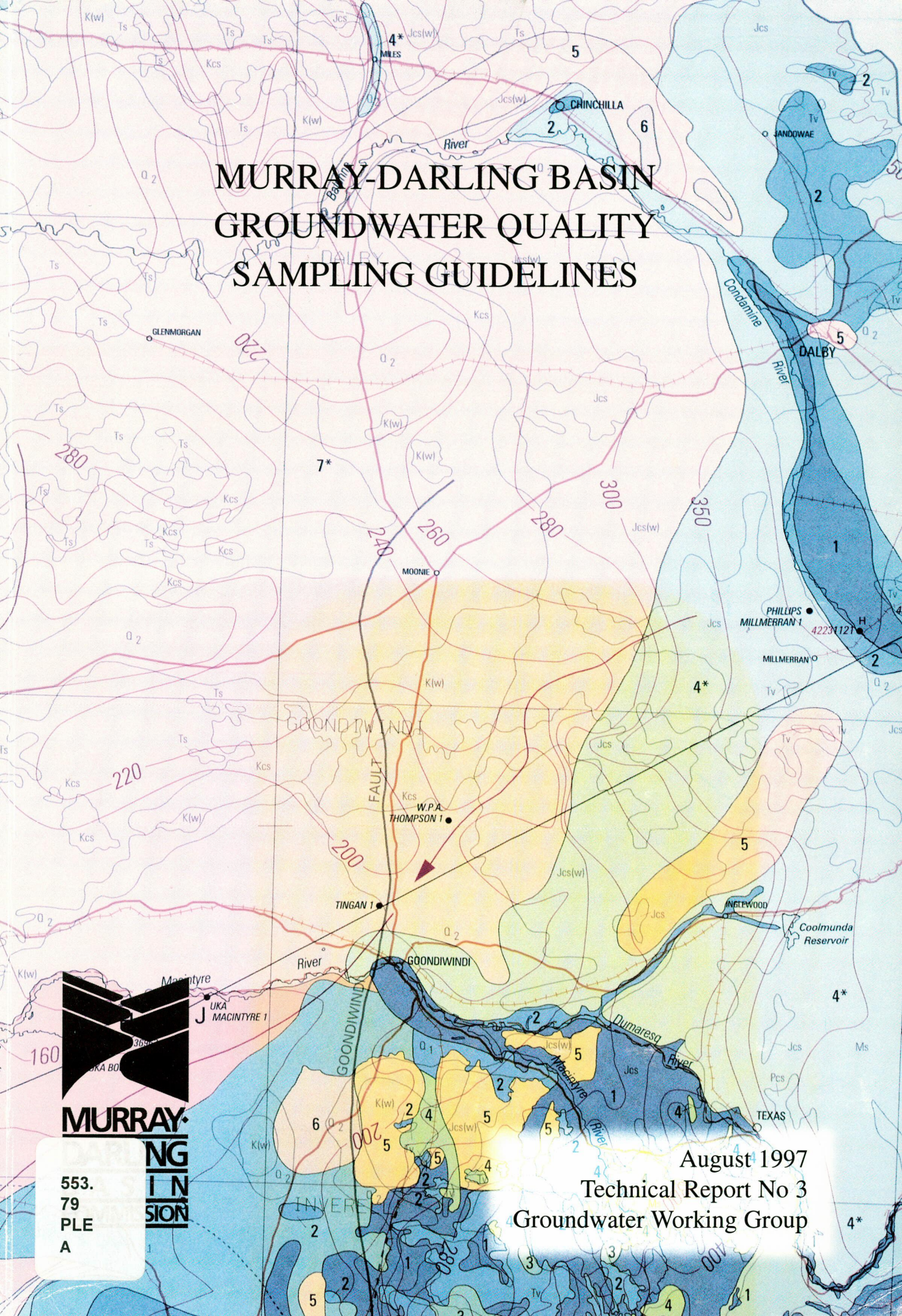


MURRAY-DARLING BASIN GROUNDWATER QUALITY SAMPLING GUIDELINES



MURRAY-DARLING BASIN

553.
79
PLE
A

August 1997
Technical Report No 3
Groundwater Working Group

DATE DUE

RAECO

553.
79
PLE

PLEASE, Patty
Murray-Darling Basin,
groundwater quality sampling
guidelines
Donation

~~8046A~~

553.
79
PLE

MURRAY-DARLING BASIN,
GROUNDWATER QUALITY
SAMPLING GUIDELINES

NPWS
LIBRARY



8618 A

98FEB

Date
Borrowed

B. Lake

Level 8

27/4/04

22/6/04
2MS ✓
4/8/04

Please Print Clearly

BORROWER	Location	Date Borrowed	

Please Print Clearly

MURRAY-DARLING BASIN
GROUNDWATER QUALITY
SAMPLING GUIDELINES

Department of Environment,
Climate Change & Water NSW
LIBRARY - HURSTVILLE

Shelf no:

ID no: 111175

August 1997
Technical Report No 3
Groundwater Working Group

MURRAY-DARLING BASIN

GROUNDWATER QUALITY

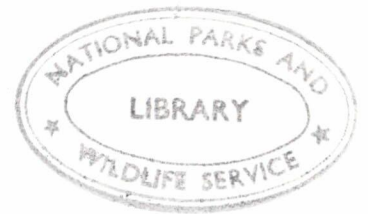
SAMPLING GUIDELINES

Compiled by Patty Please on behalf of the NRMS funded Murray-Darling Basin
Groundwater Quality Project

Agencies Involved:

Department of Land and Water Conservation (NSW)
Department of Mines and Energy (SA)
Department of Natural Resources (Qld)
Sinclair Knight Merz (Vic)
Australian Geological Survey Organisation (Commonwealth)

ISBN 1 875209 74 3



FOREWORD

The Murray-Darling Basin Commission is publishing the *Murray-Darling Basin Groundwater Quality Sampling Guidelines* to promote the management of groundwater and its related impacts in the Basin. When the Commission's Groundwater Working Group was established in the early 1980s groundwater was seen primarily as a resource. However it also poses a major threat.

High and rising water tables are causing water logging and salinity problems for both irrigation and dryland agriculture, towns along the inland slopes of the Great Dividing Range and the environment, in many parts of the Basin. These problems are expected to intensify in the future.

The groundwater situation in the Murray-Darling Basin is changing rapidly. However long term monitoring information for many parts of the Basin is lacking, particularly in dryland catchments such as those in the upland areas of the southern part of the Basin where the threat of dryland salinity is high. This publication has been prepared to help fill that gap. It is part of a broader project whose primary objective is to determine the basic design, key parameters and research requirements for the establishment of a groundwater quality monitoring program for the Basin, and to ensure its implementation.

As a preliminary step in this process the working group decided that an agreed set of groundwater quality sampling guidelines should be documented and distributed to agencies and individuals involved in groundwater quality sampling. The adoption of a more uniform, accurate and reliable set of sampling procedures will produce data that is comparable throughout the Basin and be an important step in assisting us to get a comprehensive understanding of groundwater trends across the region.

A handwritten signature in black ink, appearing to read "John Lovering".

Professor John Lovering

President

Murray-Darling Basin Commission

PREFACE

This publication was prepared as part of Stage 1 of the Groundwater Quality in the Murray-Darling Basin Project. The project is funded through the Murray-Darling Basin Commission's Natural Resource Management Strategy and operates as a partnership between New South Wales, Queensland, South Australia, Victoria and the Commonwealth.

The approach taken in the production of this document was as follows:

- 1) Existing documents on groundwater quality sampling from the States, Commonwealth and the USA were reviewed and compared.
- 2) Information relating to the main sub-topics (see Table of Contents) was extracted. Emphasis was put on finding information that would provide an explanation for the various procedures involved in sampling.
- 3) Output from (2) was compiled into a document to provide guidance on the main procedures that need to be followed for a credible groundwater quality sampling program.

Members of the team involved in the development of the guidelines include:

Patty Please (Editor)	AGSO
Steve Barnett	DMESA
Robert Ellis	QDNR
Ray Evans	AGSO
Rick Evans	Sinclair Knight Merz
George Gates	DLWC

This document has been approved for use by various representatives from the State water agencies and the Commonwealth, including those listed above.

TABLE OF CONTENTS

	Page No.
1. INTRODUCTION	1
2. GROUNDWATER SAMPLING OBJECTIVES AND PRINCIPLES	3
3. PLANNING AND PREPARATION	4
4. INDICATOR SELECTION	6
5. LOCATION AND FREQUENCY	8
6. SAMPLING DEVICES	10
7. DECONTAMINATION	13
8. BORE PURGING	15
9. FIELD MEASUREMENTS	17
10. FILTRATION	20
11. CONTAINERS, PRESERVATION, HOLDING AND TRANSPORT	21
12. CHAIN OF CUSTODY RECORDS	27
13. QUALITY ASSURANCE/QUALITY CONTROL	33
14. PROBLEMS COMMONLY ENCOUNTERED WITH GROUNDWATER SAMPLING	36
15. SUMMARY OF GROUNDWATER SAMPLING GUIDELINES	38
16. REFERENCES	40

TABLES

	Page No.
1. RECOMMENDED KEY INDICATORS FOR GROUNDWATER ISSUES	6
2. RECOMMENDED KEY INDICATORS FOR GROUNDWATER USES	7
3. SAMPLING DEVICES: THEIR ADVANTAGES AND DISADVANTAGES	11
4. PREFERRED MATERIALS FOR USE IN GROUNDWATER SAMPLING DEVICES	12
5. SAMPLING CONTAINERS, PRESERVATION AND HOLDING TIMES	24
6. SUMMARY OF GROUNDWATER PROTOCOL	38

FORMS

1. WATER QUALITY PURGING INFORMATION	18
2. SAMPLE SUMMARY SHEET	19
3. CHAIN OF CUSTODY/SAMPLE ANALYSIS REQUEST FORM	31

APPENDICES

1. FIELD EQUIPMENT CHECKLIST	43
2. SUMMARY OF PUBLICATIONS ASSESSED FOR MURRAY-DARLING BASIN GROUNDWATER SAMPLING	44
3. TOPICS ADDRESSED IN SELECTED SAMPLING MANUALS	45

INTRODUCTION

This document aims to provide a set of guidelines for groundwater quality sampling with an emphasis on regional monitoring networks. The guidelines were developed as part of the Groundwater Quality in the Murray-Darling Basin Project. This is a Murray-Darling Basin Commission – Natural Resources Management Strategy funded project involving the four States within the Basin and the Commonwealth. The objective of this project is to determine the basic design, key parameters and research requirements for the establishment of a groundwater quality monitoring program for the Murray-Darling Basin and to ensure its implementation.

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

There exist some recent publications by the State agencies on sampling (ie Jiwan & Gates, 1992, Rayment & Poplawski, 1992) and a document on sampling for contaminated sites (AWRC, 1991). Although these documents are very relevant to the issues they address there is need to provide a set of sampling guidelines that can act as a standard across state boundaries. The purpose of this report is to outline a recommended set of groundwater sampling protocols that focuses on regional monitoring and sources of contamination throughout the Murray-Darling Basin. A uniform, accurate and reliable set of sampling procedures will ensure that comparable data of a known standard is collected throughout the basin. Ultimately, this allows for greater confidence in the interpretation of any Basin-wide data.

This document provides a general overview for practical purposes and covers the elements of effective groundwater sampling and the basic capabilities for routine applications. It outlines the procedures for sampling from the bore site to delivery at the laboratory. It does not include bore construction and development or laboratory analyses. It is a general field manual including sampling for physical parameters, major ions, metals, nutrients, pesticides and microbiology. It is not aimed for use by researchers requiring specialised sampling methods for specific studies. There has been an emphasis on trying to include explanations for the various procedures.

The main issues and procedures of groundwater sampling covered in this document include:

- 1) Planning and the selection of appropriate indicators, locations and frequency;
- 2) Selection of the various sampling devices available;
- 3) Decontamination and bore purging procedures;

- 4) Field measurements and filtration of samples;
- 5) Determination of container, preservation methods and holding time, including transport to a laboratory;
- 6) The significance of and steps involved in Chain of Custody documentation;
- 7) The elements of a QA/QC program;
- 8) A summary of the standard sampling guidelines and some commonly encountered problems.

This set of recommended guidelines is very much a compilation of existing groundwater sampling documents. Appendix 2 and 3 summarise the various reports that contributed to this one. These documents may provide additional information and discussion on procedures given in this report. The core of this document has been based on A Practical Guide to Groundwater Sampling – 1st Edition (Jiwan & Gates, 1992).

1. GROUNDWATER SAMPLING OBJECTIVES AND PRINCIPLES

There are many different reasons for sampling groundwater. These include meeting regulatory requirements, industrial or municipal waste disposal site monitoring, ambient ground-water quality monitoring, research, and general bacteriological and chemical quality monitoring. Each of these different objectives can result in a different set of protocols for sampling. This document is mainly focussed on ambient and regional monitoring.

The ultimate objective of any groundwater sampling program is to obtain a representative sample of groundwater and to try to maintain the sample integrity from field to laboratory. This means that the relative proportions of all components must be the same in the sample as in the material being sampled and that there must be a minimum of disturbance to the sample during the sampling process.

The time and resources allocated for the construction of bores for groundwater monitoring, combined with a sampling program, can involve quite large sums of money. Because of this it is very important that proper sampling procedures are followed and resources are not wasted.

When utilising any set of sampling protocols it is important to remember that they must be tailored to the actual site conditions, the information needs of the program and the time/cost limitations imposed on the program.

Groundwater, and therefore groundwater sampling, is unusual by its nature. Some of its unique features include:

- The necessity of having a bore or similar structure to obtain a sample. This is a major part of the cost of any monitoring system and can have the effect of disturbing the chemistry of the sample.
- The quality of groundwater can be variable over quite short distances. This can be ambient water quality variability or it can be affected by anthropogenic factors (ie. pesticide contamination, septic tank leakage). An understanding of the hydrogeology and flow dynamics of the system is important before any water quality sampling is undertaken.
- Groundwater suffers from the 'out of sight - out of mind' syndrome. Water quality problems in groundwater are unseen and therefore easily ignored

With the developing scarcity of good quality water resources, it is becoming increasingly important that the quality as well as the quantity of groundwater supplies are managed properly.

2. PLANNING AND PREPARATION

(adapted from P. Garrett, 1988)

Careful planning and preparation of a groundwater sampling trip is very important and can save time and reduce the number of minor and major difficulties that commonly occur with fieldwork. The following are suggestions of things to consider before going on a groundwater sampling field trip. These elements can be set out in a Work Plan for routine sampling and will ensure more efficient use of time with future work. A suggested checklist of equipment to take into the field can be found in Appendix 1. The objectives of the trip will determine what equipment is necessary but the list is useful as a reminder.

Depending on the nature of the suspected contamination, there may be Occupational Health and Safety (OH&S) issues to be addressed in the collection, handling and transport of groundwater samples and by-products. Personal OH&S issues should be addressed in a Work Plan and include details of the level of protective clothing required and procedures to be used. Such plans may require input from qualified OH&S professionals to ensure all aspects are covered..

- 1) Check with your **client**, especially if off-site wells are to be sampled. Be aware of liabilities that your actions may incur in the name of your client or your own agency/firm.
- 2) Call **home well-owners** to inform them of what you are doing and to arrange access and a time for sampling. This could include providing them with a summary sheet of the project for their information and results from their bore.
- 3) Coordinate with the **laboratory**. They will need to schedule in your sample set. Discuss any problems you foresee with procedures, containers, etc. and collect all necessary sample bottles, trip blanks and spike solutions as required.
- 4) Plan how and when you will get the **samples back to the laboratory**, cool and as quickly as possible. This is especially relevant for bacterial samples.
- 5) Organise and review **maps and diagrams** for the area to be sampled. Include bore details and coordinates.
- 6) Be sure you know the **diameter** of the wells you want to sample: your sampling gear must be the right size.
- 7) Choose the **order of sampling**. Try to keep cross-contamination to a minimum, ie. sample from the suspected least contaminated bore to the most contaminated.
- 8) **Test** all equipment for the trip by performing a 'test run' on a local bore.
- 9) Fill out as much **paperwork** as possible before you leave. That includes chain of custody and shipping forms - if appropriate.

10) Call the **local council or police station** if you are sampling where people may be suspicious of your motives. Carry a few business cards.

3. INDICATOR SELECTION

There are three basic criteria used in selecting appropriate indicators for groundwater studies:

- relevance to the issues identified
- acceptable precision
- cost (collection, preservation and analysis)

Some indicators will be selected for immediate management decisions. For example identification and definition of a pollution plume will need very specific water quality measurements at many locations and at closely spaced time intervals. Once however the source and processes of contaminant flow are established, then key indicators at regular intervals (say 3 monthly) would be sufficient monitoring. Guidelines on safe levels for drinking water are documented in Australian Drinking Water Guidelines (NH&MRC, 1995) and guidelines for other water uses can be found in Australian Water Quality Guidelines for Fresh and Marine Waters (ANZECC, 1992).

Table 1 shows recommended key indicators for important groundwater issues while Table 2 shows key indicators for different groundwater uses.

Table 1

Recommended Key Indicators for Groundwater Issues

ISSUE	INDICATOR(S)
Salinity	Electrical conductivity, pH, major anions/cations (when necessary)
Iron Bacteria	Gallionella Crenothrix and Leptothrix. iron (soluble), iron (total)
Regional Resource Evaluation and Management	Electrical conductivity, pH, major anions/cations (including nitrate, silica)
Organic Pollution	Hydrocarbons (as appropriate)
Inorganic Pollution	Heavy metals, nitrate, phosphate, others as appropriate
Pesticides	As appropriate
Biological Contamination	E. coli, faecal streptococci, bacteria, viruses, nitrate, nitrogen and ammonia
Bore Corrosion	pH, dissolved gases (CO ₂ , O ₂ , H ₂ S), electrical conductivity, iron (soluble), iron (total), anions/cations

Note: Major anions include - CO₃, HCO₃, SO₄, Cl, NO₃. Major cations include - Ca, Mg, Na, K

Table 2

Recommended Key Indicators for Groundwater Uses

USE	KEY INDICATORS
Potable Water Supply	Bacteria, total coliforms, faecal coliforms, cyanobacteria, DO, BOD, pH, turbidity, odour, colour, taste, hardness, major anions/cations, nutrients, metals, organics. radioactivity, aesthetic chemicals, filtrable residue.
Agricultural Water Supply (including stock)	Bacteria, E. coli, faecal coliforms, pH, salinity, major anions/cations, nutrients, DO, BOD, organics.
Irrigation	pH, salinity, major anions/cations, nutrients, photo toxic trace elements, bacteria, algae, SAR.
Industrial Water Supply	Varies according to particular industry but usually includes pH, colour, turbidity, taste, hardness, major anions/cations, dissolved solids, total iron.
Recreation	Bacteria, algae, faecal coliforms, pH, odour, colour, salinity, nutrients, biostimulants, toxicants. Varies.
Edible fish and crustacea and protection of ecosystems and water associated wildlife.	pH, DO, salinity, suspended solids, turbidity, colour, nutrients, biostimulants, toxicants.

When selecting what indicators are to be included in a groundwater study it is important to confer with the analysing laboratory on the detection limits for each indicator. All analytical results should be interpreted with respect to the detection limit.

4. LOCATION AND FREQUENCY

Location

The selection of optimal sampling location will depend on the purpose of the program and the aquifer characteristics. For the purpose of this document there are two main categories of monitoring/sampling.

1) Ambient/Regional Monitoring

This type of monitoring aims at understanding the characteristic regional water quality variations and changes over time. It is usually accomplished through routine sampling of bores - either in a dedicated monitoring network or production bores, where no network is available. Generally, rigorous well construction and sampling procedures are not required for these projects and the objective of sampling is to detect gross changes in water quality on a regional basis.

When monitoring to identify extensive diffuse pollution of aquifers it may be worthwhile constructing some purpose-drilled boreholes. This could include shallow observation bores screened over different depth intervals in the aquifer. The distribution should be spread over the area of interest and sited according to the different hydrogeological and land-use conditions. Depending on the size of the project, one or more bores should be placed to determine natural groundwater quality outside the area of suspect contamination.

2) Point-Source Monitoring

This type of monitoring is conducted at a potential pollution source, ie waste disposal sites and feedlots. The objective of point-source monitoring is to detect and quantify the extent and the migration of the pollution plume. Sampling will be necessary both upgradient, to determine natural groundwater conditions, and downgradient of the source, to determine changes in water quality due to land use.

Sampling Bores

The use of existing **production bores** for sampling is the cheapest method available. High yielding bores can provide good representative samples. Care should be taken to ensure that aeration of the sample has not occurred due to pumping.

If there are **existing monitoring bores** in the area then these can also be used for samples.

Depending on funds available for the program, a range of **new monitoring bores** can be constructed. The use of specialist knowledge will ensure the proper design in terms of construction materials used and their effect on the quality of groundwater. PVC, stainless steel or Teflon are different materials that can be used for casing depending on what is required in terms of sample parameters and detection limits.

In all cases it is imperative to have bore information on these sites in the form of driller's logs, lithological logs and/or construction details. Information on bore yield

and water quality, from previous bore performance or sampling work, will assist in determining issues such as purge volume and rate.

Frequency

The frequency of water quality measurement is dependent on the issue being examined and the variation in quality of the groundwater in both a temporal and spatial sense, although quality changes in groundwater are usually much more gradual than those in surface waters. In some aquifers there are factors producing seasonal variations in quality and in other cases - particularly where groundwater pollution is occurring - there are short-term variations of between several hours and a few days. These variations should be recognised before a long-term sampling programme is defined.

For quality surveillance of potable supplies, the temporal variation is a very significant factor. For most determinands a monthly, or less frequent sampling, is normally adequate. In bores where microbiological contamination is a potential problem, more frequent sampling is advisable.

Continuous monitoring of pH, temperature and electrical conductivity at a few key sites is useful for identifying the rate of quality change. This information can then be used in the project area to determine the optimum sampling frequency. Continuous monitoring results from pumped bores can be used to indicate when quality variations of the pumped water are not occurring and a representative sample can be taken. With high pump rates extra care should be taken to avoid aeration of the sample.

Statistical techniques can help determine the value of individual sites within a network or alternatively if more sites are necessary. For resource inventory monitoring, such as statewide and regional water quality networks, managers should regularly review the sampling networks to determine if appropriate locations are being measured to address the issues at hand.



5. SAMPLING DEVICES

There are a variety of devices which can be used for sampling. An important consideration when selecting a sampling device is the change in water quality that may occur during the process of sampling. For example degassing can occur during pumping. Analytical error introduced during sampling becomes important in environmental studies because, even though very low analytical limits are achievable in the laboratory, detectable levels are sometimes limited practically by sampling device performance or by errors introduced by cross-contamination.

Table 3 lists a range of sampling devices and gives their advantages and disadvantages. This information should be considered when planning a sampling program. For sampling of shallow, low yield bores bailers may be the most appropriate sampler. For routine monitoring of deeper bores a submersible pump is the preferred device. If this is not available then a bailed sample should be taken after the appropriate purging of the bore.

Table 4 provides information on the preferred material for use in groundwater sampling devices. The material selected will depend on the accuracy and precision of the information required, including equipment handling and decontamination, as well as cost. For routine monitoring of a regional network, materials from order 2 to 7 would be suitable in both rigid and flexible materials.

PVC is rigid and non-porous. It has good general chemical resistance except for low-molecular weight ketones, aldehydes and chlorinated solvents. PVC is fine for inorganic analyses but may introduce a bias with some organic compounds.

Polyethylene materials are not recommended because they tend to adsorb trace metals.

Teflon is the most commonly used material for specialist sampling devices, however it is primarily limited by cost. Teflon exhibits inertness to chemical attack, has poor sorptive properties and a very low leaching potential. Monitoring bores and sampling devices used for the detection of very low concentrations of pollutants are sometimes made of Teflon. Other non-metal devices may be suitable in place of Teflon if the device is single use, ie. disposable bailers.

Stainless steel is another expensive material used for high quality monitoring programs. The usual choice is 316 quality stainless steel. However, stainless steel bailers are readily available in a range of sizes and, with the appropriate cleaning and handling, can be re-used indefinitely. They are the most commonly used sampling device for general groundwater monitoring.

When utilising production bores for sampling it is important to be aware that pumping equipment may affect chemical analysis, ie. some oil from oil lubricated pumps can contaminate the water sample.

Table 3

Sampling Devices: Their Advantages and Disadvantages

(after Jiwan & Gates, 1992)

Sampling Equipment	Advantages	Disadvantages
1. Bailer	<ul style="list-style-type: none"> • Can be constructed from variety of material compatible with parameter of interest • Can be different diameter and length to suit the sampling point • No external power source required • Easy to clean or disposable • Inexpensive and readily available • Lower surface area to volume ratio reduces outgassing of volatile organics 	<ul style="list-style-type: none"> • 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 within the water column that the sample represents • Can be impractical to remove casing storage (stagnant) water in a deep bore with a bailer • Aeration may result during transfer of sample from bailer to sample bottle • When used in deep installations, more prolonged sample handling may effect air-sensitive chemical constituents • Bailer check valves may fail to function properly • Swabbing effect of bailers that fit tightly into a bore casing may include fines from the formation to enter the bore
2. Syringe Devices	<ul style="list-style-type: none"> • Neither aeration nor outgassing of the sample occurs as it does not come in contact with atmosphere • Can be made of inert or any material • Inexpensive, highly portable and simple to operate • Can be used in small diameter wells • Sample can be collected at various intervals • Can be used as sample container 	<ul style="list-style-type: none"> • Inefficient for collecting large samples • Syringes can not be used for evacuating stagnant water • Syringes are relatively new in this application and may not be as readily available as other sampling devices • Sample contamination by components of "home-made" syringe sampling devices is possible unless fabrication materials are carefully selected • The use of syringes is limited to water with a low suspended solids content • Some leakage may occur around the plunger when syringes are used to sample water containing high level of suspended solids
3. Air-lift sampler	<ul style="list-style-type: none"> • Relatively portable • Readily available • Inexpensive • Some are suitable for well development - depends on yield rate of device 	<ul style="list-style-type: none"> • Causes changes in carbon dioxide concentration and thus not suitable for sampling for pH-sensitive parameters • Because of degassing effect on sample it is not appropriate method of sampling for detailed chemical analyses • Oxygenation is impossible to avoid unless elaborate precautions are taken
4. Suction-lift pumps	<ul style="list-style-type: none"> • Highly portable • Easily available • Flow rate can easily be controlled • Inexpensive • Can be constructed in small diameter 	<ul style="list-style-type: none"> • Limited sampling depth (6-8m) • Loss of dissolved gases and volatiles due to vacuum effect • Potential of hydrocarbon contamination of samples due to use of petrol or diesel for running the pump • Use of centrifugal pumps results in aeration and turbulence.
5. Gas-operated pump	<ul style="list-style-type: none"> • 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 	<ul style="list-style-type: none"> • 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 • CO₂ may be driven from the sample causing a pH shift
6. Bladder pump	<ul style="list-style-type: none"> • 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 	<ul style="list-style-type: none"> • Non-continuous flow • Low flow rate • Time consuming to purge bore
7. Submersible pump	<ul style="list-style-type: none"> • Constructed from various materials • Wide range of diameter • Readily available • High pumping rates are possible for evacuation of large volumes • Provides a continuous sample over extended periods of time 	<ul style="list-style-type: none"> • Conventional units are unable to pump sediment laden water without incurring damage to pump • Smallest diameter pump is relatively expensive • Most of submersible pumps are too large for 50mm diameter pumps • Must be able to pump at a low rate for sampling and a high rate for purging
8. Inertial pump	<ul style="list-style-type: none"> • Simple construction, inexpensive • Manual, gas or electric motor driven • Good for sediment clogged bores • If dedicated, it avoids cross-contamination 	<ul style="list-style-type: none"> • 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 non being properly purged. • Low flow capacity

Table 4

Preferred Materials for Use in Groundwater Sampling Devices

(Adopted from Canter et al, 1988)

A. Rigid Material

Order of Preference	Material
1	Teflon
2	Stainless steel
3	Polyvinyl Chloride (PVC)
4,2	Low-carbon steel
5	Galvanised steel
6	Carbon steel
7	Copper

B. Flexible Materials

Order of Preference	Material
1	Teflon
2	Polypropylene
3	Flexible PVC/Linear Polyethylene
4	Viton
5	Conventional Polyethylene
6	Tygon
7	Silicone/Neoprene

6. DECONTAMINATION

Decontamination of sampling equipment is recommended for all sampling work and considered essential when sampling for microbiological parameters, organics and low concentration constituents, ie. pesticides. It is not routine for major ion analyses. The purpose of decontamination is to ensure the sampling equipment is clean and contains no trace of the previously sampled groundwater that can cause erroneous analytical results (cross-contamination). Decontamination of equipment should be completed before each bore sampling.

Equipment

Plastic sheets

Clean sterile gloves

Concentrated sodium hypochlorite bleach (12-20%) or biodegradable P-free detergent for non-microbiological sampling

CAUTION: Operator should be familiar with the safety aspects of sodium hypochlorite

Large tank distilled water

Contaminant-free water, eg. from town supply. (Do not use farm or tank water as it may be contaminated)

Solution of 70% ethanol and 30% water

Hand spray pumps

2 large containers that will hold the bailer or pump hose and pump

Procedure

- Decontaminate pump away from sampling site
- Place plastic sheets around sample site to prevent contamination from ground material.
- It is advisable to wear clean, sterile gloves and protective clothing when performing the decontamination process.
- Prepare bleach or detergent solution in large container 4 hours prior to use to allow it to kill any bacteria.
 - 20 L contaminant-free water
 - 100 ml concentrated sodium hypochlorite bleach
- Place pump into container and pump until the pump hose is full of bleach solution. If using bailer, run several litres of bleach/detergent solution through equipment.
- For microbiological samples, trap bleach solution with foil or Glad-Wrap at the ends. The hose doesn't need to be totally full as the gas from the solution does the work.

- The pump and pump hose can then sit in the remaining solution in the container so that the outer hose is decontaminated as well. If a bailer is being used, scrub the outside with the solution.
- Wait 15 minutes minimum for microbiological samples.
- Pump approximately 20 L of distilled water through the pump and line and rinse the external hose. Similarly, rinse bailer. If distilled water is not available, then contaminant-free water may be used as a second choice.
- Take a Before Blank sample and End of Line Blank sample - ie a sample of contaminant-free water before it is pumped through the system and a sample after it has been pumped through the system. This should be done at the beginning and end of each sampling event. This is part of the QA/QC procedure to check on the effectiveness of the decontamination process (see Section 12).
- After allowing the equipment to air-dry the equipment is now ready for sampling.
- If the hose gets dirty/dusty spray with the solution of 70% ethanol plus 30% water in hand pumps. If solution is not available, use distilled water.

If contamination is suspected, the wastewater resulting from the decontamination process may require containment and disposal to a treatment facility. If this is the case, DO NOT dispose to groundwater or local drainage.

7. BORE PURGING

The principle of bore purging is to evacuate the stagnant water in the well casing prior to sampling so as to provide a representative sample of in-situ groundwater.

The number of bore volumes to be pumped before collection of water samples depends upon bore depth, hydraulic properties, sampling methodology and program requirements. There is no set number of volumes to be pumped that fits all situations. The aim is to obtain water from the geologic materials being monitored with minimum disturbance of the regional flow system and the collected sample.

It is generally agreed that a minimum of 3 casing volumes of water should be evacuated as well as attaining the stabilisation of pH, temperature and electrical conductivity of the discharging water. This results from this procedure should be documented - pumping rate, volumes pumped, chemical parameter measurements.

The following examples illustrate the method for calculating bore volumes.

$$\text{Volume} = \Pi r^2 h$$

Given:

15m deep, 50mm diameter piezometer (approx. 2 inch)
Static level about 4.5m below ground surface

Calculation:

$$\begin{aligned}\text{One bore volume} &= (15 - 4.5) \times 25^2 \times 3.14 \times 10^{-6} \\ &= 20.6 \text{ litres}\end{aligned}$$

Record the static water level (SWL) prior to pumping. If possible, the groundwater level should also be recorded during purging to monitor bore performance to determine possible maintenance requirements, especially with deep bores.

The pump should be located several metres above the screen and the pump rate should be set to maintain constant drawdown a few metres above the pump if possible. If the pump is too close to the screen, high entrance velocities and turbulence may result in a change of chemistry. Once a constant flow rate has been achieved the pump can be manually lifted to near the top of the water column and the bore “vacuumed” ie: the stagnant water which has been sitting in the casing well above the slotted level is directly pumped out. When using a bailer, purge from the screened interval. Use a calibrated bucket/container to record the volume of water being discharged.

The chemical stability of the discharge water is indicated when three successive measurements of pH, temperature and EC, taken at intervals of 5 minutes or more, differ by less than the following amount:

pH	0.1 unit
temperature	0.2 degrees Celsius
EC	5 percent

If the chemical stability has not been attained after four casing volumes of water have been removed, it is advised that sampling can commence if notes are made clearly describing the stabilisation problem. Continuously operated production wells need to be pumped only to chemical stability.

Periods of long pumping may lead to sampling water which is not in-situ or is at some depth other than that at which the bore is screened. Overpumping may also introduce groundwater from a distance source that may dilute or concentrate certain components and result in erratic or misleading data.

Low-yield bores (bores that are incapable of yielding three casing volumes) present a difficult situation. The following procedure is recommended: The operator should evacuate bores to dryness once. As soon as the bore recovers sufficiently, the first sample can be tested for pH, temperature and electrical conductivity. If full recovery exceeds two hours the sample should be extracted as soon as sufficient volume is available for a sample for each parameter.

It is important to note that some pumps cause volatilisation and produce high pressure differentials and thus may cause variability in the analysis of pH, EC, metals and volatile organic samples. They are, however, acceptable for purging the bores if sufficient time is allowed to let the water stabilise prior to sampling. Where possible sample should be taken with pump set at lowest rate.

When purging equipment must be reused, it should be decontaminated using the same procedures required for the sampling equipment. (See Section 6 for Decontamination.)

There may be an issue with the disposal of potentially contaminated water extracted from the bore during purging. Some containment may be required where disposal to ground will create a risk to the environment.

8. FIELD MEASUREMENTS

The optimal situation for chemical analysis of all parameters would be to determine them on site. Unfortunately there is a limited number of suitable, portable instruments for this purpose. The standard procedure is to take pH, temperature and electrical conductivity readings (include dissolved oxygen and redox potential if required) on site. All field instruments should be calibrated and verified prior to field use and then calibrated again when in the field.

The purpose of these readings are:

- to ensure purging has removed a sufficient quantity of water (see Section 7).
- to provide valid on site measurements of pH, temperature, electrical conductivity (Eh and redox potential if required)
- to compare with laboratory measurements to check for chemical changes due to holding time and transport. Temperature and pressure changes during the sampling process have the effect of altering these parameters.

The basic procedure follows:

- It is recommended that a flow-through cell with probes is used for this procedure. This allows for continuous measurement and prevents contact between the sample and atmosphere. If a flow-through cell is not available, measure in a container with the discharge pipe placed at the base of the container. This will reduce contact with the atmosphere.
- Calibrate the probes at the beginning and end of each working day (minimum) and when accuracy of equipment is suspect. Be aware that the value of the standards for calibration change as the temperature changes. Note calibration in log book.
- Rinse the probes with distilled water. The probes should be used in accordance with the operation manual supplied by the manufacturer. Make sure to keep a copy with the probes.
- Record initial chemistry readings and then take at least one set of readings per volume pumped. Also record flow rate.

The two forms (pages 18 and 19) are examples of the data that can be recorded in the field.

Form 1. WATER QUALITY PURGING INFORMATION

Site ID

Datum =
Altitude =
N =
E =

Bore No

Date

Measured W.L. (m) =	
Measured Total Depth. (m) =	
Casing Height (m) =	
Radius of bore (cm) =	
Casing Material	
Slots/Screen (m)	
Pump Depth (m)	
Average Flow Rate (L/min)	
Pumping Time (min)	

Reduced W.L. (m) =		Measured W.L. - Casing height
Reduced T. D. (m) =		Measured T.D. - Casing height
Water column (cm)		Reduced T.D. - Reduced W.L. x 100
Approx casing volume (L)		$3.1415 \times \text{radius}^2 \times \text{water column} \times 10^{-3}$
Approx volume removed (L)		Pumping time x average flow rate

Results During Pumping

Time	Flow Rate L/min	pH	Temp Deg C	D.O. mg/L	Redox mV	EC scale =	Salinity ‰ Refract
------	--------------------	----	---------------	--------------	-------------	---------------	-----------------------

Comments

Form 2. SAMPLE SUMMARY SHEET

Page ____ of ____

REGION/UNIT PROJECT MANAGER:

URGENCY: 0-1 Week []
 1-2 Weeks []
 >2 Weeks []

Please forward a copy of this sheet with samples and post or fax another copy to:

PROJECT NAME: ACCOUNT CODE:

SAMPLED BY: SAMPLE METHOD:

FIELD MEASUREMENTS

Sample Number	Sample Date	Site Name	Bore Lic. Number	Sample Depth	Appearance	pH	EC (μS/cm)	T (°C)	Preservative Y/N	Other Info

LAB USE ONLY: Checked and logged by: _____
 Received in good order: yes/no _____
 Work Order Number: _____
 Date Received: _____

9. FILTRATION

On-site filtration is a necessary step in the process of groundwater quality sampling if determination is required of the 'dissolved' fraction. If the 'total' constituents are required then you do not filter. Also, filtering is not undertaken for microbiological constituents.

Reasons for filtering include:

- Removal of particulate matter
- The adsorption-desorption equilibrium between water, sediments and particles occurs within 72 hours.
- Bacterial growth can cause the redistribution of metal ions between solution and particulate phases.

The common standard pore size of filter used in groundwater quality sampling is 0.45 μm . This size filter does not remove all particulates from water. It removes phytoplankton and most bacteria but fails to remove the colloidal fraction (0.1 - 0.001 μm) of biological and non-biological origin. The pore size of the filter will vary downwards as the mass of material on the filter accumulates. If the filter is not changed when an excessive build-up of material occurs, it may result in total clogging of the filter.

A wide range of filtration media exist. These include cellulose nitrate, cellulose acetate and glass fibre filters. Cellulose nitrate filters are commonly used for major ions, and metals. One of the advantages is that they are relatively inexpensive. The more expensive cellulose acetate membrane filters are used for nutrients to prevent contamination. They are relatively inert and have well defined pore sizes. Glass fibre filters block less regularly but do not have a well-defined pore size. They are used for ³⁶Chlorine samples.

Filtration should be performed on-site as soon as possible after collection. Clean the filter in the same way as the container used for holding the sample (see Section 10). Filter papers should be handled using forceps. It is useful to have at least two filter systems to provide a separate one for trace metals.

The mechanism for filtration can be either with a vacuum or under pressure. In either case, only low pressures (<30 kPA) must be used to avoid rupture of living cells and release of organics/metals into the soluble phase.

It is recommended that this procedure is documented and the results be reported as 'filterable' species, quoting the appropriate pore size of the filter.

10. CONTAINERS, PRESERVATION, HOLDING TIME AND TRANSPORT

The purpose of using particular handling, container and preservation techniques is to try to maintain the sample integrity as much as possible between the point of sampling and the place of analysis. It is important that the decisions concerning these procedures are made at the planning phase of any water quality sampling program.

The sampling containers and preservation techniques to be used for various parameters are detailed in Table 5. Further information can be obtained from the Australian Standard AS 2031-1986 "Selection of Containers and Preservation of Water Samples for Chemical and Microbiological Analyses". The laboratory doing the analysis should always be consulted when a choice of techniques exists. The samples need to be carefully tracked/documentated before entering the laboratory so that all stages of their transport can be checked.

Containers

The selection and preparation of the containers is important because of the effect it can have on the water sample. Plastics, unless pre-treated can release heavy metals or organics into the sample and act as ion exchange resins. Glass can release or exchange elements of interest into the water sample.

The most common form of pre-treatment for containers is acid washing followed by thorough rinsing with high purity water. The acid leaches heavy metals adhering to the container wall and reduces the ion exchange properties of the container. Bacteriological sample bottles must be sterile and remain so during transport. Pesticide sample bottles should be initially cleaned with detergent and pesticide-free water then rinsed with pesticide-free water and, finally, cleaned with methanol.

Preservation

The preservation methods are based on the retardation of biological, chemical and physical changes and vary greatly in their effectiveness. They should be employed only when the sample cannot be analysed immediately (or within a few hours of collection). If preservation is necessary then it should be done as soon as possible after the sample has been collected. It is important to be aware that preservation will affect the sample in some way. For example, preservation for trace metal analysis samples by acidification will alter the speciation of the metals.

CAUTION: It is recommended that staff familiarise themselves with the safety aspects of using preservatives.

The main preservation methods are:

- 1) Temperature Control

The most common and simplest change of temperature procedure is to keep the samples in storage at 4°C. This minimises microbial activity.

For some parameters, such as some nutrients, freezing is used as a method of preservation. In this case, samples are best frozen in small aliquots. Sealable polyethylene bags (150 mL capacity) are useful containers for this purpose. If using polyethylene bottles, make sure they are stored upright and contain sufficient air space to allow for expansion. Quick freezing with dry ice is recommended as the most satisfactory approach. **CAUTION:** Dry ice can result in frostbite, suffocation if used in confined spaces and pH shifts due to absorption.

Samples must be allowed to reach ambient temperature and be thoroughly mixed before analysis.

2) Acidification

Acidification to below pH 2 has become standard practice for the preservation of samples for trace metal analysis. The function of this step is to prevent adsorption of metals onto the container walls by minimising ion exchange effects. Acidification prior to filtration will result in the release of metals bound to particulates and this will contribute to the results upon analysis. If the requirement is for dissolved metals only then acidification should occur **AFTER** filtration.

In other cases, the pH adjustment can be to a different level to hold the analyte in a more stable form. Change of pH can also be used to reduce biological activity.

Select an acid that will not interfere with the analysis. For example, do not use nitric acid when analysing for nitrates.

3) Prevention of Redox Changes

Loss of certain substances occurs through redox reactions. A number of oxidants can be used to prevent this process. For example, a draft Australian Standard for mercury determination uses nascent bromine.

4) Solvent Extraction

This method is used to separate the analytes from the matrix and is a recommended procedure for trace organics (ie pesticides). Although it is recommended that this procedure be carried out in the field, it is usually done in the laboratory because it is an unwieldy procedure. The samples are usually stored at 4°C in the interim.

Preservation of samples is difficult because almost all methods interfere to some degree with the analytical tests. Chemical preservatives should only be used when they do not interfere with the examination being made and should be selected accordingly.

Holding and Transport

It is necessary to maintain a dialogue with the analyst particularly with respect to holding time. The holding time is the period between collection of the sample and commencement of analysis - NOT delivery to the laboratory. Therefore, the samples should be delivered to the laboratory without any delay so that the requested analyses can be performed within the specified allowable holding time.

During transportation the following precautions must be taken:

- Bottle caps are secured tightly
- Samples are protected from the effects of light and excessive heat
- Glass bottles are cushioned
- Sample labels do not become lost or damaged
- Samples requiring preservation are transported after preservation.

Table 5

SAMPLING CONTAINERS, PRESERVATION AND HOLDING TIMES

Measurement/ Parameter	Recommended Container	Volume Required (min) mL	Preservation/Treatment	Maximum Holding Period
PHYSICAL PROPERTIES				
General	P	250	Completely fill bottle and store at 4°C	Various - see below
Colour	GB, G, P	100	Store in dark, cool 4°C	24 hours
Dissolved Oxygen	G only	300		Field determination preferred
Electrical Conductivity	P,G,T	100	If field determination not taken, completely fill bottle and store at 4°C	Field determination preferred (24 hours)
Hardness	P,G	200	Fill bottle completely. Add HNO ₃ to pH<2 or store at 4°C	7 days
Odour	G	200	Cool 4°C	Field determination preferred (24 hours)
pH	P,GB,T	100		Field determination preferred
Residue filterable non-filterable total Settleable matter	P,G	100 100 100 1000	Cool 4°C	7 days
Temperature	P,G			Field determination preferred
Turbidity	P,G	100	Cool 4°C	Field determination preferred (24 hours)
MAJOR IONS/ INORGANIC/NON- METALLIC				
General	P,G	1000	Filter, Store at 4°C	6 months
Alkalinity	P,G	200	Cool 4°C	24 hours
Bromide	P,G	500	Cool 4°C	28 days
Chloride	P,G	100	None required	6 months
Chlorine	P,G	200	Field determination	No holding time
Cyanides	P,G	500	Cool 4°C, Add NaOH to pH 12	24 hours
Fluoride	P,G	500	None required	28 days
Iodide	P,G	500	Cool 4°C, Store in dark	7 days
Silica	P only	200	Store at 4°C if not analysed within 24 hours	24 hours
Sulphate	P,G	200	Cool 4°C	7 days
Sulphide (Total)	P	500	Add 2ml Zinc acetate solution, Cool 4°C	7 days
Sulphite	P,G	50	Field determination	No holding time
METALS				
Total Dissolved Metals	P,G	1000	Filter on site. Add HNO ₃ to pH<2	6 months
Suspended (Filterable) Metals	P,G	1000	Filter on site.	6 months
Total Metals	P,G	1000	Add HNO ₃ to pH<2 For Ag use dark bottles	6 months
Mercury (Dissolved)	GB	500	Filter on site. Add HNO ₃ to pH<1, add potassium dichromate to 0.05% m/V	3 days
Mercury (Total)	GB	500	As for dissolved analysis but do not filter	3 days
NUTRIENTS				
Ammonia, Nitrate, Nitrite, Total Kjeldahl Nitrogen	P,G	500	Cool 4°C or freeze.	6 hours if cool/7 days if frozen
Phosphorus (all forms)	P,G	300	Cool 4°C or freeze	6 hours if cool/28 days if frozen
Phosphorus (soluble)	P,G	300	Filter on site. Cool 4°C	24 hours
PESTICIDES				
General	Prepared glass or Teflon. Use Aluminium or PTFE lined bottle caps	1000	Immediately after collection store at 4°C. Samples should arrive refrigerated to the lab within 48 hours of sampling.	2 weeks
BACTERIA				
General	Sterile GB	40	Store at 4°C	24 hours

Adapted from M.R. Scaif et al, 1981, Manual of Ground-Water Quality Sampling Procedures

Where P = Plastic
G = Glass
T = Teflon
GB = Borosilicate Glass

For parameters not listed here please consult the Laboratory Manager or the following document:
AS2031-1986 Selection of Container and Preservation of Samples for Chemical and Microbiological Analysis

Sampling for Specific Purposes

Below are some more specific instructions for sampling different parameter groups.

Major Ions

- Filter sample if required.
- Rinse sample bottle at least 3 times (use filtrate if sample has been filtered).
- If not filtering, take sample, fill bottle to overflowing, preferably by placing a small delivery tube at the bottom of the bottle and expelling the entrapped air in the bottle.
- Preserve (if necessary), seal and store at the appropriate temperature.

Metals

- Pre-prepare bottles by rinsing with 5% HNO₃ then with deionised water.
- Filter sample as required (See Section 9).
- Pour in sample, seal and store.

Nutrients

- Sample 500mL in a bottle. For environmental monitoring, these bottles should be prepared (sterilised) and supplied by a laboratory.
- Preserve and store sample on ice or freeze

Stable Isotopes

- Check with laboratory for specific instructions

Pesticides

- Preparation of bottles should include cleaning with detergent and pesticide-free water, rinsing with pesticide-free water and, finally, cleaning with methanol.
- If glass bottles are to be used, bake at 450°C for 2 hours after cleaning.
- The bottle tops should have a Teflon or aluminium liner to prevent contact of lid with water. It is advisable to obtain these prepared bottles from a laboratory.

Bacteria

- Undertake the decontamination procedure of the pumping equipment after each sampling event.
- Use only prepared sterile containers, preferably Borosilicate glass. Do NOT rinse micro sample bottles.
- Use clean, sterile equipment. Do not remove lid from container until you are ready to take the sample. It is suggested that, as part of the decontamination process, you spray the end of the discharge hose with 70% ethanol or sodium hypochlorite and allow to evaporate.
- When taking sample, take care not to touch bottle tip or stopper with delivery pipe or fingers.
- Seal and store.
- Samples can also be taken by lowering bottle down the bore, but care must be taken not to touch the side of the bore with the sample bottle.
- It is advisable to take replicate samples as it is often found that bacteria are not detected in every sample from a bore.
- Sample should be stored on ice and delivered to the laboratory in the same day. Do not freeze. Temperature should not exceed 10°C nor fall below 4°C,

11. CHAIN OF CUSTODY RECORDS

The collection and analysis of groundwater samples usually requires a substantial investment of resources in terms of equipment, facilities and staff. If inadequate information is recorded, regarding the circumstances of collection and subsequent disposition of the sample, then the resulting data could be rendered useless. If sampling programs are related to legal action then proper documentation is crucial.

Documentation of the sample history is referred to as chain of custody records. The field recording practices should be of a level that the sampling event can be reconstructed. There are four main components of chain of custody documentation:

- the Chain of Custody record
- sample labels
- field logbook/sample record
- sample analysis request record

Chain of Custody Records

To establish the documentation necessary to trace sample possession from the time of collection, a chain of custody record must be filled out and should accompany every sample or group of individually identified samples. This practice is especially important in the advent of litigation. Copies of this document should be made available to the laboratory, the requesting agency and one for the field book. They can contain the following information:

- Sample Identification Number
- Project title
- Date and time of sample collection
- Signature and name of sample collector
- Number of containers and their type
- Method of transport
- Condition of samples when received by the laboratory
- Specific comments and remarks
- Date and time of each change of custody
- Signatures of people in the Chain of Custody sample handover

Prior to signature the number of samples, label details and sample condition should be checked against the Chain of Custody.

Sample Labels

Sample labels are necessary to prevent misidentification of samples. Paper labels or tags should be used and should include at least the following information:

- Bore number or licence number including a unique sample code that distinguishes field samples, duplicates, spikes or blanks. The laboratory should not be cognisant of the code.
- Project name or number
- Signature or initials of sample collector
- Sampling interval or depth (m)
- Date and time of sample collection
- Location of sample collection
- Type of preservation used

Labels should be affixed to the sample container prior to or at the time of sampling. The labels should be filled out at the time of sample collection. The exact sample location and type of sample must be recorded in the field logbook.

Labelling of any boxes used for archiving or sample storage should include:

- Job Number
- Location
- Site
- Depth Interval
- Date
- Disposition

Field Logbook/Sample Record

Information pertinent to the sampling effort must be recorded in a field sampling log. All entries should be made in indelible ink and all corrections should follow error

correction protocol of one line through the error and initial and date of correction. Field personnel should also record all information on the appropriate sampling forms

The following list suggests some of the main items that could be recorded in a logbook or sampling workplan, depending on the individual situation:

- Project title
- Purpose of sampling
- Location, description and photographs of sampling point
- Details of sampling site (elevation of casing, casing diameter and depth, integrity of casing, casing type, screen depth, interval sampled, condition of bore)
- Name and address of field contact
- Reference to procedures for preparation of reagents or supplies which become an integral part of the sample (eg, filters and absorbing reagents)
- Identification of sampling crew members
- Number and volume of sample taken
- Sample method
- Sample preservation including storage method
- Date and time of collection
- Collector's sample identification number
- Sample distribution and transportation method (eg, laboratory name and cartage agent)
- References such as maps of the sampling site
- Field observations
- Field measurements
- Signature and date by the personnel responsible for observations
- Decontamination procedures
- Specific comments and remarks

The logbook should be kept under strict chain of custody and stored in a location so as to make it accessible to the project manager and associated project staff. Some of the information can be gathered and prepared prior to sampling as a workplan.

Sample Analysis Request Form

The Sample Analysis Request Form is a document outlining what is required from the laboratory in terms of analysis. It should include the variables to be analysed and the total number and type of samples being sent to the lab.

An example of a Chain of Custody/Sample Analysis Request Form is on pages 29 and 30.

CHAIN OF CUSTODY/SAMPLE ANALYSIS REQUEST FORM

General Information:

PROJECT NAME:

Name of Organisation:

Address of Organisation:

Name of Person Requesting Analysis:

Account Code:

Telephone Number: Fax Number:

Sample Data:

Bore No.: Licence No.:

Map No.: Map Reference:

Weather Conditions:

Sample Depth: Sample Device:

Decontamination: Bore Volumes Purged:

Samplers (names and signatures):

.....

Chain of Custody:

Relinquished By (name and sign.)	Received By (name and signature)	Date and Time

12. QUALITY ASSURANCE/QUALITY CONTROL

Quality assurance is a set of operating principles that when carefully followed during sample collection and analysis will produce data of known, consistent and defensible quality. Most analysts use a level of quality control techniques to obtain credible results, but a comprehensive quality assurance/quality control (QA/QC) programme requires systematic use of QA/QC measures throughout the sampling and analytical process.

In a broad sense, the elements of undertaking such a QA/QC procedure are:

- establishment of the information needs and the rationale for their implementation
- documentation of statistical and other accompanying investigations to validate the statistical design
- documentation of the sampling sites and procedures
- use of qualified personnel for sample collection and field analysis
- use of a certified/accredited laboratory (ie NATA registered) for analysing the samples in the field and/or in the laboratory
- use of a certified database and adoption of standard procedures for data handling (NWQMS, 1996, draft)

The use of such a program establishes the correct use of procedures and methods during the sampling program. In terms of field sampling procedure and laboratory analysis, the QA/QC process is used to check accuracy and precision with the use of duplicates, spikes and blanks.

Accuracy is the ability of the laboratory to report what is in the sample and can be measured by the use of spiked samples. Precision is the ability of the laboratory to reproduce results and is determined by submitting duplicate samples from the same source. Discussions of whether significant changes have occurred in groundwater quality must be tempered by the accuracy and precision performance for specific chemical constituents.

Sensitivity and completeness are further measures of sampling performances. Sensitivity relates to the limit of detection and the method detection limit for a particular chemical constituent. The method detection limit is the lowest concentration of a particular chemical constituent which can be measured reliably in a sample. Completeness is a measure of the amount of data meeting the data evaluation criteria obtained from a measurement system compared to the amount that was expected to be obtained.

It is not necessary to analyse for every parameter for QA/QC purposes. Choose the more sensitive parameters or ones of primary interest.

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.

Duplicates

These are duplicate water samples that should preferably be the split of one sample or they can be two samples bottled in immediate succession and put through similar filtering, preservation, holding and analysis. Their purpose is to test for precision. Depending on the nature of the sampling project, duplicates can be taken anywhere in the range from every tenth sample to every twentieth sample. Duplicate results can be compared as relative percent difference (RPD).

$$\begin{array}{l} \text{Relative} \\ \text{Percent} \\ \text{Difference} \end{array} = \frac{\text{Sample A} - \text{Sample B}}{\text{Average Sample A} + \text{B}} \times 100$$

Spikes

A spike is a sample in which a known amount of a compound being analysed is added (or spiked) into the sample. It tests the accuracy of the analytical system and any degradation or chemical alteration of the sample from the point of collection to analysis. The spike is used to determine if you can get back as much as you put in and

the results are expressed in terms of the percent recovery with regard to the amount added. The spike solutions are transported to the field and added during the sampling process. It is recommended that they be taken whenever a duplicate is taken and that each laboratory involved in the analysis program receive a spiked sample.

$$\% \text{ Recovery} = \frac{\text{Spike Result} - \text{Unspiked Sample Result}}{\text{Concentration Added}} \times 100$$

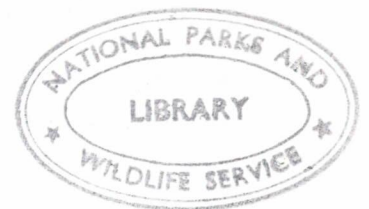
The distribution of the type and number of quality-assurance samples will not be equal among the different types of analyses because some of the types of samples require more comprehensive quality assurance than others (ie pesticides and microbiology) and different types of samples may be affected by different conditions.

Some additional recommendations in conducting field quality assurance are:

- Select wells ahead of time for quality-assurance sampling to help assure good coverage of different field conditions. However, if field conditions indicate the potential for sampling differences, the duplicate program can be restructured. Changes and reasons for changes should be documented.
- Intensify quality assurance when there are significant changes in sample collection procedures, including equipment changes.
- Conduct the different types of quality-assurance for a particular constituent class at the same sampling sites to help in interpretation of the results.

A QA/QC program will enable quantitative corrections for systematic errors (bias) during the sampling and analytical process. The QA/QC program should be made in consultation with the laboratory and will depend on the nature of the sampling project. It is especially important that these procedures are performed for the most sensitive chemical constituents. It is important that the laboratory does not know which are the QA/QC samples as all analyses should be treated equally.

A fully valid set of groundwater analytical data should include analytical performance data (eg. method, accuracy, precision, detection and quantitation limits) reported along with each set of results



13. PROBLEMS COMMONLY ENCOUNTERED WITH GROUNDWATER SAMPLING

(adapted from Jiwan & Gates, 1992)

The following list highlights some of the problems associated with groundwater sampling that can result in a chemical analysis being unrepresentative of the groundwater. Techniques to overcome the problems are also described.

- Stagnant waters are subject to evaporation and may contain animal and plant life which is not representative of natural groundwaters. If the bore has not been pumped recently, it will be necessary to purge the bore (See Section 7).
- Contamination of a water sample by entrained sediment is a common problem when the bore has not been developed properly or low aquifer yields have not allowed for proper development. In this situation the sample should be filtered at the bore head and both the liquid and solid samples sent for analysis. This process can take a while when the sediment load is heavy.
- Release of carbon dioxide during pumping may cause an increase in pH which in turn may cause many metallic ions to come out of solution. Sample at a very slow pump rate (1 to 5 litres per minute) or bail.
- The chemistry of the sample can alter as a result of oxidation. This can occur either in the pump or can be caused by water cascading into a bore installed in tight formations or by purging, such that the water level falls to the screen interval and allows the aquifer to be exposed to the air. Groundwater usually exists in a reduced state, therefore some of the common chemical changes that occur include:

- oxidation of organics
- oxidation of sulphide to sulphate
- oxidation of ferrous iron and precipitation of ferric hydroxide
- oxidation of ammonium to nitrate
- oxidation of manganese and precipitation of manganese dioxide or similar hydrous oxide.

Problems with oxidation can largely be avoided by monitoring the oxidation state of the bore during pumping (Eh meter) and taking a sample only after the water has stabilised.

- Cross-contamination of water samples due to chemical residue in the pump or sampling equipment can cause erroneous results. This includes the improper handling of sampling equipment on the ground where it can become contaminated. Decontamination of all sampling equipment is important between each sampling when high precision of results is necessary.
- The time lag between collection of a sample and analysis together with the correct preservation of the sample are two important aspects of sampling which are often

misunderstood.. Table 5 shows the preferred methods of preservation and the maximum time a sample can be held in storage.

- Poor sampling logs/records have in the past resulted in a mix-up of samples. Section 11 reviews the documentation that should accompany a sample. It should be filled out at the time of sample collection with a copy for the project manager. Where appropriate, Chain of Custody forms should also be filled out.
- To date there have either been poorly designed or no quality assurance/quality control programs to ensure that the analytical results accurately express the actual concentrations of solutes in the water as they exist in the field situation. A QA/QC program should be built into all new work programs.
- The selection of equipment for sample collection can also present problems. Many of these “tools” have not been proven reliable in specific hydrogeological situations. Table 3 sets out the advantages and disadvantages for a variety of sampling equipment.

As a result of the unique nature of groundwater there is a need to be diligent with sampling procedure. A few of the problems that occur repeatedly with sampling programs include:

- When using existing bores, there are often only poor bore construction records available or none at all.
- Untrained personnel are used for sampling programs. There are many steps to sampling and each one needs to be understood in order to carry them out properly and to be able to make decisions on them in the field.
- It is difficult to do more than the minimum of determinations on-site.

14. SUMMARY OF GROUNDWATER SAMPLING PROTOCOL

The following Table outlines in step form the requirements for a generalised sampling protocol for situations like a regional groundwater quality investigation.

Table 6

Groundwater Sampling Protocol Summary

Step	Goal	Recommendation
Preparation	To integrate sampling and analysis functions	Confer with laboratory personnel about the objectives of the program and the choice of best techniques for collection, preservation and testing.
Set-up	To prevent ground contamination and have everything ready for the sampling process	Prepare field record sheets and record data in logbooks. Place plastic sheeting around well area to prevent direct contact with ground and lay out equipment. Calibrate probes, preferably everyday or when accuracy is in doubt during the sampling program.
De-contamination	To clean sampling equipment and prevent cross-contamination.	Use bleach or detergent solution. Clean system internally and externally. Consider disposal of decontamination solution.
Hydrologic Measurements	Establish non-pumping water level	Measure depth to water, total depth of well and height of casing to +1mm.
Bore Purging	To remove stagnant water	Pump a minimum of 3 bore volumes until pH, temperature, EC and Eh have stabilised. Record volume, rate, duration and time of purge.
Pumping /Bailing to Obtain Sample	To collect samples with minimal disturbance of sample chemistry	Collect samples using appropriate pump device/bailer. Use low pump rate for gas-sensitive parameters. Higher rates can be used for inorganic parameters.
Field Measurements	To avoid bias in determination of parameters/constituents which do not store well, eg gases, pH, alkalinity.	Analysis for determinations of gases, alkalinity, temperature, pH, EC, DO, and Eh should be carried out in the field. The best system is a flow-through chamber fitted with probes. Record results.
Sample Collection	To collect samples with minimal disturbance of sample chemistry	Use containers as recommended in Table 5. Ideally run a plastic hose from the bore head outlet to the bottom of the sampling bottle (Do not use plastic with organics).
Filtration	To determine 'soluble' constituents and preserve sample. To be carried out in the field as soon as possible after collection	Standard filter is 0.45 µm. Use with vacuum or pressure pump. Filter trace metals, inorganics, anions/cations, alkalinity. Do not filter for microbiology, some stable isotopes and organic compounds.
Rinse and Fill	To collect samples with minimal disturbance of sample chemistry	Rinse the sample container and cap 3 to 4 times taking care of disposing the water away from the sampling site. If sample requires filtering then use filtered water for rinsing. Fill to overflow and expel completely any air trapped in the sample bottle. If sample is to be frozen, leave air space for expansion. If container has pre-prepared preserving material in it do not rinse and allow to overflow. Cap container as soon as possible.

Sample Preservation/ Storage and Transport	To minimise chemical alteration of samples prior to analysis by temperature control and/or addition of preservative.	Follow preservation method and maximum sample holding period as recommended in Table 5. Document preservation method and holding time and make sure bottles are properly labelled. Store securely and at appropriate temperature for transport.
QA/QC	To ensure analytical results accurately represent water in the field and to permit any correction of analytical result for changes which may occur after sample collection.	Collect blank, duplicate and spiked samples. There should be a minimum of 5% samples submitted as blind duplicates to a laboratory.
Chain of Custody Documentation	To be able to follow the sample history of each sample.	Ensure that each sample procedure is properly documented on the appropriate form and that there are sufficient copies for filing.

Adapted from Jiwan & Gates, 1992

15. REFERENCES

- ANZECC, 1992, Australian Water Quality Guidelines for Fresh and Marine Waters.
- ANZECC and ARMCANZ, Draft 1995, National Water Quality Management Strategy, Guidelines for Water Quality Monitoring and Reporting.
- AWRC, 1991. A Preliminary Guide to the Standard Operating Procedures for Sampling Contaminated Groundwater, Australian Water Resources Council Water Management Committee, Occasional Paper WRMC No. 2.
- Barcelona, M.J., Gibb, J.P., and Miller, R.A., 1984. A Guide to the Selection of Materials for Monitoring Well Construction and Ground-Water Sampling, Illinois State Water Survey for U.S. Environmental Protection Agency, Report Number EPA-600/2-84-024.
- Canter, L.W., Knox, R.C., and Fairchild, D.M., 1988. Groundwater Quality Protection, Lewis Publishers Inc., Michigan, 2nd Edition.
- Garrett, P., 1988. How to Sample Ground Water and Soils - A Manual for the Back Pocket, National Water Well Association.
- Hardy, M.A., Leahy, P. P., and Alley, W.M., 1989. Well Installation and Documentation, and Ground-Water Sampling Protocols for the Pilot National Water-Quality Assessment Program, U.S.G.S. Open-File Report 89-396.
- ISO/TC 147/SC 6 N 120. Guidance on the Sampling of Groundwater.
- Jiwan, J. and Gates, G., 1992. A Practical Guide to Groundwater Sampling - 1st Edition, NSW Department of Water Resources Technical Services Division TS92 080
- MDBC Groundwater Working Group, 1993. Groundwater Quality Monitoring Proposal - Murray-Darling Basin, Report to the Murray-Darling Basin Commission.
- NH&MRC/ARMCANZ, (1995), Australian Drinking Water Guidelines.
- Nielsen, D.M., 1991. Practical Handbook of Ground-Water Monitoring, Lewis Publishers, Inc.
- Rayment, G.E. and Poplawski, W.A. (Editors), 1992. Training Notes on Sampling for Water Quality Monitoring, Queensland Department of Primary Industries - Land Use and Fisheries and Water Resources Commission.
- Scalf, M.R., McNabb, J.F., Dunlap, W.J. and Cosby, R.L., 1981. Manual of Ground-Water Quality Sampling Procedures, U.S.E.P.A.

Technical Support Section, Unpublished. Procedures and Notes for Pumping and Sampling of Low Yield/Small Diameter Bores for Water Quality Assessment, Australian Geological Survey Organisation.

1987. A Guide to the Sampling and Analysis of Water and Wastewater - 5th Edition, Victorian Environment Protection Authority, Publication No. 254.

APPENDICES

APPENDIX 1: FIELD EQUIPMENT CHECKLIST

Field notebook, pencils, pens and markers
Map of well locations
Key for wells
Lubricant for locks (WD40 or graphite)
Water level gauge
Tape measure
Paper towels
Folding table and chairs
Conductivity meter and standard solutions for calibration of probes
Thermometer
pH meter and buffer solutions
Spare batteries for all instruments
Beakers, stirrers, wash bottle, funnels, tissue-wipes
Twine (Teflon, nylon, etc)
Bailer (<40 mm in diameter) made of appropriate material
Pump and tubing made of appropriate material
Pump reel and frame
Electric cable
Generator
Fuel and oil
Buckets (calibrated in litres)
Tape
Garden hose
Plastic sheet
Stopwatch or watch that indicates seconds
Chain of Custody and other forms
Sample Containers (bring 20% more than required), all sealed clean and labelled.
Trip blanks and spike solutions
Filtering kits
Acid Box: items for preservation and chemical treatment of samples in field.
Portable iceboxes or coolers and cooler bricks
Max/Min thermometer
Decontamination vessels - washed, rinsed and distilled
Detergent solution (biodegradable), ethanol, concentrated bleach
Deionised water, distilled water
Garden spray cans for wash fluids
Gloves, boots, overalls
Raingear or warm clothing
Sun protective lotion, hat, sunglasses, insect repellent
Camera and film
Toolbox
Soil Auger, shovel
Soil sample containers
Torch, calculator
Business cards/ID, money

MURRAY-DARLING BASIN GROUNDWATER QUALITY MONITORING PROJECT

APPENDIX 2: SUMMARY OF PUBLICATIONS ASSESSED FOR MDB GROUNDWATER SAMPLING

	NSW	QLD	SA	VIC	AGSO	COMM	MDBC	USGS USEPA	INTER- NAT
Agencies involved /contacted	DLWC EPA	DWR DEH	DMESA DENR SA Water	RWC (Sinclair- Knight-Merz) DCNR EPA	Groundwater Quality Project, EGG Technical Group, EGG	DPIE - AWRC - NWQMS The EPA River Monitoring	MDBC - Groundwater Working Group	USGS - NAWQAP USEPA	UNEP WHO UNESCO WMO
Documentation of Sampling Protocols	1992, Jiwan, J and Gates, G, A Practical Guide to Groundwater Sampling	1) 1991, McNeil, V et al -comments on sampling 2) 1992, Rayment & Poplawski, Training Notes on Sampling for WQ Monitoring 3) Hydrographic Porcedure No. 10, Water Quality Sampling, DPI-WR. Very much focussed on surface water. 4) DEH - to do in future 5) Poplawski to do after NWQMS completed.	ISO/TC 147/SC 6 N 120 - Guidance on the Sampling of Groundwater. Australian Centre for Water Quality Sampling Manual, NATA approved.	1) USEPA Guidelines and AWRC Guidelines for ISO 9000 accreditation 2) 1987, Vic EPA, A Guide to the Sampling and Analysis of Water and Wastewater - 5th Edition	1995, unpublished, Procedures and Notes for Pumping and Sampling of Low Yield for Small Diameter Bores for Water Quality Assessment	1) 1991, AWRC- WRMC, A Preliminary Guide to the Standard Operating Procedures for Sampling Contaminated Groundwater 2) NSW EPA doc. to be put into NWQMS doc. on Monitoring and Reporting (analyses only) 3) NWQMS documents - mainly surface water and no detail 4) National River Health Program - not yet available	1993, MDBC- GWG, Groundwater Monitoring Proposal - General Comments - Min. Preservation Requirements	1) 1989, USGS Open File Report 89-396, Well Installation and Documentation, and Ground-Water Sampling Protocols for the Pilot National Water-Quality Assessment Program 2) 1981, USEPA Report No. 600/2- 81-160, Manual of Ground-Water Sampling Procedures	1987, WHO, GEMS/Water Operational Guide (GEMS is the Global Environmental Monitoring System)
Document studied	as above	1992, Rayment & Poplawski, Training Notes on Sampling for WQ Monitoring	as above	1987, Vic EPA, A Guide to the Sampling and Analysis of Water and Wastewater - 5th Edition	as above	1991, AWRC- WRMC, A Preliminary Guide to the Standard Operating Procedures for Sampling Contaminated Groundwater	as above	as above	as above)
Main Document Sources	1) 1985, Barcelona et al, Practical Guide for Sampling Illinois State Water 2) Gibbs et al, Procedures for Collection of Representative Water Quality Data from Monitoring Wells	1) 1985, Barcelona et al, Practical Guide for Sampling Illinois State Water 2) 1988, Garrett, P, How to Sample Groundwater and Soils, A Manual for the Back Pocket	No source document referenced	No source document referenced Mention in text of: 1) Australian Standard AS2031- 1986 (containers) 2) Reference list for Methods of Analysis	No source document referenced	1) Dames and Moore SOPs 2) Sampling Guidelines - Industrial Wastes and Pollution Control Samples, WAWA 2) A Guide to the Sampling and Analysis of Water and Wastewater, Vic EPA	1992, Jiwan, J and Gates, G, A Practical Guide to Groundwater Sampling	Various references: 1) 1984, Barcelona et al 2) 1982, Claassen, HC 3) 1981, Pettyjohn et al 4) + many more older references	This document does not constitute a formal publication. 1978, UNESCO/WHO, Water Quality Surveys - a guide for the collection and interpretation of water quality data; Studies and Reports in Hydrology No. 23
Summary of document focus	Purpose: to obtain representative groundwater samples - very specific. Excludes pesticides and organics Very detailed methodology with numerous Tables outlining steps.	Training notes for surface and groundwater. Different chapters by different authors. Moderately descriptive and some Tables.	This international standard is one of a group of standards dealing with the sampling of specific types of water. It is very descriptive and general and useful for the principles of sampling.	Covers all water bodies. Flexible guidelines aimed at pollution monitoring. Very general.	Step-by-step field process specific to AGSO's Groundwater Quality Assessment Program.	Detailed SOPs (Standard Operating Procedures) specific to contaminated groundwater. Full process: drilling to well abandonment. Quite specific.	A few pages on groundwater sampling principles and Minimum Preservation Requirements.	1) Report covers Well Selection, Installation and Sampling for groundwater specific to NAWQA Program. Descriptive with some Tables. 2) Report covers hydrogeological and sampling principles in depth. Also, construction of wells, drilling, development. Sampling section is detailed on samplers but not very strong on other aspects.	Technical document for GEMS. Focuses primarily on surface water and analytical methods.

MURRAY-DARLING BASIN GROUNDWATER QUALITY MONITORING PROJECT

APPENDIX 3: TOPICS ADDRESSED IN SELECTED SAMPLING MANUALS

The headings on this row are associated with the publications referenced in Table 1	NSW	QLD	SA	VIC	AGSO	AWRC	MDBC GWG	USGS	USEPA
Principles	X	X 1 chapter	X	X linked to EP Act 1970		X in document text	X	X linked to NAWQAP	X
Preparation					X very detailed field equipment			X minor	X data
Indicators	X				X			X	
Location & Frequency	X	X	X					X	X location
Devices/Pumps	X	X	X limited on pumps	X bail vs. pump		X	X minor	X	X drawings
Materials for Devices	X	X				X minor		X minor	X minor
Decontamination	mentioned but no detail		X minor - flaming		X very detailed	X		X	X for micro
Purging	X very thorough	X	X minor	X minor	X	X	X	X	X minor
Field Measurements	X	X	X minor		X	X	X minor	X	X minor
Filtration	mentioned but no detail	X SW + GW + effects	X	X general	X	X		X	
Containers/ Preservation/Holding/. Transport	X	X SW + GW + effects	X general	X general	X	X	X	X	X
Chain of Custody Documentation	X	X SW + GW	X minor	X general	X	X		X	X linked to Chain of Custody
QA/QC	X + spiking solutions				X for different chemical programs		X minor	X	
Problems	X 9 points	X 1 chapter				X in document text			X in document text
Summary of Protocol	X total process	X for different chemical programs			X? not really a summary	X 18 point list		X linked with preservation + containers	
Documentation/Forms (distributed to other sections)	X	X	X 14 point list	X 8 point list	X	X		X	X 18 point list + Chain of Custody Procedure
Items peripheral to groundwater sampling protocol									
Drilling/Soil Sampling						X		X	X
Monitoring/Well Installation		X				X		X	X
Surface Water Sampling		X		X		X			
Interpretation of Results		X							

National Parks & Wildlife Service



18883

