safety management in all activities. Some of the safety procedures to be followed that are specific to groundwater field sampling are provided below.

Safety procedures before beginning a field groundwater sampling:

- Ensure that all equipment and materials are available as per the field equipment checklist (Appendix 3).
- Groundwater sampling equipment is often bulky and heavy and should be loaded onto vehicles using appropriate heavy lifting devices, and securely attached or tied down so as not to come loose during transport.
- Where possible groundwater sampling equipment should be divided and stored in smaller and lighter units/cases (eg. <15 kg per piece where possible).

Safety procedures at the sampling site:

- Before approaching the bore or immediate sampling area, look carefully at the general area to identify any possible hazards.
- Determine the location(s) of the nearest health care facility(s) to the sampling site or area, and map out the quickest routes to get there.
- Avoid contact with electrical lines or connections, especially if water or wet ground is present in the field.
- Pumps that are deployed down a hole should be secured to effectively counter balance the weight of water-filled tubing down the hole.
- Generators should be regularly tested, and earthed to prevent electrical accidents at waterlogged sites. An automated trip-out device should be used, and all cable connections protected from moisture.
- The engines, exhausts, and some pipes close to an operating pump can be extremely hot, so take care not to touch any surface which might cause a burn.
- Be extremely careful with glass acid vials for sample preservation. The acid itself is extremely hazardous and must be washed off your skin or clothing immediately if you contact it.
- There should be at least two members of a sampling crew, so pay attention to your partner, their whereabouts, physical condition, etc., and be ready to help out if necessary.

12. Acknowledgement

We would like to extend our appreciation to Steven Lewis from Geoscience Australia and Karina Budd from National Residue Survey for their input to this field guide. We would like to thank John Spring and John Wischusen from Geoscience Australia and Wendy Timms, University of New South Wales for reviewing the manual and providing us with constructive criticisms and suggestions.

13. Glossary

The glossary has been adapted from Waterwatch (2005).

Aquifer A rock or soil formation capable of receiving, storing, transmitting and yielding significant quantities of water; aquifer types are confined, unconfined, and artesian.

Aquitard A rock or soil formation that is relatively impermeable and not capable of receiving, storing, transmitting and yielding significant quantities of water.

Artesian aquifer A confined aquifer in which the pressure head of the groundwater rises above the upper confining layer of the aquifer. If the pressure is sufficient to cause the bore to flow at the surface, it is called a flowing artesian aquifer.

Artesian bore A bore sunk into an artesian aquifer in which water rises from an underground water-containing layer under its own pressure.

Bore, well A hole sunk into the ground for abstraction of water from an aquifer or for observation purposes. A well is generally of larger diameter than a borehole and dug rather than drilled.

Casing A tube used as a temporary or permanent lining for a borehole in order to prevent the solid aquifer material from entering the borehole or to ensure groundwater only enters the borehole at specific depths through a screen.

Catchment The area of land, which intercepts rainfall and contributes the collected water to surface water (streams, rivers, wetlands) or groundwater.

Confined aquifer An aquifer that is sandwiched between two layers of relatively impermeable material (e.g. clay or unfractured granite) called aquitards. Groundwater in a confined aquifer is under pressure significantly greater than atmospheric pressure.

Discharge Water flow from an aquifer (e.g. from a natural spring or water bore).

Discharge zone Area where groundwater reaches the surface.

Flow rate Speed with which groundwater moves through the ground.

Flowing artesian bore	When the top of a bore in a confined aquifer is below the potentiometric surface, water will flow out of the well under pressure.
Hydraulic gradient	Slope of the groundwater surface between two points in an aquifer. The difference in hydraulic head between two measuring points within a porous medium, divided by the distance between the two points.
Hydraulic conductivity	A rate of flow indicating the ease with which water will pass through aquifer material
Head	The fluid potential for flow through porous media largely comprised of pressure head and elevation head. Hydraulic head has been defined as the water level above a zero datum (mean sea level) of water in a bore tapping an aquifer that is open to the atmosphere.
Permeable	Permeability is a measure of the ease with which a fluid will move through a porous material (e.g. sand and gravel or rock). A geologic unit is permeable if groundwater moves easily through it.
Permeability	Ability of a material (generally an earth material) to transmit fluids (water) through its pores when subjected to pressure or a difference in head. Expressed in units of volume of fluid (water) per unit time per cross section area of material for a given hydraulic head.
Piezometer	Small diameter bore open at a point or short length in the aquifer to allow measurement of hydraulic head at that point or short length.
Potentiometric surface	The level to which water in a confined aquifer would rise if unaffected by pressure from the surrounding rocks and sediments.
Precipitation	Water falling onto the surface of the earth in the form of rain, hail or snow.
Recharge	Water infiltrating to replenish an aquifer; either natural, through movement of precipitation into an aquifer, or artificial through pumping of water into an aquifer.

Recharge area	An area through which water from a groundwater catchment percolates to replenish (recharge) an aquifer; an unconfined aquifer is recharged by rainfall throughout its distribution; confined aquifers are recharged in specific areas where water leaks from overlying aquifers, or where the aquifer rises to meet the surface. Recharge of confined artesian aquifers is often at some distance 'upflow' from points of extraction and discharge.
Run-off	The portion of rainfall, melted snow, or irrigation water that flows across the ground surface instead of soaking into the soil. Runoff can pick up pollutants from the air or land carry them to streams, lakes or oceans.
Salinity	The amount of salt dissolved in water. In the field, salinity measurements are usually expressed in terms of electrical conductivity either in µS/cm or dS/m. The measure of total dissolved (or soluble) salt, i.e. mineral constituents in water. Water resources are classified on the basis of salinity in terms of Total Dissolved Solids (TDS) or Total Soluble Salts (TSS).
Seawater intrusion	The inland or up-gradient intrusion of seawater into a layer of fresh groundwater.
Saturated zone	Rock or soil, in which every available space is filled with water.
Sustainable yield	The volume of groundwater that can be annually extracted from a groundwater basin without causing adverse effects.
Transpiration	The process of absorption of water by plants, usually through the roots, the movement of water through plants, and the loss of the water to the atmosphere through small openings on the underside of leaves called stomata.
Turbidity	Turbidity is caused by the presence of fine suspended matter such as clay, silt or colloidal material. It gives water a muddy or milky appearance due to the scattering of light by the suspended material.
Unconfined aquifer	An aquifer whose upper boundary is made up of permeable material that transmits water readily.
Water table	The upper surface of groundwater within the unconfined aquifer. Swamps or lakes in low-lying areas may be surface expressions of the water table.
Well	*See* Bore

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APPENDIX 1: FIELD EQUIPMENT CHECKLIST

EQUIPMENT LIST	CHECK	EQUIPMENT LIST	CHECK
Purging/sampling equipment		**Kit bag/tool box**	
Water level probe and batteries		Tape (gaffa, masking)	
Water quality meters		Disposable gloves	
Standards to calibrate the water quality meter		Tools—spanner/shifter/ Stillson wrench/ screw drivers	
Pump, tubing		Paper towel	
Folding table and chairs		Disinfectant wipes	
Generator		Garbage bags	
Bailers & cord		Ziplock bags for samples	
Sample bottles		Leather gloves	
Labels for samples		Spare pump motors	
Eskies and ice		**Safety equipment**	
Decontamination		First-aid kit	
Buckets		Sunscreen	
Demineralised water		Drinking water	
Detergent solution		Mobile phone	
Sponges, scrubbing brush		PPE – wide-brimmed hat	
Plastic groundsheet		– wet weather gear	
Documentation		– steel-capped boots	
Sampling plan		– sunglasses	
Map of bore locations		– work pants	
Site plans		– long-sleeved cotton shirts for hot weather	
Bore records		**Miscellaneous**	
Field notebook		Calculator	
Chain of Custody		Digital camera and batteries/charger	
Pens & textus		Bore key	
MSDS		GPS and batteries	
		Business/ID cards	

APPENDIX 2: BORE INFORMATION AND FIELD ANALYSES SHEET

FIELD ID	DATUM USED:
	Alt =
	S =
Sample ID / Date	E =

Measured T.D. (m)		
Measured W.L. (m)		
Casing Height (m)		
Radius of bore (m)		
Slots/Screen @ (m)		
Pump Depth (m)		
Pump Time On		
Pump Time Off		
Pumping Time (min)		
Average Flow Rate (L/min) (from Flow rate conversion chart)		
Reduced T.D.(m)		Measured T.D. - Casing height
Reduced W.L.(m)		Measured W.L. - Casing height
Water column (m)		Reduced T.D. - Reduced W.L.
Approximate casing volume (L)		3.1416 x radius^2 x water column x 1000
Approximate vol. removed (L)		Pumping time x Average flow rate

Field analyses:

TIME	FLOW RATE (L/MIN)	PH	TEMP °C	D.O. (MG/L)	REDOX MV	EC µS/CM

Comments Redox probe correction factor to apply to above Redox values = mV

APPENDIX 3: FLOW RATE CONVERSION CHART

For converting time taken (in seconds) to fill a 10 L container, to litres per minute
Formula = (60 divided by seconds taken to fill 10 L container) x 10 = L per minute

SECONDS	L/MIN.	SECONDS	L/MIN.
10	60	51	11.7
11	54.5	52	11.5
12	50	53	11.3
13	46.1	54	11.1
14	42.8	55	10.9
15	40	56	10.7
16	37.5	57	10.5
17	35.3	58	10.3
18	33.3	59	10.1
19	31.6	60	10
20	30	61	9.8
21	28.5	62	9.7
22	27.2	63	9.5
23	26.1	64	9.4
24	25	65	9.2
25	24	66	9.1
26	23.1	67	8.9
27	22.2	68	8.8
28	21.4	69	8.7
29	20.7	70	8.5
30	20	71	8.4
31	19.3	72	8.3
32	18.7	73	8.2
33	18.2	74	8.1
34	17.6	75	8
35	17.1	76	7.9
36	16.6	77	7.8
37	16.2	78	7.7
38	15.8	79	7.6
39	15.4	80	7.5
40	15	81	7.4
41	14.6	82	7.3
42	14.3	83	7.2
43	13.9	84	7.1
44	13.6	85	7
45	13.3	86	6.9
46	13	87	6.9
47	12.7	88	6.8
48	12.5	89	6.7
49	12.2	90	6.6
50	12	91	6.6

APPENDIX 4: CHAIN OF CUSTODY RECORD

Project Name		Laboratory contact	
Name and address of organisation		Telephone	
Project contact		Contract/Project/Job No.	
Telephone			

SAMPLE ID	SAMPLE LOCATION	SAMPLE TYPE (WATER, SOIL, SEDIMENT)	SAMPLE PRESERVATION	SAMPLING		NO. OF CONTAINERS	ANALYSIS REQUESTED	COMMENTS
				DATE	TIME			
Sampled by:			Signature					

SAMPLE RELINQUISHED BY: SAMPLE RECEIVED BY:

NAME AND ORGANISATION	SIGNATURE	DATE	TIME	SAMPLE CONDITION	NAME AND ORGANISATION	SIGNATURE	DATE	TIME	SAMPLE CONDITION

APPENDIX 5: FIELD PARAMETER CALIBRATION RECORDS

DATE	pH STANDARD 1 (4.0)	pH READING	pH STANDARD 2 (7)	EC STANDARD 1 ( )	EC READING	EC STANDARD 2 ( )	EC READING	DO STANDARD	DO READING	TEMP (°C)	DO MEMBRANE CHANGE DATE	SIGNATURE