A National Protocol for State of the Environment Groundwater Sampling in New Zealand
## Contents

### Part One: Introduction

**Purpose of the Protocol**

**Development of the protocol**

**What the protocol covers**

**Organisation and use of this document**

### Part Two: The Sampling Protocol

1. **Pre-sampling**
   - 1.1 Check site details
   - 1.2 Gather equipment
   - 1.3 Calibrate field meters

2. **On-site preparation**
   - 2.1 Confirm you have the correct sampling site
   - 2.2 Confirm appropriate sample point
   - 2.3 Check calibration of field meter(s)
   - 2.4 Clean sampling equipment

3. **Purging**
   - 3.1 Measure depth to water
   - 3.2 Calculate the volume of water to be purged
   - 3.3 Install portable pump if necessary
   - 3.4 Initiate pumping
   - 3.5 Monitor field parameters during purging
   - 3.6 Assess adequacy of purging

4. **Collect samples**
   - 4.1 General
   - 4.2 Preparing to collect samples
   - 4.3 Collect samples in isolation from the atmosphere (if required)
   - 4.4 Collect filtered, acid-preserved samples (if required)
   - 4.5 Collect filtered, unpreserved samples (if required)
   - 4.6 Collect unfiltered, unpreserved samples (if required)
   - 4.7 Collect sterile unfiltered, unpreserved samples (if required)

5. **Site clean-up**

6. **Sample storage, transport and delivery**


### Appendix 2: Sample field sheet

1. **Site details**
2. **Field information**
3. **Sample field sheet**

### Appendix 3: Information that should be recorded regarding each Sampling Site

### Screen shot of a typical ‘WELLS’ database screen

### Appendix 4: Recommended gear list

### Appendix 5: Instructions for isolating a pressure tank

### References
Tables
Table 1: Recommended sampling methods for typical determinands
Table 2: Summary of calibration procedures for field measurements

Figures
Figure 1: Calibrating a field meter using a pH 7 standard solution
Figure 2: Name plates on bores are a useful way to confirm the correct site is being sampled
Figures 3 and 4: An appropriate sample point should be as close to the well head as possible, in good condition and upstream of any pressure cylinders wherever possible
Figure 5: Water level in non-artesian conditions can be measured using a dip tape and the depth recorded relative to a known point on the well
Figure 6: Artesian head can be measured using a clear tube and a staff gauge
Figure 7: When purging, ensure the discharge is away from the well so that water does not pond around the well casing
Figure 8: A suitable pump rate will ensure laminar flow from the outlet point (left), aerated flow (right) is not appropriate
Figure 9: Water from the pump outlet can be passed through an open container (left) or a flow cell (right)
Figure 10: Filling a sample bottle – note the tilting and laminar flow
Figure 11: Typical sample bottles with clear labels
Figure 12: With the nylon tube all the way to the bottle on the sample bottle, fill the bottle slowly and smoothly until all air has been displaced and water overflows from the bottle
Figure 13: Tap the cap underwater to remove any air bubbles and then cap the sample bottle underwater
Figure 14: Typical syringe and 0.45 µm disposable filter
Figure 15: Position the filter and syringe above the bottle, ensuring not to touch the bottle with the filter to avoid contamination
Figure 16: Attach the in-line filter to the sample point using clean tubing
Figure 17: Filling a sample bottle using an in-line filter – note the tilted bottle and laminar flow
Figure 18: Chilly bins should be packed with at least five frozen chemical pads (top right) or 3 kg of ice (bottom). Too few pads will not keep the samples at or below 4ºC (top left). Overnight couriering requires the chilly bin to re-packed with ice (bottom).
Figure 19: Flaming a metal sample point
Figure 20: Spraying a sample point with an ethanol solution
Figure 21: Filling sterile bottle with gloved hands – note minimal aeration
Part One: Introduction

Purpose of the Protocol

This document describes a standardised protocol for the collection of groundwater samples in New Zealand for the purpose of State of the Environment (SOE) monitoring. SOE monitoring aims to:

- characterise the ambient groundwater quality on a regional scale
- identify significant groundwater quality issues, such as spatial or temporal trends in quality, which may result from pressure on the resource such as land use, point source discharges and non-point source discharges
- assess compliance with groundwater quality management objectives
- provide data to assess the effectiveness of groundwater management policies.

It is well established that analytical results can be heavily influenced by the way a groundwater sample is collected, preserved and transported prior to analysis. While there are numerous existing guidelines to assist samplers, they typically present a number of options for sampling without providing a recognised best-practice procedure that is appropriate for New Zealand conditions. As a result, several different methods for SOE groundwater sampling are currently in use in New Zealand. Thus SOE monitoring data may not be readily comparable between different regions, and even within a single region, older groundwater quality data may not be directly comparable to newer data.

The aim of this sampling protocol is to facilitate robust assessments of groundwater quality, particularly at an inter-regional and national scale. Use of this protocol will:

- ensure groundwater samples are representative of groundwater in the aquifer
- ensure results from samples which are taken in different regions, at different times, and/or by different samplers can be compared with more confidence.

It is important to note that this protocol is not a mandatory requirement or official national guideline. Any sampler may choose to collect a non-compliant sample at any time based on professional judgement. It is acknowledged that there may be practical constraints to following this protocol in certain cases. However, it is hoped that, as a minimum, labelling and recording samples as ‘compliant’ or ‘non-compliant’ with the protocol will become a standard practice for all SOE groundwater samples. This will lead to improved awareness of the status of results from around the country.

Development of the protocol

The need for a standardised groundwater sampling protocol was identified as a priority by the Regional Groundwater Forum (RGF) in 2004. The RGF comprises groundwater scientists from all regional and unitary councils in New Zealand. The protocol has been developed by a working group of groundwater scientists from GNS Science, Greater Wellington Regional Council, Environment Canterbury and Marlborough District Council, under contract to the Ministry for the Environment.
A draft version of the sampling protocol was produced in August 2005 (see Daughney et al 2006). It was developed by collating and condensing existing guidelines into a single best-practice procedure. The draft protocol described step-by-step instructions for well purging, sample collection and treatment, and other critical steps in groundwater sampling. Justification for each step in the protocol was provided through reference to existing national and international groundwater sampling guidelines.

In September 2005, the draft protocol was reviewed by members of the RGF and by representatives from United States Geological Survey, the British Geological Survey, and the Australian CSIRO. The reviewers made several recommendations for modification to the sampling procedures specified in the draft protocol. Many of the recommended changes seemed to be based on adherence to common industry practice without reference to published scientific literature. A search of the scientific literature did not shed light on the magnitude of the possible biases that might be caused by particular sampling methods, or indeed whether or not these potential biases would be significant for typical SOE groundwater sampling conditions in New Zealand.

In March and April 2006, a field trial was undertaken to assess the possible effects of different sampling procedures on the chemistry of groundwater samples collected from typical SOE monitoring sites in New Zealand. The field trial involved 49 SOE monitoring sites in the Wellington (including Wairarapa), Marlborough and Canterbury regions, and set out to address specific questions raised by the reviewers. The results of the field trial justified several modifications to the procedures specified in the draft groundwater sampling protocol (Daughney et al 2006).

This current version of the protocol (October 2006) is updated in accordance with the recommendations of the national and international reviewers and the results of the field trial. This version of the protocol may be updated in the future, following its release for general use in New Zealand in late 2006.

**What the protocol covers**

The protocol is a prescriptive field procedure for the collection, preservation and transport of groundwater samples. This protocol includes detailed instructions for:

- off-site preparation for sampling
- on-site preparation for sampling
- purging of standing water from the well and field measurement of pH, conductivity and temperature
- collection and preservation of samples
- site clean up
- sample storage, transport and delivery to the laboratory.
In accordance with standard analyses conducted for the purpose of SOE monitoring in New Zealand, this protocol includes instructions for collection of:

- unfiltered, unpreserved samples collected in isolation from the atmosphere, which are suitable for the analysis of chlorofluorocarbons (CFCs), sulphur hexafluoride ($SF_6$) and some other dissolved gases
- filtered, acid-preserved samples, which are suitable for analysis of major cations and some metals
- filtered, unpreserved samples, which are suitable for analysis of major anions and nutrients
- unfiltered, unpreserved (raw) samples, which are suitable for analysis of pH, conductivity, alkalinity and isotopes of oxygen and hydrogen (including tritium)
- sterile unfiltered, unpreserved samples, which are suitable for analysis of microbiological indicators.

This protocol does not apply to collection of groundwater samples for the analysis of parameters which are not usually monitored for SOE purposes in New Zealand. Many “non-SOE” parameters have unique sampling requirements and therefore have been excluded from the protocol. However, aspects of this protocol may still be applicable to sampling for these parameters, for example the purging criteria. Sampling for these parameters should be discussed with the laboratory that will ultimately perform the analysis. Otherwise, assume that this protocol is not suitable for:

- organic carbon compounds, including volatiles and non-aqueous phase liquids (see Rosen et al 1999)
- pesticides
- metals at concentrations less than 0.01 g m$^{-3}$ (see Rosen et al 1999)
- geothermal samples (gasy or hot) (see Rosen et al 1999; Stansfield et al 2001)
- sulphide (a specific preservative is required; see Rosen et al 1999)
- cyanide (a specific preservative is required; see Rosen et al 1999)
- isotopes of nitrogen, sulphur or carbon (large sample volumes or special reagents may be required; see Rosen et al 1999).

This protocol does not include instructions for monitoring network design or site selection. The protocol is strictly a field procedure, and it is therefore assumed that the wells being sampled form part of a well-designed groundwater monitoring network. In accordance with most SOE monitoring sites in New Zealand, this protocol is intended for sampling of bores and wells. The suitability of any site for SOE monitoring is addressed only to the extent of confirming the ability of the site to be purged and sampled in compliance with the protocol. Hughes (2000) provides advice on selection of wells for SOE monitoring. Rosen et al (1999) and Hughes (2000) provide recommendations on the timing and frequency of sampling suitable for New Zealand. See Sinton (1986) and Hughes (2000) for information on sampling springs and seeps.
This protocol does not provide guidance on quality assurance (QA) or quality control (QC) of data. Although QA/QC measures are an essential component of a monitoring programme, these measures are not discussed here because this protocol is limited to field actions required for the collection of samples. Hughes (2000), Crowcroft and Scoble (1997) and Standards New Zealand (1998) discuss the use of these QA/QC methods. Commonly used QA/QC methods include duplicate samples, blanks, spiked samples, control standards and inter-laboratory comparisons.

This protocol does not provide specific guidance on sampling safety or etiquette. Although sampling safety and etiquette are crucial in any sampling programme, they are not discussed here because, as stated above, the protocol is limited to the field actions required for sample collection. Measures that should be taken to ensure the safety of sampling staff are discussed by Rosen et al (1997), Crowcroft and Scoble (1997), Standards New Zealand (1998a), Hughes (2000) and Stansfield (2001). Rosen et al (1997) and Hughes (2000) discuss appropriate sampling etiquette that minimises any inconvenience to well owners.

**Organisation and use of this document**

The protocol comprises four parts:

- this guideline document, describing the sampling procedures in detail and providing the rationale behind them
- a flow diagram for use in the field, providing a simplified step-by-step two-page guide that is cross-referenced to the more detailed guideline (Appendix 1 of this document)
- an example field sheet that can be used for recording information in the field (Appendix 2 of this document)
- a separate report that describes and interprets results from the field trials (Daughney et al 2006).

This protocol separates the actions which are **required** for compliance with this protocol from the actions which are **recommended** for collection of samples. For all procedural steps, essential actions are indicated by the words “must” and “required”, whereas non-essential optional actions are indicated by the words “should” and “recommended”. For example, Step 2.2 states that all samples **must** be collected from a sample point that is in good condition, and that all samples **should** be collected upstream of any pressure tank or similar device. These instructions indicate that any sample which is collected from a corroded sample point will be non-compliant with this protocol, whereas a sample collected downstream from a pressure tank will be compliant with this protocol (although the sampler should observe the recommendation to collect the sample from upstream of the pressure tank if possible).

In the organisation of this document, an effort has been made to list all essential actions at the beginning of the description of each sampling step, followed by a list of actions which are recommended as best-practice but not required for compliance with this protocol. The description of recommended actions is kept to a minimum for the sake of brevity.
This protocol is intended to provide a stand-alone reference for groundwater sampling. For all *required* actions, reference to other existing guidelines is provided only for justification, and is not intended to imply that other guidelines should be consulted prior to sampling. For some *recommended* actions, the reader is directed to other existing guidelines simply in order to keep this protocol document as brief as possible. The protocol does not include a glossary, but certain terms that might be unfamiliar to some readers are defined in the text at their first occurrence. For definitions of any other terms used in this document, readers are directed to Standards New Zealand (1998a).
Part Two: The Sampling Protocol

This section describes the procedural steps of the protocol and the rationale behind these steps. Each step is cross-referenced to the accompanying field guide (Appendix 1).

1 Pre-sampling

The following pre-sampling steps are recommended because proper preparation will facilitate the sampling programme and ensure the collection of meaningful data. These steps would typically be completed before leaving the office, either the day before or the morning of the sampling event.

Sampling in dry conditions is not required for compliance with this protocol, but it is recommended for the comfort and safety of sampling staff, and to prevent contamination of the sample from rain and/or windborne particles. It is therefore advisable to check the weather forecast to decide whether or not the sampling event should take place. It is the sampler’s responsibility to exercise professional judgement as to whether or not sampling in poor weather conditions will compromise sample quality or personal safety.

1.1 Check site details

Certain information should be compiled in order to provide a context for interpretation of groundwater quality data from any monitoring site. This information should include, for example, the name, location and depth of each well that is to be sampled (see Appendix 3). Although not mandatory for compliance with this protocol, the sampler should check that the relevant information for each site is available, complete and up to date (Hughes 2000; Standards New Zealand 1998a). Any data or information gaps should be addressed prior to sampling.

1.2 Gather equipment

a General

See Appendix 4 for a list of equipment that is recommended for groundwater sampling (Crowcroft and Scoble 1997; Stansfield 2001). Note that individual sample sites will have different equipment requirements. The sampler must ensure all of the equipment that will be required for the sites to be sampled is available and in good working order.

b Bottles

Bottles must be new or pre-cleaned. Specifications for bottle materials and cleaning methods for particular types of samples are given in Step 4 and Table 1. Instructions for cleaning bottles according to particular methods (eg, acid washing, detergent washing, baking, sterilising) are provided in Standards New Zealand (1998a).
A preservative is required for some types of samples (eg, an acid preservative for samples to be analysed for cations). It is recommended that the preservative is added directly to the sample bottles (either by the laboratory or by the sampler) prior to the sampling event. In this case, the sampler must confirm and record that the preservative has in fact been added to all bottles where it is required. Alternatively, if preservative is not added to the bottle before sampling, it is acceptable for the sampler to add the preservative to the bottle in the field after the sample has been collected (see Step 4).

c  Chilling samples

Some standard laboratory methods for certain analytes (eg, nutrients) require samples to be chilled to below 4°C immediately after collection and for the duration of their transport to the laboratory (see Step 4). Compliance with this protocol does not require that chilling is accomplished in any particular way, but the sampler must ensure samples are chilled according to the laboratory’s requirements. One commonly used approach that has been shown to chill samples effectively (Daughney et al 2006) is to use a chilly bin (ca 20–40 litres) which is packed with at least five frozen chemical ice packs (“slicka” pads) or at least 3 kg of ice (one typical service station size bag) (see Step 4). If this approach is to be used, the sampler must ensure chemical ice packs are pre-frozen or that ice is available, and then transfer the required quantity into the chilly bin immediately prior to the sampling event.

1.3 Calibrate field meters

This protocol requires field measurement of temperature, conductivity and pH (see Step 3). Calibration is the act of adjusting a meter’s settings so that it displays the proper reading when sensors are immersed in solutions with known values of the pH, conductivity or temperature (or other parameter of interest). Standards are the solutions with known values of pH, conductivity or temperature (or other parameter of interest) that are used for calibration.

Compliance with this protocol requires the sampler to ensure the temperature, conductivity and pH meters are maintained and calibrated according to the manufacturer’s instructions. The sampler must also check that temperature correction functions for conductivity and pH are working properly, as described below. These steps are usually most easily accomplished before leaving the office on the day of sampling.

General guidelines for calibration of temperature, conductivity and pH are summarised in Table 2. All meters should be calibrated as often as recommended by the manufacturer, or at the minimum intervals given below. Standard solutions used for calibration should cover the range expected for the samples to be measured, and should be within the manufacturer’s recommended shelf life. Note that probes and sensing devices must be allowed sufficient time to equilibrate with standard solutions during calibration.
a **Temperature**

The temperature meter must be calibrated as often as recommended by the manufacturer or at least once per year (Rosen et al 1999).

For many modern temperature meters, adjustments of the calibration can only be performed by the manufacturer. In this case, it is the sampler’s responsibility to ensure the meter is sent to the manufacture as required for regular servicing.

Alternatively, the temperature calibration of some meters can be set by the user. In this case, temperature calibration can be performed using a constant temperature bath and a reference thermometer (Rosen et al 1999; Radtke et al 2004). The temperature calibration should include measurement of at least three different standards that cover the range of temperatures expected for the groundwater to be sampled. Standards of in the range 5–25°C are appropriate for most SOE groundwater monitoring sites in New Zealand.¹

The accuracy of the temperature calibration should be checked at least once every six months. This should be accomplished by measuring at least one solution with a known temperature that is within the range of the calibration. The calibration is acceptable if the measured temperature is within ±0.2°C of the true (known) temperature (Radtke et al 2004). If the measured temperature is not within ±0.2°C of the true (known) temperature, the temperature probe should be recalibrated or replaced.

b **Conductivity**

The conductivity meter must be calibrated as often as recommended by the manufacturer or at least at the beginning of each sampling day (Rosen et al 1999; Radtke et al 2005).

For most modern conductivity meters, the calibration must be set by the sampler using at least one standard solution. Standard solutions can be purchased from the meter manufacturer or prepared as described by Rosen et al (1999). Standard solutions in the range 50–750 μS/cm at 25°C are suitable for most SOE sites in New Zealand.¹ Standard solutions should be kept at room temperature to facilitate the check of the temperature compensation function (see Step 1.3.d).

The accuracy of the conductivity calibration must be assessed at each sampling location before samples are collected (see Step 2.3).

¹ The median of temperature measurements made in the New Zealand National Groundwater Monitoring Programme since 1990 is 14°C, with 90 percent of measurements between 11 and 19°C (Daughney and Reeves, 2003). The median of conductivity measurements is 200 μS/cm at 25°C, with 90 percent of measurements between 50 and 750 μS/cm at 25°C. The median of field pH measurements is 6.8, with 90 percent of measurements between pH 6.0 and 8.0.


**c pH**

The pH meter must be calibrated as often as recommended by the manufacturer or at least at the beginning of each sampling day (Rosen et al 1999; Radtke et al 2003).

For most modern conductivity meters, the calibration must be set by the sampler using at least two standard solutions, one standard in the range of pH 4 to 7, and one standard in the range of pH 7 to 10. Standard solutions can be purchased from the meter manufacturer. Rosen et al (1999) recommend that the calibration always begin with the standard closest to pH 7, because most groundwaters are closer to pH 7 than to pH 4 or 10. Standard solutions should be kept at room temperature to facilitate the check of the temperature compensation function (see Step 1.3.d).

The accuracy of the pH calibration must be assessed at each sampling location before samples are collected (see Step 2.3).

**Figure 1: Calibrating a field meter using a pH 7 standard solution**

![Calibrating a field meter using a pH 7 standard solution](image)

**d Temperature compensation functions for conductivity and pH**

If the conductivity or pH meter has an automatic temperature compensation function, compliance with this protocol requires the sampler to confirm that it is functioning properly. Calibrate the pH and conductivity meters as described above, using room temperature standards. Check the temperature compensation function by measuring at least one conductivity standard solution and one pH standard solution which have been kept in the refrigerator overnight. The temperature compensation functions are working effectively if the chilled samples read within ± 6% of the expected values (Daughney et al 2006).

If the conductivity or pH meter lacks a temperature correction function, or if the temperature correction is not working correctly, then the pH and conductivity meters must be calibrated at each site prior to sampling, using standard solutions at the expected groundwater temperature.
e  Calibration for other parameters

Field measurements of parameters other than temperature, conductivity and pH are not required for compliance with this protocol. However, if such measurements are to be made, the relevant meters must be calibrated at appropriate intervals according to the manufacturers’ instructions (see Rosen et al 1999; Wilde and Radtke, chapter sections variously dated). Note that the accuracy of the calibrations for some parameters should be assessed at each sampling location before the collection of samples (see Step 2.3).
2 On-site preparation

The following steps must be completed at each sampling location prior to the collection of any samples, so that the groundwater quality data can be meaningfully interpreted within the context of an SOE programme. It is the sampler’s responsibility to ensure all field work is conducted safely and with appropriate etiquette (see Rosen et al 1999; Hughes 2000; Stansfield 2001).

2.1 Confirm you have the correct sampling site

The *sampling site* is the well, bore or other location from which the samples will be collected. For compliance with this protocol, the sampler must ensure the correct site is being sampled. This can be accomplished by:

- having made a previous visit to the same site
- confirming a grid reference with a GPS unit and ensuring a match between the site to be sampled and a photograph or a written description, or
- confirming the site name or identification number by reference to a physical label at the site, if such a label exists. Figure 2 is an example of a marked bore.

For sites that have not been sampled previously, site details listed in Appendix 3 should be recorded to facilitate repeat sampling of the same site.

*Figure 2: Name plates on bores are a useful way to confirm the correct site is being sampled*

Source: Hawkes Bay Regional Council, 2006
2.2 Confirm appropriate sample point

The sample point is the tap, fitting, hose or other such outlet from which water will actually be collected. Some sampling sites may have more than one sample point. In such cases, the sampler must select the most appropriate sample point, document it, and ensure samples are collected from the same sample point in the future. An appropriate sampling point is one that minimises the purging time (see Step 3) and minimises the potential for contamination or alteration of the sample (refer Figures 3 and 4). Note that it is acceptable to attach a short length of clean hose to the tap or well head, because this can assist with maintenance of laminar flow.

a Minimising the purging time

The sample point must be as far upstream as possible in the reticulation system. This minimises the volume of water which must be purged through the delivery and/or reticulation system before samples can be collected (see Step 3). This also minimises the length of the sample delivery line, thereby reducing the risk that the sample could be altered in any way, for example due to depressurisation or exposure to light, heat or air.

b Minimise the potential for contamination

Samples must be collected from a sample point which is in good condition. It is acceptable to attach a short length of clean hose (ca 2 m or less) to the tap or well head (eg, to assist with maintenance of laminar flow), but the hose outlet must not be allowed to touch the ground. Do not collect samples from a tap, fitting or hose that is corroded, leaking, or otherwise in poor condition. If there is any indication that the integrity of the site has been compromised, samples should not be collected.

c Storage tanks and pressure cylinders

Wherever possible, samples should be collected from a point that is upstream of any storage tank or pressure cylinder. If the sample point is downstream of a pressure tank or cylinder, the tank or cylinder should be isolated from the delivery line as described in Appendix 5. This will ensure samples are not tainted by standing, possibly contaminated water from the tank or cylinder. This approach is advocated by USGS (various references), Rosen et al (1999), Hughes (2000) and Stansfield (2001). Always obtain the site owner’s consent before isolating or draining a pressure cylinder.
Figures 3 and 4: An appropriate sample point should be as close to the well head as possible, in good condition and upstream of any pressure cylinders wherever possible.

2.3 Check calibration of field meter(s)

Compliance with this protocol requires that the accuracy of calibrations for conductivity and pH be checked at each site prior to collection of any samples (Rosen et al 1999; Wilde, chapter sections variously dated). This is because conductivity and especially pH sensors can drift and lose their calibrations over the course of a day and accurate measurements of these parameters are essential for assessing the adequacy of the purging operation (see Step 3). This protocol does not require that the accuracy of calibrations for other field parameters be assessed at each
site, although this is recommended for parameters such as temperature, dissolved oxygen and oxidation-reduction potential (Wilde and Radtke, chapter sections variously dated).

Calibration accuracy must be assessed by measuring at least one standard solution with a known value of the parameter of interest. The following criteria indicate acceptable calibrations:

- measured (predicted) conductivity is within ±6% of the true (known) conductivity (Daughney et al 2006)
- measured (predicted) pH is within ±3% or 0.1 pH units of the true (known) pH (Radtke et al 2003; Daughney et al 2006).

Note that field measurements of conductivity and pH must be properly temperature compensated. This can be achieved by using a meter with an automatic temperature-compensation function which has been shown to be functioning correctly (see Step 1.3.d). If the meter does not have a temperature compensation function or if it is not functioning properly, then the calibration checks must be performed using standard solutions kept at ambient groundwater temperature. In this case, record the measurement temperature so that the corresponding conductivity and pH at 25°C can be determined (see Radtke et al 2005).

If the conductivity or pH calibrations do not meet with the criteria specified above, on-site recalibration is required. If on-site recalibration cannot be achieved then it is not possible to assess the adequacy of purging (see Step 3), and thus any samples collected from the site will not comply with this protocol.

2.4 Clean sampling equipment

The sampler must exercise professional judgement to ensure all sampling equipment is sufficiently clean before sample collection. This is required to avoid sample contamination and cross-contamination between sites.

At a minimum, all equipment should be rinsed thoroughly with distilled water after sampling at each site, and, if dirtied during storage or transport, again before sampling at the next site (Rosen et al 1999; Hughes 2000; Stansfield 2001; Wilde 2004). This includes pumps, pump tubing, dip probes, water level tapes and any other equipment that might contact the sample water. Basins, brushes and other materials used for cleaning should themselves not be prone to leach the analytes of interest into cleaning solutions. Note that more rigorous equipment decontamination is required if the site is severely contaminated (see Wilde 2004), but such contamination is not normally encountered in SOE monitoring in New Zealand.

3 Purging

Purging is the removal of standing water from a well and its replacement with fresh formation water. Purging is essential because standing water in the well may not be chemically representative of groundwater in the aquifer some distance away from the well (Rosen et al 1999; Wilde et al 1999; Hughes 2000, Daughney et al 2006). The steps presented below are relevant to most SOE monitoring sites in New Zealand and must be followed unless:

- the sample collection interval is sealed with packers
- drawdown occurs rapidly but recovery to approximately 90 percent cannot be achieved before samples are collected, or
- a purge minimisation device or low-flow purging technique is used (in this event, modify the purging protocol as described by Wilde et al 1999).

### 3.1 Measure depth to water

A measurement of the depth to water in the well under ambient (non-pumping) conditions is useful for calculating the volume of water to be purged (see Step 3.2) and for general interpretation of water quality data from the site. However, at some SOE sites in New Zealand, access to the well is poor and thus it is not possible to measure depth to water. Additionally, if the pump is running, measurement of depth to water may not be representative of ambient conditions.

For non-artesian conditions, depth to water should be measured using a dip tape, according to the manufacturers’ instructions (see also Rosen et al 1999, Figure 5). Record also a description of the datum from which the measurement is made, for example ground level or the top of the well casing. The same measuring point should be used each time the well is measured.

Figure 5: Water level in non-artesian conditions can be measured using a dip tape and the depth recorded relative to a known point on the well

Take care to ensure the tape does not become snared on any pump or equipment in the well. Although not required for compliance with this protocol, it is possible to measure artesian groundwater pressure with a pressure gauge or a transparent pipe as described by Rosen et al (1999, Figure 6).
3.2 Calculate the volume of water to be purged

A certain minimum volume of water must be extracted from a well before samples are collected, in order to ensure the samples will be representative of the in situ conditions within the aquifer (Daughney et al 2006). In this sampling protocol, the term *purge volume* is used to describe an incremental fraction of the total volume of water extracted from the bore during the purging operation. The purge volume is equal to the volume of water in the well under ambient (non-pumping) conditions:

\[
\text{Purge Volume} = 3.14 \times [\text{well depth} - \text{depth to water}] \times \left(\frac{\text{well radius}}{2}\right)^2 \times 1000
\]

Note that:

- the purging operation requires extraction of *at least three times* the calculated purge volume and may require extraction of many more than three times the calculated purge volume
- if the depth to water under ambient (non-pumping) conditions cannot be determined for any reason, assume “depth to water” = 0 in the equation above
- well depth, depth to water, and well radius must be expressed in metres in order to derive the purge volume in litres. Well depth can be obtained from the drilling log or through the use of the dip tape. Well radius refers to the casing dimension and not to the dimension of the bore
- if it is not possible to determine depth to water and if the well depth is unknown, then purge volume cannot be calculated. In this case, any samples collected from the well will not comply with this protocol. However, in instances where samples are to be collected from such sites, the sampler should calculate an approximate purge volume by
overestimating the likely depth of the well. An estimate of maximum likely well depth can often be obtained by examining the drilling logs of wells that are nearby.

3.3 Install portable pump if necessary

If the well is equipped with a dedicated pump, proceed to Step 3.4. Otherwise, a portable pump or bailer must be used to collect the groundwater sample, as described below.

a Suitable pumping equipment

Rosen et al (1999) and Lane et al (2003) describe different pump types that can be used for purging and groundwater sampling.

- Portable submersible pumps (positive pressure or positive displacement) are recommended for compliance with this protocol.
- Peristaltic pumps, vacuum lift pumps and bailers are not recommended, due to possible biases associated with them (Lane et al 2003). However, provided other steps in this protocol can be satisfied (eg, purging of a sufficient volume of water, stabilisation of field parameters), samples collected using these pumping systems will be compliant with this protocol.

The pump, pump tubing, and all other equipment that contacts the sample must be chemically inert and suitable for the target analytes (Lane et al 2003):

- stainless steel (all grades), if uncorroded, is suitable for the inorganic parameters relevant to this protocol. Metals other than stainless steel are not suitable, unless samples will only be analysed for CFCs, in which case refrigeration grade copper tubing is acceptable.
- glass is suitable for the inorganic parameters relevant to this protocol.
- plastics made of fluorocarbon, polyethylene, polypropylene, PVC and silicone are suitable for the parameters relevant to this protocol. For CFC sampling, either nylon or refrigeration grade copper tubing is required, but fluorocarbon tubing is not appropriate (see Step 4).

b Pump installation

The sampler must ensure the portable pump is used in accordance with the manufacturer’s instructions (see also Crowcroft and Scoble 1997). The pump should be positioned so that its intake is at least one metre below static water level and a minimum distance above the top of the screened/open interval of 10 times the well diameter (for example, 1500 mm for a 150 mm well diameter) (Wilde et al 1999). This will ensure the sample is representative of the entire screened or open interval of the well. The pump line should be fitted with a non-return valve to prevent contamination of the well with residual water in the pump tubing. It is advisable to place a dip tape or other water level sensor in the well to permit measurement of the water level during purging.
3.4 Initiate pumping

Upon arrival at the site, if the well is equipped with a dedicated pump which has been running continuously and for long enough to have removed one purge volume of water (see Step 3.2), record the time and date of arrival on site and proceed to Step 3.5. Otherwise, record the time, date and water level and initiate pumping. Ensure the outflow from the pump is disposed of away from the well so that it does not pond around the well casing (Rosen et al 1999; Wilde et al 1999, Figure 7).

Figure 7: When purging, ensure the discharge is away from the well so that water does not pond around the well casing

Compliance with this protocol does not require a specific pumping rate during purging. The sampler must use their professional judgement so that the pumping rate suits the well construction, aquifer characteristics and pumping equipment. A suitable pumping rate produces a continuous stream of water from the pump outlet or sample point without turbulence, entrainment of air, or pump cavitation (refer Figure 8). As a guideline, Wilson (1995), Rosen et al (1999) and Wilde et al (1999) recommend that pumping rates during purging should be 0.1-1 litre per minute. Pumping should not be halted during purging, and the pumping rate should be kept constant throughout purging (Wilde et al 1999). If the pumping rate must be changed, it should be changed gradually, taking care not to cause turbulence.
Compliance with this protocol requires determination of the pumping rate during purging. This is most easily accomplished by recording the time required to fill a container of known volume, such as a 10 litre bucket. Alternatively, if the site is fitted with an in-line flow meter, the pump rate can be determined by recording changes in the flow meter readings over time. With either approach, the measurements should be repeated on at least three separate occasions during purging in order to obtain at least three separate estimates of the pumping rate, all of which should be recorded on the sampling log.

Compliance with this protocol does not require minimisation of drawdown during purging. However, if possible, the water level in the well should be continuously monitored throughout the purging operation. Values of drawdown should be recorded on at least three separate occasions during purging, and again immediately prior to collection of samples. Ideally, purging should not cause drawdown of more than 0.3 m if the pump inlet is above the screened interval of the well, or more than 0.15 m if the pump inlet is within the screened interval. If drawdown exceeds these criteria, the pumping rate should be modified appropriately, where possible and practical and at the sampler’s discretion.

### 3.5 Monitor field parameters during purging

Temperature, conductivity and pH must be monitored during purging in order to assess the adequacy (completeness) of the purging operation (see Step 3.6). Values of all three field parameters must be recorded at least four separate times during purging. The first measurement must be made as soon as possible after the initiation of pumping. Subsequent measurements must be made at intervals corresponding to the time required to extract at least one purge volume from the well (see Step 3.2). Thus the second, third and fourth sets of field measurements are made after extraction of about one, two, and three purge volumes, respectively.

The water does not need to be rigorously isolated from the atmosphere for the measurement of these parameters (Rosen et al 1999; Wilde et al 2000; Hughes 2000; Daughney et al 2006).
Water from the pump outlet can be passed through a sealed flow cell or through a short length of clean hose and into an open container such as a 10-litre plastic bucket (refer Figure 9). In either case, the probes and the water inlet should be placed as low as possible inside the container, and water should be allowed to continuously flow out, or overflow from, the container or flow cell. The flow of water past the sensors must be continuous and laminar. The flow rate through the flow cell or open container must be slow enough to prevent introduction of air or gas bubbles, but fast enough to prevent shifts in the temperature or chemical composition of the sample.

Figure 9: Water from the pump outlet can be passed through an open container (left) or a flow cell (right)

Measurements of other field parameters, such as dissolved oxygen, redox potential or turbidity, are useful but are not required. For field measurement of other parameters, refer to Rosen et al (1999) or Wilde et al (2000) to determine if isolation from the atmosphere is critical. If isolation from the atmosphere is critical, field measurements must be made in an air-tight flow cell; if not, measurements can be made in a sealed flow cell or in an open container as described above.

3.6 Assess adequacy of purging

The following criteria for assessing adequacy of purging have been based on a variety of sampling guidelines (Crowcroft and Scoble 1997; Wilson 1995; Standards New Zealand 1998b; Rosen et al 1999; Wilde et al 1999; Hughes 2000; Stansfield 2001). Daughney et al (2006) have confirmed that these criteria are appropriate for New Zealand SOE groundwater monitoring sites.

The purging operation is complete if:

- the container in which field measurements are made and the tubing that connects it to the pump have both been rinsed with a quantity of well water that exceeds three times their volume and
- the field values of temperature, conductivity and pH have been measured on at least four separate occasions, each measurement at least one purge volume apart (see Step 3.5) and the differences between the last two measurements are the same within the following limits:
  - Temperature \(\pm 0.2 \, ^\circ C\) and
  - Conductivity \(\pm 3\%\) (\(\pm 5\%\) if <100 \(\mu S/cm\) at 25 \(^\circ C\)) and
  - pH \(\pm 0.1\) pH unit.
Continue the purging operation by making measurements after extraction of each purge volume until simultaneous stabilisation of all three field parameters is achieved. Once the criteria have been met, record the date and time that stabilisation was achieved, and record the field measurements as final values. If the criteria relevant to the site and situation cannot be met even after prolonged pumping, any samples collected from the well will not be in compliance with this protocol.

Field parameters other than the above can also be monitored to assess adequacy of purging, but are not required for compliance with this protocol. The following stabilisation criteria are recommended for dissolved oxygen and turbidity:

- Dissolved oxygen ±0.3 mg/L
- Turbidity ±10%
4 Collect samples

4.1 General

For compliance with this protocol, all samples must be collected directly from the pump outlet, sample point or outlet of a short length (<2 m) of clean tubing attached to the sample point. Collection of samples from an intermediate container such as a bucket or pail has been common practice in New Zealand (Rosen et al 1999), but this practice is no longer recommended (Daughney et al 2006). Collection of samples from the pump outlet requires that the pump be left running continuously during sampling.

If samples are to be collected for tritium, ensure nobody with a luminous watch is nearby during sampling. The light source of some of these watches is tritium and may contaminate the sample.

The order in which the Filtered, acid-preserved, filtered, unpreserved and unfiltered, unpreserved samples are collected is not important. Thus Steps 4.3 to 4.6 can be completed in any order. Sterile unfiltered, unpreserved samples (Step 4.8) must be collected after all other samples. This is because the requirements for sterilisation could potentially influence the chemistry of samples collected afterwards. Note that sterilisation of the sample point requires the pump to be turned off briefly.

The bottle volume and material must suit analytical requirements (see below and the summary in Table 1 on page 37). New or pre-cleaned bottles are required and are normally supplied by the analytical laboratory (alternatively, refer to Standards New Zealand (1998a) or Rosen et al (1999) for instructions on cleaning bottles for samples to be analysed for particular parameters).

Certain general guidelines for filling bottles must be followed (see Rosen et al 1999, Wilde et al 1999, Hughes 2000, and Figure 10). All sample bottles must be filled quickly but carefully to prevent aeration and entrapment of air bubbles. Tilt the sample bottle during filling to help to exclude air, and remove air bubbles by tapping the sides of the bottle lightly with your fingers. In all cases, avoid contact between the mouth of the sample bottle and your hands or the sample point. Do not smoke while collecting samples, and always avoid vehicle fumes and other potential sources of contamination close to the sample point. Always double check that container lids are tightly sealed. It is advisable to tape the cap to the bottle with electrical tape, winding the tape in a clockwise direction when looking down at the top of the bottle.
It is the sampler’s responsibility to take all practical and reasonable measures to ensure samples are not damaged during shipping to the analytical facility (Rosen et al 1999; Wilde et al 2004). Samples should be placed in individual, sealed, water-tight plastic bags during shipping. Do not use foam or vermiculite as packing materials. Samples for some analytes must be chilled immediately after collection and for the duration of their transport to the laboratory (see Step 4.5.c).

4.2 Preparing to collect samples

a Label bottles

All samples must be labelled. Each sample label must be unique and must be recorded on a corresponding sampling sheet. This protocol does not require a specific labelling style, but at the minimum, the label must include the site name (or similar identifier), sample date and time, and sampler’s name (Hughes 2000, Figure 11).

It is recommended that bottles are labelled prior to sample collection. Rosen et al (1999) recommend on-site labelling to prevent accidental switching of pre-labelled bottles. Blue or black indelible ink is recommended; red ink is not recommended because it can fade in sunlight. Certain kinds of tape can come off the bottles if they get wet, so labels on tape should be avoided.
b Reduce pumping rate if required

The pump rate during sampling must be low enough to permit laminar flow at the sampling point, without aeration of the sample (Wilson 1995; Rosen et al 1999; Hughes 2000).

This protocol does not require a specific pumping rate, but it is recommended the pumping rate during sampling should be the same as the pump rate during purging (0.1–1 litre per minute) (Wilde et al 2000). If the pump rate must be decreased after purging, it should be decreased gradually, without causing turbulence.

4.3 Collect samples in isolation from the atmosphere (if required)

Unfiltered, unpreserved samples collected in isolation from the atmosphere are required for analysis of dissolved gases such as CFCs and SF₆ (refer Table 1 on page 37). Collection of these samples requires the great care to avoid contact of water by air during sampling, or entrapment of air in the sample bottle (Rosen et al 1999).

a Bottle type

Glass bottles are required for samples to be analysed for CFCs or SF₆. A capacity of 125 ml is required for CFCs, and 1 litre for SF₆. The laboratory should supply special caps for the SF₆ bottles, which have nylon seals to prevent any air bubbles from being caught in the neck.

b Filling method

Attach a 5 mm diameter nylon tube to the sample point using grease-free fittings, or thrust the tube about 2 m through the sample point and into the water supply pipe. This tube allows the sample bottle to be filled without aeration.

If a sample is to be collected for analysis of CFCs, use the outflow from the nylon tube to fill a large beaker or pail completely. The beaker should ideally be glass or stainless steel but plastics such as polyethylene and polypropylene are acceptable. The beaker or pail must be large enough to permit complete immersion of the sample bottle and its manipulation and capping underwater.

Insert the free end of the nylon tube all the way to the bottom of a glass bottle. Fill the bottle slowly and smoothly until all air has been displaced and water overflows from the bottle (refer Figure 12). Each and every air bubble on the inside of the glass must be removed by tilting, rotating and tapping the bottle. After the bottle is filled, slowly remove the nylon tube, leaving the bottle filled to the brim.
Figure 12: With the nylon tube all the way to the bottle on the sample bottle, fill the bottle slowly and smoothly until all air has been displaced and water overflows from the bottle


For a sample to be analysed for SF$_6$, cap the bottle. For a sample to be analysed for CFCs, submerge the cap in the beaker and tap it underwater to remove any air bubbles (refer Figure 13). Submerge the bottle completely in the beaker, then cap the bottle tightly underwater.

Figure 13: Tap the cap underwater to remove any air bubbles and then cap the sample bottle underwater
It is vital to ensure no air has been trapped in samples that will be analysed for CFCs or SF$_6$. After the bottle has been filled and capped, invert it, and tap it to check for air bubbles. If bubbles are present, empty the bottle and start again. If no bubbles are present then dry the bottle, retighten the cap and tape the cap to the bottle with electrical tape, winding the tape in a clockwise direction when looking down at the top of the bottle. Note that small bubbles may form in the sample bottles after collection. As long as these are not air bubbles trapped at the time of sampling and the bottle is closed tightly, this is acceptable.

Finally, remove the nylon hose from the sample point after sample collection is complete.

c Preservation, transport and storage

Samples to be analysed for CFCs and SF$_6$ must be stored upright, in an area that is cool or at room temperature. Do not chill or expose to excessive heat, such as in the back of a sun-exposed vehicle. Retighten the caps of all bottles at the end of the day. Ship without delay, but avoid air-freighting.

4.4 Collect filtered, acid-preserved samples (if required)

Filtered, acid-preserved samples collected according to this protocol are suitable for analysis of major cations and some metals, including calcium, magnesium, sodium, potassium, iron, manganese, aluminium, antimony, arsenic, barium, beryllium, cadmium, chromium, cobalt, copper, lead, lithium, nickel, selenium, silver, tin, uranium, vanadium, zinc and some others (see Table 1 on page 37; Standards New Zealand 1998a; Rosen et al 1999). Daughney et al (2006) have shown that SiO$_2$ can be analysed in a filtered, acid-preserved sample as recommended by Rosen et al (1999) or in a filtered, unpreserved sample as recommended by Standards New Zealand (1998a).

Filtered, acid-preserved samples collected according to this protocol are NOT suitable for analysis of:

- any cation or metal at concentration less than 0.01 g m$^{-3}$
- mercury, which is typically preserved with a chromium solution that would interfere with the analysis of other metals
- arsenic if the hydride technique is to be used for analysis, in which case HCl should be used as the preservative instead of HNO$_3$ (Standards New Zealand 1998a). These samples are also unsuitable for differentiation of As (III) vs. As (V) (see McClesky et al 2004 and references therein).

Filtration can be accomplished either with a syringe and syringe-tip filter or with an in-line cartridge filter. Daughney et al (2006) have shown that either filtration method will produce the same results. In either case, the filter membrane must have a nominal pore size between 0.1 and 0.45 µm. Cellulose acetate filter membranes are recommended (Standards New Zealand 1998a; Rosen et al 1999). A pore size of 0.45 µm is used routinely for most studies at present (Wilde et al 2004).
a  **Bottle type**

The filtered, acid-preserved sample must be collected in a new or acid-washed plastic bottle (polyethylene, polypropylene or similar) (Standards New Zealand 1998a; Rosen et al 1999; Stansfield 2001). See Standards New Zealand (1998a) for instructions for acid-washing. The bottle volume must suit analytical requirements.

b  **Filling method using a syringe-tip filter**

Fill a plastic syringe (polyethylene, polypropylene or similar, 60–100 ml capacity) directly from the sample point. Smoothly discharge the water to waste, and then refill the syringe. Repeat this procedure until the syringe has been field-rinsed three times. After the third rinse, refill the syringe as described above.

Affix a syringe-tip filter to the syringe outlet, ensuring that your hands and any other sources of potential contamination are kept away from the syringe outlet and the inlet and outlet of the filter (refer Figure 14). Individually wrapped filters are recommended. It is a good idea to retain the packing case because it provides a clean place to temporarily store the filter in the event the syringe needs to be refilled during sampling (see below).

**Figure 14: Typical syringe and 0.45 µm disposable filter**

If the acid preservative was added to the bottle beforehand:

- Discharge approximately 20 mL of water from the syringe to waste, in order to field-rinse the filter. Do not field-rinse the filter with a significantly greater volume of the sample, because this can cause clogging of the membrane and reduction of the nominal pore size

- Position the filter outlet over the sample bottle, ensuring that your hands and any other sources of contamination are kept away from the sample water, the filter outlet and the threads and inner surfaces of the bottle and cap

- Fill the bottle quickly and efficiently but with minimal aeration, by depressing the syringe plunger to pass water through the filter and into the bottle (refer Figure 15). Do not pre-rinse the bottle with sample water. The bottle should only be filled to the shoulder, to avoid flushing out the preservative.
• If the syringe must be refilled, follow the steps outlined below.
• Finally, cap the bottle tightly. Invert the bottle to mix the sample with the preservative.

**Figure 15:** Position the filter and syringe above the bottle, ensuring not to touch the bottle with the filter to avoid contamination

If the acid preservative is to be added to the bottle after sample collection:

• Position the filter outlet over the sample bottle, ensuring that your hands and any other sources of contamination are kept away from the sample water, the filter outlet and the threads and inner surfaces of the bottle and cap.
• Discharge water from the syringe into the bottle until it is approximately one-tenth full. Cap the bottle, shake to wet all interior surfaces, then uncap the bottle and pour out the water to waste. This provides a sufficient and simultaneous field-rinse of the filter and the bottle. Do not field-rinse the filter and bottle with a significantly greater volume of sample, because this can cause clogging of the filter membrane and reduction of the nominal pore size.
• Re-position the filter outlet over the sample bottle as described above, then fill the bottle quickly and efficiently but with minimal aeration, by depressing the syringe plunger to pass water through the filter and into the bottle. Fill the bottle only to the shoulder, to allow room for addition of the preservative.
• If the syringe must be refilled, follow the steps outlined below.
• Add the acid preservative to the bottle following instructions given below.
• Finally, cap the bottle tightly. Invert the bottle to mix the sample with the preservative.
If the syringe must be refilled during sampling:

- Remove the filter cartridge from the syringe outlet, ensuring that your hands and any other sources of potential contamination are kept away from the syringe outlet and the inlet and outlet of the filter. Place the filter in a clean location, for example back into the case or packing material supplied by the manufacturer.
- Refill the syringe directly from the sampling point as described above.
- Re-fix the filter to the syringe outlet as described above, and resume collection of the filtered sample.

c Filling method using an in-line filter

Affix an in-line filter to the sample point using fittings and tubing as required (refer Figure 16). Ensure your hands and any other sources of potential contamination are kept away from the tubing and the inlet and outlet of the filter.

**Figure 16: Attach the in-line filter to the sample point using clean tubing**

Allow approximately 100 ml of water to pass through the filter cartridge to waste, in order to field-rinse the filter. Do not field-rinse the filter with a significantly greater volume of sample, because this can cause clogging of the cartridge and reduction of the nominal pore size.

If the acid preservative was added to the bottle beforehand:

- Position the filter outlet over the sample bottle, ensuring that your hands and any other sources of contamination are kept away from the sample water, the filter outlet and the threads and inner surfaces of the bottle and cap.
- Fill the bottle quickly, efficiently, and with minimal aeration directly from the outlet of the filter cartridge. Do not pre-rinse the bottle with sample water. The bottle must only be filled to the shoulder, to avoid flushing out the preservative (refer Figure 17).
- Cap the bottle tightly. Invert the bottle to mix the sample with the preservative.
If the acid preservative is to be added to the bottle after sample collection:

- Position the filter outlet over the sample bottle, ensuring that your hands and any other sources of contamination are kept away from the sample water, the filter outlet and the threads and inner surfaces of the bottle and cap.

- Fill the bottle from the outlet of the filter cartridge until the bottle until it is approximately one-tenth full. Cap the bottle, shake to wet all interior surfaces, then uncap the bottle and pour out the water to waste. This provides a sufficient and simultaneous field-rinse of the filter and the bottle. Do not field-rinse the filter and bottle with a significantly greater volume of sample, because this can cause clogging of the filter membrane and reduction of the nominal pore size.

- Re-position the filter outlet over the sample bottle as described above, and fill the bottle quickly and efficiently but with minimal aeration. Fill the bottle only to the shoulder, to allow room for addition of the preservative.

- Add the acid preservative to the bottle following the instructions given below.

- Finally, cap the bottle tightly. Invert the bottle to mix the sample with the preservative.

### Preservation, transport and storage

Samples to be analysed for cations and/or metals must be preserved via addition of concentrated nitric acid (HNO₃) to pH < 2. Add one drop for sample volume less than 100 ml, with one additional drop for each additional 100 ml sample volume (Standards New Zealand 1998a; Rosen et al 1999, Wilde et al 2004). Refer to information provided by the supplier for safe practices regarding handling of concentrated HNO₃. The acid preservative can be added to the bottle either by the laboratory that supplies the bottles or by the sampler. In the latter case, the preservative can be added either before or after the collection of the sample, either before or after arrival on site.
Acid-preserved samples do not need to be chilled during transport to the analytical laboratory, but chilling will not affect the analytical results, and so it may be convenient to transport the filtered preserved samples along with samples that do require chilling (eg, Step 4.5). Samples must not be frozen, so should not be shipped with dry ice or other coolants with freezing temperatures below 0°C.

Acid-preserved samples for cation and/or metal analysis should be analysed within 2–3 weeks of collection, but have a shelf life of up to six months (Standards New Zealand 1998a).

### 4.5 Collect filtered, unpreserved samples (if required)

Filtered, unpreserved samples collected according to this protocol are suitable for analysis of major anions and nutrients, including chloride, bromide, fluoride, iodide, sulphate, nitrate, nitrite (filtration removes the need for HgCl₂ preservative), ammonium, total Kjeldahl nitrogen, total nitrogen, phosphate, total phosphorus, and some others (see Table 1 on page 37, and also Standards New Zealand 1998a, Rosen et al 1999). Daughney et al (2006) have shown that SiO₂ can be analysed in a filtered, acid-preserved sample as recommended by Rosen et al (1999) or in a filtered, unpreserved sample as recommended by Standards New Zealand (1998a).

#### a Bottle type

The filtered, unpreserved sample must be collected in a new or pre-cleaned plastic bottle (polyethylene, polypropylene or similar) (Standards New Zealand 1998a; Rosen et al 1999; Wilde et al 2004). If the sample is to be analysed for nutrients or bromide, the bottle must be opaque (Standards New Zealand 1998a; Rosen et al 1999; Wilde et al 2004). This is because these analytes can be directly affected by light, or can be transformed by micro-organisms that are stimulated by light. Fluorocarbon plastic bottles are not suitable for samples to be analysed for fluoride (Standards New Zealand 1998a).

#### b Filling method

If a syringe-tip filter is employed, fill the bottle for this sample as described in Step 4.4(b). If an in-line filter is used, fill the bottle as described in Step 4.4(c).

#### c Preservation, transport and storage

Samples to be analysed for nutrients must be chilled to 4°C immediately after collection and maintained at 4°C for the duration of their transport to the laboratory (Rosen et al 1999; Wilde et al 2004). Samples must not be frozen, so should not be shipped with dry ice or other coolants with freezing temperatures below 0°C.
It is the sampler’s responsibility to ensure samples are chilled appropriately after collection and for their duration of transport to the laboratory. Compliance with this protocol does not require any specific method for chilling samples, but the following methods have been shown to be effective in New Zealand (Daughney et al 2006). Chilly bins (20–40 litre capacity) should be packed with at least five frozen chemical packs or at least 3 kg of ice (one typical service station size bag, refer Figure 18). To maintain the temperature below 4°C, chilly bins should be repacked with at least 3 kg of ice no more than six hours after leaving the office at the start of the day of sampling. Chilly bins should be repacked with a fresh quantity of ice (ca 3 kg) before dispatch to the laboratory.

Figure 18: Chilly bins should be packed with at least five frozen chemical pads (top right) or 3 kg of ice (bottom). Too few pads will not keep the samples at or below 4°C (top left). Overnight couriering requires the chilly bin to re-packed with ice (bottom).

The following holding times apply to chilled filtered, unpreserved samples to be analysed for particular parameters (Standards New Zealand 1998a; Rosen et al 1999):

- nitrite, nitrate, total Kjeldahl nitrogen, total nitrogen, phosphate, or total phosphorus should be analysed as soon as possible and must be analysed within 24 hours of sample collection.
- ammonium must be analysed within four days of sample collection.
- sulphate must be analysed within seven days of sample collection.
- other anions must be analysed within one month of sample collection.
4.6 Collect unfiltered, unpreserved samples (if required)

Unfiltered, unpreserved (raw) samples collected according to this protocol are suitable for laboratory analysis of conductivity, pH, alkalinity, bicarbonate, carbonate, oxygen-18 ($^{18}$O), deuterium ($^{2}$H) and tritium ($^{3}$H) (Rosen et al 1999; Stansfield, 2001). Samples collected as described below are not suitable for analysis of isotopes of nitrogen, carbon or sulphur (refer to Rosen et al 1999). Although compliance with this protocol requires that conductivity and pH are measured in the field, measurement in the laboratory provides confirmation of field measurements and can be used as a check that the sample was not accidentally mislabelled or compromised during transport.

a Bottle type

The unfiltered, unpreserved sample should be collected in a plastic bottle (polyethylene, polypropylene or similar), but glass is also acceptable (Rosen et al 1999). The bottle must be new or detergent-washed (Rosen et al 1999; Standards New Zealand 1998a).

Separate samples are ordinarily required for pH/anions and the oxygen and hydrogen isotopes. The sample collected for tritium can also be analysed for $^{18}$O and $^{2}$H (only about 20 mL of water is required for these latter analyses).

b Filling method

Fill the bottle completely with water from the sample point. Ensure aeration and turbulence are minimised, and that your hands and any other sources of contamination are kept away from the sample water and the threads and inner surfaces of the bottle and cap. Cap the bottle, shake to wet all interior surfaces, then uncap the bottle and pour out the water to waste. Repeat this procedure three times to field-rinse the bottle.

Fill the bottle quickly and efficiently but with minimal aeration, again avoiding potential contamination by your hands or from other sources. Fill the bottle completely (ie, until it overflows). Tap the bottle during filling to dislodge air bubbles. It is important to minimise entrapment of air for samples to be analysed for pH, alkalinity, tritium, and some other parameters (Standards New Zealand 1998a, Rosen et al 1999, Stansfield 2001). If the sample is to be analysed only for $^{18}$O and $^{2}$H, then it can be filled to the top or a small airspace can be left in the bottle.

Finally, cap the bottle tightly. Invert the bottle and check for entrapped air bubbles. If any air is present inside the bottle, re-open it and add more sample water. Retighten the cap after a few hours.

c Preservation, transport and storage

Samples to be analysed for pH, conductivity, alkalinity, bicarbonate and/or carbonate do not need to be chilled during transport to the analytical laboratory. However, chilling will not affect the analytical results, and so it may be convenient to transport the samples along with other samples that do require chilling (eg, Step 4.6). Samples must not be frozen, so should not be shipped with dry ice or other coolants with freezing temperatures below 0°C.
Samples for analysis of \(^{18}\text{O},\, ^{2}\text{H}\) and tritium should be stored upright and they should not be chilled or exposed to excessive heat.

The following holding times apply to unfiltered, unpreserved samples to be analysed for particular parameters (Standards New Zealand 1998a; Rosen et al 1999):

- pH, alkalinity, bicarbonate and carbonate should be analysed as soon as possible and must be analysed within 24 hours of sample collection
- conductivity should be analysed within one month of sample collection
- \(^{18}\text{O},\, ^{2}\text{H}\) and tritium should be shipped for analysis as soon as possible, but there is no recommended maximum shelf life.

4.7 Collect sterile unfiltered, unpreserved samples (if required)

Sterile, unfiltered, unpreserved samples collected according to this protocol are suitable for laboratory analysis of microbiological indicator parameters, including faecal indicator bacteria (eg, the enterococci and coliform groups), faecal indicator viruses, and protozoan pathogens (eg, Cryptosporidium, Giardia).

The sterile, unfiltered, unpreserved sample must be collected after all other samples for analysis of isotopes, gases and major cation and anions (Rosen et al 1999, Hughes 2000, Stansfield 2001, Myers and Wilde 2003). This is because collection of a sterile sample may require installation of a metallic fitting suitable for sterilisation by flaming, or sterilisation of the sample point using a bleach or ethanol solution. These procedures have the potential to affect cation, metal and anion concentrations in samples collected afterwards.

a Preparation for sample collection

The sampler must wear clean (preferably sterile), powder-free latex gloves (Myers and Wilde, 2003). Sterilisation of the pump, pump tubing, dip tape or other equipment used during sampling, is recommended but not required for compliance with this protocol. Refer to Myers and Wilde (2003) for instructions on sterilisation of different types of equipment. If the sampling equipment is not sterilised prior to collection of samples for microbiological analysis, collection of equipment blanks is recommended (see Myers and Wilde (2003) for details).

Turn the pump off to permit sterilisation of the sampling point before the sample is collected (Standards New Zealand 1998a; Stansfield 2001; Wilde et al 2003). After flow from the sample point has stopped, one of the following methods is appropriate for sterilisation:

- Use a butane or propane burner (lighter or portable torch) to flame the nozzle or sample point directly, starting at the nozzle and working back to the body of the tap until the water held in the nozzle boils (refer Figure 19). Methylated spirit flames are not acceptable because they are not hot enough for disinfection. Note that this procedure is only suitable for metal sample points.
• Immerse, spray or swab the outside and as much of the inside of the sample point as possible using a solution of either 70 percent (v/v) ethanol or 10 percent (m/v) sodium hypochlorite (refer Figure 20). Allow the disinfectant solution to act for two to three minutes. This procedure is suitable for plastic or metal fittings.

After sterilisation of the sample point, turn the pump back on. Allow a sufficient volume of water to pass through the sample point to ensure it is cooled (if flamed for sterilisation) and that any residual ethanol and/or sodium hypochlorite has been flushed out of the fittings.
b  **Bottle type**

Bottles for collection of microbiological samples must be pre-sterilised, and can be new or pre-washed (Standards New Zealand 1998a; Rosen et al 1999; Hughes 2000; Stansfield 2001; Myers and Wilde 2003). Bottles are usually plastic (Rosen et al 1999), but glass, metal and autoclavable plastics are all suitable (Standards New Zealand 1998a; Stansfield 2001). Pre-sterilised bottles are typically provided by the laboratory (alternatively, see Myers and Wilde 2003 for appropriate methods for bottle sterilisation). Pre-sterilised bottles are often sealed in sterile plastic bags, and the lids may be sealed with heat-sensitive tape. If the bag or the tape seal is broken, the bottle should not be used (Hughes 2000).

c  **Filling method**

Fill the bottle directly from the sample point quickly and efficiently but with minimal aeration. Avoid potential contamination by your hands or from other sources. The bottle should be filled almost completely, leaving a small air space, so that the bottle can be mixed by shaking before it is tested (refer Rosen et al 1999 and Figure 21).

*Figure 21: Filling sterile bottle with gloved hands – note minimal aeration*

![Filling sterile bottle with gloved hands](image)

**d  Preservation, transport and storage**

Samples for microbiological analysis must be chilled immediately to below 4°C and maintained at this temperature in the dark for the duration of their transport to the laboratory (Rosen et al 1999; Myers and Wilde 2003). Samples for microbiological analysis must not be frozen. See Step 4.6(c) for general guidelines on chilling samples.
If chlorine is used as a disinfectant for a water supply, the chlorine residual must be neutralised when the sample is collected, in order to obtain meaningful microbiological data (Rosen et al 1999; Myers and Wilde 2003). The chlorine residual can be neutralised via addition of sodium thiosulphate (0.1 ml of a 3 percent solution will neutralise up to 5 mg/L FAC in a 120 ml sample). The sodium thiosulphate must be sterile, so it should be added to each sample bottle before autoclaving.

The following holding times apply to chilled samples to be analysed for particular microbiological parameters (Standards New Zealand 1998a; Rosen et al 1999; Myers and Wilde 2003):

- the enterococci and coliform groups of bacteria should be analysed within six hours and not more than 24 hours of sample collection.
- faecal indicator viruses must be analysed within 48 hours of sample collection.
- protozoan pathogens (*Cryptosporidium, Giardia*) must be analysed within 96 hours of sample collection.
5 Site clean-up

Sampling equipment should be cleaned before departure from each site. All pumps, pump tubing, dip tapes, flow cells and similar equipment should be thoroughly rinsed with distilled water immediately after sampling, then wrapped and transported in clean plastic bags (Stansfield 2001; Wilde 2004). Visually inspect the pump and tubing for signs of corrosion and wear. If there is any visual indication that the condition of the sampling gear has deteriorated during the sampling interval, then samples collected will not be in compliance with this protocol (corrosion can occur rapidly in some situations, for example if the water is very saline or has a high sulphide content).

6 Sample storage, transport and delivery

Check bottles upon return from the field to ensure all sites have been sampled, and that sample integrity has not been compromised.

Deliver or courier samples to your analytical laboratory (see above for maximum acceptable holding times). It is the sampler’s responsibility to take adequate measures to ensure samples are suitably chilled, if required, during transport to the laboratory. A guideline is to repack a standard size chilly bin (20–40 litre capacity) with at least 3 kg of ice to ensure samples reach the laboratory at a temperature of no more than 4ºC (Daughney et al 2006).

For compliance with this protocol, analyses must be conducted by a laboratory with an accreditation that is in compliance with NZS/ISO/IEC Standard 17025 (Standards New Zealand, 1999).

For information related to sample disposal see Rosen et al (1999).
### Table 1: Recommended sampling methods for typical determinands

<table>
<thead>
<tr>
<th>Determinand</th>
<th>Bottle type</th>
<th>Sample type</th>
<th>Preservation and transport</th>
<th>Holding time</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkalinity</td>
<td>P or G</td>
<td>UF UP</td>
<td>Chill to 4°C</td>
<td>24 hours</td>
<td>Analyse as soon as possible after collection</td>
</tr>
<tr>
<td>Ammonia</td>
<td>P (O)</td>
<td>FF UP</td>
<td>Chill to 4°C</td>
<td>24 hours</td>
<td>Analyse as soon as possible after collection</td>
</tr>
<tr>
<td>Arsenic</td>
<td>P</td>
<td>FF AP</td>
<td>Acidify with nitric acid</td>
<td>1 month</td>
<td>Acidify with hydrochloric acid for the hydride technique</td>
</tr>
<tr>
<td>Bicarbonate</td>
<td>P or G</td>
<td>UF UP</td>
<td>Chill to 4°C</td>
<td>24 hours</td>
<td>Analyse as soon as possible after collection</td>
</tr>
<tr>
<td>Boron</td>
<td>P</td>
<td>FF UP</td>
<td>Chill to 4°C</td>
<td>24 hours</td>
<td></td>
</tr>
<tr>
<td>Bromide</td>
<td>P (O)</td>
<td>FF UP</td>
<td>Chill to 4°C</td>
<td>24 hours</td>
<td></td>
</tr>
<tr>
<td>Calcium</td>
<td>P</td>
<td>FF AP</td>
<td>Acidify with nitric acid</td>
<td>1 month</td>
<td></td>
</tr>
<tr>
<td>Carbonate</td>
<td>P or G</td>
<td>UF UP</td>
<td>Chill to 4°C</td>
<td>24 hours</td>
<td>Analyse as soon as possible after collection</td>
</tr>
<tr>
<td>Carbon dioxide, free</td>
<td>P or G</td>
<td>UF UP</td>
<td>Chill to 4°C</td>
<td>24 hours</td>
<td>Analyse as soon as possible after collection</td>
</tr>
<tr>
<td>Chloride</td>
<td>P</td>
<td>FF UP</td>
<td>Chill to 4°C</td>
<td>1 month</td>
<td></td>
</tr>
<tr>
<td>Chlorofluorocarbons (CFCs)</td>
<td>G</td>
<td>UF UP AF</td>
<td></td>
<td></td>
<td>Avoid contact of sample water by ambient air</td>
</tr>
<tr>
<td>Chromium</td>
<td>P (AW)</td>
<td>FF AP</td>
<td>Acidify with nitric acid</td>
<td>1 month</td>
<td></td>
</tr>
<tr>
<td>Copper</td>
<td>P (AW)</td>
<td>FF AP</td>
<td>Acidify with nitric acid</td>
<td>1 month</td>
<td></td>
</tr>
<tr>
<td>Deuterium (¹H)</td>
<td>P or G</td>
<td>UF UP</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electrical conductivity</td>
<td>P or G</td>
<td>UF UP</td>
<td>Chill to 4°C</td>
<td>24 hours</td>
<td>Must also be measured in the field</td>
</tr>
<tr>
<td>Fluoride</td>
<td>P</td>
<td>FF UP</td>
<td>Chill to 4°C</td>
<td>1 month</td>
<td>Fluorocarbon plastics are not suitable</td>
</tr>
<tr>
<td>Iron</td>
<td>P (AW)</td>
<td>FF AP</td>
<td>Acidify with nitric acid</td>
<td>1 month</td>
<td></td>
</tr>
<tr>
<td>Lead</td>
<td>P (AW)</td>
<td>FF AP</td>
<td>Acidify with nitric acid</td>
<td>1 month</td>
<td></td>
</tr>
<tr>
<td>Magnesium</td>
<td>P</td>
<td>FF AP</td>
<td>Acidify with nitric acid</td>
<td>1 month</td>
<td></td>
</tr>
<tr>
<td>Manganese</td>
<td>P (AW)</td>
<td>FF AP</td>
<td>Acidify with nitric acid</td>
<td>1 month</td>
<td></td>
</tr>
<tr>
<td>Microbiological, coliform bacteria</td>
<td>P (S)</td>
<td>UF UP S</td>
<td></td>
<td>24 hours</td>
<td></td>
</tr>
<tr>
<td>Microbiological, enterococci</td>
<td>P (S)</td>
<td>UF UP S</td>
<td></td>
<td>24 hours</td>
<td></td>
</tr>
<tr>
<td>Microbiological, faecal viruses</td>
<td>P (S)</td>
<td>UF UP S</td>
<td></td>
<td>48 hours</td>
<td></td>
</tr>
<tr>
<td>Microbiological, protozoa</td>
<td>P (S)</td>
<td>UF UP S</td>
<td></td>
<td>96 hours</td>
<td></td>
</tr>
<tr>
<td>Nitrate</td>
<td>P (O)</td>
<td>FF UP</td>
<td>Chill to 4°C</td>
<td>24 hours</td>
<td>Analyse as soon as possible after collection</td>
</tr>
<tr>
<td>Nitrite</td>
<td>P (O)</td>
<td>FF UP</td>
<td>Chill to 4°C</td>
<td>24 hours</td>
<td>Analyse as soon as possible after collection</td>
</tr>
<tr>
<td>Nitrogen, total kjeldahl</td>
<td>P (O)</td>
<td>FF UP</td>
<td>Chill to 4°C</td>
<td>24 hours</td>
<td>Analyse as soon as possible after collection</td>
</tr>
<tr>
<td>Nitrogen, total</td>
<td>P (O)</td>
<td>FF UP</td>
<td>Chill to 4°C</td>
<td>24 hours</td>
<td>Analyse as soon as possible after collection</td>
</tr>
<tr>
<td>Oxygen-18 (¹⁸O)</td>
<td>P or G</td>
<td>UF UP</td>
<td>Chill to 4°C</td>
<td>24 hours</td>
<td>Must also be measured in the field</td>
</tr>
<tr>
<td>pH</td>
<td>P or G</td>
<td>UF UP</td>
<td>Chill to 4°C</td>
<td>24 hours</td>
<td>Analyse as soon as possible after collection</td>
</tr>
<tr>
<td>Phosphorus, dissolved reactive</td>
<td>P (O)</td>
<td>FF UP</td>
<td>Chill to 4°C</td>
<td>24 hours</td>
<td>Analyse as soon as possible after collection</td>
</tr>
<tr>
<td>Phosphorus, total</td>
<td>P (O)</td>
<td>FF UP</td>
<td>Chill to 4°C</td>
<td>24 hours</td>
<td>Analyse as soon as possible after collection</td>
</tr>
<tr>
<td>Potassium</td>
<td>P</td>
<td>FF UP</td>
<td>Acidify with nitric acid</td>
<td>1 month</td>
<td></td>
</tr>
<tr>
<td>Determinand</td>
<td>Bottle type¹</td>
<td>Sample type²</td>
<td>Preservation and transport</td>
<td>Holding time</td>
<td>Comments</td>
</tr>
<tr>
<td>-------------------------------------</td>
<td>--------------</td>
<td>--------------</td>
<td>----------------------------</td>
<td>--------------</td>
<td>----------</td>
</tr>
<tr>
<td>Silica, reactive</td>
<td>P</td>
<td>FF UP</td>
<td>Chill to 4°C</td>
<td>24 hours</td>
<td></td>
</tr>
<tr>
<td></td>
<td>P</td>
<td>FF AP</td>
<td>Acidify with nitric acid</td>
<td>1 month</td>
<td></td>
</tr>
<tr>
<td>Sodium</td>
<td>P</td>
<td>FF AP</td>
<td>Acidify with nitric acid</td>
<td>1 month</td>
<td></td>
</tr>
<tr>
<td>Sulphur hexafluoride (SF₆)</td>
<td>G</td>
<td>UF UP AF</td>
<td>1 month</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulphate</td>
<td>P</td>
<td>FF UP</td>
<td>Chill to 4°C</td>
<td>7 days</td>
<td></td>
</tr>
<tr>
<td>Tritium (³H)</td>
<td>P</td>
<td>FF UP</td>
<td>Acidify with nitric acid</td>
<td>1 month</td>
<td></td>
</tr>
<tr>
<td>Zinc</td>
<td>P</td>
<td>FF AP</td>
<td>Acidify with nitric acid</td>
<td>1 month</td>
<td></td>
</tr>
</tbody>
</table>

Notes:
1. All bottles must be new or appropriately washed. Please check with your laboratory for volume requirements.
   - P = Plastic bottle (polyethylene, polypropylene or similar)
   - P (O) = Opaque plastic bottle for nutrients and bromide
   - P (AW) = Plastic acid-washed bottle
   - P (S) = Plastic sterilised bottle
   - G = Glass.
2. UF UP = Unfiltered and unpreserved sample (fill bottle completely to exclude air).
   - UF UP S = Unfiltered and unpreserved, sterile sample
   - UF UP AF = Unfiltered and unpreserved sample collected in isolation from ambient air
   - FF UP = Field–filtered and unpreserved sample
   - FF AP = Field–filtered and nitric-acid preserved sample

Table 2: Summary of calibration procedures for field measurements

<table>
<thead>
<tr>
<th>Determinand</th>
<th>Required calibration frequency</th>
<th>Number of standards</th>
<th>Recommended range of standards</th>
<th>Required frequency of calibration checks</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrical conductivity</td>
<td>Yearly</td>
<td>3</td>
<td>5–25°C</td>
<td>Six-monthly</td>
<td>Calibration is usually performed by manufacturer. If using more than one standard, begin calibration with standard closest to pH 7.</td>
</tr>
<tr>
<td>pH</td>
<td>Daily before sampling</td>
<td>1</td>
<td>4–10 pH units at 25°C</td>
<td>At each site before sampling</td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td>Daily before sampling</td>
<td>1</td>
<td>50–750 µS/cm at 25°C</td>
<td>At each site before sampling</td>
<td></td>
</tr>
</tbody>
</table>

Instructions in RED must be done  
See over for further explanations

**Step 1: Pre-sampling**
- 1.1 Check site details
- 1.2 Gather equipment
- 1.3 Calibrate field meters

**pH:** Calibrate at the start of each day. Use at least 2 standard solutions (pH 4, 7 or 10)

**Conductivity:** Calibrate at the start of each day. Use at least 1 standard (50–750 μS/cm)

**Temperature:** Calibrate annually. Use at least 1 standard solution (5–25°C)

**Check temperature compensation for pH & conductivity calibrations:** using chilled standard solutions

**If temperature compensation function is not working, re-calibration is required at each site. Use standard solutions at ambient groundwater temperature**

**Step 2: On-site Preparation**
- 2.1 Confirm correct site
- 2.2 Confirm appropriate sampling point
- 2.3 Check meter calibration
- 2.4 Clean sampling equipment

Check calibration at each site using at least 1 standard solution for pH and 1 standard solution for conductivity. The meter reading must be within ±6% of expected value

If the specified criteria cannot be met on-site calibration is required

If re-calibration cannot be achieved the meter must not be used

**Step 3: Purging**
- 3.1 Measure depth to water
- 3.2 Calculate volume to be purged
- 3.3 Install pump if necessary
- 3.4 Initiate pumping if necessary
- 3.5 Monitor field parameters
- 3.6 Assess adequacy of purging

One Purge Volume (litres) = \( 3.14 \times (D-W)^2 R^2 \times 1000 \)

D = well depth in metres
W = depth to water in metres
R = radius in metres

Continue purging until:
- 1. Container/flow cell and tubing have been rinsed with a quantity of water exceeding 3 times their volume AND
- 2. Temperature, pH & conductivity have been measured on at least 4 occasions, each measurement one purge volume apart AND
- 3. The difference between the last two measurements are within the limits:
  - Temperature: ±0.2°C AND
  - Conductivity: ±3% AND
  - pH: ±0.1 pH units

**Step 4: Sample Collection**
- 4.2 Preparation
  - a. Label bottles
  - b. Reduce pump rate if required
  - 4.3-4.7 Collect samples in any order as required:
    - Isolated from atmosphere
    - Filtered and preserved
    - Unfiltered and preserved
  - 4.6 Collect sterile unfiltered unpreserved sample if required:
    - a. Stop pump and sterilize sample point
    - b. Wear clean, sterile gloves

**Step 6: Sample storage, transport and delivery**

Some types of samples require appropriate measures to ensure that adequate chilling during storage and transport.

**During the day:** Samples should be kept in a chilli bin, with at least 5 frozen pads, or 3 kg of ice.

**Overnight Costume:** Replace frozen pads/ice used during the day with at least 3 kg of ice for overnight transport.

Minimise airspace in chilli bin.

**Step 5: Site Clean-up**
- Clean and rinse all sampling equipment between sites
1.2 A preservative is required for some types of sample, (e.g. an acid preservative for samples to be analysed for cations). Be prepared to chill samples (e.g. for nutrients) to 1–4°C immediately after collection and for the duration of transport to the laboratory.

2.2 An appropriate sampling point is one that minimises the purging time (see Step 3) and minimises the potential for contamination or alteration of the sample. It is acceptable to collect samples from a short length of clean hose attached to the tap or wellhead.

3.2 For calculation of purge volume:
   - Well depth, depth to water, and well radius must be expressed in meters in order to derive the purge volume in litres.
   - If the depth to water under ambient (non-pumping) conditions cannot be determined for any reason, assume “depth to water” = 0.
   - Well depth can be obtained from the drilling log or through the use of the dip tape.
   - Well radius refers to the casing dimension and not to the dimension of the bore.
   - If it is not possible to determine depth to water and if the well depth is unknown, then purge volume cannot be calculated. In this case, any samples collected from the well will not comply with this protocol.

3.3 The pump should be installed so that its intake is positioned at least 1 m below the static water level and a minimum distance above the top of the screened/open interval of 10 times the well diameter (for example, 1500mm for a 150mm well diameter). This will ensure that the sample is representative of the entire screened or open interval of the well.

3.4 A suitable pumping rate produces a continuous stream of water from the pump outlet or sample point without turbulence, entrainment of air or pump cavitation. Compliance with this protocol requires determination of the pumping rate during purging.

3.6 For assessment of adequacy of purging, note that:
   - The purging operation requires extraction of at least three times the calculated purge volume and may require extraction of many more than three times the calculated purge volume.
   - The field values of temperature, conductivity and pH must be measured on at least four separate occasions, each measurement at least one purge volume apart.
   - The differences between the last two sets of field measurements must be the same within the following limits:
     - Temperature: ±0.2 °C, AND
     - Conductivity: ±3% (±5% if <100 μS/cm at 25 °C), AND
     - pH: ±0.1 pH unit

4.3-4.7 All samples must be collected sequentially from the sample point or from a short length of clean tubing attached to the sample point. The filtered acid-preserved, filtered unpreserved, unfiltered unpreserved samples and the samples collected in isolation from the atmosphere can be collected in any order.

4.8 Sterile samples must be collected after all other samples. This is because the requirements for sterilisation could potentially influence the chemistry of samples collected afterwards. Note that sterilisation of the sample point requires the pump to be turned off briefly.

Refer to Groundwater Sampling Protocol for further detailed explanations when required
Appendix 2: Sample field sheet

This appendix includes a sample field sheet that can be used to record information during sampling. The use of this particular field sheet is not required for compliance with this protocol. However, recording of information to this level of detail is to help qualify and quantify parameters which are measured or visually observed in the field, and to aid in the later interpretation of the analytical results. It is important that the sampler records field data in a way that will be comprehensible to other users of the data. In order to help achieve this, explanations of the information to be recorded on the field sheet are provided below.

1 Site details

Site name: The site name is a unique identifier for the well, bore, spring or other sample location. It can be composed of any combination of letters and numbers as long as it is unique and easily understood by the sampler. It is advisable to record the name permanently in a database, along with other site details that would not change between sampling events (eg, site location, screened interval, bore depth, etc). This information is used to help identify and locate the bore, to determine pump placement, and to calculate purge volumes.

Screen: The top and bottom of the screened or open interval of the bore. Specify units of measurement (eg, metres below ground surface or metres from top of casing). This information is required to ensure correct placement of any portable pump used.

Depth: Total depth of the bore. Specify units of measurement (eg, metres below ground surface or metres from top of casing).

Grid reference: This specifies the location of the site in some co-ordinate system (eg, New Zealand Map Grid). It is typically given as an Easting and a Northing. Can be used as a check on whether the correct bore is being sampled. Be sure to record the coordinate system used.

MP: Measuring point. This is the point from which water level is measured. It is typically the top of casing, top of flange plate or top of measuring plug.

MP RL: Measuring point reference level. This is the reference level of the bore relative to a known datum. This datum is typically, but not necessarily, given in metres above or below mean sea level.

Fittings required: If special fittings are required to obtain a sample from the bore, this note is useful to ensure the correct fittings are brought to the site.

Location: This is a description of the location of the bore, for example “behind white shed”. These instructions should be detailed enough for a new sampler to be able to locate the site without any difficulty. Give reference to gates, driveways, raceways and obvious landmarks.

Contact details: As most SOE sites are private bores, it is important to keep in regular contact with the land owner.

Collection instructions: This can include information on how to start a pump, or free-flow a bore. Include any information needed to allow a sample to be taken from the bore.
2 Field information

**Date:** Date sample collected.

**Collected by:** Sampler(s) name/s. Useful when analysing data.

**Time:** Time sample collected. Differentiates from time when pumping was started. Be sure to state whether the time given is referenced to daylight savings time or standard time.

**Bore water level:** Water level above or below the measuring point. A level below MP should be negative, above MP (artesian) positive. State units of measurement (eg, metres).

**Pump on:** Whether or not the pump is operating on arrival.

**Time pump on:** Time that the pump is turned on (if known).

**Pump method:** Will generally be a pumped sample, but may be a bailed or free-flowing sample.

**Calculated purge volume:** This is the volume of water in the bore, as calculated and described in Step 3.2.

**Minimum total purge volume:** The minimum total purge volume is the volume calculated above multiplied by three. See Step 3.2.

**Estimated discharge rate:** Generally recorded in litres per second. Measure using the water meter on the bore, or if no meter is present, measure using a bucket and a stopwatch.

**Required purge time:** This is calculated from the purge volume and the discharge rate.

**Sample appearance at completion of pumping:** This is a useful qualitative indicator of sample appearance. Samples can be described as clear or turbid based on the cloudiness of the sample or the amount of suspended sediment it contains. Groundwater samples can often have a coloured appearance. Typical colours range from a red/rusty colour to a slightly yellow colour. Bores which have remained stagnant for a long time often appear coloured at the start of pumping. Groundwater in peaty areas often has a yellow tinge. A description of odour can also be a useful qualitative measure. In reducing groundwater systems an ‘eggy’ smell can often be detected as hydrogen sulphide (H₂S) leaves the water. The degree of odour is often categorised as slight, moderate or strong. Other odours used to describe a groundwater sample include ‘iron odour’ or ‘metallic odour’.

**Samples:** Indicates what samples were collected from the site, whether or not each sample was compliant or non-compliant with the protocol, and also records an identification number for each sample. If any sample is non-compliant with the protocol, ensure the reasons for this are noted under the comments.
## 3 Sample field sheet

<table>
<thead>
<tr>
<th>Site name:</th>
<th>Grid ref:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Screen:</td>
<td>- m / - m</td>
</tr>
<tr>
<td>Depth:</td>
<td>m</td>
</tr>
<tr>
<td>Location:</td>
<td>MP:</td>
</tr>
<tr>
<td>Fitting required:</td>
<td></td>
</tr>
<tr>
<td>Contact details:</td>
<td></td>
</tr>
<tr>
<td>Collection instructions:</td>
<td></td>
</tr>
</tbody>
</table>

### Date: ____________________________  Pump on: Yes / No

### Collected by: _____________________  Time pump on: ________________

### Time: ________________ NZST / NZDT  Calculated purge volume: ________________

### Bore w/l: ___________mm above/below MP  Calculated total purge volume: ___________ litres

### Pump method: pumped / bailed / free flowed  Required purge time: ___________ min

#### Sample appearance at commencement of pumping:

<table>
<thead>
<tr>
<th>Clear / Turbid Colourless / Colour</th>
<th>Odourless / Odour</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>Meter</th>
<th>Criteria</th>
<th>Start time</th>
<th>Measurements at intermediate times</th>
<th>Final time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp</td>
<td>°C</td>
<td></td>
<td>± 0.2 °C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cond</td>
<td>µScm⁻¹</td>
<td></td>
<td>± 3 %</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>± 5% if &lt;100</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>pH units</td>
<td></td>
<td>± 0.1 pH unit</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Other</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Other</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

#### Sample appearance at completion of pumping:

<table>
<thead>
<tr>
<th>Clear / Turid Colourless / Colour</th>
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<tr>
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<td></td>
</tr>
<tr>
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<td></td>
</tr>
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<tr>
<td>Additional</td>
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#### Comments:

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Appendix 3: Information that should be recorded regarding each Sampling Site

Certain information should be recorded regarding each sampling location in order to facilitate interpretation of groundwater quality data within an SOE programme. Much of this data relates to the ownership, location, surrounding land use and the physical construction of the bore. It is advisable to use a database to store all of this information. Several regional councils in New Zealand use the ‘WELLS’ database originally constructed by Environment Canterbury. A screen shot of site information from this database is provided below. Note that some of the information about the site should be taken into the field on each sampling event, to ensure the site can be positively identified before sampling (see Step 1 and Appendix 2).

Information that should be recorded regarding each sampling location:

- Site number
- Site name
- Site location
- Easting
- Northing
- Accuracy of easting and northing (eg, ±10 m)
- Owner/occupier details
- Sample site location information
- Sampling instructions
- Land use within 10 metres
- Land use within 100 metres
- Land use within 500 metres
- Bore/water use
- Details of well head protection
- Well construction details
- Depth of screened/source interval
- Source aquifer
- Miscellaneous notes
Screen shot of a typical ‘WELLS’ database screen

Source: Greater Wellington Regional Council.
Appendix 4: Recommended gear list

The following is a list of recommended equipment for routine groundwater sampling. It is not intended to be an exhaustive list of equipment, as every sampling programme will have its own requirements, but this list should provide basic guidance as to equipment requirements for standard SOE sampling in New Zealand:

- Sample bottles, filters, syringes
- Field sheets (see example in Appendix 2)
- Field meter and calibration solutions
- Flow cell
- Sample tubing
- Water level probe
- Staff gauge (for measuring artesian head)
- Graduated bucket
- Gloves (powder-free latex)
- Gas torch for flame sterilisation or alcohol and swabs
- Toolbox (should include basic tools such as screwdrivers, adjustable spanners, hammer, pliers, groove joint pliers, pipe/stillson wrench, electrical tape, thread tape)
- Assorted plumbing fittings, hose clips and plugs
- Calculator
- Stopwatch
- Pen, pencil and permanent marker
- Portable pump (if required) and generator
- Cell phone
- First aid kit
- Paper towels
- Hand sanitiser
- Zip-lock bags (for grouping bottles from each site)
- Rubbish bags
- Chilly bin/s
- Ice and/or slika pads
- Groundsheet
Appendix 5: Instructions for isolating a pressure tank

Many groundwater delivery systems utilise pressure tanks. These tanks are designed to:

- maintain water pressure within the delivery system
- provide a minimum storage of useable water to prevent frequent recycling of the pump.

Tanks work by containing a volume of air that is compressed by water in the system thereby maintaining pressure within the system. Draw-off causes water to be released from the tank which allows the air to expand and the pressure falls. Reduction of pressure below a certain point will cause the pump to start which will refill the tank and deliver water to the rest of the system.

There are two types of pressure tanks:

- plain steel – in these tanks there is a water-air contact. Automatic air volume valves are required to maintain the air volume otherwise the air may dissolve into the water. This causes the air volume of the tank and, consequently, its effectiveness to decrease
- diaphragm – in these tanks there is no water-air contact; the two are separated by a rubber diaphragm. These tanks may be identified by the air valve at the top of the tank.

The figures below show a diaphragm tank with its sides cut away. In the first picture the rubber bladder can be seen flush against the tank inlet. In the second picture the bladder has been lifted away from the inlet as it would be when filled with water.

Tanks pose a problem for groundwater sampling because their storage function means additional flushing is required to ensure a sample collected after the tank has been drained does not contain any water which may have been stored for an unknown period of time. Consequently, the collection of a groundwater sample from a system with a pressure tank should be done only if the tank can be isolated from the delivery system. There are a number of ways of achieving this situation:

- sample from a point upstream of the pressure tank
- if the tank is sufficiently small, drain the tank, flush the well, re-drain the tank, re-start the pump and sample
- drain the tank and add air pressure to push the diaphragm against the inlet/outlet point thereby isolating the tank space from the delivery system. Flush the well and sample and then return tank to its operating air pressure.
The following procedure is used by the USGS’ Denver office to isolate pressure tanks (J Bails personal communication):

1. Note the water pressure in-line (there should be a gauge right next to the tank) and in the tank. Pressure tanks have a valve on top, usually under a plastic screw cap.
2. Run the water in the house and note the pressures (from the in-line gauge) where the pump kicks in and when it shuts off.
3. Double check the pressure in the tank, right after the pump runs. The pressure is usually a bit higher than when the initial check is done.
4. Turn off power to the pump. There is usually a fuse box with a big switch on it near the pump, or it may be controlled through the main breaker box.
5. Open up a few taps and release the water pressure from the plumbing.
6. With the plumbing drained, check the pressure in the tank again. This is the pressure you need to return the tank to when you are finished, so write the value down.
7. With the taps still open, pressurise the tank with the air compressor through the valve on top; 80 psi should be sufficient. Make sure it is more than the maximum pressure you recorded in step 3.
8. Close the inside taps used to drain the system.
9. Make sure that you have at least two outside taps that you can turn on with hoses on them. Running inside taps while sampling may overload the septic system if one is fitted, so do not use them. If needed, you can use a splitter on the taps you plan to sample from.
10. Make sure you are ready to purge: meters calibrated, outside taps open, etc.
11. Turn on the power to the pump.
12. Make sure that the pump is not cycling on and off; you should be able to see this in the in-line pressure gauge. It will swing wildly, and you will hear the pressure switch for the pump going on and off. If the pump is cycling on and off, you do not have enough taps open. You will know when things are okay when the in-line pressure gauge holds steady at a pressure less than the shut-off pressure noted in step 2. (If there is a tap in the plumbing near the pressure tank, and you can attach a hose and run it to waste outside, this almost guarantees the pump will not cycle on and off. Check this a few times during the sampling.)
13. When you are finished with the sampling turn off the power to the pump again. Leave taps open.
14. Release the pressure on the tank until you are back to the pressure you recorded in step 6.
15. Close all taps.
16. Turn on the power to the pump, open and close a few taps to remove the air from the system.
17. Note the in-line pressure as the pump pressurises the plumbing and turns itself off – it should be what you noted before.
18. Check the pressure in the tank. It should be what you noted before.
19. Turn on some taps and watch the pressure gauge as the pump goes through a cycle. Make sure that the pump is turning on and shutting off at the same levels noted before. This setting is controlled by the switch and should not be affected at all by what you have done. This is just a check to make sure, and it usually is right-on.

20. Replace the plastic cap back on the valve and you are finished.

Equipment required to remove the pressure tank from the sample pathway:
- air compressor capable of delivering at least 90 psi
- air compressor hose with schraeder valve fitting (car tyre valve)
- low-range air pressure gauge (0–50 psi)
- high-range air pressure gauge (0–100 psi).
References


