National Environmental Monitoring Standards

# Water Quality

## Part 1 of 4: Sampling, Measuring, Processing and Archiving of Discrete Groundwater Quality Data

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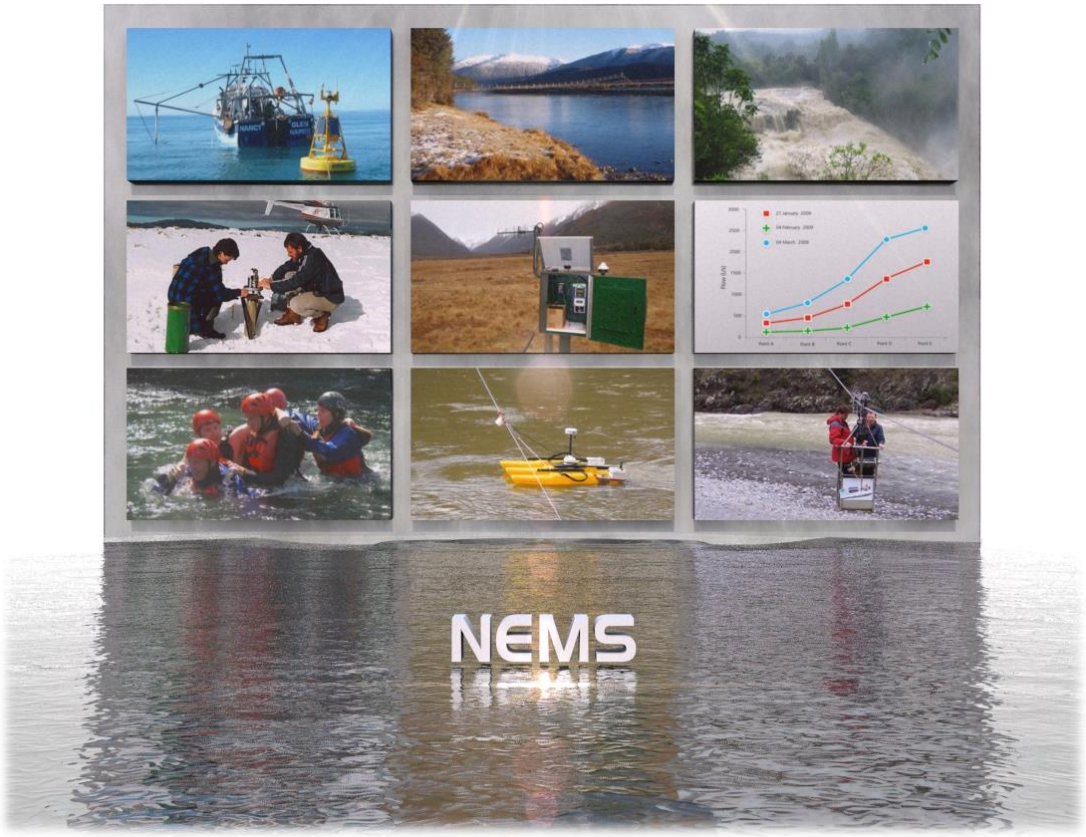

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# The National Environmental Monitoring Standards

The current suite of National Environmental Monitoring Standards (NEMS) documents, Best Practice Guidelines, *Glossary* and *Quality Code Schema* can be found at http://www.nems.org.nz.

## Implementation

When implementing the Standards, current legislation relating to health and safety in New Zealand and subsequent amendments and the NEMS Codes of Practice shall be complied with.

## Limitations

It is assumed that as a minimum, the reader of these documents has undertaken industry-based training and has a basic understanding of environmental monitoring techniques. Instructions for manufacturer-specific instrumentation and methodologies are not included in this document.

The information contained in these NEMS documents relies upon material and data derived from a number of third-party sources.

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## Development

The National Environmental Monitoring Standards (NEMS) Steering Group has prepared a series of environmental monitoring standards on authority from the regional chief executive officers (RCEOs) and the Ministry for the Environment (MfE).

The strategy that led to the development of these Standards was established by Jeff Watson (Chair) and Rob Christie (Project Director) in 2014. Implementation of the strategy has been overseen by a Steering Group that currently comprises Jeff Watson, Phillip Downes, Martin Doyle, Michael Ede, Glenn Ellery, Jon Marks, Charles Pearson, Jochen Schmidt, Pierre Tellier and Raelene Mercer (Project Manager).

The development of this Standard involved consultation with regional and unitary councils across New Zealand, analytical laboratory industry representatives, the National Institute for Water and Atmospheric Research Ltd (NIWA) and the Institute of Geological and Nuclear Sciences Ltd (GNS Science). These agencies are responsible for a significant amount of discrete water quality sampling of fresh and near-shore coastal waters across New Zealand. It is recommended that this Standard is adopted throughout New Zealand and all data collected are processed and quality coded appropriately to facilitate data sharing. The degree of rigour with which the Standard and associated best practice may be applied will depend on the quality of data sought.

This document has been prepared by a core working group comprising Juliet Milne (lead technical writer – NIWA), Magali Moreau (GNS Science), Peter Robinson (Robinson Scientific and formerly Hill Laboratories), Maree Patterson (Horizons Regional Council), Rob Davies-Colley (NIWA), Rob Donald (Bay of Plenty Regional Council), David Brown (Horizons Regional Council) and Jarrod Walker (Auckland Council). Mike Ede (Marlborough District Council) and Jochen Schmidt (NIWA) were the NEMS Steering Group representatives. Olivier Ausseil (Aquanet Consulting) was appointed as Water Quality NEMS Project Co-ordinator in early 2017.

The core working group was supported by representatives from the regional sector's Groundwater Forum (GWF), Surface Water Integrated Management (SWIM), Coastal and Environmental Data (formerly Local Authority Environmental Monitoring Group, LAEMG) Special Interest Groups (SIGs). Members of these SIGs contributed material, attended meetings and/or provided review comments. Particular thanks go to Adrian Meredith (Environment Canterbury), Carl Hanson (Environment Canterbury), Roger Hodson (Environment Southland), David Evans (Environment Canterbury), Karlien Heyns (Marlborough District Council), Pete Wilson (Waikato Regional Council), Mark Gall (NIWA), Trevor James (Tasman District Council), Pete Davidson (Marlborough District Council), Richard Griffiths (Northland Regional Council), Marta Scott (Environment Canterbury), Bill Vant (Waikato Regional Council), Abby Matthews (Horizons Regional Council), Chris Daughney (GNS Science), Paul Scholes (BoPRC), Regan Phipps (Taranaki Regional Council), Lesley Bolton-Ritchie (Environment Canterbury), Claire Conwell (Greater Wellington Regional Council), Rachel Webster (Environment Canterbury), Lisa Scott (Environment Canterbury) and Jeff Cooke (Hawke's Bay Regional Council).

The working group would like to express their thanks to:

- the laboratory specialists who attended workshops and provided information on laboratory testing requirements: You-Sing Yong (Watercare Services Ltd), Ara Heron (Hill Laboratories), Jane Sherrard (Hill Laboratories), Mike Crump (NIWA), Rob Deacon (Eurofins ELS), Tracy Morrison-Judd (Eurofins ELS), Sunita Raju (Eurofins ELS), Stuart Sanderson (GNS Science) and Adrian Spence (Bay of Plenty Regional Council)
- all those who submitted feedback on the draft (October 2017) version of this NEMS, in particular –
    - members of the GWF that drafted the revised low-flow sampling guidance, and
    - laboratory staff at Hill Laboratories, Watercare Services Ltd, Eurofins ELS, NIWA, GNS Science, Bay of Plenty Regional Council and Taranaki Regional Council that participated in an interlaboratory comparison in late 2017 to inform revisions to some of laboratory test method details, and
- the NEMS Steering Group for their oversight and the review undertaken, which is gratefully acknowledged.

## Funding

The Ministry for the Environment (MfE) and Envirolink (through the Ministry of Business, Innovation and Employment, MBIE) provided the direct financial support to this NEMS *Water Quality* project.

In addition, the following organisations provided in-kind time to this project:

- Auckland Council (AC)
- Bay of Plenty Regional Council (BoPRC)
- Environment Canterbury Regional Council (ECan)
- Environment Southland (ES)
- Eurofins ELS
- GNS Science
- Greater Wellington Regional Council (GWRC)
- Hawke's Bay Regional Council (HBRC)
- Hill Laboratories
- Horizons Regional Council (HRC)
- Marlborough District Council (MDC)
- National Institute of Water and Atmospheric Research Ltd (NIWA)
- Northland Regional Council (NRC)
- Otago Regional Council (ORC)
- Taranaki Regional Council (TRC)
- Tasman District Council (TDC)
- West Coast Regional Council (WCRC)
- Waikato Regional Council (WRC)
- Watercare Services Ltd

## Review

This document will be reviewed by the NEMS Steering Group in March 2020, and thereafter once every two years. Further details on the review process can be found at http://www.nems.org.nz.

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# Normative References

This Standard should be read in conjunction with the following references:

- NEMS Code of Practice *Safe Acquisition of Field Data In and Around Fresh Water*
- NEMS *Dissolved Oxygen* (continuous measurements)
- NEMS *Glossary*
- NEMS *Quality Code Schema*
- NEMS *Turbidity* (continuous measurements)
- NEMS *Water Level* (continuous measurements)
- NEMS *Water Quality – Part 2 (Rivers), Part 3 (Lakes)* and *Part 4 (Coastal Waters),* and
- NEMS *Water Temperature* (continuous measurements).

# About This Standard

## Introduction

Discrete (grab or spot) sampling of groundwater quality is carried out across New Zealand for many purposes. Water quality measurements help in our understanding of groundwater and associated ecosystems, the impacts land use may have on groundwater, and the suitability of groundwater for specific uses, such as irrigation and stock watering.

This Standard has been prepared principally for field technicians, programme managers and environmental scientists or consultants who collect, quality check or report on discrete water quality data. The primary focus is on groundwater quality data acquisition (sampling and measurement), quality assurance and archiving associated with long-term monitoring programmes, including State of the Environment (SoE) monitoring programmes. The principal purpose of SoE water quality monitoring is to assess state (condition) and trends through time.

Assembling a valuable long-term groundwater quality data record requires a robust monitoring design underpinned by a consistent approach to in situ measurements, water sample collection, laboratory measurements and data management. This is because groundwater quality can vary both in time and space, and is subject to many influences. These influences can include groundwater-rock interaction, water abstraction, saltwater intrusion, biological processes and diffuse source contaminant discharges.

Discrete groundwater quality sampling is used by many agencies for a broad range of purposes other than long-term monitoring for SoE reporting, such as investigating specific contamination issues, informing policy effectiveness, characterising natural waters, and assessing public health or the effects of consented activities. While sampling for these purposes is not specifically addressed in this document, much of the guidance around in situ (field) measurements, water sample collection and handling, and data management are applicable to other uses of discrete water quality data. This Standard, therefore, provides a normative reference for most discrete groundwater quality sampling and measurements carried out across New Zealand.

This document forms Part 1 of a four-part document series on discrete water quality sampling and measurement. The other three parts address rivers, lakes and near-shore coastal waters. The four water domains are documented separately because there are important differences in sample collection and measurement requirements between the domains. However, consistency in content is maintained across the documents where possible to help facilitate an integrated approach to water monitoring and management.

## Objective

The objective of this Standard is to ensure discrete groundwater sample collection, measurements and associated data processing and quality assurance are consistent and reliable across New Zealand. This document is made up of two sections: the first section is the Standard and the second section contains supporting information that practitioners are required to implement in order to achieve the Standard.

## Scope

The Standard covers groundwater and natural springs issuing from fissures or river banks where the outlet can be located. It focuses specifically on long-term (including SoE) monitoring programmes. Some of the methods presented may not be applicable to some specific forms of monitoring, such as consent or potable supply monitoring.

The Standard addresses all processes associated with:

- field work preparation
- sampling point selection
- sampling equipment preparation and use, including decontamination
- field observations (visit metadata) and measurements (during sampling)
- water sample collection methods
- water sample handling and transport
- laboratory processing and test methods, reports, quality checks and accreditation
- reconciliation between field and laboratory water quality data
- quality assurance (QA) procedures
- data quality coding, and
- data archiving.

Discrete water samples are collected for a defined monitoring objective(s). This objective will influence the selection of sampling site(s), water quality variables to measure, the timing and frequency of sampling, and the water sample collection and measurement methods. It is beyond the scope of this document to address monitoring objectives and sample design elements pertaining to a long-term monitoring programme.

The following suite of water quality variables are addressed in this Standard. This suite represents those variables typically measured on a routine or periodic and ongoing basis as part of long-term groundwater SoE programmes. Some common environmental tracers have also been included. The list of variables is not fully prescriptive for environmental monitoring and alternative specialist advice should be sought for variables not included here.

| Variable | | Nomenclature[1] |
|---|---|---|
| *Physico-chemical properties* | | |
| Water temperature – field | | Temp |
| Dissolved oxygen – field percentage saturation | | DO % sat |
| Dissolved oxygen – field | | DO |
| Carbon dioxide, free | | CO2 |
| pH – field | | pH – field |
| pH – laboratory | | pH |
| Specific conductivity – field | (also known in this Standard as electrical conductivity at 25°C) | SpC – field |
| Specific conductivity – laboratory | | SpC |
| Total dissolved salts – field | | TDS – field |
| Total dissolved solids | | TDS |
| *Nutrients, anions, cations and metals (dissolved form[2])* | | |
| Aluminium | | Al diss |
| Ammoniacal nitrogen | | NH4-N |
| Arsenic | | As diss |
| Bicarbonate | | HCO3 diss |
| Bromide | | Br diss |
| Cadmium | | Cd diss |
| Calcium | | Ca diss |
| Carbonate | | CO3 diss |
| Chloride | | Cl diss |
| Chromium | | Cr diss |
| Copper | | Cu diss |
| Dissolved reactive phosphorus | | DRP |
| Fluoride | | F diss |
| Iron | | Fe diss |
| Lead | | Pb diss |
| Magnesium | | Mg diss |
| Manganese | | Mn diss |
| Nitrate nitrogen | | NO3-N |
| Nitrite nitrogen | | NO2-N |
| Nitrite-nitrate nitrogen (also known as total oxidised nitrogen) | | NNN |
| Potassium | | K diss |
| Silica (reactive) | | SiO2 diss reactive |
| Sodium | | Na diss |
| Sulphate | | SO4 diss |
| Total (dissolved) alkalinity | | Alkt |
| Total (dissolved) hardness | | Hard |

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| Variable | Nomenclature[1] |
|---|---|
| Total phosphorus | TP |
| Zinc | Zn diss |
| *Metals and metalloids (total form[2])* | |
| Aluminium (Al total), Arsenic (As total), Cadmium (Cd total), Copper (Cu total), Chromium (Cr total), Lead (Pb total) and Zinc (Zn total) | As left |
| *Microbiological properties* | |
| *Escherichia coli (E. coli)* | EC |
| Faecal coliforms | FC |
| *Environmental tracers* | |
| Radon | 222Rn |
| Sulphur hexafluoride | SF6 |
| Chlorofluorocarbons –11 | CFC -11 |
| Chlorofluorocarbons –12 | CFC -12 |
| Chlorofluorocarbons –13 | CFC -13 |
| Deuterium | 2H |
| Oxygen-18 | 18O |
| Tritium | 3H |
| *Other* | |
| Dissolved organic carbon[3] (non-purgeable) | DOC |

*[1] Nomenclature varies both in the literature and in practice. Adoption of the nomenclature in this table is recommended for the storage and/or exchange of water quality data to improve consistency in inter-regional and national reporting in New Zealand.*

*[2] Variables may exist in groundwater in either particulate or dissolved form. Particulate matter includes living and dead plankton, precipitates, adsorbate to particulates, etc. A "total form" includes dissolved and particulate forms.*

*[3] Not typically measured in groundwater but included for relevance to groundwater ecosystems and because some groundwater sites may be monitored for an understanding of connections with overlying surface waters.*

The following variables are also included in this Standard but at the present time there is insufficient guidance available to inform quality coding. Until such time as guidance is developed, measurements of these variables shall be coded QC 200 – unverified.

| Variable | Nomenclature |
|---|---|
| Oxidation-reduction potential | ORP |

## Relationship with Existing Guideline Documents

This Standard has been prepared giving consideration to general principles outlined in the ANZECC (2000) *Australian guidelines for water quality monitoring and reporting*. It updates and supersedes sampling and testing guidance provided in:

- *A national protocol for State of the Environment groundwater sampling in New Zealand* (Daughney *et al*., 2006), which provided the starting basis for much of this NEMS, notably subsection 2.2, Section 4, and Annexes B and E of the supporting documentation to the Standard, and
- *Freshwater monitoring protocols and quality assurance* (Davies-Colley *et al*., 2012), prepared as part of the National Environmental Monitoring and Reporting (NEMaR) project.

## Data Fit for Purpose

This Standard requires all collected data to be assigned a quality code.

Data that are collected, processed and archived in a verifiable and consistent manner according to this Standard can meet the highest quality code (QC 600). Data that do not meet QC 600 shall be coded appropriately.

> *Note: Enduring use – It is important to note that data that are coded QC 500 or QC 400 may be restricted in their use for a wide range of (yet unknown) purposes sometime in the future.*

# The Standard – Discrete Water Quality (Groundwater)

As a means of achieving discrete groundwater quality data of the highest quality under this Standard (i.e. QC 600), the following requirements and best practice prerequisites shall apply:

| **Field measurements and sample collection** | | | | |
|---|---|---|---|---|
| Certification | | Water samples, field measurements and associated metadata shall be collected by trained staff following a recorded procedure that is consistent with the supporting information contained in this Standard. | | |
| Measurement Units, Accuracy and Resolution | **Variable** | **Measurement unit** | **Sensor accuracy** | **Measurement resolution** |
| | Water temperature (Temp) | °C | ± 0.3°C | 0.1°C |
| | Dissolved oxygen – saturation (DO % Sat) | % | ± 3% between 0 and 200% | 0.1%, corrected to barometric pressure |
| | Dissolved oxygen – concentration (DO) | mg/L [1] | ± 0.3 mg/L between 0 and 20 mg/L | 0.01 mg/L, corrected to barometric pressure |
| | Specific conductivity (SpC – field) | µS/cm at 25°C [2] | ± 1 µS/cm (or ± 0.5% for full scale error) | 0.1 |
| | pH (pH – field) | pH units @ 25°C | ± 0.2 pH units | 0.01 |
| Validation and Calibration | Records | Records of field meter calibration and validation shall be kept. | | |
| | Water temperature | 12-monthly validation checks against two traceable reference thermometers involving at least a 5-point validation process in accordance with the NEMS *Water Temperature*. | | |

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| | | |
|---|---|---|
| Validation and Calibration (con.) | Dissolved oxygen | Validation on each sampling day before deployment using 100% saturated air or water. Validation passes when the measurement is within ± 0.5% saturation.<br><br>If validation fails, perform a single-point calibration using 100% saturated air or water.<br><br>Whenever the sensor cap or membrane is replaced, or consistently low DO concentrations are expected, perform a 2-point calibration using firstly 100% saturated air or water and secondly 0% saturation.<br><br>*Alternative option for 'high quality' sensors:*<br>Validation and calibration is performed in full accordance with the requirements of Annex G. Validation is achieved when a subsequent DO measurement is within ± 0.5% saturation in a 100% saturated air or water solution after the measurement was made (calibration before, and a successful validation after the measurement, as per Annex G). |
| | Specific conductivity | Validation on each sampling day before deployment using at least two standard solutions. Validation passes when the measurement is within:<br>• standards ≤ 10 uS/cm: ± 25%<br>• standards > 10 and ≤ 200 uS/cm: ± 15%<br>• standards > 200 uS/cm: ± 5%<br><br>If validation fails, calibrate the sensor using a standard higher than the concentration in the water to be measured and validate in a range close to expected measurements.<br><br>At the minimum, field validation shall be repeated once at the end of day in 148 uS/cm standard solution.<br><br>*Alternative option for 'high quality' sensors:*<br>Validation and calibration is performed in full accordance with the requirements of Annex G. Validation is achieved when a subsequent conductivity measurement in a calibration standard is in the range:<br>• standards ≤ 10 uS/cm: ± 25%<br>• standards > 10 and ≤ 200 uS/cm: ± 15%<br>• standards > 200 uS/cm: ± 5%<br>(Calibration before, and a successful validation after the measurement, as per Annex G). |

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| | | |
|---|---|---|
| Validation and Calibration (con.) | pH | A minimum of a 2-point calibration on each day of use with standard buffer solutions of pH 4, 7 and pH 9 or 10. To pass calibration, the meter's millivolts reading in pH 7 buffer shall be 0 mV ± the manufacturer's specifications (typically 35–45 mV).<br>Validation at the end of each day using a standard solution of pH 7. To pass validation, pH shall be in the range 6.8 to 7.2.<br>*Alternative option for 'high quality' sensors:*<br>Validation and calibration is performed in full accordance with the requirements of Annex G. Validation is achieved when a subsequent pH measurement is in the range 6.8 to 7.2 in pH 7.0 buffer (calibration before, and a successful validation after the measurement, as per Annex G). |
| Site Location and Stationarity | | The site location for field measurements and water sample collection shall be clearly identifiable and retained through time. |
| Site Metadata | | Site metadata, including site name, location, altitude, photographs and landowner details, shall be recorded and reviewed at least annually. |
| Site Visit Metadata (field record form) | | A field record form shall be completed of the location, date and time of field measurements and/or water sample collection, including the environmental conditions under which these were collected, field meter(s) make, model and ID number, and the depth to groundwater. |
| Timing of Measurements | Accuracy and resolution | The timing of sample collection shall be recorded as a single visit time to the nearest 5 minutes that is representative of the time the final field meter measurements were made. |
| | Time zone | Time shall be expressed as New Zealand Standard Time (NZST).<br>*Note: Do not use New Zealand Daylight Time (NZDT).* |
| Field Equipment Deployment | Meters | The meter sensor(s) shall be deployed in the main flow and time allowed to stabilise in accordance with the manufacturer's specifications. |
| | Dissolved oxygen | If electrochemical sensors are used, a mechanical stirrer shall be used to ensure the velocity of water past the sensor exceeds 0.3 m/s. Alternatively, a flow cell shall be used. |

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| | | |
|---|---|---|
| Sample Collection, Processing and Handling | Sampling point | Water samples shall be collected where groundwater is visibly flowing. For low flow sampling, water samples shall be collected at the well head. For springs, water samples shall be collected as close to the outflow as practical. |
| | Purging (excluding low flow conditions) | Groundwater from wells shall be purged prior to sample collection. Purging is complete when either:<br>• at least three times the calculated purge volume has been extracted, or<br>• where low flow sampling has been performed, at least the total volume of water in the pump and tubing, plus the volume of the drawdown in the well, has been purged,<br>and groundwater temperature, specific conductivity and pH have been measured on at least four separate occasions, with the differences between the last two measurements meeting the following criteria:<br>• water temperature: ± 0.2°C, and<br>• specific conductivity: ± 5% if ≤ 100 µS/cm and ± 3% if > 100 µS/cm, and<br>• pH: ± 0.1 pH unit. |
| | Low flow purging and sampling | Low-flow purging and sampling shall only be performed where the following criteria can be met:<br>• the well head is secure, sealed to prevent surface water and rain water infiltration<br>• the well construction details are known, including screen interval<br>• static water level and drawdown can be measured during purging and sampling<br>• the pump intake is within the screen interval<br>• a variable-rate, low-flow pump is used, and<br>• field variables are measured in a flow cell.<br><br>Purging is complete when the above criteria for purging are met, DO measurements are stable (last two measurements are within ± 0.3 mg/L of each other), and the water level is stable (last two measurements within ± 0.1 m of each other). |
| | Sampling equipment | Sampling equipment, including unpreserved sample bottles, syringes, tubing and buckets where applicable, shall be field-rinsed three times.<br><br>*Note: Do not field rinse the sterile microbial sample bottle.* |

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| | | |
|---|---|---|
| Sample Collection, Processing and Handling (con.) | Bottle type and filling requirements | Correct laboratory sample bottle(s) shall be used for the variable(s) to be measured with filling requirements met as follows (and outlined in Table 3, Section 5.4.3):<br>• *Specific conductivity, pH and total dissolved solids:* Unpreserved bottle filled with no air gap<br>• *Nutrients:* Unpreserved field-filtered bottle filled without air gap OR where sulphuric acid preservative is used, filled to shoulder and sample inverted to mix<br>• *Anions, cations, total hardness, total alkalinity and metals:* Unpreserved bottle filled with no air gap, OR where acid preservative is used, filled to shoulder and sample inverted to mix<br>• *Microbial samples:* Sterile unpreserved bottle filled directly with a small air gap<br>• *Environmental tracers:* Unpreserved glass bottle (or plastic bottle for 2H, 18O and 3H) filled with no air gap<br>• *Dissolved organic carbon*: Unpreserved and furnaced brown glass bottle filled with no air gap.<br>All unpreserved bottles shall be field rinsed prior to sample collection except sterile bottles for microbial testing. |
| | Sample Filtration | Samples collected for soluble nutrient, metal, anion or cation measurement shall be filtered to 0.45 µm in the field at the time of collection. |
| | Sample handling | Samples shall be promptly removed from the light and transferred to chilled storage bins to rapidly reduce the sample temperature to below 10°C. Microbial samples shall not be subject to freezing at any time, even in part. |
| | Sample traceability and integrity | Samples shall be unequivocally identifiable and accompanied by a completed Chain of Custody form that enables sample traceability from the field to the laboratory. |
| **Laboratory measurements** | | |
| Certification | | The laboratory shall hold current IANZ accreditation for the test method used to measure each water quality variable. |
| Sample Arrival at the Laboratory | Documentation | Laboratory staff shall record confirmation of the date and time of receipt of samples on the accompanying Chain of Custody form, together with:<br>• sample temperature on arrival (°C), and<br>• any anomalies in sample condition with the potential to impact the laboratory measurement (e.g. damaged or incorrectly filled sample bottle). |
| | Temperature | Unpreserved and microbial samples shall be less than 10°C (or at a temperature less than the sample collection temperature where samples are delivered within 2 hours of collection), unfrozen and free of ice crystals. |
| | Processing and testing time frames | All microbial, pH, free carbon dioxide and alkalinity testing shall commence within 36 hours of sample collection. |

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| | Variable | Measurement unit | Test method(s) | Method detection limit[3] |
|---|---|---|---|---|
| Test Method and Measurement Requirements | pH | pH units at 25°C | APHA 4500-$H^+$ B | 0.1[4] |
| | Specific conductivity (SpC) | µS/cm at 25°C | APHA 2510 B | 1[4] |
| | Carbon dioxide, free (CO2) | mg/L | APHA 4500-CO2 D | 1.0 at 25°C |
| | Total dissolved solids (TDS) | | APHA 2540 C | 10 |
| | *Nutrients, anions, cations and metals (dissolved form)* | | | |
| | Aluminium (Al diss) | mg/L | APHA 3125 B | 0.005 |
| | Ammoniacal nitrogen (NH4-N) | | APHA 4500-NH3 H | 0.005 |
| | Arsenic (As diss) | | APHA 3125 B | 0.001 |
| | Bicarbonate (HCO3 diss) | mg/L $CaCO_3$ | APHA 4500-CO2 D or APHA 2320 | 1.0 at 25°C |
| | Bromide (Br diss) | mg/L | APHA 4110 B | 0.05 |
| | Cadmium | | APHA 3125 B | 0.0001 |
| | Calcium (Ca diss) | | APHA 3120 B or APHA 3125 B | 0.05 |
| | Carbonate (CO3 diss) | mg/L $CaCO_3$ | APHA 4500-CO2 D or APHA 2320 | 1.0 at 25°C |
| | Chloride (Cl diss) | mg/L | APHA 4110 B | 0.5 |
| | Chromium (Cr diss | | APHA 3125 B | 0.0005 |
| | Copper (Cu diss) | | | |

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| | Variable | Measurement unit | Test method(s) | Method detection limit[3] |
|---|---|---|---|---|
| Test Method and Measurement Requirements (con.) | Dissolved reactive phosphorus (DRP) | mg/L | APHA 4500-P G | 0.004 |
| | Fluoride (F diss) | | APHA 4110 B or APHA 4500-F C or G | 0.05 |
| | Iron (Fe diss) | | APHA 3120 B or APHA 3125 B | 0.01 |
| | Lead (Pb diss) | | APHA 3125 B | 0.0001 |
| | Magnesium (Mg diss) | | APHA 3120 B or APHA 3125 B | 0.01 |
| | Manganese (Mn diss) | | APHA 3120 B or APHA 3125 B | |
| | Nitrate nitrogen (NO3-N) | | APHA 4500-NO3 I or APHA 4110 B | 0.002 |
| | Nitrite nitrogen (NO2-N) | | | |
| | Nitrite-nitrate nitrogen (NNN) | | | 0.01 |
| | Potassium (K diss) | | APHA 3120 B or APHA 3125 B | 0.1 |
| | Silica (SiO2 diss reactive) | mg/L as $SiO_2$ | APHA 4500-SiO2-F *or* APHA 3120 B | |
| | Sodium (Na diss) | mg/L | APHA 3120 B or APHA 3125 B | 0.02 |
| | Sulphate (SO4 diss) | | APHA 4110 B | 0.5 |
| | Total alkalinity (Alkt) | mg/L $CaCO_3$ | APHA 2320 B | 1 at 25°C[4] |

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| | Variable | Measurement unit | Test method(s) | Method detection limit[3] |
|---|---|---|---|---|
| Test Method and Measurement Requirements (con.) | Total anion/ total cation balance check | % difference | APHA 1030 E | N/A |
| | Total hardness (Hard) | mg/L $CaCO_3$ | APHA 2340 B | 1 |
| | Zinc (Zn diss) | mg/L | APHA 3125 B | 0.001 |
| | *Metals and metalloids (total form)* | | | |
| | Aluminium (Al total) | mg/L | APHA3030 E or F nitric and/or hydrochloric acid digestion, then analysis by APHA 3125 B | 0.005 |
| | Arsenic (As total) | | | 0.001 |
| | Cadmium (Cd total) | | | 0.0001 |
| | Chromium (Cr total) | | | 0.0005 |
| | Copper (Cu total) | | | 0.0005 |
| | Lead (Pb total) | | | 0.0001 |
| | Zinc (Zn total) | | | 0.001 |
| | *Microbial* | | | |
| | Faecal coliforms (FC) | cfu/100 mL | APHA 9222 D | 1 |
| | *E. coli* (EC) | MPN/100 mL | APHA 9223 B | 1 |
| | *Environmental Tracers* | | | |
| | Radon (222Rn) | Bq/L | Radiometric detection. Low level scintillation detectors | 0.1 |
| | Sulphur hexafluoride (SF6) | fmol/kg | Gas chromatography with electron capture detection | 0.02 |

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| | Variable | Measurement unit | Test method(s) | Method detection limit[3] |
|---|---|---|---|---|
| Test Method and Measurement Requirements (con.) | Chlorofluoro-carbons – 11 (CFC – 11) | pmol/kg | Gas chromatography with electron capture detection | 0.03 |
| | Chlorofluoro-carbons – 12 (CFC – 12) | | | |
| | Chlorofluoro-carbons – 13 (CFC – 13) | | | |
| | Deuterium (2H) | per mL | Mass spectrometry, GVI Isoprime coupled with AquaPrep | 1 |
| | Oxygen-18 (18O) | | | 0.1 |
| | Tritium (3H) | TU | Radiometric detection. Electrolytic enrichment + low level scintillation detectors | 0.03 |
| | *Other* | | | |
| | Dissolved organic carbon (DOC) | mg/L | APHA 5310 C | 0.3 |
| Measurement Resolution | All laboratory measurements shall be reported to one, two or three significant figures as dictated by the uncertainty of measurement for the test method. | | | |
| Data records | The laboratory measurements shall be provided in a report that specifies the:<br>• date and time of both sample collection and receipt at the laboratory<br>• form of measurement made (e.g. dissolved vs total)<br>• measurement value and units<br>• uncertainty of measurement (at a 95% confidence level)<br>• measurement method and standard method detection limit, including details of any modifications made to these (e.g. from diluting samples), and<br>• any anomalies with the condition of the sample upon receipt (e.g. temperature on arrival, bottle type and/or filling) or the subsequent measurement value, including unexpected differences between dissolved and total nutrient concentrations. | | | |
| Quality coding | All data shall be quality coded as per the Quality Codes flowchart. | | | |

*[1] mg/L is equivalent to g/m³, g m⁻³ or ppm.*

*[2] 1 µS/cm is equivalent to 0.1 mS/m.*

*[3] The specified method detection limits (MDLs) represent the minimum required for 'high quality 'or 'unimpacted' groundwaters. This Standard does not preclude the*

*use of higher MDLs for the specified test method provided that this does not result in more than one censored value (< MDL) in every 10 measurements.*

*[4] Represents a measurement resolution rather than a method detection limit.*

The following summarises additional best practice measures. These measures are recommended but are not required to meet QC 600.

| | | |
|---|---|---|
| Field Documentation | Site visit metadata | Arrival and departure times at a site are recorded on the field record form. A photograph of the site is taken at least annually using a camera with geo-referencing capability. |
| | Electronic data capture | Visit metadata and field measurements are recorded electronically in the field. Where paper forms are unavoidable, waterproof paper is used. |
| Field Measurements | Field meters | Field meters are validated in the field at each site before use. |
| | | Field measurements are logged for the period of sensor deployment. |
| | | Where field measurements are greater than the highest standard solution used for validation, revalidation is performed using an appropriate standard. |
| | Dissolved oxygen | Optical sensors are deployed as part of a multi-probe meter. |
| | pH | pH is measured as a supporting variable where ammoniacal nitrogen and/or metals are measured. |
| | Quality assurance | As a minimum, a 12-monthly interagency audit is performed to verify measurement practices. This exercise should include:<br>• field meter calibration, deployment and measurement<br>• all other field measurements and observations, and<br>• water sample collection, pre-treatment and handling, with blind duplicate water samples dispatched for laboratory analysis. |
| Sample Integrity | Microbial samples | The pump and associated sampling equipment are sterilised prior to sample collection. |
| | Sample identification | Water sample bottles are clearly and permanently labelled with a unique identification number which is referenced on the field sampling and Chain of Custody records. |

*Continued on next page…*

| | | |
|---|---|---|
| Sample Integrity (con.) | Holding times | Water samples are dispatched to the laboratory within 24 hours, otherwise stored in dark, cool (4°C optimum, unless advised otherwise by the laboratory for preserved samples) and secure conditions. |
| | Field blanks | Field blanks are used on a routine (six-monthly) basis as part of quality assurance. |
| Laboratory Measurements | Detection limits | Laboratory method detection limits are 10-fold lower than the measured sample concentration wherever possible. |
| | Sample retention | Laboratories store water samples for at least 30 days to permit retesting where required and appropriate. |
| Data Reporting and Checks | Laboratory reports | Uncensored (or 'best estimate') measurement values are provided by the laboratory together with uncertainty of measurement values. |
| | Quality assurance | Measurements reported by the laboratory are checked by the collection agency within 2 weeks of receipt to enable sample retesting if necessary. |
| | | The historical site measurement range and relationships with other variables are used as a guide to check the 'validity' of measurements. |
| Archiving | Original and final records | File, archive indefinitely, and back up regularly in a time-series database:<br>• site and field visit metadata<br>• field meter validation results and calibration details<br>• field measurements together with meter/sensor make and model<br>• censored and uncensored laboratory values together with associated uncertainty of measurement values<br>• date, time and condition of samples received at the laboratory, and<br>• any sample or measurement anomalies, including quality checks performed on these. |
| Consistency of Record | Field and laboratory methodology changes | If measurement methods are changed, duplicate measurements using both the old and new methods are carried out for a period of time (at least 12 months where sampling occurs monthly) to provide sufficient data to enable a conversion factor to be derived to 'align' the old and the new data. |
| Data Auditing | *Quality assurance requirements are under development.* | |

# 1 Preparatory Work in the Office

## In This Section

This section outlines matters that need to be addressed prior to leaving the office that shall be documented in a Field and Office Manual. These items include health and safety considerations, monitoring programme quality assurance measures, field record forms, water quality variables to be measured, field equipment, sample bottle requirements and preservatives/pre-treatment, and sample handling.

## 1.1 Field and Office Manual

Field measurements and sample collection are critical steps in a monitoring programme so it is important that everyone involved with these understands the monitoring objective(s) and procedures, and has received sufficient training to carry out all assigned tasks and procedures correctly. The objectives and procedures shall be documented in a Field and Office Manual (or equivalent) that also addresses, in detail, matters set out in the remainder of this section. This manual shall also contain office-based quality checking procedures, as outlined in Section 6.

## 1.2 Health and Safety

Collection of field measurements and water samples from groundwater has some elements of danger that shall be considered in a Health and Safety Plan, prepared in accordance with your own organisational processes.

Safe access to routine monitoring sites in all weather conditions is particularly important. Only trained personnel shall be involved in fieldwork and suitable lone worker procedures are required if lone work is unavoidable.

Appropriate personal protection equipment, such as hi-visibility clothing and floatation aids, should be provided to ensure safety. Gloves should be worn when sampling groundwaters likely to present a significant health risk (e.g. wells with known sewage contamination). Where possible, avoid using generators or purge pumps in the rain.

For further guidance on safety precautions when collecting discrete water samples, refer to the NEMS Code of Practice *Safe Acquisition of Field Data In and Around Fresh Water*.

## 1.3 Quality Assurance

Quality assurance (QA) (and quality control (QC)) programmes are mandatory components of laboratory practice to ensure measurements are accurate.

However, field work is the first step in carrying out an examination of water quality and any errors caused by improper field measurements, sample collection or sample pre-treatment, transport or storage cannot be corrected. Quality assurance procedures are therefore necessary to monitor the effectiveness of the field methodology and demonstrate that the various stages of fieldwork are adequately managed to minimise errors. This ensures that data obtained both directly (e.g. field measurements) or indirectly from the field (e.g. laboratory tests on water samples) are robust.

The QA programme should comprise all the steps taken to ensure that valid measurements are produced. This includes documented evidence that field personnel are trained and competent, field equipment is well maintained and calibrated/validated, and appropriate sample collection, preservation and handling methods are employed. Particular emphasis should be given to correct execution and recording of on-site measurements and completion of field record forms. This is best done through field inter-comparison exercises with another experienced monitoring agency (e.g. Davies-Colley *et al.*, 2017). Regular internal training and checks are also recommended.

### 1.3.1 Annual Field Audit

As best practice, this Standard recommends that field protocols are verified once every 12 months through an inter-agency field QA sampling exercise. This QA exercise should seek to:

1. validate the reproducibility of field measurements (e.g. dissolved oxygen), and
2. deliver to the laboratory 'dependable' samples that are representative of the groundwater at the site and remain unchanged during transit to the laboratory.

The QA field exercise shall target specific practices around:

- field meter calibration/validation, deployment and measurements
- execution and recording of other on-site measurements (e.g. water depth)
- collection and handling of water samples, including bottle labelling, sample pre-treatment or preservation and sample dispatch, and
- completion of sample records/field record forms, including metadata.

The exercise requires two or more staff of different agencies to simultaneously, but independently, complete the tasks above and dispatch a set of duplicate water samples to the same laboratory. Alternatively, an 'auditor' (with appropriate training) from an independent agency can accompany field staff on a routine sampling 'run' and check their field protocols – including through collection of duplicate field measurements and water samples.

### 1.3.2 Field Blanks

Field blanks are samples obtained in the field using distilled water. It is recommended as best practice that field blanks are collected from at least one site on a regular (e.g. six-monthly) basis) to check for any background contamination arising from the sample bottle, collection or handling. A field blank should be submitted to the laboratory for analysis in the same type of bottle as the groundwater samples against which it will be compared.

### 1.3.3 Other Checks

There are a number of checks that can be made by the sampling agency to test other aspects of the field practice and various aspects of the laboratory testing that could affect data accuracy. These include collection of replicate (2 or more) samples, provision of external duplicate samples (dispatch of a second set of samples to another laboratory), or provision of samples of known concentrations (e.g. standard reference). The need for these checks should be considered during monitoring programme design.

Replicate samples should be assigned a false name so that the laboratory does not know the actual location of collection. The choice of sample to be duplicated could be chosen at random or a sample from a 'reference' site with low levels of most variables could be split routinely.

## 1.4 Field Record Forms

A standard field record form shall be used to record field visit metadata (both observations and field measurements). This form provides a vital record that verifies the location, timing, methods and conditions under which field measurements and sampling was carried out, along with other factors that may influence the data being collected; for example, presence of potential contaminant sources. This record is also essential for later reconciliation with water quality results received from the laboratory (Section 6).

Electronic field record forms are becoming increasingly common and have the advantage of offering more efficient data capture and the ability to build in automated calculations and checks of imputed data to ensure records are correct at the time they are made. If paper forms are used, waterproof paper is recommended to protect the integrity of the record.

Metadata that shall be recorded when visiting groundwater monitoring sites are outlined in subsection 4.4. An example field record form is provided in Annex B.

Field personnel shall be trained on how to correctly complete field records.

*Note: Use of customised groundwater monitoring field record forms with pre-printed site names and site numbers, and standardised text options for sampling method, field meter details and weather conditions, will reduce time spent filling out the form on site and provide for consistent record keeping.*

## 1.5 Water Quality Variables

The water quality variables to be measured in the field (i.e. in situ) or on water samples submitted to the laboratory will depend on the monitoring objective(s). The suite of water quality variables presented in the Scope of this document (p. x) represent those that are typically measured on a routine, or periodic, and ongoing basis as part of long-term (e.g. State of the Environment, SoE) groundwater monitoring programmes.

There is considerable commonality in groundwater quality variables with those typically measured across the river (Part 2), lake (Part 3) and coastal water (Part 4) domains. Further alignment in variables between groundwater and surface water may be an important consideration where an integrated assessment of catchment water quality is a monitoring objective.

## 1.6 Monitoring Equipment

A list of the monitoring equipment that will generally be required is given in Annex C. The core equipment includes:

- an instrument (multivariable field meter) to measure water temperature, dissolved oxygen, specific conductivity and pH
- a pump, tubing, flow-through cell, sampling manifold and associated equipment for groundwater purging and sample collection
- field record forms to record visit metadata and field measurements, and sample bottles and cool, dark storage (e.g. chilly bin with slush ice).

A GPS receiver and a camera with geo-referencing capability may also be useful.

Portable submersible pumps (positive pressure or positive displacement) are recommended (e.g. bladder pump, positive displacement pneumatic pump) for purging and groundwater sampling. Peristaltic pumps, vacuum lift pumps and bailers are not recommended due to possible biases associated with them. However, provided other requirements of this Standard are satisfied (e.g. purging of a sufficient volume of water, stabilisation of field water quality variables), samples collected using these pumping systems will be satisfactory.

The pump, pump tubing and all other equipment that contacts the water sample shall, as far as practical, comprise materials that are inert with respect to the variables to be measured. In general, plastics made of fluorocarbon, polyethylene, polypropylene, PVC and silicone are suitable for the variables relevant to this Standard. The key exception is CFCs where either nylon or refrigeration-grade copper tubing is required.

Glass and stainless steel (all grades), if uncorroded, are both suitable for the inorganic variables relevant to this Standard.

It is essential that all equipment and devices are properly maintained and cleaned to avoid contamination of water samples.

## 1.7 Field Meters

Some groundwater quality variables (e.g. water temperature, dissolved oxygen, pH) need to be measured on site using field meters because they change rapidly once groundwater is removed from its natural environment. Stable measurements of these variables are also used to indicate when purging is complete and water samples can be collected.

### 1.7.1 Calibration and Validation

Regular calibration and validation of field meters are necessary because sensors, especially pH sensors, can drift and lose their calibration – even over the course of a day. The procedure involves adjusting a meter's settings so that the meter obtains an accurate measurement when its sensors are immersed in solutions with known values (referred to as 'standard solutions') of the variable of interest. In contrast, validation involves a check to ensure that there is no drift in sensor calibration.

This Standard requires all field meters to be calibrated and/or validated prior to a field visit and records of these procedures to be kept. Requirements and acceptance criteria for calibration and validation are outlined in subsection 3.1.

## 1.8 Sample Bottles

The type (e.g. plastic, glass) and size of sample bottles required will depend on the water quality variables of interest and associated laboratory analytical method. Sample bottles, including filling instructions, pre-treatment and preservation requirements, are summarised in Table 3, in subsection 5.4.3, for the water quality variables listed in the Scope of this document (p. x). It is recommended that a programme and laboratory-specific sample bottle guide is included in the Field and Office Manual. Where possible, plastic bottles should be used to reduce weight and potential for breakage. For some variables (e.g. DOC, CFCs), glass bottles are required.

New or suitably pre-cleaned sample bottles are required and are normally supplied by the analytical laboratory. It is usually possible for several variables to be measured from the same sampling bottle, provided the material, collection, preservation and transport requirements are the same (e.g. nutrient, anion and cation measurements may be performed from a single 500 mL bottle). However, *E. coli* and other microbiological indicators shall be measured on a separate sterile bottle collected on the same visit.

High-precision measurement of selected variables (e.g. tracers) may require a larger sample volume.

Due to the low cost-effectiveness of cleaning used sample bottles and increased capability for recycling, it is increasingly common to use new laboratory-rated sample bottles on each sampling occasion. Where sample bottles are reused,

bottles shall be scrupulously clean to avoid sample cross-contamination. The cleaning agent shall be selected with consideration for the future use of the bottle. Polyethylene bottles reused for nutrient testing should be cleaned with 10% chromic acid and then rinsed multiple times with distilled water.

### 1.8.1 Labels

All sample bottles shall be uniquely labelled as outlined in subsection 4.3.1. Waterproof labels are recommended to avoid labels coming off the bottles if they get wet. On-site labelling (in blue or black indelible ink) is also recommended to prevent accidental switching of pre-labelled bottles.

*Note: Use of customised sample bottle labels with pre-printed site names and numbers can reduce labelling time in the field.*

## 1.9 Sample Filtering

Once groundwater is removed from an aquifer, some key chemical variables (water temperature, pH and oxidation state) will rapidly change, which may induce precipitation (e.g. calcite or calcium carbonate, iron, manganese) (e.g. Rosen *et al*. 1999). Microbial activity may also alter groundwater chemical composition. It is therefore a requirement of this Standard to filter in the field any groundwater samples collected for dissolved nutrient, metal or trace element analysis. Filtration of a groundwater sample through a 0.45 µm pore size filter will separate particulate and aqueous fractions in the sample and remove micro-organisms. Specific details on field filtering are outlined in subsection 4.3.3.

## 1.10 Sample Storage and Transport

Labelled samples collected for laboratory testing should be placed in a storage/shipping container (e.g. chilly bin) promptly and not left exposed to sunlight where they may be subject to warming and photochemical degradation (subsection 4.6).

Firmly sealed samples should ideally be placed in an ice slush (ice equilibrated with water) inside the storage bin so that samples are evenly and quickly chilled (ideal temperature range between 4 and 10°C). Once the initial temperature has reduced, samples may be transferred to a separate holding bin with other chilled samples, and frozen slicker pads used to maintain the samples in a chilled state. The number of bins and amount of ice and chemical packs required will vary with season, the number of water samples collected and the size of available bins. It may be necessary to equip the sampling vehicle with a small fridge to ensure that the samples are kept below the desired storage temperature during summer conditions.

Chilly bins may need to be repacked with a fresh quantity of ice or frozen slicker pads before dispatch to the laboratory, especially in summer. Unless prior

arrangements have been made with the analytical laboratory, sampling should not be scheduled on Fridays or directly prior to public holidays, to ensure that the laboratory can receive and process samples promptly. In general, the shorter the time that elapses between collection of samples and their analysis, the more reliable the analytical results will be.

## 1.11 Chain of Custody

A completed Chain of Custody (CoC) form (Annex D) shall accompany water samples to provide an audit trail from sample dispatch (subsection 4.9) to sample arrival at the laboratory, and a record of sample condition on arrival at the laboratory (subsection 5.2). The CoC information shall be used to provide a quality assurance check on sample integrity (subsection 6.2.1.2).

*Note: Use of a customised CoC form with pre-printed sampler details, site names, site numbers and sample test requirements can reduce time spent filling out the form before sample dispatch.*

## 1.12 Managing Measurement Method Changes

Long-term monitoring programmes should ideally retain the same measurement methods and associated instruments to avoid the potential for 'step' changes which can arise when a change is made to either one of these. However, this is unrealistic, particularly with developments in methods and instrumentation over time.

If field meters or measurement methods need to be changed, there should be a period of duplicate measurement using both the old and new meters and/or methods. Monthly parallel measurements for a period of time (e.g. 12 months for a programme based on monthly sampling) is recommended to provide sufficient data to enable a conversion factor to be derived to 'align' the old and the new methods (or meters). Similarly, if laboratory analytical methods need to be changed, there may need to be a period of duplicate analyses using both the old and new test methods. This is discussed in more detail in subsection 5.7.

The exact measurement method used shall be linked with each sample result in the monitoring agency's database (see subsection 6.1.3) to allow for any potential 'step' changes in data to be tracked.

# 2 Monitoring Site Location

## In This Section

This section focuses on monitoring site considerations, specifically locating the point where field measurements and water sample collection will occur, and site metadata requirements. It also provides a brief overview of on-site health and safety considerations.

## 2.1 Groundwater Types

Groundwater may be confined, semi-confined or unconfined but in practice, the degree of confinement does not affect sample collection, only the time required for purging. For most unconfined aquifers, it is expected that winter water samples represent high water level conditions, whereas summer samples are more representative of low water level conditions. Note that springs and wells may run dry during the summer. Purging time and possible water level variations should be considered when planning the sampling trip.

## 2.2 Site (Point) Location

### 2.2.1 Spring

The optimum location for field measurements and water sample collection is as close to the spring outlet as is safe, where water is seen to move out of the ground. Where a spring creates a pool, it might be necessary to step into the water to get close to the rising spring water. Care should be taken on approaching the outlet as depth may be difficult to judge.

Field measurements and water samples should only be taken from where water is flowing.

### 2.2.2 Well

The monitoring point is the tap, fitting, hose or other such outlet from which water will actually be collected. Some wells may have more than one point where water can be accessed. In such cases, the most appropriate sample point should be selected and documented to ensure field measurements and water samples are collected from the same point in the future. An appropriate point is one that minimises purging time and potential for contamination or alteration of the sample.

A short length of clean hose (~2 m or less) can be connected to the tap or well head (e.g. to assist with maintenance of laminar flow), but the hose outlet should not touch the ground. The tubing may then be connected to a Teflon or other

chemically inert (e.g. brass) manifold in order to measure field variables (a flow-through cell is recommended) and/or fill more than one sample bottle at the same time. Alternatively, the tubing end may be used to directly collect samples.

Water samples should not be collected from a tap, fitting or hose that is corroded, leaking or otherwise in poor condition. Record any indication that the integrity of the site has been compromised (e.g. cracked concrete pad, well head allowing rainwater to enter the well) on the field record form, noting samples have not been collected.

To minimise the purging time, the sample point shall be located as far upstream as possible in the reticulation system, thus reducing the volume of water to purge through this system before samples can be collected. This also minimises the length of the sample delivery line, thereby reducing the risk that the sample could be altered in any way (e.g. due to depressurisation or exposure to light, heat or air). If a suitable sampling point is not present, seek permission from the well owner to install one on the well head.

### 2.2.3 Storage Tanks and Pressure Cylinders

Wherever possible, water samples shall 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, obtain the site owner's consent to isolate the tank or cylinder from the delivery line as described in Annex E. This will ensure that field measurements and water samples are not impacted by standing (possibly contaminated) water from the tank or cylinder.

## 2.3 Site Metadata

Site metadata shall be recorded, including:

- name of source aquifer (where known)
- site name and number
- site location; for example, GPS units or latitude/longitude coordinates expressed to a minimum of 6 decimal places
- site altitude
- start date of monitoring
- related sites and records, including the nearest weather station
- relevant environmental characteristics and features; for example, immediate land use within 10, 100 and 500 metres
- well/water use
- well protection details, including measurement of the top of casing relative to the ground
- well screen interval
- photographs of the site
- land owner/occupier contact details and, where relevant, associated procedures for accessing the site, and

- specific health and safety considerations.

Adequate mechanisms shall be put in place to store all relevant site-related metadata with the actual data records (see Section 6).

Site metadata shall be reviewed and updated as necessary, at least annually.

## 2.4 On-site Risk Assessment

Field personnel should carry out a rapid personal risk assessment upon arrival at the site. This assessment should be used to determine if:

- it is safe to carry out sampling and/or field measurements in the usual manner, or
- sampling and/or field measurements can only be attempted with suitable modifications.

If conditions are considered to make field measurements or sampling unsafe, they should not be attempted. Such conditions include adverse weather such as heavy rain or snow that make ground conditions hazardous. Record any health and safety issues on the field record form and update the Health and Safety Plan (subsection 1.2) as appropriate.

# 3 Field Meters

## In This Section

This section focuses on field meters, primarily field meter calibration, validation and maintenance requirements. Although information on field meters for measuring oxygen reduction potential (ORP) is included here, further information is required before quality codes can be assigned to measurements of this variable.

## 3.1 Field Meter Sensors, Calibration and Validation

Records shall be kept of field meter specifications, and calibration and validation details. An example calibration record form is provided in Annex F.

Calibration and validation solutions shall target the range of concentrations expected in the field (as indicated by historical records). All standard solutions should be used within the expiry date, with a small portion decanted for each calibration and used once to avoid contamination of the standards. Some solutions (e.g. pH buffers) may need to be kept in the dark.

Field meter sensors should be given sufficient time to equilibrate with standard solutions during calibration.

*The calibration and verification protocols outlined in this section were developed for traditional handheld sensors used in the environmental water quality domains. Instrumentation is improving and 'high quality' sondes may increasingly be used on a routine basis for "spot" field measurements; such instruments may require less frequent calibration and this Standard provides for the use of the alternative calibration/validation protocol provided in Annex G.*

*Note: If difficulty is experienced with calibrating or validating specific conductivity or pH sensors, a water sample can be collected for these measurements to be made in the laboratory.*

### 3.1.1 Water Temperature

Water temperature is best measured with a platinum resistance thermometer, of which a PT100 sensor is the most common type. Thermocouple and thermistor temperature sensors are also suitable.

This Standard requires a manufacturer's sensor accuracy of ± 0.3°C to be eligible for the highest quality code (QC 600). An accuracy of ± 0.5°C is acceptable as a lower quality measurement.

Recommended sensor calibration and validation practices are summarised in Table 1.

### 3.1.2 Dissolved Oxygen

Under this Standard, dissolved oxygen (DO), both percentage saturation and absolute concentration, shall be measured using:

- optical sensors, or
- galvanic or electrochemical (membrane) sensors used with a mechanical stirrer to ensure the velocity of water past the sensor always exceeds 0.3 m/s (see NEMS *Dissolved Oxygen*).

*Note: In practice, it can be difficult to measure the velocity of water past the sensor. For this reason, optical DO measurements are preferable to ensure eligibility for the highest quality code (QC 600).*

The manufacturer's sensor accuracy shall be:

- ± 3% in the 0 to 200% saturation range, and
- ± 0.3 mg/L in the 0 to 20 mg/L concentration range.

Recommended sensor calibration and validation practices are summarised in Table 1.

To take a DO measurement, the meter's sensor first measures the partial pressure of oxygen. The sensor then calculates the percentage DO saturation with corrections for temperature, barometric pressure and often specific conductivity. DO concentration, then, is determined based on temperature.

Dissolved oxygen readings shall be corrected to barometric pressure. Barometric pressure correction is built into most handheld DO meters but care is needed when using sensors that do not have barometers built in (e.g. sondes designed for continuous water quality monitoring). If barometric pressure is not built in, raw barometric pressure (i.e. not corrected to sea level) shall be measured at every site using a handheld barometer for a manual calculation to be performed (or at a nearby site with altitude correction applied). Refer to the NEMS *Dissolved* Oxygen (continuous measurements) pressure correction tables or:

$$DO\%\ Saturation_{LOCAL} = DO\%\ saturation_{RAW} \times Barometric\ pressure \div 1013.25$$

*Where:*

- *Barometric pressure is measured in hPa (equivalent to millibars)*
- *1013.25 is one standard atmosphere at sea level in hPa*

Barometric pressure ($P_{atm}$) change with altitude ($h_{alt}$) is given by:

$$P_{atm} = 1013.25 \times (1 - 2.25577\ 10^{-5}\ h_{alt})^{5.25588}$$

Therefore, at an altitude of 400 m, the pressure is 95% of sea level, and at 1000 m, saturation DO is 87% of the sea-level value.

*Note: Some meters can display corrected DO or uncorrected DO. When the handheld has a barometer attached, it is important to check that the meter is reporting the*

*corrected DO (some instruments call this 'Local DO%' and this is what you should set your meter to read).*

### 3.1.3 Specific Conductivity

Specific conductivity (SpC) in this Standard is the measurement of electrical conductivity corrected to a reference water temperature of 25°C. The manufacturer's sensor accuracy shall be ± 1 µS/cm or ± 0.5% for full scale error.

*Note: Conductivity is always referenced to a standard temperature. This NEMS specifies 25°C. Some meters allow you to change the temperature standard, and it is possible to purchase calibration solutions to other standards. Correction to 25°C (the most commonly used correction temperature) was selected for national consistency.*

Recommended sensor calibration and validation practices are summarised in Table 1.

If the sensor includes a temperature correction function, check that this function is working properly before leaving the office by:

- calibrating the sensor using a standard solution kept at room temperature that has a conductivity value higher than that expected in the field
- checking the instrument is set to compensate for temperature (i.e. typically an option of 'SP Cond' or similar will be displayed by the instrument), and
- validating the calibration by placing the sensor in a prepared calibration solution that is close to the measurement range expected in the field.

If the sensor lacks a temperature correction function, or if the temperature correction function is not working correctly, then the sensor should be calibrated at each site prior to sampling, using standard solutions at the expected water temperature.

*Note: In practice, this may be difficult to do, so measurement on a water sample(s) submitted to the laboratory is preferable.*

At the minimum under this Standard, field validation shall be repeated once at the end of day using a standard solution with a SpC value similar to values measured in the field. If validation fails, this will impact on the quality coding assignment for all SpC measurements collected across the course of the day.

If a field meter sensor is being used at both freshwater and saline sites on the same day, a conductivity standard around 12,880 µS/cm is recommended for validation purposes. The accuracy of conductivity measurements that are taken from very clean freshwaters or very saline waters may be compromised unless the sensor is validated specifically for these sites. Therefore, a different sensor for fresh and saline waters is preferred.

### 3.1.4 pH

This Standard recommends pH measurements using an ion-specific electrode (ISE) glass sensor. The manufacturer's sensor accuracy specification shall be ± 0.2 pH

units. Field pH measurements shall be corrected to a reference water temperature of 25°C.

*Note: pH is always referenced to a standard temperature. This NEMS specifies 25°C. Some meters allow you to change the temperature standard, and it is possible to purchase calibration solutions to other standards. Correction to 25°C (the most commonly used correction temperature) was selected for national consistency.*

Recommended sensor calibration and validation practices are summarised in Table 1.

If the sensor includes a temperature correction function, check that this function is working properly before leaving the office by calibrating the sensor using a standard pH buffer solution kept at room temperature.

If the sensor lacks a temperature correction function, or if the temperature correction function is not working correctly, then the sensor should be calibrated at each site prior to sampling, using standard solutions at the measured local water temperature.

*Note: In practice, this may be difficult to do, so measurement on an air-tight water sample(s) submitted to the laboratory may be necessary.*

End-of-day validation is a requirement of the Standard as pH sensors are prone to drift. If this validation fails, this will impact on the quality coding assignment for all pH measurements collected across the course of the day.

### 3.1.5 Oxygen-Reduction Potential (ORP)

ORP is usually available as part of a combined pH sensor. It is measured as the voltage (difference in potential) between a chemically inert (platinum) electrode and a reference electrode of the pH sensor. Sensor accuracy should be within ± 20 mV.

ORP is a non-specific measurement that represents the net status of all the oxidation and reduction reactions in the water. The measured potential is reflective of a combination of the effects of all the dissolved redox-active species in the water; for example, the salts of many metals and strong oxidising (chlorine) and reducing (sulfite ion) agents.

ORP measurement results are relative to the reference electrode used in the sensor. This means readings from two ORP sensors measuring the same solution will often be different if the sensors use different reference electrodes. Through known relationships, measurement values can be converted to other reference electrode systems.

ORP shows an inverse relationship with water temperature which should be accounted for when calibrating the sensor.

Sensor calibration and validation practices will be instrument-specific. General good practice recommendations are summarised in Table 1.

**Table 1: Summary of recommended calibration and validation practices for selected water quality variables measured in the field**

| Field meter/ variable | Calibration | Validation |
|---|---|---|
| Water Temperature (Temp) | Factory calibrated. If validation fails, replace or repair sensor. | 12-monthly validation checks against two traceable reference thermometers in accordance with the NEMS *Water Temperature* (involving at least a 5-point validation process with measurements made across a temperature range of −5 to 50°C). Replace sensor if validation fails.<br>*Note: The annual check is the minimum requirement and has been set by* the NEMS *Water Temperature; 5 data validation points reflects the non-linear temperature calibration. More frequent (e.g. quarterly) 2-point validation is recommended.* |
| Dissolved Oxygen (DO % Sat & DO) | Single-point calibration using 100% saturated air or water on each sampling day in the office before use if validation fails.<br>Whenever the sensor cap or membrane is replaced, perform a 2-point calibration using firstly 100% saturated air or water and secondly 0% saturation (the latter via nitrogen gas or sodium sulphite ($Na_2SO_3$) to remove the oxygen. (Use of a calibration chamber can assist when using gas.)<br>No field measurements should be made for 2 hrs after a 0% calibration with $Na_2SO_3$has been performed. | Validation on each day of use before you leave the office with 100% saturated air or water. Validation passes if the measured value is within ± 0.5%.<br>If validation fails, calibrate the sensor.<br>*Note: It may take up to 30 min for the calibration cup to become fully saturated. Tip: Leaving the sensor in a moist cup overnight (with meter off) may help. Also store the sensor with a damp sponge.* |

*Continued on next page…*

| | | |
|---|---|---|
| Specific Conductivity (SpC) – field<br><br>(and Total Dissolved Salts) | Calibrate sensor monthly using a standard higher than the concentration in the water to be measured (around 1414 µS/cm) then revalidate in a standard solution range close to the expected measurements (~148 µS/cm). Validation passes if within 15% or between 126 and 170 µS/cm.<br><br>Clean the sensor, recalibrate or change the standard solution if calibration fails. | Validation on day of use before you leave the office with standard buffer solutions. Validation passes when the measurement is within:<br>• standards < 10 µS/cm: ± 25%<br>• standards ≥ 10 and < 200 µS/cm: ± 15%<br>• standards ≥ 200 µS/cm: ± 5%<br><br>If validation fails, calibrate the sensor using a standard higher than the concentration in the water to be measured (around 1414 µS/cm) then revalidate in a standard solution range close to the expected measurements; for example, ~148 µS/cm passes if within 15% or between 126 and 170 µS/cm. Clean the sensor, calibrate again or change the standard solution if it doesn't pass.<br><br>At the minimum, field validation should be repeated once at the end of day in a standard solution of 148 µS/cm. If validation fails, adjust the quality coding assignment for all SpC measurements collected across the course of the day (see Section 6). |
| pH<br>(pH – field) | A 2- or 3-point calibration on each sampling day before use with laboratory-prepared standard buffer solutions of pH 7, 4 and 9 or 10 (to cover the range of expected field measurements). One of the calibration points needs to be pH 7.<br><br>A 3-point calibration is considered best practice. This is important where measurements taken during a sampling run are expected to vary widely (e.g. in the range 7-9). | Perform a validation check using the pH 7 solution at least once at the start and end of the day. To pass validation, pH should be in the range ± 0.2 pH units of the temperature-adjusted pH solution (record temperature).<br><br>Also record the millivolts (mV) which provide an indicator of sensor condition. At pH 7, the mV should be 0 with a tolerance range (changes with temperature) as per the manufacturer's specifications (typically ± 35–40 or 60 for EXO-sondes). If outside the accepted mV range, replace the electrolyte solution (where possible), the sensor or part of the sensor (e.g. reference junction, glass bulb).<br><br>pH measurements drift so end-of-day validation is important. If this validation fails, adjust the quality coding assignment for all pH measurements collected across the course of the day (see Section 6). |

*Continued on next page…*

| | | |
|---|---|---|
| Oxygen Reduction Potential (ORP) | Single-point calibration of the pH sensor (used as a reference for the ORP electrode), after pH calibration, on day of use using a standard solution recommended by the meter's manufacturer (typically ZoBells solution at 223–233 mV). Calibration passes if the measurement is within ± 30mV at a reference temperature of 25°C. | Validate at end of day in the same standard solution used for calibration. |

## 3.2 Field Meter Maintenance

Maintenance of field meters and associated sensors is critical for accurate measurements. Inadequate maintenance is a key reason why sensor calibration or validation may fail. Inadequate maintenance can also slow sensor stabilisation time (e.g. pH sensors if the electrolyte solution in the reference junction and/or the glass bulb are not maintained as required).

Field meters shall be maintained in accordance with the manufacturer's instructions. This may include at least an annual service of the meter and replacement of sensors. Table 2 outlines good maintenance practices for field meters used to measure selected water quality variables.

It is important not to use standard solutions after they have expired and avoid using solutions more than once. Sensors should be rinsed in used standard solution before a fresh solution is used for validation/calibration.

**Table 2: Summary of good maintenance practices for field meters used to measure selected water quality variables**

| Field meter/ variable | Maintenance |
|---|---|
| Dissolved Oxygen | Daily rinse/wipe down of the sensor after use. Store the sensor with a damp sponge to maintain a fully saturated environment ahead of calibration/validation.<br><br>For optical sensors, replace sensor cap as per manufacturer's recommendations (likely to be no more than 2-yearly). May need to re-load into the meter the sensor membrane coefficients supplied with the sensor cap.<br><br>For galvanic or electrochemical sensors, check the integrity of the membrane before each use. Change membrane 3–6 monthly and sand the anode to remove oxide build-up.<br><br>As best practice, regardless of sensor type, perform a 2-point calibration every 6 months as part of regular maintenance. |
| Specific Conductivity | Clean daily in water, or as required, checking cells for no debris, etc. Most sensors are supplied with a small brush or swabs to assist with cleaning. |
| pH and ORP | Rinse daily, carefully wiping the glass bulb with a sponge or swab as needed.<br><br>Monthly maintenance on top of routine calibration and validation. Keep sensor clean and moist. Place sensor in potassium chloride (KCI) or pH 4 buffer solution if storing for > 30 days. Track mV records to know when to replace solutions or sensors. Sensors often only last a year.<br><br>Reference junctions often only last 9 months on sensors. It is important to monitor the mV in pH 7 buffer to help determine the state of the electrolyte solution. If the mV reading is outside of the manufacturer's specification, the sensor is no longer meeting the accuracy specified by the supplier and the electrolyte solution must be replaced. |

## 3.3 Field Meter Measurement Records

Section 4 addresses groundwater field measurements in detail. The following notes apply to recording of field meter measurements:

- The equipment used to make field measurements shall be recorded on the field record form (see subsection 4.4). For field meters, this shall include meter make and model, and a unique identifier for the specific instrument(s) used; for example, serial number, assigned number.
- Records of DO measurements shall be corrected to barometric pressure and altitude (and salinity where relevant).

- For ORP measurements, the water temperature and reference electrode shall also be recorded to facilitate comparisons between measurement results.
- Field meter measurements shall be recorded at the following resolution:
    - Water temperature: 0.1°C
    - Dissolved oxygen – saturation: 0.1%, corrected to barometric pressure
    - Dissolved oxygen – concentration: 0.01 mg/L, corrected to barometric pressure
    - Specific conductivity: 0.1 µS/cm
    - pH: 0.01 pH units.

# 4 Field Measurements and Water Sample Collection

## In This Section

This section focuses on groundwater field measurements and sample collection. This includes purging, sample bottle filling, sample filtering, visit metadata, cleaning of field meters and sampling equipment upon completion at the site, and sample transport and handling.

## 4.1 Purging

All wells shall be purged prior to sampling to remove the standing water and replace it 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.

Low-flow sampling may be required for low-yielding, small-diameter wells (see subsection 4.1.5). Manual bailing may also be used but is a less preferable method.

The steps to purging are outlined further below and shall be followed unless:

- the sample collection interval is sealed with packers to perform sampling or pump testing
- drawdown occurs rapidly but recovery to approximately 90% cannot be achieved during the first, second or third bail before water samples are collected, or
- a purge minimisation device or a low-flow purging technique is used.

### 4.1.1 Depth to Water Measurement

Measurement of the depth to water in the well under ambient (non-pumped) conditions is required to calculate the volume of water to be purged (and for general interpretation of water quality data from the site). However, at some sites access to the well may be poor, preventing measurement of the depth to water. In such cases, the purging volume should be calculated assuming the well is full.

For non-artesian conditions, depth to water shall be measured using a dip tape, according to the manufacturer's instructions (Figure 1). Record a description of the datum from which the measurement is made (e.g. ground level or the top of the well casing). The same measuring point shall be used each time the water depth is measured.

Guidance on groundwater level measurements is provided in NEMS *Water Level.*

**Figure 1 – 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**

Photograph: Environment Canterbury.

It is possible to measure artesian groundwater pressure with a pressure gauge or a transparent pipe (Figure 2).

**Figure 2 – Artesian head can be measured using a clear tube and a staff gauge**

Photograph: Environment Canterbury.

Where possible, measure the depth to water in the well under ambient (non-pumped) conditions. If the pump is running, measurement of depth to water may not represent ambient conditions.

*Note: Groundwater monitoring wells that have a cap can sometimes be under pressure due to an increase in piezometric surface elevation, artesian conditions, etc. This can lead to rising water levels in the well when depressurised. In this situation, it is advisable to take measurements at a couple of intervals subsequent to opening the well to verify that the water level has stabilised.*

### 4.1.2 Calculation of the Purging Volume

The purge volume is equal to the volume of water in the well under ambient (non-pumping) conditions:

$$Purge\,Volume = 3.14 \times [well\ depth - depth\ to\ water][well\ radius]^2 \times 1000$$

Note that:

- All measurements are expressed in metres (m).
- The purging operation requires extraction of at least three times the calculated purge volume.
- If the depth to water under ambient (non-pumping) conditions cannot be determined for any reason, either assume 'depth to water' = 0 in the equation above or use historical water level measurements at the well or a nearby well screen at a similar depth.
- Well depth, depth to water, and well radius shall 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 the purge volume cannot be calculated. In this case, an approximate purge volume shall be determined by overestimating the likely depth of the well; for example, an estimate of maximum likely well depth can often be obtained by examining the drilling logs of nearby wells.

### 4.1.3 Purging Operation

If the well is not equipped with a dedicated pump, a portable pump (or bailer in small wells) shall be used to purge the well and collect the groundwater sample.

The portable pump should be used in accordance with the manufacturer's instructions. The pump shall be positioned so that its intake is at least 1 metre below the static water level and a minimum distance above the top of the screened/open interval of 10 times the well diameter (e.g. 1500 mm for a 150 mm well diameter). It may be installed at the mid-point of the screened interval. 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. A dip tape or other water level sensor placed in the well will permit measurement of the water level during purging.

### 4.1.4 Pumping

Upon arrival at the site, if the well is equipped with a dedicated pump that has been running continuously and for long enough to have removed one purge volume of water, record the time and date of arrival on site and proceed to collection of field measurements. 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.

Best judgement should be used to determine the pumping rate, giving consideration to 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 (Figure 3).

**Figure 3 – A suitable pump rate will ensure laminar flow from the outlet point (left); aerated flow (right) is not appropriate**

Photographs: Daughney *et al*. (2006).

Recommended pumping rates during purging are 0.1–1 L/min. Pumping should not be halted during purging, and the pumping rate should be kept constant throughout purging. If the pumping rate must be changed, it should be changed gradually, taking care not to create turbulence.

The pumping rate needs to be determined during purging by recording the time required to fill a container of known volume (e.g. a 10 L bucket) or, if the site is fitted with an in-line flow meter, by recording changes in the flow meter readings over time. With either approach, the measurements shall be repeated on at least three separate occasions during purging and recorded.

If possible, the water level in the well should be continuously monitored throughout the purging operation. Values of drawdown shall be recorded on at least three separate occasions during purging, and again immediately prior to collection of water 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 reduced appropriately, where possible and practical.

### 4.1.5 Low-flow Purging

Low-flow purging and sampling is a specialised technique that is only appropriate where the following criteria can be met:

- the well head is secure, sealed to prevent surface water and rain water infiltration
- the well construction details are known, including screen interval
  *Note: This rules out dug wells and brick-lined wells without a proper screen)*
- static water level and drawdown can be measured during purging and sampling
- the pump intake is within the screen interval
- a variable-rate, low-flow pump is used
- drawdown, pH, specific conductivity, water temperature and DO are measured during purging (ORP and turbidity measurements are optional)
- field variables are measured in a flow cell, and
- the water sample is collected at the well head.

#### 4.1.5.1 Procedure

- Measure and record the initial water level in the well
- Install the pump – lower the pump as gently as possible to minimise disturbance of the standing water column
- The pump intake must be within the screen interval of the well
  *Note: It is recommended that the pump intake is at the mid-point of the screen or, if the initial water level is within the screen interval, then the pump intake should be at the midpoint between the bottom of the screen and the initial water level.*
- Record the position of the pump intake
- Measure and record the water level after the pump is in place to ensure that it has returned to the initial level)
- Purge the well at a low pumping rate until the water level in the well stabilises
  *Note: The water should be clear under low-flow purging. If this is not the case, the well has likely not been properly developed.*
- Maintain drawdown of the water level at less than 0.1 m
  *Note: If this is not possible, a drawdown up to 1 m is acceptable if the water level stabilises.*
- Record the flow rate and the stabilised drawdown level
- Measure, as a minimum water temperature, specific conductivity, DO and pH every 5 minutes until stable. At least one flow-through cell volume should be exchanged between measurement readings or the time interval between readings should be increased, and
  *Note: Water temperature, specific conductivity, DO and pH should be measured on four separate occasions, with the differences between the last two*

*measurements falling within the stabilisation limits outlined in subsection 4.1.6. Of these variables, DO is the most likely to change with purging.*

- Ensure that the final purge volume is at least the total volume of water in the pump and tubing, plus the volume of the drawdown in the well. Record the total purged volume.

### 4.1.6 Field Measurements

This section focuses on field measurements from wells during purging. For springs, deploy the field meter in the main flow before making your field observations (see subsection 4.4) and read after making these observations to allow time for the reading to stabilise. This may take at least 10 minutes or more depending on the measurements being made.

#### 4.1.6.1 Water Temperature, Specific Conductivity and pH

Water temperature, specific conductivity and pH shall be measured during purging in order to assess the completeness of the purging operation. Values of all three of these field variables shall be recorded at least four separate times during purging. The first measurement shall be made as soon as possible after the initiation of pumping. Subsequent measurements should be made at intervals corresponding to the time required to extract at least one purge volume from the well (i.e. the second, third and fourth sets of field measurements are made after extraction of about one, two and three purge volumes, respectively).

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 L plastic bucket (Figure 4). In either case, the field meter sensors and the water inlet should be placed as low as possible inside the container, and water allowed to continuously flow out, or overflow from, the container or flow cell. The flow of water past the sensors should be continuous and laminar. The flow rate through the flow cell or open container shall 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 water to be sampled.

*Note: Placement of sensors in a bucket for the collection of field measurements is not recommended. Greater consistency is achieved in field measurements when a flow cell is used – measurements such as DO should be made in flowing water, preferably with an optical sensor (refer subsection 3.1.2).*

**Figure 4 – Water from the pump outlet can be passed through an open container (left) or a flow cell (right)**

Photographs: Daughney *et al*. (2006).

#### 4.1.6.2 Other Field Variables

Measurements of other field variables, such as dissolved oxygen (DO) or ORP (also turbidity – not covered in this Standard), are additional variables that can be used to assess the adequacy of purging. However, it is not a requirement of this Standard to use these variables.

### 4.1.7 Purging Assessment

The purging operation is complete once three purge volumes have been extracted and 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
- water temperature, specific conductivity and pH have been measured on at least four separate occasions, with the differences between the last two measurements falling within the following limits:
  - water temperature: ± 0.2°C, and
  - specific conductivity: ± 3% (± 5% if < 100 µS/cm at 25°C), and
  - pH: ± 0.1 pH unit.

Continue the purging operation by making measurements after extraction of each purge volume until simultaneous stabilisation of all three field variables is achieved. Once the criteria have been met, record the time that stabilisation was achieved, and record the field measurements as final values. Record on the field record form if the purging criteria cannot be met, even after prolonged pumping.

The following stabilisation criteria are recommended if DO and/or turbidity are also monitored to assess adequacy of purging:

- dissolved oxygen: ± 0.3 mg/L, and
- turbidity: ± 10%.

## 4.2 Sample Collection Point

All groundwater samples shall be collected directly from the pump outlet, sample point, a manifold device, or outlet of a short length (~2 m or less) of clean tubing attached to the sample point. The pump should be left running continuously during sampling.

## 4.3 Sample Bottles and Filling

Sample bottle, volume and filling requirements depend on the water quality variables of interest (see Table 3 in subsection 5.4). An air pocket facilitates mixing before sub-sampling and is crucial for testing some variables (e.g. *E. coli*) while complete isolation of air is critical for testing of other variables (e.g. alkalinity, tritium, radon). Ensure that sample bottle caps are tightly sealed after filling.

When sampling involves multiple bottles, the order in which the samples are collected is not important. However, if a metallic fitting is used, microbial samples should be collected after all other samples.

Sterilisation of the pump, pump tubing, dip tape or other equipment used during sample collection for microbiological analysis is recommended but not a requirement of this Standard. Metallic fittings are suitable for sterilisation by flaming. Sterilisation of the sample point using a bleach or ethanol solution is not recommended.

*Note: Sterilisation of the sample point requires the pump to be turned off briefly.*

If sampling equipment is not sterilised prior to collection of microbial samples, collection of equipment blanks is recommended.

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 avoid vehicle fumes and other potential sources of contamination close to the sample point. If samples are being collected for tritium analysis, ensure that field personnel are not wearing a luminous watch – the light source of some of these watches is tritium and may contaminate the sample.

If the collected sample is potentially compromised in any way, record this on the field record form.

<u>Unpreserved bottles</u>

Rinse three times in the water to be sampled before collecting the final sample volume. If a sample is collected for laboratory pH measurement, ensure that the sample is air-tight.

<u>Unpreserved sterile bottles (for microbiological testing)</u>

Fill without rinsing and avoid contact with the inside of lid and bottle. Leave a small ~1 cm air gap at the top to facilitate re-mixing at the laboratory.

Preserved bottles

Fill bottles containing acids or other preservatives slowly to avoid overfilling (or fill from another larger unpreserved collection bottle that has been rinsed at least twice in the water to be sampled). Fill to the neck, cap the bottle and invert gently to mix.

*Note: Immersing or overfilling of bottles containing preservatives will displace the preservative and affect the integrity of the sample.*

### 4.3.1 Bottle Labels

All sample bottles shall be uniquely labelled with, at the minimum, the site name and site code (or sample number), sample date and time, and sampler's name.

### 4.3.2 General Bottle Filling Procedure

#### 4.3.2.1 Springs

When filling sample bottles, avoid any surface microlayer that is potentially present and may not be visible; for example, bacteria and nutrients, as well as hydrophobic compounds, foams and floatable scums, may be concentrated at the water surface. Also take extreme care to avoid disturbing bottom sediments during sample collection.

The following procedure shall be used for filling all **unpreserved** water sample bottles (illustrated in Figure 5):

1. Prior to immersion in the water, remove the sample bottle cap taking care to avoid touching the underside of the cap or the neck threads of the sample bottle.
2. Facing upstream, fill the sample bottle after rinsing at least twice with spring water.
3. Submerge bottle with the opening pointing straight down.
4. At the desired depth (~0.2 to 0.3 m), gently tip the bottle up into the flow, allowing air to escape and water to enter the bottle (this avoids entrainment of material on the water surface into the bottle).
5. Secure bottle cap under water then remove to an iced container for storage.

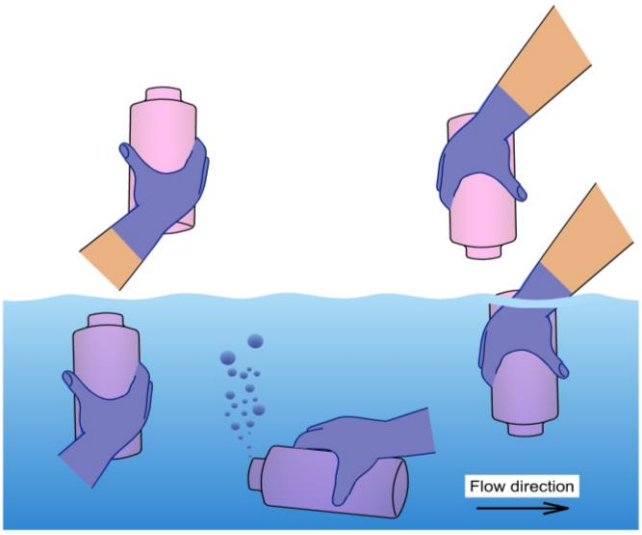



**Figure 5 – Sampling technique for unpreserved sample bottles**

*The sample bottle is gently dipped upside down into the water. Turn towards the spring flow. Hold for 3 seconds. Turn upwards and lift out of the water.*

Source: Modified from Hébert and Legare (2000, Octobre).

#### 4.3.2.2 Wells

It is recommended that the pumping rate during sampling is the same as the pump rate during purging. If the pump rate must be decreased after purging, it should be decreased gradually, without causing turbulence. An indicative rate suitable for filling bottle is 0.1 to 1 L per minute, which is too slow for standard purging. A flow-splitter may be used to control the flow into the sample bottle.

All sample bottles should be filled quickly but carefully to prevent aeration and entrapment of air bubbles (Figure 6). 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.

**Figure 6 – Filling a sample bottle**

*Note the tilting and laminar flow.*

Photograph: Daughney *et al*. (2006).

#### 4.3.2.3 Samples in Complete Isolation from the Atmosphere

Water samples requiring complete isolation from the air (e.g. for radon, CFC or $SF_6$ analysis) shall be collected by connecting a nylon tube to the sample point or directly into the water supply pipe. Fill the sample bottle slowly and smoothly from the other end of the tube until all air has been displaced and water overflows from the bottle (Figure 7). Alternatively, fill a glass or stainless-steel container large enough to permit complete immersion and capping of the sample bottle under water. 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. 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.

**Figure 7 – Collection of a water sample in isolation from the air**

*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*

Photograph: Daughney *et al*. (2006).

### 4.3.3 Sample Filtration

As outlined in subsection 1.9, filtration to 0.45 µm upon sample collection is required to separate particulate and aqueous fractions of a water sample and to remove micro-organisms when samples are collected for dissolved metal or trace element analysis.

Filtration can be carried out using either a syringe and syringe-tip filter or with an in-line cartridge filter; either filtration method will produce the same results. Cellulose acetate filter membranes are recommended.

*Note: If for some reason field filtering is not possible, or surface springs are sampled, unfiltered sample bottles shall be filled completely, removed from the light, chilled and freighted promptly to the laboratory to enable laboratory filtering to be completed within 36 hours of sample collection.*

#### 4.3.3.1 Syringe-tip Filter

Filtering should be performed using a plastic (polyethylene, polypropylene or similar, 50–100 mL capacity) syringe and 0.45 µm filter (Figure 8).

1. Fill and discharge the syringe with sample point water on three occasions before refilling the syringe.
2. Attach a clean filter on the end of the syringe, avoiding contamination of the syringe and filter outlets from fingers, and discharge approximately 20 mL of water from the syringe to waste in order to field-rinse the filter.
3. Depress the syringe plunger to push the remainder of the sample through the filter into the appropriate sample bottle, taking care to avoid contamination of the threads and inner surfaces of the bottle and cap.


**Figure 8 – Typical syringe and 0.45 µm disposable filter**

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

Photographs: Daughney *et al*. (2006).

If the syringe must be refilled or filter replaced during sampling, take care to ensure 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. When refilling the syringe, place the filter in a clean location; for example, back into the packing material it was supplied in.

#### 4.3.3.2 In-line Filter

The filtering procedure is similar to that using a syringe. Affix an in-line filter to the sample point using fittings and tubing as required (Figure 9). Ensure your

hands and any other sources of potential contamination are kept away from the tubing and the inlet and outlet of the filter. Before filling the sample bottle, field-rinse the filter by allowing approximately 100 mL of water to pass through the filter cartridge to waste.

**Figure 9 – An in-line filter attached to the sample point using clean tubing**

Photograph: Daughney *et al*. (2006).

## 4.4 Visit Metadata (Observations)

A standard form shall be used to record field metadata (observations) on each visit to the site to collect field measurements and water samples. This form shall include:

- the site location
- the sample site name and number (e.g. GW335, Tom Morrison's well)
- any unique sample ID number assigned
- the name(s) of the field personnel
- information on field measurements made at specific locations
- date and time (in NZST) of field measurements
- the point of sample collection (e.g. outlet tap 2)
- protocols used, including any deviations from standard field measurement and/or sampling protocols or if there were any difficulties with calibration/validation of field meters or sample collection
- the weather conditions at the time of measurements
- if there is any notable or unusual appearance or smell
- general sample colouration (clear/colourless, turbid or brown)
- confirmation that samples were field filtered, and
- notes of any other site-related factors that may influence the data being collected (e.g. integrity of bore/well head) or significant changes in adjacent land use (e.g. stock effluent application in vicinity of well/bore).

An example field record form is provided in Annex B. A photograph of the site can provide useful additional metadata.

## 4.5 Site and Visit Identifiers

Each field measurement and water sample shall be referenced against existing unique identifiers for the monitoring site and the sampling event. This ensures that field and laboratory measurements can be related to each other. Therefore, organisational conventions for site identifiers and sampling event identifiers shall be maintained and recorded as metadata for each field measurement and water sample.

## 4.6 Time Records

The timing of field measurements and sample collection shall be recorded as a single site visit time to the nearest 5 minutes. This visit time shall be the time at which the final field meter measurements are recorded. It is recommended that arrival and departure times at a site are also recorded on the field record form so as to bracket other activities on site (e.g. purging, water sampling) that take finite time to conduct.

All times shall be recorded in New Zealand Standard Time (NZST). Accurate time recording can be assured using a device that is regularly synchronised with reference time; for example, a smartphone or smartwatch.

## 4.7 Finishing at the Site

Sampling equipment should be properly cleaned before departure from each site to avoid sample contamination and cross-contamination between sites. All pumps, pump tubing, dip tapes, flow cells and similar equipment should be thoroughly rinsed with water immediately after sampling, then wrapped and transported in clean plastic bags. If the sampling gear is visually dirty or muddy, then distilled water should be used as rinse water. Visually inspect the pump and tubing for signs of corrosion and wear; for example, this is possible if the water is very saline or has a high sulphide content.

## 4.8 Sample Transport and Handling

To maintain sample integrity for subsequent laboratory testing, sample bottles shall be removed from the light, chilled (using an ice slush) and freighted promptly (preferably within 24 hours) to the laboratory for processing within 36 hours. If that is not possible, interim refrigeration (but not freezing) is recommended. Exceptions include samples that have already been stabilised through filtering and/or the use of sample bottles containing acid preservatives.

In summer, repack chilly bins with a fresh quantity of ice or frozen slicker pads before dispatch to the laboratory to ensure samples remain chilled during transportation.

*Note: Daughney et al. (2006) demonstrated that at least five frozen chemical packs or at least 3 kg of ice (i.e. one typical service station size bag) are needed for chilling water samples in a 20–40 L capacity chilly bin. To maintain sample temperatures within the target range, 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 sampling day.*

Place samples in individual, sealed, water-tight plastic bags. Ensure the samples are carefully packed to avoid damage during shipping and stored upright (vertical) in the bin. Care shall also be taken to avoid icing inside sterile sample bottles which might compromise microbial measurements. These bottles may be wrapped in bubble wrap for protection (Figure 10).

Each packed chilly bin weight should not exceed 25 kg to meet courier acceptance criteria. Record the courier ticket number(s) on the field record form to assist with prompt tracing of any chilly bins lost or delayed in transit to the laboratory.

**Figure 10 – Examples of chilly bin packing**

*Chilly bins should be packed with at least five frozen chemical pads (top right) or 3 kg of ice (bottom). Too few pads (top left) will not keep the samples below 10°C. Overnight couriering requires the chilly bin to re-packed with ice. Chilly bins also may be packed with frozen chemical packs and bubble wrap.*

Photographs: Andrew Yuill.

## 4.9 Chain of Custody

A Chain of Custody (CoC) form (Annex D) shall be completed and inserted (within a sealed waterproof bag) inside the chilly bin. As a minimum, the CoC shall include:

- the date and time of sample collection and dispatch
- if water samples have been filtered
- the laboratory tests required (if not already pre-printed on the form)
- anything unusual about the samples, if relevant (e.g. possible saline influence), and
- the name of the person dispatching the samples.

If more than one chilly bin is dispatched, either place a copy of the CoC into each bin or include a waterproof note confirming the number of bins and which contains the CoC (e.g. “Bin 2 of 2 – see CoC in Bin 1”).

# 5 Laboratory Measurements on Water Samples

## In This Section

This section focuses on activities undertaken in the laboratory. It addresses laboratory certification, receipt of water samples at the laboratory, sample preparation (filtration and dilution), test methods, reporting, quality checks and managing changes in test methods or laboratories.

## 5.1 Laboratory Certification

Under this Standard, water samples shall be tested at a laboratory accredited by International Accreditation New Zealand (IANZ) for each test method to ensure that the laboratory has appropriate quality practices in place to provide reliable results.

IANZ is an independent organisation which operates under its own Act of Parliament and audits laboratories against NZS/IEC/ISO 17025. An experienced auditor from IANZ visits accredited laboratories accompanied by one or more technical experts. The IANZ representative audits laboratory management and record keeping, staff training, calibration of equipment, internal audits, etc. The technical expert audits laboratory methods and ensures the staff carrying out the testing are following the documented test procedure and are knowledgeable about what they are doing.

*Note: Further information about IANZ can be found at www.ianz.govt.nz, and the accreditation status of each laboratory and their test methods found using the 'Directory' tab.*

## 5.2 Sample Receipt

Water samples shall be registered for testing on arrival at the laboratory. This shall include completion of the CoC form (Annex D) that accompanied the samples and prompt (same day) return of this form to the sampling agency with a laboratory reference or job number.

### 5.2.1 Date and Time of Arrival

Laboratory staff shall record the date and time (in NZST) of samples on arrival at the laboratory and record this on the CoC.

### 5.2.2 Sample Temperature and Condition on Arrival

Laboratory staff shall measure the temperature of samples on arrival at the laboratory (e.g. through the use of a calibrated dual beam infrared thermometer or 'laser gun' inside each chilly bin) and record this on the CoC. Laboratory staff shall also inspect the condition of samples and record any anomalies on the CoC and in their sample notes for inclusion in reporting of sample test results (see subsection 5.5). For example, this shall include:

- damaged or incorrect sample bottles for the variables of interest
- unsatisfactory filling procedures (e.g. large head space in unpreserved samples), and
- frozen or partially frozen samples.

## 5.3 Sample Preparation

### 5.3.1 Filtration

Where required (e.g. for soluble inorganic nutrients and dissolved metals where samples were not field filtered), filtration to 0.45 µm shall be carried out on unpreserved samples on the day of sample arrival at the laboratory.

### 5.3.2 Acid preservatives

For some variables (e.g. total phosphorus), the laboratory may add acid to water samples on the day of receipt to preserve the samples prior to analysis.

### 5.3.3 Dilution

There are two cases where dilution may be required to obtain a measurement:

1. when the measured sample concentration is expected to be outside the range for which the test equipment may be calibrated; for example, microbiological tests such as faecal coliforms and *E. coli* where analysts will often carry out the test on several dilutions of the sample to try and ensure the colonies on a plate are within the acceptable range for counting.
2. post-measurement, where the measured variable is outside the upper end of the calibration range and a diluted sample is reanalysed. The measurement must then be corrected for dilution prior to being reported. This information should be included as a comment on the laboratory report.

Dilution of samples introduces uncertainty, both from the physical process of dilution (e.g. measuring volumes) and because dilution is done with deionised water which will change the chemistry of the sample (e.g. precipitates may dissolve or disaggregate).

## 5.4 Sample Measurement

A laboratory provides a controlled environment for the analysis of water samples. As a result, accuracy and precision of measurements are often significantly better than measurements made in the field. All laboratory analytical equipment is calibrated and rigorously checked before use.

### 5.4.1 Measurement Range

Every laboratory test method is calibrated over a range of concentrations appropriate to the method; for example, pH is 3 buffers, some organics are 7. The lower measurement end is set by the method detection limit (MDL), and the higher measurement end is set by the maximum signal the instrument can determine without distortion. Sample concentrations greater than the high value can be determined by dilution, or by taking a smaller sample for analysis.

The upper end of the measurement range is important, as samples with concentrations above this will have a greater uncertainty of measurement (UoM) because of the extra or varied steps in the determination.

*Note: The UoM should be considered when selecting a test method (and using the resulting data).*

### 5.4.2 Detection Limits and UoM

The method detection limit (MDL) for a laboratory test, also known as the limit of detection (or LOD), is statistically determined as the minimum concentration that the laboratory can be 95% confident is above zero. The detection limits for test methods under this Standard are set out in Table 3. These can be considered minimum detection limits; for nutrients, anions and cations, lower (ultra-trace) detection limits may be desirable for some 'very clean' waters.

All laboratory measurements are accompanied by an uncertainty factor (Figure 11). The UoM for a specific test may be reduced by analysis of duplicate samples, or by the laboratory using specific areas, instruments and staff dedicated to high-precision analysis.

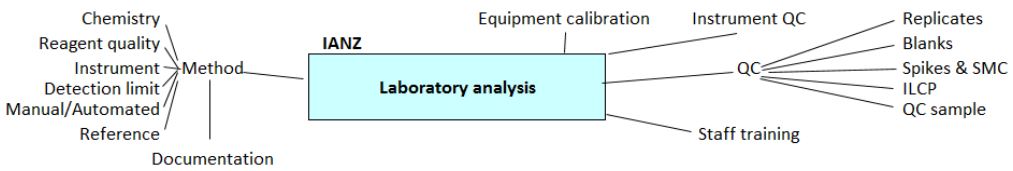



**Figure 11 – Common laboratory-specific uncertainties in the water measurement process**

*See subsection 5.6 for Quality Control (QC) measures.*

Source: Peter Robinson.

*Note: This Standard does not preclude the use of higher MDLs for the specified test method provided that this does not result in more than one censored value in every 10 measurements. As a general rule, the MDL should be approximately 1/10th of the measured value and the aim is to minimise the number of censored data in a dataset where temporal trends are of interest.*

### 5.4.3 Test Method

Table 3 sets out the test methods that shall be performed on groundwater samples collected under this Standard. For many variables, there are multiple methods available but the method(s) specified have been determined as the most appropriate for long-term (e.g. SoE) groundwater quality monitoring programmes.

Most of the methods listed are standard methods for the examination of water from the American Public Health Association (APHA). In some cases, laboratories may modify a standard method (e.g. to reduce a matrix effect that prevents obtaining a measurement) or because of new instrumentation. This Standard requires modifications to methods to be clearly identified on the laboratory report.

It is recognised that methods need to be periodically reviewed, as more precise measurements and new methods may become available as technology advances.

Some guiding principles for selecting analytical laboratories and methods are:

- The laboratory shall hold current IANZ accreditation for the method (see subsection 5.1). This means that the laboratory has been independently certified to perform the required test(s).
- The expected range in concentration that a particular variable will likely fall within shall align with the measurement range of the test method (where possible).
- Consistency in test method is important, especially if data are to be compared against historic data or with data from another programme. At the very least, the basic chemistry used for a test should not be changed except for a compelling reason; for example, a much cheaper test is developed (see subsection 5.7).

Laboratories may offer test methods with 'screen' or 'trace' (lower) method detection limits. Usually the same chemistry will be involved but trace methods may use larger volumes of samples or specific instrument settings. Trace methods will cost more than screen methods but are essential to track changes in contaminant concentrations in 'clean' waters. The UoM for both methods will be similar near their detection limit (around 67% where the MDL is determined from 7 samples), but a low-level result on the screen test will be mid-range on the trace method, so the result will have a lower UoM at the same concentration using the trace test.

*Note: 'Ultra trace' (lowest) method detection limits may also be available.*

**Table 3: Sample bottle and filling requirements and laboratory test method details for groundwater quality variables under this Standard**

*This table assumes filtering of samples, where required, occurs in the field. Unless specified otherwise, the sample bottle may be polyethylene, PVC or glass. "No head space" (compared with "filled to the top") means filled air tight, often through capping the sample bottle under water. ICP-OES = inductively coupled plasma optical emission spectrometry; ICP-MS = Inductively coupled plasma mass spectrometry.*

| Variable | Units | Bottle type, preservative and filling | Recommended minimum sample volume (mL) | Method(s) and description | Method detection limit (MDL) | Method modifications and comments |
|---|---|---|---|---|---|---|
| pH | pH units at 25°C | Unpreserved, no head space | 100 | APHA 4500-H+ B, pH meter | 0.1* | Should be measured within 24 hours of collection.<br>* Measurement resolution, not MDL |
| Specific Conductivity (SpC) | µS/cm at 25°C | | | APHA 2510 B, conductivity meter, 25°C | 1* | * Measurement resolution, not MDL |
| Total Dissolved Solids (TDS) | | Unpreserved, filled to the top | | APHA 2540 C, gravimetric | 10 | Modifications may include lower drying temperature than 180°C. |
| *Nutrients, anions, cations and metals (dissolved)* | | | | | | |
| Nitrate Nitrogen (NO3-N) | mg/L | Unpreserved, no head space | 100 | APHA 4500-NO3 I, flow injection analyser (FIA)<br>OR<br>APHA 4110 B, ion chromatography | 0.002 | Field filtered sample.<br>If measured using APHA 4500-NO3 I, NO3-N is calculated: = NNN – NO2-N. |
| Nitrite Nitrogen (NO2-N) | | | | | | |
| Nitrite-Nitrate Nitrogen (NNN) | | | | | 0.01 | If measured using APHA 4110 B, NNN is calculated: = NO3-N + NO2-N). |

*Continued on next page…*

| Variable | Units | Bottle type, preservative and filling | Recommended minimum sample volume (mL) | Method(s) and description | Method detection limit (MDL) | Method modifications and comments |
|---|---|---|---|---|---|---|
| Ammoniacal Nitrogen (NH4-N) | mg/L | Unpreserved, no head space, OR, where acid preservative is used, filled to shoulder and sample inverted to mix | 100 | APHA 4500-NH3 H, flow injection analyser | 0.005 | Field filtered sample. |
| Dissolved Reactive Phosphorus (DRP) | | Unpreserved, no head space | 100 | APHA 4500-P G, flow injection analyser | 0.004 | Field filtered sample.<br>Modifications may include stronger acid strength to remove silica interference. |
| Dissolved Organic Carbon (DOC) | | Furnaced brown glass bottle, no headspace | 125 | APHA 5310 C | 0.3 | Samples should be acidified and 'purged' before analysis (i.e. here DOC is dissolved non-purgeable organic carbon or DNPOC). |
| Bicarbonate (HCO3 diss) | | Unpreserved, no head space OR, where acid preservative is used*, filled to shoulder and sample inverted to mix | 500 | APHA 4500-CO2 D,<br>OR<br>APHA 2320 B titration | 1.0 at 25°C | Field filtered sample. Filtering represents a modification of method APHA 2320 B. |
| Bromide (Br diss) | | | | APHA 4110 B, ion chromatography | 0.05 | Field filtered sample. |

*Continued on next page…*

| Variable | Units | Bottle type, preservative and filling | Recommended minimum sample volume (mL) | Method(s) and description | Method detection limit (MDL) | Method modifications and comments |
|---|---|---|---|---|---|---|
| Calcium (Ca diss)* | mg/L | Unpreserved, no head space OR, where acid preservative is used*, filled to shoulder and sample inverted to mix | 500 | APHA 3120 B, ICP-OES<br>OR<br>APHA 3125 B ICP-MS | 0.05 | Field filtered sample.<br>* Nitric acid preserved |
| Carbonate (CO3 diss) | | | | APHA 4500-CO2 D,<br>OR<br>APHA 2320 B titration | 1.0 at 25°C | Field filtered sample. Filtering represents a modification of method APHA 2320 B. |
| Chloride (Cl diss) | | | | APHA 4110 B, ion chromatography | 0.5 | Field filtered sample. |
| Fluoride (F diss) | | | | APHA 4110 B, ion chromatography<br>OR<br>APHA 4500-F C or G, ion selective electrode | 0.05 | |
| Iron (Fe diss)* | | | | APHA 3120 B, ICP-OES<br>OR<br>APHA 3125 B ICP-MS | 0.01 | Field filtered sample. Where APHA 3125 B is used for Mg, this will represent a method modification (Mg is not specifically covered by the test method).<br>* Nitric acid preserved |
| Magnesium (Mg diss)* | | | | | | |
| Manganese (Mn diss)* | | | | | | |

*Continued on next page…*

| Variable | Units | Bottle type, preservative and filling | Recommended minimum sample volume (mL) | Method(s) and description | Method detection limit (MDL) | Method modifications and comments |
|---|---|---|---|---|---|---|
| Potassium (K diss)* | mg/L | Unpreserved, no head space OR, where acid preservative is used*, filled to shoulder and sample inverted to mix | 500 | APHA 3120 B, ICP-OES<br>OR<br>APHA 3125 B ICP-MS | 0.1 | Field filtered sample. Where APHA 3125 B is used for K, this will represent a method modification (K is not specifically covered by the test method).<br>* Nitric acid preserved |
| Silica (SiO2 diss reactive) | | | | APHA 4500-SiO2-F<br>OR<br>APHA 3120 B | | Dissolved reactive silica. Field filtered. |
| Sodium (Na diss)* | | | | APHA 3120 B, ICP-OES<br>OR<br>APHA 3125 B ICP-MS | 0.02 | Field filtered sample. Where APHA 3125 B is used for Na, this will represent a method modification (Na is not specifically covered by the test method).<br>* Nitric acid preserved |
| Sulphate (SO4 diss) | | | | APHA 4110 B, ion chromatography | 0.5 | Field filtered sample. |
| Total alkalinity (Alkt) | mg/L $CaCO_3$ | | | APHA 2320 B, auto titration | 1 | |

*Continued on next page…*

| Variable | Units | Bottle type, preservative and filling | Recommended minimum sample volume (mL) | Method(s) and description | Method detection limit (MDL) | Method modifications and comments |
|---|---|---|---|---|---|---|
| Total Anion/ Total Cation Balance Check | % difference | | | APHA 1030 E, calculation | 0.1* | Measurement resolution and not MDL. |
| Total Hardness (Hard) | mg/L $CaCO_3$ | | | APHA 2340 B, calculation | 1 | Field filtered sample. Calculated from dissolved calcium and dissolved magnesium. |
| Aluminium (Al diss) | mg/L | Nitric acid preserved, filled to shoulder and sample inverted to mix | 100 | APHA 3125 B, ICP-MS | 0.005 | Field filtered sample. |
| Arsenic (As diss) | | | | | 0.001 | |
| Cadmium (Cd diss) | | | | | 0.0001 | |
| Chromium (Cr diss) | | | | | 0.0005 | |
| Copper (Cu diss) | | | | | 0.0005 | |
| Lead (Pb diss) | | | | | 0.0001 | |
| Zinc (Zn diss) | | | | | 0.001 | |

*Continued on next page…*

| Variable | Units | Bottle type, preservative and filling | Recommended minimum sample volume (mL) | Method(s) and description | Method detection limit (MDL) | Method modifications and comments |
|---|---|---|---|---|---|---|
| *Metals and metalloids (total)* | | | | | | |
| Aluminium (Al total) | mg/L | Nitric acid preserved, filled to shoulder and sample inverted to mix | 100 | APHA 3030 E* (nitric) *or* F (hydrochloric) acid digestion, then analysis by APHA 3125 B (ICP-MS) | 0.005 | * An acceptable modification to APHA 3030 E is to use a laboratory-validated combination of concentrated nitric acid and hydrochloric acid. This may be necessary to ensure full recovery of some metals (e.g. chromium) in certain sample matrices. |
| Arsenic (As total) | | | | | 0.001 | |
| Cadmium (Cd total) | | | | | 0.0001 | |
| Chromium (Cr total) | | | | | 0.0005 | |
| Copper (Cu total) | | | | | 0.0005 | |
| Lead (Pb total) | | | | | 0.0001 | |
| Zinc (Zn total) | | | | | 0.001 | |
| *Microbial* | | | | | | |
| Faecal Coliforms (FC) | cfu/100 mL | Sterile, filled with small head space left | 100 | APHA 9222 D | 1 | A single larger 400 mL sterile bottle can be used where both indicator bacteria are to be tested. |
| *E. coli* (EC) | MPN/100 mL | | | APHA 9223 B | | |

*Continued on next page…*

| Variable | Units | Bottle type, preservative and filling | Recommended minimum sample volume (mL) | Method(s) and description | Method detection limit (MDL) | Method modifications and comments |
|---|---|---|---|---|---|---|
| *Environmental tracers* | | | | | | |
| Radon (222Rn) | Bq/L | Unpreserved glass bottle, no head space | 100 | Radiometric detection Low-level scintillation detectors | 0.1 | |
| Sulphur hexafluoride (SF6) | fmol/kg | | 1000 | Gas chromatography with electron capture detection | 0.02 | The laboratory should supply special caps with nylon seals for the SF 6 bottle to prevent any air bubbles from being caught in the neck. |
| Chlorofluorocarbons – 11 (CFC – 11) | pmol/kg | | 125 | | 0.03 | |
| Chlorofluorocarbons – 12 (CFC – 12) | | | | | | |
| Chlorofluorocarbons – 13 (CFC – 13) | | | | | | |
| Deuterium (2H) | per mL | | 100 | Mass spectrometry, GVI Isoprime coupled with AquaPrep | 1 | |
| Oxygen-18 (18O) | | | | | 0.1 | |
| Tritium (3H) | TU | | | Radiometric detection Electrolytic enrichment + low level scintillation detectors | 0.03 | |

#### 5.4.3.1 pH

This Standard requires measurement of pH in the field to inform completion of purging and the timing of groundwater sample collection (refer subsection 4.3). If this is not possible, or a spring sample has been collected, pH can be measured in the laboratory but the measurement shall be considered a separate variable (pH – lab). This is because pH rapidly changes once groundwater is removed from an aquifer. It is therefore typically very difficult to reconcile field and laboratory pH measurements.

#### 5.4.3.2 Faecal Coliforms and *E. coli*

Multiple test methods exist for microbial indicator bacteria. This Standard requires the methods specified in Table 3 to be used. In the case of *E. coli*, the enzyme substrate method (APHA 9223 B, Colilert) is preferred because, although less precise than membrane filtration (e.g. APHA 9222 G):

- This is a superior method based on biochemistry
- Measurement up to 2419 *E. coli* per 100 mL is possible without sample dilution
- This method has less chance for error or failure
- Membrane filtration methods do not perform well on turbid or sediment-laden water samples and may require dilutions to be performed that can stress the micro-organisms and result in 'under-recovery', and
- It is the current method of choice for measurement of *E. coli* in potable waters (MoH 2008), providing for cost efficiencies where groundwater is sampled for both SoE and drinking water purposes.

Sample dilutions should be performed where a water sample is expected to render an *E. coli* count >2419 MPN per 100mL.

Enzyme substrate and membrane filtration methods use different processes and therefore do not necessarily produce equivalent results. For this reason, the use of test methods other than the enzyme substrate method shall not be eligible for a quality coding rating higher than QC 500.

#### 5.4.3.3 Anions and Cations

There are several analytical methods in use for determination of some anions and cations (e.g. flow injection analysis and ion chromatography). The methods specified in this NEMS were shown in a recent national interlaboratory comparison (of surface water samples) to produce comparable results (Milne and Robinson 2019). The anion and cation sums, when expressed as milliequivalents per litre (meq/L), should balance because natural waters are electrically neutral. Where the full anion-cation suite is measured, laboratories should perform an anion-cation balance check using the APHA equation below. This Standard requires the balance to agree within ± 5%. The exception is where waters are of low ionic strength (i.e. at an anion sum of 3 meq/L), in which case the balance shall

agree within ± 0.2 meq/L or ± 7%. Unrounded data should be used in anion-cation balance calculations.

$$\% \text{ difference} = 100 \times \frac{\Sigma \text{ cations} - \Sigma \text{ anions}}{\Sigma \text{ cations} + \Sigma \text{ anions}}$$

*And the typical criteria for acceptance are as follows:*

| *Anion sum meg/L* | *Acceptable difference* |
|---|---|
| *00.0 –3.0* | *± 0.2 meq/L* |
| *03.0 – 10.0* | *± 2%* |
| *10.0 – 800* | *± 5%* |

## 5.5 Laboratory Reports

All analytical reports should be checked by a key technical person (KTP) and must be validated in order to be released to the client.

The official laboratory report shall, as a minimum, include for each measurement:

- the name of the sample and time it was collected
- the date and time of receipt of the sample at the laboratory
- whether the sample was laboratory or field filtered (for each applicable measurement)
- the variable measured, measurement value, unit of measurement and associated UoM (at a 95% confidence level)
- the measurement method and standard limit of detection, including details of any modifications made to these
- comments on any anomalies with the condition of the sample upon receipt (e.g. temperature on arrival, bottle type and/or filling) and supporting commentary from the analyst in the advent of difficulties with testing the sample (e.g. insufficient sample for analysis or a matrix effect that prevented the standard detection limit from being achieved) or an unusual result (e.g. if a test result for the dissolved fraction of a nutrient is higher than the results of its total fraction), and
- the maximum time the laboratory will hold the sample to provide for retesting, if requested.

Laboratory reports shall be supplied to the monitoring agency digitally, locked to prevent inadvertent editing. Unofficial reports may also be supplied in the form of spreadsheet (.csv) and/or database (.xml) files for convenience. Results contained in these unofficial files shall be checked by the monitoring agency against the official report (see subsection 6.3).

Although the laboratory performs internal checks, it does not hold the long-term history of a particular monitoring site or any metadata that was not included on the CoC. It is recommended that the monitoring agency, who holds all metadata,

systematically checks laboratory results as soon as possible; for example, against previous results. If this is undertaken within a reasonable time frame (preferably two weeks, but coinciding with the laboratory's maximum sample holding time), it is possible for the monitoring agency to query unusual measurements which may trigger re-analysis. Sometimes analysis cannot be repeated, either because of the analyte or because of the test method; for example, microbiological tests such as faecal coliforms and *E. coli* which must be performed on a 'fresh' water sample.

### 5.5.1 'Censored' Results

Censored values are those that only partially known, either above or below a test MDL. The censored (validated) measurement value is considered the laboratory's official result and shall be reported as '>' (greater than) the maximum value of the calibrated range or '<' (less than) the lower MDL.

As best practice under this Standard, laboratories shall also supply the 'uncensored' (i.e. raw unrounded) measurement and the associated uncertainty of measurement (UoM).

## 5.6 Laboratory Quality Checks

Laboratories are required to have robust quality checks in place as part of obtaining and maintaining their IANZ accreditation. This includes participation in an Inter-Laboratory Comparison Programme (ILCP), where water samples are received from an external supplier to measure the laboratory's performance against that of other participating laboratories.

Each laboratory worksheet will typically have most of the following:

- calibration standards
- blanks (i.e. reagents only, no sample)
- replicates (usually duplicate)
- spikes (usually the same sample as replicated), and
- quality control (QC) sample(s).

A worksheet may also have a routine repeat (i.e. a sample from a previous worksheet that is re-analysed).

The analytical report signatory (i.e. the KTP) will also carry out data validation checks before signing the report. With water quality data, these checks include, but are not limited to, such things as:

- dilution calculation checks
- anion-cation balance (if sufficient data available), and
- ensuring that reported total concentrations are greater than or equal to reported dissolved concentrations for the same variable, within UoM (e.g. As total ≥ As diss).

*Note: Laboratories can provide a QC report on request (usually for a charge).*

## 5.7 Managing Changes in Laboratory Methods

Because the objective of most long-term water quality monitoring programmes is to be able to detect changes through time, long-term monitoring programmes would ideally retain the same laboratory, test method and associated instruments to avoid the potential for 'step' changes that can arise when a change is made to any one of these. However, this is unrealistic, particularly with changes in laboratory contracts and developments in methods and instrumentation over time; for example, automation of manual tests, discontinuation of reagents. The best that can be expected is that the basic chemistry used for a test be kept constant as far as possible.

If laboratory analytical methods need to be changed, there should be a period of duplicate analyses using both the old and new test methods. Monthly parallel testing for a period of time (e.g. 12 months for a programme based on monthly sampling) is recommended to provide sufficient data to determine if a conversion factor can be derived to 'align' the old and the new methods (or laboratories). This is particularly important for nutrient test methods, where 'step' changes have been reported (e.g. Davies-Colley & McBride, 2016). Note that this procedure is not foolproof and adds to the analytical costs; the optimum situation is to have all analyses done by the same high-quality laboratory.

The exact test method used shall be linked with each sample result in the monitoring agency's database (see subsection 6.1.3) to allow for any potential 'step' changes in data to be tracked. Laboratory contracts should stipulate that any test method changes on the part of the laboratory are communicated and agreed prior to implementation.

# 6 Data Processing and Quality Assurance

## In This Section

This section contains information on the processing, storage and quality assurance (QA) of water quality data and associated metadata.

## 6.1 Data Types

Discrete water quality data can be split into several data types:

- site metadata (subsection 2.3), which are specific to the site location and may change with time but generally not on each site visit
- visit metadata (subsection 4.4), which are specific observations made about where and when field measurements and water samples were collected,
- water quality data, which generally consist of both field measurements and laboratory measurements made on one or more water samples, and
- information about the data including length of record and other information relevant to the data set including Quality Code.

All data types shall be stored in a database.

### 6.1.1 Site Metadata

Adequate mechanisms shall be put in place to store all relevant site-related metadata listed in subsection 2.4.

### 6.1.2 Visit Metadata

Visit metadata is recorded on a field record form, either in paper or electronic format. Adequate mechanisms shall be put in place to store all relevant visit-related metadata listed in subsection 4.4, together with the water quality measurement values (subsection 6.1.3).

### 6.1.3 Measurements and Associated Metadata

Each water quality measurement shall be stored with:

- its associated measurement date, time and units
- field instrumentation (make, model and number) or laboratory name, location and test method (whichever is applicable)
- clear reference to its associated form (dissolved, total, reactive, etc.), where applicable (e.g. nutrients and metals)
- all relevant visit-related metadata, including the name(s) of personnel conducting field measurements and sampling (subsection 4.4)
- relevant laboratory comments (subsection 5.5) where applicable, and

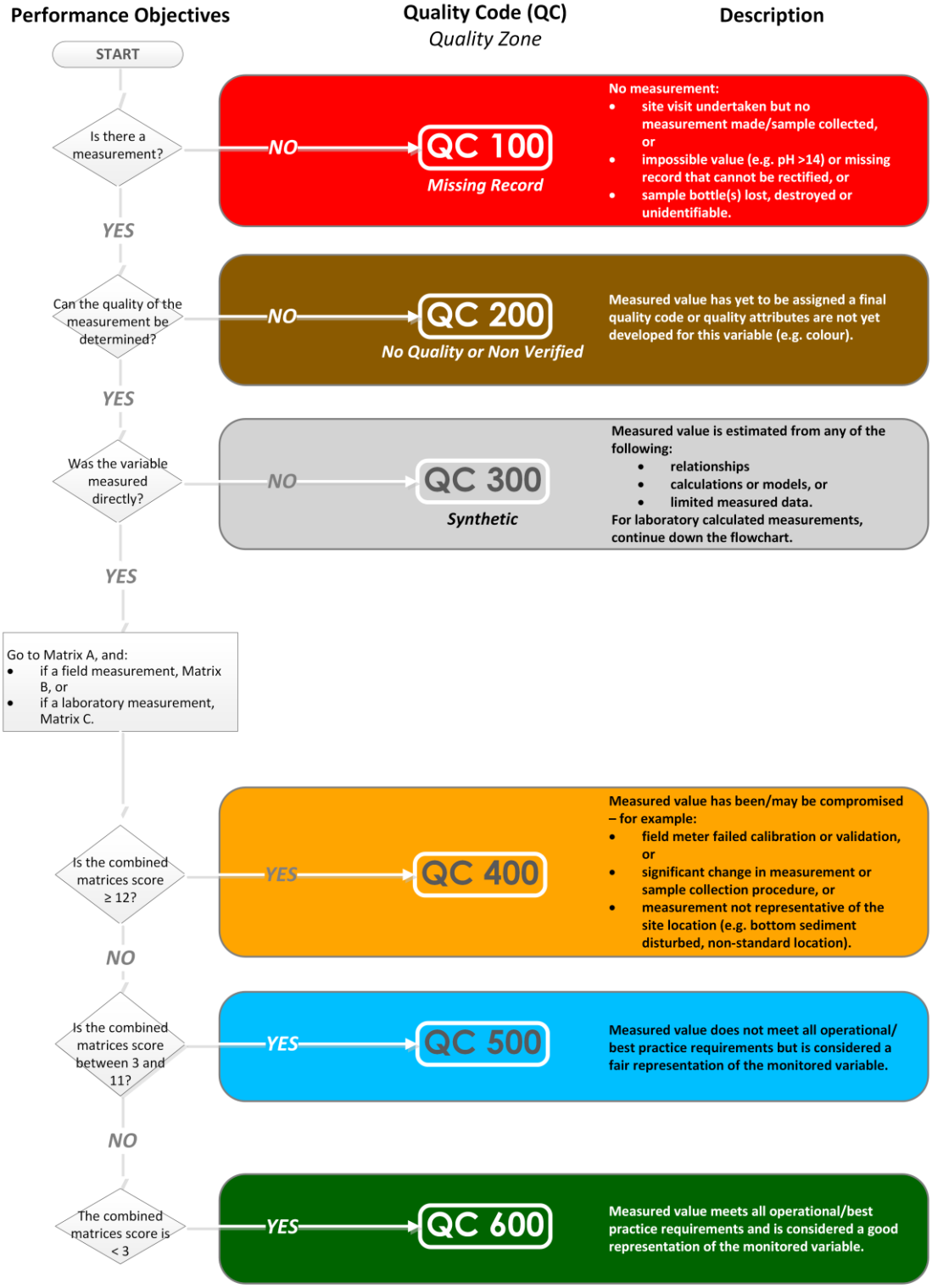
- its associated quality code (subsection 6.2.1).

## 6.2 Data Processing and Quality Coding

Processing of discrete water quality data primarily includes assignment of quality codes through consideration of field practices, sample handling and transport transit conditions, documentation and laboratory practices. It may also include adjustment of water quality data based on known errors; for example, correction of a pH value recorded as 18.1 beside a water temperature of 7.1 (in this case a data transcription error). Any adjustments to data should be documented.

## 6.2.1 Quality Codes – Discrete Water Quality

All individual water quality variable measurements shall be quality coded in accordance with the NEMS *Quality Coding Schema*. The schema comprises six 'parent' codes and permits valid comparisons within and across multiple data series. Use the following flowchart as a framework to assign quality codes to all field and laboratory measurement data.



*Note: The NEMS Quality Code Schema permits valid comparisons within a data series and across multiple data series. A monitoring agency may choose to add more definition to the coding scheme through the use of 'child' codes.*

In most cases, discrete water quality data collected as part of long-term (e.g. SoE) monitoring will fall under one of QC 400, QC 500 or QC 600. Three matrices follow that provide a framework for assigning one of these quality codes to individual water quality measurements. The matrices are:

Matrix A: General procedures and site visit
Matrix B: Field variable measurements, and
Matrix C: Laboratory variable measurements.

To assign a quality code to a field measurement variable, follow Matrices A and B and determine the total number of points. To assign a quality code to a water quality variable measured in the laboratory, follow Matrices A and C and determine the total number of points.

Total Points
(All matrices)

| | |
|---|---|
| QC 600 | < 3 points |
| QC 500 | 3–11 points |
| QC 400 | 12+ points |

*Note 1: If 3 or more criteria are in the '3 points' column, the data are deemed to be QC 400.*

*Note 2: If water temperature obtains a code of QC 500 on any occasion, then temperature-dependent field measurements of dissolved oxygen, specific conductivity and pH can also only obtain a maximum of QC 500. Dissolved oxygen measurements of > 100% saturation shall also obtain a maximum of QC 500.*

*Note 3: Quality considerations for oxygen reduction potential (ORP) field measurements require further development. Measurements of this variable shall be coded QC 200 in the interim.*

*Note 4: Child codes may be used to provide for a more detailed breakdown of data quality. Refer to the NEMS Quality Code Schema.*

# Matrix A: General Procedures and Site Visit

Quality coding of all discrete water quality data shall firstly address the following criteria.

*Note: The first two criteria represent system 'completeness and currency' checks.*

| Criteria | 12 points | 3 Points | 1 Point | 0 Points |
|---|---|---|---|---|
| **Field and Office Manual** *(subsection 1.1)* | Manual lacks documented quality assurance procedures for sampling, measurement or data management | Manual lacks documented quality assurance procedures for some aspects of sampling, measurement and data management | | Manual maintained in accordance with the Standard, including quality assurance procedures for all aspects of sampling, measurement and data management |
| **Site Metadata** *(subsection 2.3)* | | Site metadata partially or not documented | Site metadata documented in accordance with the Standard but in need of updating | Site metadata documented in accordance with the Standard and checked/updated less than 12 months ago |
| **Site Location** *(subsection 2.2)* | | Different field measurement/ water sample location | | Field measurement/water sample location consistency maintained |
| **Site Condition** *(subsection 2.2)* | The integrity of the monitoring site is likely compromised, supported by visual evidence (e.g. cracked concrete pad or well head potentially allowing rain or overland flow to enter the well) | | | The monitoring site is in good condition, free from any obvious surface contamination (e.g. cracked well head) |

*Continued on next page…*

| Criteria | 12 points | 3 Points | 1 Point | 0 Points |
|---|---|---|---|---|
| **Visit Metadata** *(subsection 4.4)* | No metadata recorded other than the site, date and actual/estimated time of measurement/sample collection | Visit metadata generally recorded in accordance with the Standard but lack some details, including an identifier for the actual field meter(s) used | | Visit metadata recorded on a field record form in accordance with the Standard, including:<br>• measurement date, time and units,<br>• field meter(s) make, model and ID number, and<br>• the environmental conditions under which measurements/ water samples were collected |
| **Purging** *(subsection 4.1)* | The groundwater water is not purged prior to field measurement or sample collection | The groundwater is purged prior to finalising field measurements and sample collection but one or more purging criteria specified in the Standard are not met | | The groundwater is purged prior to finalising field measurements and sample collection in accordance with the Standard |
| **Sample Filtration** *(subsection 4.3.4 – the requirement for filtration is variable-specific)* | Samples are not filtered in accordance with the Standard in the field at the time of sample collection | | | Samples are filtered in accordance with the Standard in the field at the time of sample collection<br>OR<br>N/A (e.g. field measurements and microbial samples) |
| **Total Score** | | | | |

# Matrix B: Field Measurements

In addition to the criteria in Matrix A, quality coding of discrete water quality data collected in the field shall address the following criteria. The total score that determines the final Quality Code for each field measurement is the sum of the total score from Matrix A plus the scores of the relevant components of this Matrix B.

| Criteria | 12 points | 3 Points | 1 Point | 0 Points |
|---|---|---|---|---|
| **Applies to all variables, unless specified otherwise** | | | | |
| **Sensor Accuracy and Type** *(subsection 3.1)*<br><br>[Applies to Temp, DO % Sat, DO, SpC – field pH – field] | Sensor accuracy does not meet that specified in the Standard for the variable in question and, in the case of water temperature, sensor accuracy is poorer than ± 0.5°C.<br><br>For DO % sat and DO, an electrochemical (i.e. membrane-based) sensor is used without a mechanical stirrer or a flow cell. | Sensor accuracy deviates from that specified in the Standard for the variable in question but meets the following criteria:<br>• Temp: ± 0.5°C<br>For DO % sat and DO, an electrochemical (i.e. membrane-based) sensor is used with a mechanical stirrer or a flow cell to ensure the velocity of water past the sensor exceeds 0.3 m/s. | | Sensor accuracy meets the requirements of the Standard for the variable in question |

*Continued on next page…*

| Criteria | 12 points | 3 Points | 1 Point | 0 Points |
|---|---|---|---|---|
| **Field Meter Validation and Calibration** *(subsection 3.1)*<br><br>[Applies to Temp, DO % Sat, DO, SpC – field pH – field] | Validation and/or calibration failed or not performed, or no records available<br><br>OR<br><br>An alternative validation method under Annex G was used and a validation was not performed following measurement collection and before the next calibration | Start-of-day (pre-sampling run if using Annex G) validation and/or calibration meet the requirements of the Standard but:<br>• end-of day (post sampling run if using Annex G) validation (for SpC and pH only) failed/not performed, and/or<br>• supporting information missing (e.g. pH – mVolts, DO – raw barometric pressure) | Validation and calibration meet the requirements of the Standard, but documentation not 100% complete | Validation and calibration meet the requirements of the Standard, including documentation |
| **Measurement Resolution** *(subsection 3.3)* | Measurement resolution does not meet that specified in the Standard for the variable in question | | | Measurement resolution meets that specified in the Standard for the variable in question |
| **Measurement Correction** *(subsection 3.3)* | Supporting measurements are not collected and/or measurement is not corrected where required; for example, dissolved oxygen, pH | | | Supporting measurements are collected and measurement is corrected where required, including:<br>• dissolved oxygen is corrected for barometric pressure, and<br>• pH and SpC are reported at a reference temperature of 25°C |
| **Total Score** | | | | |

# Matrix C: Laboratory Measurements

When quality coding water quality data from the laboratory, assess each laboratory measurement against Matrix A plus the general and relevant variable criteria in the following matrix. The total score that determines the Quality Code is the sum of the total scores from Matrix A and Matrix C.

| Criteria | 12 points | 3 Points | 1 Point | 0 Points |
|---|---|---|---|---|
| **Applies to all variables, unless specified otherwise** | | | | |
| **Laboratory Certification** *(subsection 5.1)* | Laboratory does not hold current IANZ accreditation or evidence of observing standard procedures and QA/QC practices for the measurement method | Laboratory holds documentation for the measurement method and incorporates standard QA/QC practices but lacks current IANZ accreditation | | Laboratory holds current IANZ accreditation for the measurement method |
| **Traceability** *(subsections 1.11 4.9)* | Samples not identifiable and/or received without a completed Chain of Custody | Samples identifiable but not accompanied by a Chain of Custody | | Samples identifiable and accompanied by a completed Chain of Custody |
| **Sample Receipt Time** *(subsection 5.2.1)* | Unpreserved and microbial samples received > 48 hours after collection<br>OR<br>Samples for radon testing received outside of 72 hours of collection | | Unpreserved and microbial samples received within 48 hours of collection | Unpreserved and microbial samples received within 24 hours of collection<br>OR<br>Samples for radon testing received within 72 hours of collection |

*Continued on next page...*

| Criteria | 12 points | 3 Points | 1 Point | 0 Points |
|---|---|---|---|---|
| **Sample Temperature on Arrival** *(subsection 5.2.2)* | Samples arrive at or above 10°C*<br>* Or greater than the sample collection temperature where samples are delivered within 2 hours of collection<br>*Note: If microbial samples arrive frozen or with evidence of ice crystals, then code QC 100 ('no result')* | | | Samples arrive < 10°C* and the microbial sample was not subject to freezing, in whole or part<br>* Or less than the sample collection temperature where samples are delivered within 2 hours of collection |
| **Sample Bottles and Condition** *(subsection 5.2.2)* | Laboratory notifies incorrect sample bottle, filling and/or pre-treatment has likely compromised the measurement | Laboratory notifies incorrect sample bottle, filling and/or pre-treatment used but unlikely to have compromised the measurement | | Correct sample bottle used for the variable and no anomalies are identified by the laboratory in the condition of the bottles or samples |
| **Test Method** *(subsection 5.4.3)* | | The method used is not that specified in the Standard for the variable in question OR is a modified method without laboratory qualification | | The method used is that specified in the Standard for the variable in question |

*Continued on next page.....*

| Criteria | 12 points | 3 Points | 1 Point | 0 Points |
|---|---|---|---|---|
| **Anion and Cation Balance Check** *(subsection 5.4.3.2)* (Applies to anions and cations only) | The calculated anion-cation balance does not agree within ± 5%, or, where the groundwater is of low ionic strength (i.e. at an anion sum of 3 meq/L), the balance is outside of ± 7% | | | The calculated anion-cation balance agrees within ± 5%, or, where the groundwater is of low ionic strength (i.e. at an anion sum of 3 meq/L), the balance is within ± 7% |
| **Measurement Units, Detection Limit and Resolution** *(subsection 5.4.3)* | The detection limit or measurement resolution do not align with those specified in the Standard for the variable in question, including any censored value | The measurement units do not align with those specified in the Standard for the variable in question | | The measurement units, detection limit and resolution align with those specified in the Standard for the variable in question |
| **Total Score** | | | | |

#### 6.2.1.1 Considerations

Water quality data shall be coded following the quality coding framework and matrices that forms part of this Standard. The following records shall be utilised in the quality coding process:

- Field and Office Manual (subsection 1.1)
- field meter calibration, validation and maintenance (subsections 3.1 and 3.2, and Annex F)
- field record form (subsections 1.4 and 4.4, and Annex B)
- completed Chain of Custody form (subsections 1.11 and 4.6.1, and Annex D), and
- laboratory report (subsection 5.5).

Site metadata (subsection 2.3) and QA (subsection 1.3) information will also need to be consulted from time to time.

Field measurements

The initial quality code for field measurement data should be assigned by the field personnel who made the measurements.

Laboratory measurements

Quality coding of laboratory measurement data is a two-step process. The first step involves the laboratory undertaking checks identified in subsection 5.2 (time, temperature and condition of samples on arrival at the laboratory) and subsection 5.6 (quality checks) and providing comments to the monitoring agency. The second step is best carried out by a data analyst within the monitoring agency who collates all the information about the sample, including that provided by the laboratory, to assign the final quality code to the measurement value. Measurements should ideally be checked within two weeks of receipt from the laboratory to enable sample retesting if necessary (subsection 5.5).

*Note: Checking water quality measurement data only every 12 months for annual reporting is not sufficiently 'responsive' for maintaining quality data.*

It is recommended that:

- automated checks are placed on sampling dates (e.g. to limit entry to a week day), times (e.g. to limit entry to between 0700 and 1900 hours), and known measurement ranges (e.g. pH), and
- the 'validity' of water quality measurements are assessed prior to archiving by looking at:
  - the historical site measurement range (e.g. 5th and 95th percentile values of the last five years of data or the last 60 data points),

    *Note: Pre-population of historical measurement ranges for water quality variables measured in the field on the field record form can facilitate early detection at the time of collection that the*

*measurement may not be reliable, providing for instrument checks or re-measurement.*

- relationships with other variables (e.g. high dissolved magnesium or sodium concentrations typical of reduced aquifer conditions are generally consistent with low DO concentrations), and
  *Note: Scatterplots are a useful way of inspecting the data.*
- internal consistency of the analysis (e.g. anion-cation balance).

#### 6.2.1.2 Batch Coding

Undertaking quality coding in batches is recommended. The raw data archive should be copied into a processing/batch file. Any edits to the data and changes to codes should only occur in this file. When applying a quality code, a comment should sit alongside that code to enable other staff to determine why that code has been assigned.

Once a batch file is completed, a different staff member should QA the batch file before it is committed to the final archive.

#### 6.2.1.3 Data That Do Not Meet The Standard

Any field or laboratory measurement data that do not meet this Standard shall be assigned a quality value from QC 100 to QC 500.

*Note: A quality value of QC 600 shall only be assigned where this Standard and associated best practice is achieved.*

## 6.3 Data Preservation and Storage

The water quality data and visit metadata shall be stored together in a time-series data server, linked with a single date and time. A link to the following records should also be considered:

- site metadata
- field meter/instrument calibration, validation and maintenance
- quality assurance, and
- any legal requirements, confidentiality agreements and/or restrictions related to data access.

All original records shall be retained indefinitely by the monitoring agency.

### 6.3.1 Database Comments

Comments, including visit and measurement metadata, are useful to explain unusual features data users should be aware of that are not easily quality coded.

*Note: Current software packages provide several ways to build a database of comments. Comments can be entered into an unstructured file of text. If the comments are entered into an ODBC (Open Database Connectivity) database, they*

*can be accessed by any ODBC compliant software. Therefore, this method is recommended.*

### 6.3.2 Data Files

Both of the following versions of laboratory water quality data shall be retained and maintained:

- official laboratory measurement results with censored values where appropriate, and
- raw ('unadjusted') measurement data from the laboratory, together with the accompanying Uncertainty of Measurement (UoM).

Any editing or adjustments of data shall also be retained separate from the raw data. This ensures that data can be traced back to the original values. Examples of editing or adjustment include:

- correction of sample time
- correction of field measurements based on additional environmental variables such as basic sanity checks of laboratory measurement values
- re-calculation of nutrient subspecies
- replacement of an original laboratory measurement value with a retest value, and
- averaging duplicate measurement values to report a single final value.

### 6.3.3 Data Archiving

The archiving procedures, policies and systems shall consider:

- data workflow, including minimising manual entry and editing
- transparent, optimised data curation
- future data-format changes
- off-site duplication of records, and
- disaster recovery.

## 6.4 Quality Assurance

All agencies should implement a standard methodology for data audit and review.

*Note: This is to ensure standardisation of data sets that enable meaningful analyses and comparison of data within regions, across regions and nationally.*

### 6.4.1 Audit Cycle

Quality assurance processes shall include an audit of the data:

- at a frequency appropriate to the needs of the monitoring agency and end users, or

- as defined by the monitoring agency's quality management system or documented procedures.

This work shall be undertaken by a suitably qualified and experienced practitioner.

Unaudited data that are released for use shall be identified as being unaudited.

*Note: Datasets other than those under review may be included in the audit to help with comparisons. Where available, reliable data records operated by other agencies may be used.*

### 6.4.2 Minimum Audit Report Requirements

As a minimum, analyses and information required for an audit report shall cover:

- site and deployment metadata details, including catchment (if applicable) and site details
- comments and quality coding attached to the records
- data tabulations, and
- data plots.

#### 6.4.2.1 Aquifer and Site Details

The following shall be included in the audit report:

- a site details summary, and
- a location map, with locations of monitoring sites identified.

The location details summary shall:

- identify the groundwater management zone and/or aquifer
- identify other water quality data utilised in the audit report for comparison purposes or for generating a missing record (where relevant), and
- for each water quality record, identify:
  - the date and time of record collection
  - the site name and number
  - map reference
  - altitude
  - field meter/equipment details
  - sample collection method details, and
  - laboratory method details.

#### 6.4.2.2 Comments and Quality Coding

The following shall be included in the audit report:

- for each water quality record being reviewed, a copy of the filed comments for the record, and

- a copy of the quality codes of all of the data being audited.

### 6.4.3 Other Requirements

#### 6.4.3.1 Outputs

Recommended report outputs include:

- a hard copy report
- an electronic report, or
- at a minimum, an electronic document that only identifies which records have passed the audit.

#### 6.4.3.2 Audit Certification

The completed audit shall contain the name and signature of the auditor and the date that the audit was completed.

# Annex A – List of Referenced Documents

ANZECC (2000). *Australian guidelines for water quality monitoring and reporting. (National Water Quality Management Strategy No. 7.)* Canberra, Australia: Australian and New Zealand Environment and Conservation Council, & Agriculture and Resource Management Council of Australia and New Zealand.

APHA/AWWA/ WEF. (2012). *Standard methods for the examination of water and wastewater* (22nd ed.). Washington DC: Author.

Daughney, C., Jones, A., Baker, T., Hanson, C., Davidson, P., Zemansky, G., Reeves, R., & Thompson, M. (2006). *A national protocol for State of the Environment groundwater sampling in New Zealand.* Wellington, New Zealand: Ministry for the Environment.

Davies-Colley, R., Hughes, A., Verburg, P., & Storey, R. (2012). *Freshwater monitoring protocols and quality assurance*. *National environmental monitoring and reporting (NEMaR)*. NIWA Client Report HAM2012-092 prepared for the Ministry for the Environment, Wellington.

Davies-Colley, R. & McBride, G. (2016). *Accounting for changes in method in long-term nutrient data: Recommendations based on analysis of paired SoE data from Wellington rivers.* NIWA Client Report No. HAM2016-070 prepared for the Ministry for the Environment, Wellington.

Davies-Colley, R., Milne, J., Perrie, A., & Heath, M. (2017). *Inter-agency comparison of water quality measurements: A pilot QA programme between Greater Wellington Regional Council and NIWA.* Report No. 2017096HN prepared under NIWA Project ELF16508 (NEMS for Discrete Water Quality).

Hébert, S., & Legare, S. (2000, Octobre). *Suivi de la qualité de l'eau des rivières et petits cours d'eau*. Ministère de l'Environnement, Gouvernement du Québec: Quebec, Canada.

Milne, J. & Robinson, P. (2019). *An interlaboratory comparison to inform long-term fresh and coastal water quality monitoring.* NIWA Client Report No. 2018195WN prepared for Marlborough District Council.

Ministry of Health. (2008). *Drinking-Water Standards for New Zealand 2005 (Revised 2008).* Ministry of Health, Wellington.

Rosen, M., Cameron S., Taylor, C., & Reeves, R. (1999). *New Zealand guidelines for the collection of groundwater samples for chemical and isotopic analysis.* Institute of Geological and Nuclear Sciences Science Report 99/9.

U.S. Environmental Protection Agency. (1996). *Low stress (LOW flow) purging and sampling procedures for the collection of groundwater samples from monitoring wells, SOP#GW0001*. U.S. Environmental Protection Agency, Region 1, Boston, MA.

# Annex B – Example Field Record Form

*Note: This form is a guide only and can be modified as appropriate.*

**Field Record Form: Groundwater**

**Programme Name** _____

**Site Name & No.** _____

**GPS Location** Easting _____ Northing _____

**Sample Run Name** _____ *(leave blank if N/A)*

**Date** _____

**Field Personnel** _____

**Visit Metadata**

Weather o Fine o Overcast o Drizzle o Rain Rain in last 24 hours? o Y o N

Wind Direction o NW o N o NE o SE o S o SW Digital Photo o Y o N

Wind Speed o Calm o Light o Moderate o Strong

Air Temperature ____ °C

Time (NZST) Arrival on site _____ **Official visit time*** _____ Departure from site _____

* Time of final field measurements

Comments *(e.g. integrity of bore/well head, significant changes in surrounding land use, new hazards, etc.)*

| **Purging & Field Measurements** | Volume 1 _____ L | Volume 2 _____ L | Volume 3 _____ L |
|---|---|---|---|
| Water Temperature (°C) | | | |
| pH | | | |
| Specific Conductivity (µS/cm) | | | |
| Other _____ | | | |

One well purge volume _____ L

Pumping duration _____ min

Pumping volume _____ L

*Final measurements* Meter make, model & number

Water Temperature _____ °C _____

Dissolved Oxygen _____ mg/L _____

Dissolved Oxygen _____ % sat. _____

Specific Conductivity _____ µS/cm _____

pH _____ pH _____

ORP _____ mV _____

Turbidity _____ FNU _____

Depth to water _____ m Measured from _____

**Water Samples**

Sample No./ID _____ QA/QC Sample Details _____

Total No. of Bottles _____ Field Filtered o Y (No. of filters ____ ) o N

Collection Method o Pumped bore o Bailed o Grab o Bucket o Other _____

Sample Appearance o Colourless o Clear o Turbid o Other _____

Odour o Y o N

**Other Notes** *(e.g. deviation from protocols, QA/QC, courier assignment no., end of day field meter validation data)*

# Annex C – Equipment List

Equipment required for groundwater sampling may include:

- sample bottles, filters, syringes
- handheld GPS to confirm sampling point location
- field record forms (see example in Appendix B)
- 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, including 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 plastic bags (for grouping bottles from each monitoring site)
- rubbish bags
- chilly bins
- ice and/or slicker pads, and
- a groundsheet.

# Annex D – Example Chain of Custody Form

*Note: This form is a guide only and will need to be modified in consultation with the laboratory provider.*

## Chain of Custody Form for Water Samples

**Client Name** _____ **Client Contact** _____

**Client Reference** _____ **Email*** _____

**Quote/Order No.** _____ ** For return of CoC*

*Client to complete*

**Sample Dispatch** Date _____ Time (NZST) _____

Name _____ Signature _____

**Additional Notes** _____

_____

_____

*Laboratory to complete*

**Sample Arrival** Date _____ Time (NZST) _____

Name _____ Signature _____

**Sample Condition** o Room temperature o Chilled o Frozen

Temperature _____ °C

Comments *(e.g. appropriate bottle used, headspace requirements met)*

_____

_____

_____

**Job. No.** _____

**Sample Details** *(Client to complete)*

Type o Groundwater o River / Stream o Lake o Estuarine / Coastal

Have samples been field filtered? o Y o N Details _____

| *No.* | *Sample Name* | *Sample Date & Time (NZST)* | *Tests Required* |
|---|---|---|---|
| 1 | | | |
| 2 | | | |
| 3 | | | |
| 4 | | | |
| 5 | | | |
| 6 | | | |
| 7 | | | |
| 8 | | | |
| 9 | | | |
| 10 | | | |

# Annex E – Isolating a Pressure Tank

The following instructions are reproduced from Appendix 5 of Daughney *et al*. (2006).

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

- maintain water pressure within the delivery system, and
- 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 that 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, or
- 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).

# Annex F – Example Field Meter Calibration Form

*Note: This form is a guide only – for handheld meters.*

## Handheld Meter Calibration Form

**Meter ID** _____ **Date** _____

**Staff Member** _____ **Time** _____ NZST

**Sample Run Name** _____

**Barametric Pressure Checks**

Meter Reading mbar

Reference Site Reading mbar

**Dissolved Oxygen (DO)**

DO % saturation (after calibration) _____ % Pass Calibration (99.5 - 100.5 %)

DO (after calibration) _____ mg/L o Y o N

Temperature _____ °C

**Specific Conductivity**

0.001 M Meter Reading _____ µS/cm Pass Validation / Calibration (120 - 175 µS/cm)

0.001 M Validation/Calibration Value _____ µS/cm o Y o N

0.001 M Meter Reading _____ µS/cm

**pH**

| | Meter Reading | Temperature | mV pH Value |
|---|---|---|---|
| pH 7 Calibration / Validation | _____ pH units | _____ °C | _____ |
| pH 4 Calibration / Validation | _____ pH units | _____ °C | _____ |
| pH 10 Calibration / Validation | _____ pH units | _____ °C | _____ |

**ORP**

Calibration Value _____ mV Temperature _____ °C

**End of Day Validation Checks**

Staff Member _____ Time (NZST) _____

| | Meter Reading | Temperature | Passed Validation? |
|---|---|---|---|
| *Specific Conductivity* (0.001 M) | _____ µS/cm | _____ ° C | (120 - 175 µS/cm) o Y o N |
| *pH* (pH 7) | _____ pH | _____ ° C | Passed Validation? (6.7 - 7.3 pH) o Y o N |
| *ORP* | _____ mV | _____ ° C | Passed Validation? (200 - 280 mV) o Y o N |

**Comments**

# Annex G – Alternative Field Meter Calibration/Validation Protocol

The calibration and verification protocols outlined in Section 3 were developed for traditional handheld sensors used in the environmental water quality domains. Outlined below is a calibration/validation protocol that can be used for 'high quality' sondes associated with short or long-term deployments.

## 1. Develop criteria per variable on an instrument to determine sensor drift

Initial calibrations shall be completed in accordance with the relevant parts of Section 3 of this document.

Each organisation wishing to use an alternate method of validation shall develop a Standard Operating Procedure (SOP) that document the process for determining the appropriate calibration frequency. The calibration frequency shall at no stage be:

- less than the manufacturer's recommendations, or
- less than that specified in the NEMS that are in place for the relevant variable measured on a continuous basis (e.g. NEMS *Dissolved Oxygen* (continuous measurements)).

The SOP shall document the following for each field-measured variable:

- cleaning of the field instrument and the process by which this is managed to ensure that the sensor is clean and free of bio-fouling (this could be an integrated wiper, visual checks, manual cleaning)
- maintenance of the field instrument and the process for ensuring that this has taken place (e.g. DO membranes / sensor caps, pH bulbs / electrolyte / reference junctions / monitoring the pH 7.0 millivolts, etc.)
- validation checks on the field meter daily (as used) in a known standard solution (e.g. end of day), without any adjustment to the calibration
- evaluation of how the sensor drifts over a given period of time (without a follow up calibration or adjustment of the sensor's response), and
- a conservative calibration schedule of not more than half the period of measured drift within the acceptable range (e.g. if the calibration of a dissolved oxygen sensor is measured for 6 months before its drifts outside of the acceptable range then the calibration frequency shall not exceed 3 months).

## 2. Continuing calibration / verification

When an initial sensor calibration is not performed on each day of instrument use, the validity of the calibration shall be verified prior to assessing the final quality code for the data measured by the meter's sensor. It is recommended that an end of day validation be performed for each water quality variable covered by this protocol. A successful validation following variable measurement under this process will be deemed to have passed the NEMS calibration / verification protocols (i.e. assignment of

zero ‘demerit’ points in Quality Coding Matrix B: Field Measurements). Any subsequent adjustments to instrument calibrations shall be preceded by a validation as a check on the data collected under the old calibration. **Failure to validate a sensor before recalibrating shall result in a quality code of QC200 for the measured variable** (‘unverified data’, for all measurements collected since the last sensor validation).

A full calibration shall be completed in accordance with subsection 3.1 of this document following any sensor maintenance (e.g. replacement of DO membranes, sensor caps, pH bulbs, electrolyte solution, reference junctions), other than routine sensor cleaning.

## 3. Failure of any validation

Each organisation wishing to use an alternate method of validation shall develop a SOP that documents the process to be followed if sensor validation fails. As a minimum, this process shall ensure that **all measurements collected since the last “good validation” or calibration are downgraded to a maximum of QC 400**.

Following a failed validation, the organisation shall check, clean, and recalibrate the instrument’s sensor(s). It is also recommended that a review of maintenance and calibration solutions is undertaken. The calibration interval shall be reduced to half the period since the last calibration to prevent reoccurrence.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