

National Environmental Monitoring Standards

Water Quality

Part 2 of 4: Sampling, Measuring, Processing and Archiving of Discrete River Water Quality Data

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NEMS

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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 particular 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), Maree Patterson (Horizons Regional Council), Rob Davies-Colley (NIWA), Peter Robinson (Robinson Scientific and formerly Hill Laboratories), Rob Donald (Bay of Plenty Regional Council), Magali Moreau (GNS Science), Jarrod Walker (Auckland Council) and David Brown (Horizons Regional 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 Surface Water Integrated Management (SWIM), Groundwater Forum (GWF), Coastal and Environmental Data (formerly Local Authority Environmental Monitoring Group or 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).

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- Environment Canterbury Regional Council (ECan)
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- GNS Science
- Greater Wellington Regional Council (GWRC)
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- Horizons Regional Council (HRC)
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- 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 *Open Channel Flow* (continuous measurements)
- NEMS *Quality Code Schema*
- NEMS *Suspended Sediment (in preparation)*
- NEMS *Turbidity* (continuous measurements)
- NEMS *Water Level* (continuous measurements)
- NEMS *Water Quality – Part 1 (Groundwater), Part 3 (Lakes) and Part 4 (Coastal Waters)*, and
- NEMS *Water Temperature* (continuous measurements).

About This Standard

Introduction

Discrete ('grab' or 'spot') river water quality sampling is carried out across New Zealand for many purposes. Water quality measurements help in our understanding of ecosystem health and also provide important information on the suitability of rivers and streams for specific uses, such as irrigation, stock watering, recreation and mahinga kai (food gathering).

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 river water quality data acquisition (sampling and measurement), quality assurance and archiving associated with long-term State of the Environment (SoE) monitoring programmes. The principal purpose of SoE water quality monitoring is to assess state (condition) of waters and trends through time.

Assembling a valuable long-term river water 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 river water quality can vary greatly in time and space, and is subject to many influences. These influences can include water abstraction, groundwater intrusion, sediment resuspension, biological processes, and both point and diffuse source contaminant discharges.

Discrete river water 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 water quality sampling and measurements carried out in rivers and streams across New Zealand.

This document forms Part 2 of a four-part document series on discrete water quality sampling and measurement. The other three parts address groundwater, 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 domains. However, consistency in content is maintained across the documents where possible to help to facilitate an integrated approach to water monitoring and management.

Objective

The objective of this Standard is to ensure discrete river water 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 the fresh water reaches of permanently and intermittently flowing rivers and streams (herewith referred to as rivers only). For clarity, spring outflows are addressed in Part 1 of the Standard (*Groundwater*) and tidal reaches of rivers are addressed in Part 4 (*Coastal Waters*).

This Standard focuses specifically on long-term monitoring programmes (e.g. SoE monitoring) and certain methods presented may not be applicable to some specific forms of monitoring, such as consent monitoring. For sampling and testing of microbial water quality at recreational sites, existing national guidance is available in MfE/MoH (2003).

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 the sampling visit)
- 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 SoE programmes for rivers. This list is not fully prescriptive for environmental monitoring and alternative specialist advice should be sought for variables not included here.

Variable		Nomenclature ¹
<i>Physico-chemical properties</i>		
Water temperature – field		Temp
Dissolved oxygen – field percentage saturation		DO % sat
Dissolved oxygen – field		DO
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
<i>Optical properties</i>		
Visual clarity (horizontal black disk)		VC – BD
Turbidity – field ²		Turb – field
Turbidity – laboratory ²		Turb
Total suspended solids		TSS
Absorbance ³		Absorb
<i>Nutrients</i>		
Nitrate nitrogen		NO ₃ -N
Nitrite nitrogen		NO ₂ -N
Nitrite-nitrate nitrogen (also known as total oxidised nitrogen)		NNN
Ammoniacal nitrogen		NH ₄ -N
Total nitrogen – direct		TN-A
Total nitrogen – indirect		TN-K
Dissolved reactive phosphorus		DRP
Total phosphorus		TP
Dissolved organic carbon (non-purgeable)		DOC
<i>Anions and cations (dissolved, and excluding metals)⁴</i>		
Calcium (Ca diss), Magnesium (Mg diss), Sodium (Na diss), Potassium (K diss), Chloride (Cl diss), Sulphate (SO ₄ diss), Bicarbonate (HCO ₃ diss), Carbonate (CO ₃ diss), Bromide (Br diss), Fluoride (F diss), Iron (Fe diss), Manganese (Mn diss), and Silica (SiO ₂ diss reactive)		As left
Total (dissolved) hardness		Hard
Total (dissolved) Alkalinity		Alkt
<i>Metals and metalloids (dissolved)</i>		
Aluminium (Al diss), Arsenic (As diss), Cadmium (Cd diss), Copper (Cu diss), Chromium (Cr diss), Lead (Pb diss) and Zinc (Zn diss)		As left
<i>Metals and metalloids (total)</i>		
Aluminium (Al total), Arsenic (As total), Cadmium (Cd total), Copper (Cu total), Chromium (Cr total), Lead (Pb total) and Zinc (Zn total)		As left

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<i>Microbiological properties</i>	
<i>Escherichia coli (E. coli)</i>	EC
Faecal coliforms	FC
Enterococci ⁵	Ent
Chlorophyll <i>a</i> – laboratory	CHLA
Phaeophytin – laboratory	Phaeo

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 *Surrogate rather than ‘true’ measurement variable – measured as a proxy for another variable(s) and requires calibration against relevant laboratory measurements.*

³ *Measured for the purpose of calculating coloured dissolved organic matter (CDOM) which is indexed by the absorption coefficient of a filtrate at 440 nm, corrected for residual scattering.*

⁴ *Nitrate nitrogen, ammoniacal nitrogen and dissolved reactive phosphorus are also included in typical anion and cation suites.*

⁵ *Not typically measured in fresh waters but included as some SoE monitoring may have a focus on connections with downstream estuarine or coastal 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, these variables shall be coded QC 200 – unverified.

Variable	Nomenclature
Chlorophyll <i>a</i> – field (by fluorescence) ¹	CHF – field
Colour (hue) – field	Hue
Visual clarity (beam transmissometry)	VC – BT
Suspended sediment concentration ²	SSC

¹ *Surrogate rather than ‘true’ measurement variable – measured as a proxy for chlorophyll and requires calibration against relevant laboratory measurements.*

² *This variable is discussed in Section 5.4.3.3 only. Specific guidance on SSC measurement is addressed in the NEMS Suspended Sediment (in preparation) and will be added to this NEMS in a future update.*

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 *Freshwater monitoring protocols and quality assurance* (Davies-Colley et al., 2012) prepared as part of the Ministry for the Environment's 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 (Rivers)

As a means of achieving discrete river water 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.		
Equipment Specifications	Black disk	All black disk targets shall be painted with matte black paint. The viewer shall comprise a clean and unscratched viewing window and a glass 45° angle mirror.		
	Dissolved oxygen	Optical sensors shall be used to measure dissolved oxygen.		
Measurement Units, Accuracy and Resolution	Variable	Measurement unit	Measurement requirements	Measurement resolution
	Visual clarity – black disk (VC-BD)	m	<p>A minimum of two measurements shall be recorded using the appropriate diameter disk size for the following visibility ranges:</p> <ul style="list-style-type: none"> • 200 mm: >1.5 m • 60 mm: >0.5–1.5 m • 20 mm: ≤0.5 m. <p>A SHMAK (or equivalent) viewing tube may also be used for visibility measurements in the range of 0.02 to 0.5 m.</p>	1% (or 3 'significant' figures)
	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

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	Variable	Measurement unit	Sensor accuracy	Measurement resolution
Measurement Units, Accuracy and Resolution (con.)	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
	Turbidity (Turb – field) by ISO7027 near infrared light at 90° ³	FNU (Formazin Nephelometric Units)	± 0.3 from 0 to 999 FNU, and 5% for 1000 to 4000 FNU	0.1
Validation and Calibration	Records	Records of field meter calibration and validation shall be kept.		
	Black disk	At least a 12-monthly integrity check of the viewer using a reference viewer.		
	Water temperature	12-monthly validation checks against two traceable reference thermometers involving at least a 5-point validation process in accordance with the NEMS <i>Water Temperature</i> .		
	Dissolved oxygen	<p>Validation on each sampling day before deployment using 100% saturated air or water. Validation passes when the measurement is within ± 0.5% saturation.</p> <p>If validation fails, perform a single-point calibration using 100% saturated air or water.</p> <p>Whenever the sensor cap or membrane is replaced, perform a 2-point calibration using firstly 100% saturated air or water and secondly 0% saturation.</p> <p><i>Alternative option for 'high quality' sensors</i></p> <p>Validation and calibration is performed in full accordance with the requirements of Annex E. 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 E).</p>		

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Validation and Calibration (con.)	Specific conductivity	<p>Validation on each sampling day before deployment using at least two laboratory-prepared standard solutions. Validation passes when the measurement is within:</p> <ul style="list-style-type: none"> standards $\leq 10 \mu\text{S/cm}$: $\pm 25\%$ standards > 10 and $\leq 200 \mu\text{S/cm}$: $\pm 15\%$ standards $< 200 \mu\text{S/cm}$: $\pm 5\%$ <p>If validation fails, the sensor shall be calibrated using a standard higher than the concentration in the water to be measured – around $1414 \mu\text{S/cm}$ – and validate in a range close to expected measurements in a $148 \mu\text{S/cm}$ solution.</p> <p>At the minimum, field validation shall be repeated once at the end of day in $148 \mu\text{S/cm}$ standard solution.</p> <p><i>Alternative option for 'high quality' sensors</i></p> <p>Validation and calibration is performed in full accordance with the requirements of Annex E. Validation is achieved when a subsequent conductivity measurement in a calibration standard is in the range:</p> <ul style="list-style-type: none"> standards $\leq 10 \text{ uS/cm}$: $\pm 25\%$ standards > 10 and $\leq 200 \text{ uS/cm}$: $\pm 15\%$ standards $> 200 \text{ uS/cm}$: $\pm 5\%$ <p>(Calibration before, and a successful validation after the measurement, as per Annex E).</p>
	pH	<p>A minimum of a 2-point calibration on each day of use with standard buffer solutions of pH 7 and one or more of pH 4, 9 or 10. To pass calibration, the meter's millivolts reading in pH 7 buffer shall be $0 \text{ mV} \pm$ the manufacturer's specifications (typically 35–45 mV).</p> <p>Validation at the end of each day using a laboratory-prepared standard solution of pH 7. To pass validation, pH shall be in the range 6.8 to 7.2.</p> <p><i>Alternative option for 'high quality' sensors</i></p> <p>Validation and calibration is performed in full accordance with the requirements of Annex E. 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 E).</p>
	Turbidity (infrared light at 90°)	<p>For handheld meters, a single zero-point validation shall be performed monthly using distilled water and take an in situ water sample for laboratory measurement. Validation is achieved if the measurement is within $\pm 10\%$ or 2 FNU of the laboratory measurement, whichever is greater.</p>
Site Location and Stationarity		<p>The site location for field measurements and water sample collection shall be clearly identifiable and retained through time.</p>

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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 visual clarity disk size, field meter(s) make, model and ID number, and the environmental conditions (e.g. flow state) under which measurements and/or samples were collected.
Timing of Measurements	Accuracy and resolution	The timing of field measurements and sample collection shall be recorded as a single visit time to the nearest 5 minutes, with the time recorded representative of the time field meter measurements were made.
	Time zone	Time shall be expressed as New Zealand Standard Time (NZST). <i>Note: Do not use New Zealand Daylight Time (NZDT).</i>
Field Equipment Deployment	Meters	The meter sensor(s) shall be deployed in the main current and time allowed to stabilise in accordance with the manufacturer's specifications.
	Black disk	The viewer and black disk shall be deployed so that the path of sight is uniformly lit and bed disturbance plumes are avoided prior to measurement. A viewer shall be used to obtain measurements.
Sample Collection, Processing and Handling	Bottle type and filling requirements	<p>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 4, Section 5.4.3):</p> <ul style="list-style-type: none"> • <i>Specific conductivity, pH and turbidity</i>: Unpreserved bottle filled with no air gap • <i>TSS</i>: Unpreserved bottle filled to the top • <i>Nutrients</i>: Unpreserved bottle filled without air gap • <i>Dissolved organic carbon</i>: Unpreserved and furnace brown glass bottle filled with no air gap • <i>Anions, cations, total hardness, total alkalinity and metals (dissolved)</i>: Unpreserved bottle filled with no air gap • <i>Total metals</i>: Nitric or hydrochloric acid-preserved bottle, filled to shoulder and sample inverted to mix • <i>Microbial samples</i>: Sterile unpreserved bottle filled directly with a small air gap • <i>Chlorophyll a</i>: Opaque unpreserved bottle filled to the top. <p>All unpreserved bottles shall be field rinsed prior to sample collection except sterile bottles for microbial testing.</p>
	Sample collection	Samples shall be collected at approximately 0.2 m below the water's surface, facing directly into the water current.
	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.

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Sample Collection, Processing and Handling (con.)	Sample filtration	Samples collected for chlorophyll <i>a</i> , absorbance or dissolved organic carbon, nutrient, metal, anion or cation measurements shall be dispatched to the laboratory for filtering. ⁴		
	Sample traceability and integrity	Samples shall be unequivocally identifiable and accompanied by a completed Chain of Custody form that provides 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: <ul style="list-style-type: none"> • sample temperature on arrival (°C), and • 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 timeframes	All microbial, pH and turbidity testing shall commence within 36 hours of sample collection. Laboratory filtration for unpreserved samples for chlorophyll <i>a</i> , absorbance, or dissolved organic carbon, nutrient, metal, anion or cation testing shall be completed within 36 hours of sample collection.		
Test Method and Measurement Requirements	Variable	Measurement unit	Test method(s)	Method detection limit⁵
	pH	pH units at 25°C	APHA 4500-H ⁺ B	0.1 ⁶
	Specific conductivity (SpC)	µS/cm at 25°C	APHA 2510 B	1 ⁶

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	Variable	Measurement unit	Test method(s)	Method detection limit ⁵
Test Method and Measurement Requirements (con.)	<i>Optical</i>			
	Turbidity (Turb) (by near infrared light) ³	FNU	ISO 7027	0.05
	Total suspended solids (TSS)	mg/L	APHA 2540 D	1
	Absorbance (Absorb) <ul style="list-style-type: none"> • 340 nm • 440 nm • 780 nm 	m ⁻¹	APHA 5910 B	0.002
	<i>Nutrients</i>			
	Nitrate nitrogen (NO ₃ -N)	mg/L	APHA 4500-NO ₃ I (calculation)	0.002
	Nitrite nitrogen (NO ₂ -N)		APHA 4500-NO ₃ I	
	Nitrite-nitrate nitrogen (NNN)		APHA 4500-NO ₃ I	
	Ammoniacal nitrogen (NH ₄ -N)		APHA 4500-NH ₃ H	0.005
	Total nitrogen – direct (TN-A) ⁷		APHA 4500-N C <i>or</i> APHA 4500-P J potassium persulphate digestion then analysis by APHA 4500-NO ₃ I	0.01
	Dissolved reactive phosphorus (DRP)		APHA 4500-P G	0.001
	Total phosphorus (TP)		APHA 4500-P B 5 <i>or</i> J persulphate digestion then analysis by APHA 4500-P G	0.002
	Dissolved organic carbon (DOC)		APHA 5310-C	0.3

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	Variable	Measurement unit	Test method(s)	Method detection limit⁵
Test Method and Measurement Requirements (con.)	<i>Anions and cations (dissolved)</i>			
	Bicarbonate (HCO ₃ diss)	mg/L CaCO ₃	APHA 4500-CO ₂ D <i>or</i> APHA 2320	1.0 at 25°C
	Bromide (Br diss)	mg/L	APHA 4110 B	0.05
	Calcium (Ca diss)		APHA 3120 B <i>or</i> APHA 3125 B	
	Carbonate (CO ₃ diss)	mg/L CaCO ₃	APHA 4500-CO ₂ D <i>or</i> APHA 2320	1.0 at 25°C
	Chloride (Cl diss)	mg/L	APHA 4110 B	0.5
	Fluoride (F diss)		APHA 4110 B <i>or</i> APHA 4500-F C <i>or</i> G	0.05
	Iron (Fe diss)		APHA 3125 B	0.02
	Magnesium (Mg diss)		APHA 3120 B <i>or</i> APHA 3125 B	
	Manganese (Mn diss)			0.005
	Potassium (K diss)			0.05
	Silica (SiO ₂ diss reactive)		mg/L as SiO ₂	APHA 4500-SiO ₂ -F <i>or</i> APHA 3120 B
	Sodium (Na diss)	mg/L	APHA 3120 B <i>or</i> APHA 3125 B	0.02
	Sulphate (SO ₄ diss)		APHA 4110 B	0.5
	Total alkalinity (Alkt)	mg/L CaCO ₃	APHA 2320 B	1 ⁶ at 25°C
	Total anion/ total cation balance check	% difference	APHA 1030 E	0.1 ⁶
	Total hardness (Hard)	mg/L CaCO ₃	APHA 2340 B	1

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	Variable	Measurement unit	Test method(s)	Method detection limit ⁵
Test Method and Measurement Requirements (con.)	<i>Metals and metalloids (dissolved)</i>			
	Aluminium (Al diss)	mg/L	APHA 3125 B	0.005
	Arsenic (As diss)			0.001
	Cadmium (Cd diss)			0.00005
	Chromium (Cr diss)			0.0005
	Copper (Cu diss)			0.0005
	Lead (Pb diss)			0.0001
	Zinc (Zn diss)			0.001
	<i>Metals and metalloids (total)</i>			
	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)			0.001
	Copper (Cu total)			0.0005
Lead (Pb total)	0.0005			
Zinc (Zn total)	0.001			

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	Variable	Measurement unit	Test method(s)	Method detection limit ⁵
Test Method and Measurement Requirements (con.)	<i>Microbial</i>			
	Faecal coliforms (FC)	cfu/100 mL	APHA 9222 D	1
	<i>E. coli</i> (EC)	MPN/100 mL	APHA 9223 B	
	Enterococci (Ent)	MPN/100 mL	APHA 9230 D b	1
	Chlorophyll <i>a</i> (CHLA)	mg/L	APHA 10200 H and fluorometry ⁸	0.0002 ⁸
	Phaeophytin (Phaeo)			
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	<p>The laboratory measurements shall be provided in a report that specifies the:</p> <ul style="list-style-type: none"> • date and time of both sample collection and receipt at the laboratory • form of measurement made (e.g. dissolved vs total) • measurement value and units • uncertainty of measurement (at a 95% confidence level) • measurement method and standard method detection limit, including details of any modifications made to these (e.g. from diluting samples), and • 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 and 0.001 mg/L is equivalent to 1 µg/L, 1 mg/m³ or 1 ppb.

² 1 µS/cm is equivalent to 0.1 mS/m.

³ Surrogate variable measured as a proxy for one or more other variables.

⁴ Some samples may have high organic content and warrant filtering in the field for rapid preservation.

⁵ The specified method detection limits (MDLs) represent the minimum required for 'clean' river waters. 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.

⁶ Represents a measurement resolution rather than a method detection limit.

⁷ Calculation of total nitrogen by the summation of Total Kjeldahl Nitrogen and NNN (TN-indirect) may be preferred for nitrogen-rich waters where suspended sediment concentrations are typically > 20 mg/L and an existing record of TN-indirect measurements exists. See subsection 5.4.3.4.

⁸ APHA 10200 H and spectrophotometry (to a minimum method detection limit of 0.003 mg/L) is an acceptable alternative method for eutrophic rivers (defined by an annual median CHLA concentration above 0.005 mg/L). See subsection 5.4.3.8.

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 form. A photograph of the site is taken at least annually using a camera with geo-referencing capability.
	Electronic data capture	Visit meta data 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, re-validation is performed using an appropriate standard.
	Visual clarity	The viewer is equipped with a glass window to reduce potential scratching. Visibilities less than 0.1 m are better calculated from measurements on a diluted water sample using a SHMAK clarity tube.
	pH	pH is measured as a supporting variable where ammoniacal nitrogen and/or metals are measured.
	Flow/river discharge	Discharge is measured or estimated to ± 20% as a supporting variable for river water quality measurements.
	Quality assurance	As a minimum, a 12-monthly inter-agency audit is performed to verify measurement practices. This exercise should include: <ul style="list-style-type: none"> • field meter calibration, deployment and measurement • all other field measurements and observations, and • water sample collection, pre-treatment and handling, with blind duplicate water samples dispatched for laboratory analysis.

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Sample Integrity	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.
	Holding times	Water samples are dispatched to the laboratory within 24 hours of collection, otherwise stored in dark, cool (4°C optimum, unless advised otherwise by the laboratory for preserved samples) and secure conditions.
	Field blanks	For very low (oligotrophic) nutrient waters, field blanks are used on a routine (quarterly or 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 re-retesting where required and appropriate.
Reporting and Data 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 re-testing if necessary.
		The historical site measurement range and relationships with other variables shall be 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: <ul style="list-style-type: none"> • site and field visit metadata • field meter validation results and calibration details • field measurements together with meter/sensor make and model • censored and uncensored laboratory values together with associated uncertainty of measurement values • date, time and condition of samples received at the laboratory, and • 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	<i>Quality assurance requirements are under development.</i>	

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 rivers 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. Special attention to safety is needed when sampling of rivers is conducted from the shore, a bridge, a boat or by wading during high, swift and/or turbid conditions. 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 river waters likely to present a significant health risk (e.g. known sewage contamination, toxic cyanobacteria).

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 or 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 sampling personnel are trained and competent, field meters are well maintained and calibrated/validated, and appropriate sample collection, preservation and handling methods are employed. Particular emphasis shall 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 or audit. This QA exercise should seek to:

1. validate the reproducibility of field measurements (e.g. dissolved oxygen and visual clarity), and
2. deliver to the laboratory 'dependable' samples that are representative of the water body 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. black disk)
- 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 used on a regular (e.g. quarterly or six-monthly) basis when measuring river waters with very low nutrient concentrations (e.g. reference sites) to check for any background contamination arising from the sample container, collection or handling. A field blank should be submitted to the laboratory for analysis in the same type of bottle as the river water 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 rivers are outlined in subsection 2.6. 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 river monitoring field record forms with pre-printed site names and site numbers, and standardised text options for sampling method, black

disk sizes, 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. ix) 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) river monitoring programmes.

There is considerable commonality in river water quality variables with those typically measured across the groundwater (Part 1), 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

The core monitoring equipment that will generally be required includes:

- an instrument (multivariable field meter) to measure water temperature and dissolved oxygen (possibly also specific conductivity, pH, turbidity and chlorophyll *a*)
- a fixed-length or telescopic sampling pole
- a bucket with rope for bridge sampling (or for sub-sampling)
- a set of black disks and viewer (underwater periscope) for horizontal black disk measurement, and a SHMAK clarity tube
- 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.

All equipment and devices shall, as far as practical, comprise materials that are inert with respect to the variables to be measured. It is essential that all equipment and devices are properly maintained and cleaned to avoid contamination of water samples.

1.7 Field Meters

Some river water quality variables need to be measured on site using field meters because preservation of water samples for later measurement in the laboratory is either impossible (e.g. water temperature) or difficult (e.g. dissolved oxygen).

Specific conductivity, pH, turbidity and chlorophyll *a* may be measured in the field or the laboratory. However, the time taken for pH measurements to completely

stabilise can be very long in waters of low ionic strength. For this reason, pH in surface waters is usually best measured in laboratory conditions.

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 4 in subsection 5.4.3 for the water quality variables listed in the Scope of this document (p. ixi). 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), 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. nutrients, turbidity and conductivity measurements may be performed from a single 500 mL unpreserved 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. suspended solids) may require a larger sample volume to provide sufficient residue on glass fibre filters (e.g. 5 L or more from clear rivers) than samples collected from turbid waters.

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

Filtration through 0.45 µm pore size filters is an essential preparatory step to separate particulate and aqueous fractions of a water sample when samples are collected for dissolved nutrient, metal, trace element or chlorophyll-*a* analysis. Filtration also removes micro-organisms which can alter the water sample's chemical composition.

It is a requirement of this Standard to filter river water samples in the laboratory.

Filtering samples in the field can be time consuming and carries the potential for sample contamination; laboratory filtering is generally preferable.

However, filtering water samples in the field (or upon return to the office which provides a cleaner and more 'controlled' environment), including immediate preservation of the dissolved fraction of samples is recommended where:

- samples have high biochemical activity (e.g. near-dry river with high algal content)
- samples are from anoxic waters and/or waters with high organic carbon content
- samples are collected in areas of known groundwater/surface water interaction and it is intended to compare surface and groundwater sample measurements, or
- there is likely to be significant delays (e.g. two or more days) with delivery of samples to the laboratory.

To maintain sample integrity for subsequent analysis, 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.

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 4.4).

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 C) shall accompany water samples to provide an audit trail from sample dispatch (subsection 4.4) 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 and Platforms

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 monitoring platforms, and outlines key health and safety considerations, and visit metadata requirements.

2.1 Site (Point) Location

Monitoring of river water quality is about measuring the water quality characteristics at *reach* scale. The location for field measurements and water sample collection shall be in an appropriate geomorphic habitat for that reach well away from the influence of point sources, tributary stream and drain confluences and dead zones (e.g. backflow eddies) that will not have completely mixed in the river channel.

The monitoring location should be easily identifiable, preferably with a permanent location marker (e.g. warratah or external staff gauge) to ensure safe access and consistency in the location of field measurements and sample collection through time.

Field measurements and water samples shall be collected from a representative 'fully mixed' part of the channel. Samples shall be collected from 'flowing water' in a run where possible (Figure 1).

Field measurements and sample collection from pools, eddies, eddy lines, backwaters and areas immediately downstream of stream confluences and contaminant discharges (e.g. stormwater inputs) should be avoided because of the potential occurrence of 'dead zones' of poorly mixed water in which water quality characteristics may differ from the river main-stream. Although there is a degree of subjectivity in identifying riffles, runs and pools in some rivers, Figure 2 and the following simple identification guideline (based on Harding et al., 2009) may be helpful.

- **Riffle** Shallow depth, moderate to fast water velocity, with mixed currents, surface rippled and largely broken.
- **Pool** Deep, slow-flowing water with a smooth water surface, usually where the stream widens and/or deepens.
- **Run** Intermediate between riffle and pool, low to moderate depth, slow to moderate water velocity, uniform to slightly variable current, surface smooth-rippled and unbroken.

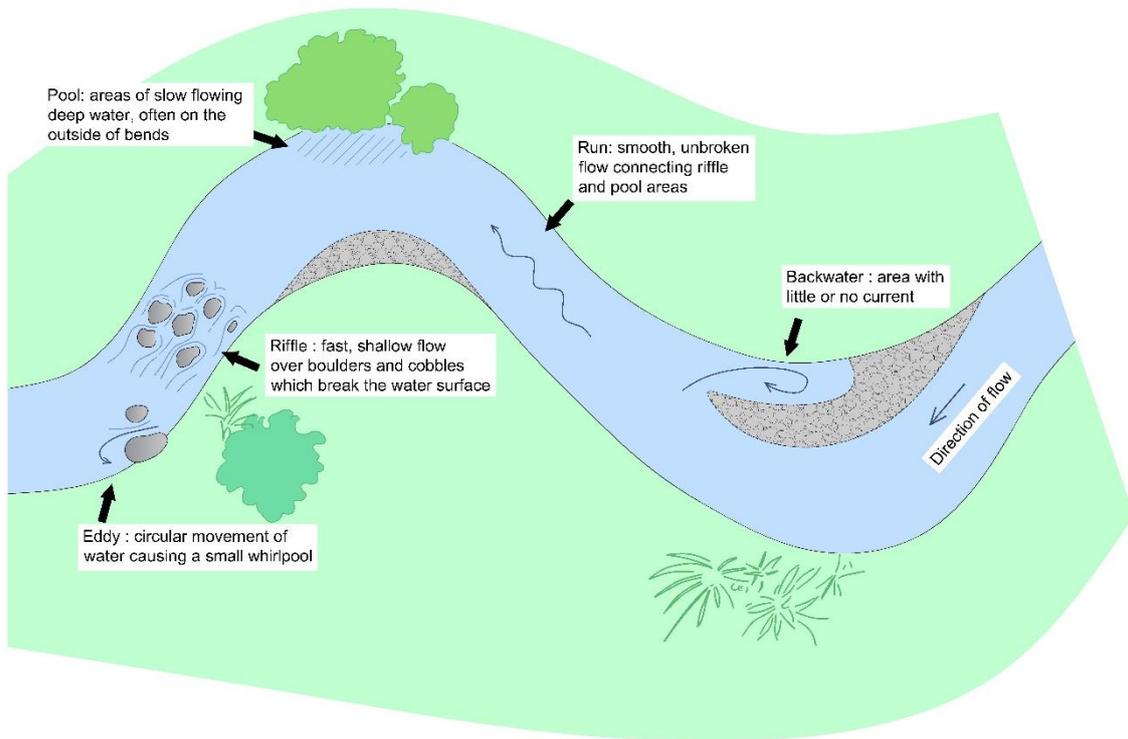


Figure 1 – Schematic of a river showing run, riffle, pool and other features

Figure: Quentin Gilkison, after Kilroy and Biggs (2002).

2.2 Site Metadata

Site metadata shall be recorded, including:

- river name
- site name and number
- site location; for example, GPS units or latitude/longitude coordinates expressed to a minimum of 6 decimal places
- site altitude
- related sites and records, including the nearest weather station and flow/level recorder
- relevant environmental characteristics and features – immediate land use/ riparian margin features (e.g. fenced/unfenced, vegetation, eroded banks) and presence of structures (e.g. stormwater or irrigation pipes)
- start date of monitoring
- typical sampling time*
- photographs of the site
- landowner contact details and, where relevant, associated procedures for accessing the site
- channel morphology and access notes, including the location of gently shelving point bars which should provide safe wading access even in elevated flows, and
- specific health and safety considerations.

** River water quality is characterised by high temporal variability on both a diurnal basis (for some variables) and a seasonal basis. Consistency as regards time of day of sampling is very important for variables that fluctuate diurnally (e.g. water temperature, DO, pH) if the data are to be used for long-term trend analysis. Inconsistent sampling times for these variables add noise to the dataset which could compromise long-term trend detection; for example, water temperature change driven by climate change. In order to achieve time-of-day consistency, sites (especially reference sites) with only spot measurements of water temperature, DO and pH should ideally be visited in the same order on each 'run' with the aim being to collect samples within ± 1 hour from a given site on each sampling 'run'. However, the requirement of sampling at the same time of day is less important for sites where continuous measurements of water temperature, DO and pH are being collected.*

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.

2.3 Monitoring Platforms

The monitoring platform shall be determined at the time of designing the monitoring programme. If a different platform from usual is used, record this on the field form as part of the visit metadata.

2.3.1 Wading

Wading is the best way to collect field measurements and water samples from rivers of wadeable depth.

Extreme care should be taken when wading in very muddy environments for health and safety reasons and to avoid sediment re-suspension affecting field measurements and water samples.

2.3.2 Bankside

Where wading is judged to be unsafe, notably for deep or swift rivers, or during very high or turbid flows, it is preferable that water samples are collected using a fixed-length or telescopic pole remotely from the river bank or river's edge, or by telescopic pole or bucket from a bridge in the centre of the channel.

2.3.3 Bridges

When wading or bankside sampling are judged to be unsafe or unsuitable (e.g. presence of a dense macrophyte bed), field measurements and water samples can be collected by telescopic pole or bucket from a nearby bridge in the centre of the channel. Sampling and field measurements should wherever possible be taken from the upstream side of the bridge. This avoids potential contamination sources from material lost from vehicles and animals crossing the bridge, stormwater and

road run-off associated with the bridge, or birds and wildlife roosting or living in or under the bridge structure.

Note: Sampling from a road or bridge will require working to an approved traffic management plan lodged with the relevant roading authority. An onsite traffic controller (TC or STMS) will also need to be present.

2.3.4 Automatic Sampling Stations

When channel access is judged to be hazardous for wading or even use of a telescopic sample pole, if an automatic sampler is installed nearby, this could be used to obtain bulk water samples and field measurements.

2.3.5 Boats

Boats may be required on large or unwadeable rivers. Boat type and size should be determined by environmental conditions, practicality, and health and safety requirements.

A kayak or small inflatable may be suitable for sampling some sites and have the advantage of being quick to deploy. Jet boats are suitable for use on shallow or braided rivers. Motorised vessels and their handlers will have to comply with all Maritime New Zealand rules and be equipped with the appropriate safety equipment.

Care shall be taken to avoid biasing field measurements and contaminating water samples with disturbance of riverbed sediment or any discharges from the boat.

2.4 Monitoring Strategies

2.4.1 General Principles

Wherever possible it is best to work from downstream to upstream so as to avoid sediment plumes created by in-channel activities.

The order of activities at the site is important, particularly for ensuring sediment plumes from bed or macrophyte disturbance are avoided. The recommended order of activities is as follows:

- visit metadata – observations of site and sample conditions (see subsection 2.6)
- deployment of field instruments – leave to equilibrate, and set logging, say at 1-minute intervals, if instruments have this capability (see subsection 3.3)
- collection of visual clarity (see subsection 3.3.2) and other optical measurements (e.g. colour)
- water sample collection, starting with microbial samples first (see subsection 4.2)
- record field meter measurements (see subsection 3.3), and

- carry out additional activities as applicable (e.g. periphyton cover assessment, gauging, continuous sensor checks, site maintenance).

The site-specific location of the activities is also an important consideration in terms of placement of field meter sensors and collection of measurements to avoid sediment plumes compromising measurements.

2.4.2 Braided Rivers

Consistency is recommended in sampling from one chosen bank and sampling the first major accessible braid. Care may be needed in braided (and other) rivers to avoid localised groundwater upwellings, often indicated by discrete dense patches of periphyton and cooler water temperatures.

2.4.3 Spring-fed Streams

For spring-fed macrophyte-dominated/ clogged streams, identify an area of clear open water for measurements and sampling. If this is not possible then clear an area of macrophytes in deeper water away from the stream edge and let any disturbed sediment flush and settle for at least 15 minutes prior to taking field measurements and water samples.

2.4.4 Shallow Rivers

When taking field measurements and sampling in very shallow conditions (e.g. summer low flows), choose the deepest part of the flowing channel.

2.5 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 only can be attempted with suitable modifications such as self-fastening to a suitable anchor point, use of harnesses and ropes, or sampling from a bridge.

If conditions are considered to make field measurements or sampling unsafe, they should not be attempted. Such conditions include rivers in major flood flow and 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.

2.6 Visit Metadata

A standard form shall be used to record field metadata (observations) on each visit to the site to collect field measurements (Section 3) and water samples (Section 4). This form shall include:

- the name of the water body
- the name of the site location
- any unique sample ID number(s) assigned
- the name(s) of the field personnel
- information on measurements made at specific locations (e.g. bridge, from the bank)
- date and time (in NZST) of field measurements
- the weather conditions at the time of measurements
- flow state (rated, gauged or estimated – at least as ‘low’, ‘moderate’, ‘high’)
- protocols used, including any deviations from standard field measurement and/or sampling protocols (e.g. water samples taken from bridge during a high flow event instead of at the regular sampling location, field filtration of samples), or if there were any difficulties with calibration/validation of field meters or sample collection
- general sample colouration (clear/colourless, turbid or brown) and if the water has any unusual smell
- the presence of any scums, foams or floatables
- notes of any other factors that may influence the data being collected; for example, presence of potential contaminant sources such as waterfowl or stock, and
- notes of significant changes in reach characteristics; for example, fodder crop grazed to bank, bulldozer in the river, bank erosion or slumping that may result in sediment entering the water.

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

2.6.1 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.

2.6.2 Time Records

The timing of field measurements and sample collection shall be recorded as a single site visit time to the nearest 5 minutes. The time recorded shall be the time at which field meter measurements are recorded. It is recommended that arrival

and departure times at a site are also logged on the field record form so as to bracket other activities on site (e.g. water sampling, visual clarity, flow estimation) that take finite time to conduct.

Note: Any prolonged delays between collection of field measurements and water samples should be recorded on the field form, with a note made of the time at which individual measurements and samples were collected. This is particularly important if the river level is rising during the field visit and/or there is a change in water clarity or colour.

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

2.7 Decontamination

All field meters, measuring equipment and sampling devices should be properly cleaned to avoid transfer of biological pests (e.g. Didymo) and contaminants between monitoring sites. Boats and trailers, if used, should also be inspected for animal and plant pests (e.g. aquatic macrophytes) prior to leaving the sampled river. This is particularly important where multiple rivers are visited on the same day.

Note the principles of 'Check, Clean, Dry' for decontamination.

3 Field Measurements

In This Section

This section focuses on field measurements. It outlines requirements for field meter sensors, calibration and validation, field meter maintenance and the collection of field measurements. Several variables (beam transmissometry and colour) included here require further information before quality codes can be assigned to measurements of these.

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 D.

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' sensors on some 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 E.

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 $\pm 0.3^{\circ}\text{C}$ to be eligible for the highest quality code (QC 600). An accuracy of $\pm 0.5^{\circ}\text{C}$ 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.

Galvanic or electrochemical (membrane) sensors shall only be 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:

- $\pm 3\%$ 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:

$$\text{DO\% Saturation}_{\text{LOCAL}} = \text{DO\% saturation}_{\text{RAW}} \times \text{Barometric pressure} \div 1013.25$$

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:

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

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 meter 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 $\pm 1 \mu\text{S}/\text{cm}$ or $\pm 0.5\%$ 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 which 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 coastal sites on the same day, a conductivity standard around 12,880 $\mu\text{S}/\text{cm}$ 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 coastal waters is preferred.

3.1.4 pH

This Standard recommends pH is measured 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 validated 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 is preferable.

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 Turbidity

This Standard requires the use of turbidity sensors that conform to ISO 7027. The manufacturer's accuracy sensor specification shall be ± 1 FNU in the range 0 to 999 FNU ($\pm 5\%$ for measurements above 1000 FNU).

The key features of ISO 7027 are:

- light source: monochromatic infrared beam with a maximum 1.5°
- convergence angle measurement wavelength: $860 \text{ nm} \pm 30 \text{ nm}$
- measurement angle: $90^\circ \pm 2.5^\circ$ (Figure 2)
- calibration standard: formazin
- reporting units: formazin nephelometric units (FNU), and
- operational range: 0–4000 FNU.

As outlined in the NEMS *Turbidity*, available turbidity sensors vary in terms of the:

- spectral sensitivity and beam geometry
- angular range of detected light
- angle between emitted and detected light beams
- wavelength of detected light
- reference suspension used for calibration, and
- turbidity range able to be measured.

Variation in the first four characteristics can produce numerically different results.

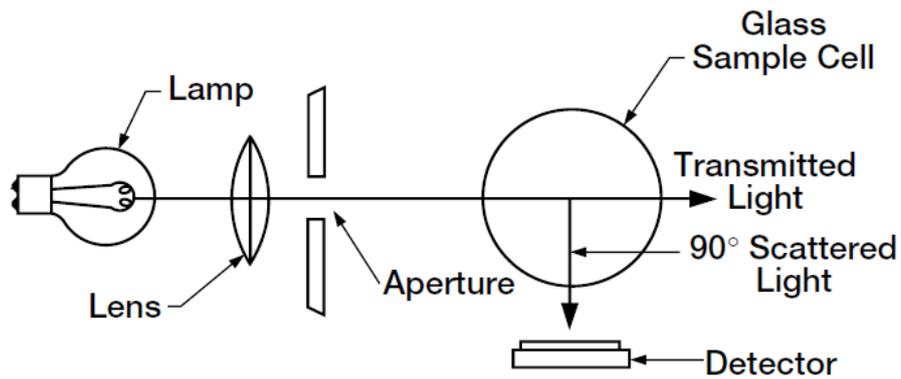


Figure 2 – Schematic of the key components of a turbidity sensor

A sensor that detects light back-scattered at an angle of 90° from the transmitted light pathway.

Source: Reproduced from NEMS Turbidity.

Most field sensors follow the ISO 7027 Standard using monochromatic, near-infrared light and are based around wastewater measurements with a higher turbidity range.

Infrared light is detected at 90° and is repeatable from a handheld meter to an ISO 7027 lab measurement. Near-infrared light measurement avoids interference by humic absorption of light and is also less influenced by sediment colour. Thus, the ISO 7027 Standard has broader field application and has been adopted in both this NEMS and NEMS *Turbidity* (continuous measurement). Field turbidity measurements obtained with a white light sensor source under APHA 2130 B or EPA 180.1 are not necessarily inter-convertible with laboratory test measurements made using the same method.

Caution: Many white light handheld sensors only measure the 180° light attenuation or ‘Ratio Off’ method. This meets the APHA or EPA Standard where turbidity is below 40 nephelometric turbidity units (NTU). Measurements above 40 NTU require backscatter measurement in addition to the attenuation which is typically called ‘Ratio On’. Without the ‘Ratio On’ feature, no direct comparison between field and laboratory turbidity measurements is possible.

In terms of quality coding under this Standard:

- Only near-infrared FNU turbidity data shall be eligible for assignment of the maximum quality code (QC 600).
- Turbidity measurements obtained from any non-conforming white light field instruments that meet the APHA 2130 B or EPA 180.1 Standard shall be reported in nephelometric turbidity units (NTU) and automatically be assigned QC 400.
- Measurements obtained from instruments that do not meet the ISO 7027 or EPA 180.1 Standard but use a backscatter-type detection system and formazin as the calibration standard should be reported in formazin backscatter units (FBU), and automatically be assigned QC 400.

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

Note: Turbidity is an index of light scattering in water. The primary purpose of measuring turbidity is to serve as a surrogate for other water quality variables; for example, suspended sediment, visual clarity.

3.1.6 Chlorophyll *a* (by Fluorescence)

Fluorescence sensors can be used to provide a surrogate (indirect) measure of chlorophyll *a* in relative fluorescence units (RFU) between 0 and 100%. A (manufacturer) sensor accuracy of ± 0.1 RFU is recommended. Narrow bandpass optics are also recommended to filter out interference from dead algal cells and reduce interference from suspended sediments in the water and dissolved organic matter.

The sensor output values can be converted into actual chlorophyll I concentrations by using a post-calibration procedure, after the chlorophyll content of discrete water samples have been analysed in the laboratory (see subsection 5.4.3.8).

Sensor calibration and validation practices are 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 <i>Water Temperature</i> (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. <i>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.</i>

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<p>Dissolved Oxygen (DO % Sat & DO)</p>	<p>Single-point calibration using 100% saturated air or water on each sampling day in the office before use if validation fails.</p> <p>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 (Na₂SO₃) to remove the oxygen. (Use of a calibration chamber can assist when using gas.)</p> <p>No field measurements should be made for 2 hrs after a 0% calibration with Na₂SO₃ has been performed.</p>	<p>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%.</p> <p>If validation fails, calibrate the sensor.</p> <p><i>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.</i></p>
<p>Specific Conductivity (SpC)</p>	<p>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.</p> <p>Clean the sensor, recalibrate, or change the standard solution if calibration fails.</p>	<p>Validation on day of use before you leave the office with standard buffer solutions. Validation passes when the measurement is within:</p> <ul style="list-style-type: none"> • standards < 10 µS/cm: ± 25% • standards ≥ 10 and < 200 µS/cm: ± 15% • standards ≥ 200 µS/cm: ± 5%. <p>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.</p> <p>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).</p>

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<p>pH (pH – field)</p>	<p>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.</p> <p>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).</p>	<p>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).</p> <p>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).</p> <p>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).</p>
<p>Turbidity (Turb – field)</p>	<p>An annual 2-point calibration at a minimum. Also carry out a single zero-point calibration if the monthly zero-point validation reads > 0.5 FNU.</p> <p>CAUTION: The high-end calibration uses formazin – ingesting formazin can cause serious illness or death. Staff must be trained in the safe use of formazin or the meter can be sent to the laboratory for calibration where H&S risks are easier to manage.</p> <p>Standard solutions comprising non-toxic polystyrene beads may also be suitable.</p>	<p>For handheld meters, each month: perform a single zero-point validation using distilled water, and verify the field meter’s performance through collection of a water sample from one monitoring site for laboratory measurement.</p> <p>Validation passes if the measurement is within $\pm 10\%$ or 2 FNU where turbidity is < 20 FNU.</p>
<p>Chlorophyll <i>a</i> (CHF – field)</p>	<p>Two-point calibration monthly using red rhodamine dye.</p> <p>Also recalibrate sensors whenever the optics or filters are changed.</p>	<p>Verify field measurements once a month at one monitoring site via collection of an in situ water sample for verification through laboratory measurement (by fluorimetry).</p>

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.

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 solution aliquots 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	<p>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.</p> <p>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.</p> <p>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.</p> <p>As best practice, regardless of sensor type, perform a 2-point calibration every 6 months as part of regular maintenance.</p>
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	<p>Rinse daily, carefully wiping the glass bulb with a sponge or swab as needed.</p> <p>Monthly maintenance on top of routine calibration and validation. Keep sensor clean and moist. Place sensor in potassium chloride (KCl) 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.</p> <p>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.</p>
Turbidity and Chlorophyll <i>a</i>	As per the manufacturer’s instructions. It is important to keep the sensor clean.

3.3 Field Measurement Collection

The equipment used to make field measurements shall be recorded on the field record form (subsection 2.6). 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.

Where field measurements need to be taken from a bucket (e.g. if sampling from a bridge), rinse the bucket in the river three times before collection of sample. Water samples required for laboratory testing should be decanted from the bucket into laboratory bottles before immersing field meter sensors in the bucket. Sensors may need to be regularly moved in the bucket to provide a stable reading.

3.3.1 Field Meters

Deploy the field meter in the main flow before making your field observations (subsection 2.6) 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. Visual water clarity and colour may be measured, and water samples collected (Section 4), while the meter(s) is equilibrating.

If field measurements are being taken to help to interpret other water quality variables measured at a site, you will need to consider the location of the meter sensor with regards to water sample collection and the representativeness of the water 'parcel' from which the sample is taken. For example, if continuous sensors and/or automatic samplers are deployed, it is important to sample very close to the continuous sensor and auto-sampler intake.

3.3.1.1 Water Temperature

Water temperature measurements shall be recorded to a resolution of 0.1°C.

3.3.1.2 Dissolved Oxygen

Dissolved oxygen measurements shall be recorded to a resolution of 0.1% (DO saturation) or 0.01 mg/L (DO concentration), corrected to barometric pressure and altitude.

3.3.1.3 Specific Conductivity

Conductivity measurements shall be recorded to a resolution of 0.1 $\mu\text{S}/\text{cm}$, corrected to a reference water temperature of 25°C.

3.3.1.4 pH

pH measurements shall be recorded to a resolution of 0.01 pH units corrected to a reference water temperature of 25°C.

Note: The thickness of the glass electrodes determines the sensor stabilisation time. Glass electrodes are very slow to equilibrate in low ionic strength natural waters and

up to 30 minutes should be allowed. Stabilisation time is greatly reduced by properly maintaining the electrolyte and replacing the glass bulb as required (see Table 2).

3.3.1.5 Turbidity

Turbidity measurements shall be recorded to a resolution of 0.1 FNU.

3.3.1.6 Chlorophyll *a*

Depending on the sensor used, the measurements may be instantaneous or an average; for example, over one minute. All raw data should be recorded to a resolution of 0.01 RFU.

3.3.2 Visual Clarity

Horizontal black disk sighting range is typically used to assess the visual clarity of rivers and streams (Figure 3). Beam transmissometry can also be used to measure visual clarity and to verify visual measurements.



Figure 3 – Black disk observations in a river

Photograph: Deborah Ballantine.

Care shall be taken to avoid bias, most commonly from shadows across the path of sight in the water or contamination of the water by plumes of disturbed fine sediment.

- Under clear sun conditions, the path of sight shall be uniformly sunlit or uniformly in shadow. No partial shadowing, such as by riparian trees, should affect the path of sight, although dense shadow cast by an unbroken canopy or a high bank, is fine. If partial shadowing is unavoidable, black disk visibility should still be measured, but with a note in the visit metadata of the likelihood of bias.
- Avoid plumes of fine sediment. Any such plume caused by wading in the channel should be fully flushed from the water volume encompassing the path of sight before visibility is recorded.

Black disk measurements should ideally be made before (or upstream of) any other activity is undertaken that will result in a disturbance of the river bed. Sighting direction in relation to current is not usually important, although disturbance plumes may clear from the path of sight more quickly if the observation is made cross-current.

The correct disk size shall be used to keep the apparent size of the disk near-constant in the ‘optically large’ range of 1–10° of arc (Table 3). Disk size shall be recorded. The SHMAK tube is equivalent to black disk visibility at sighting ranges less than 0.5 m (Kilroy & Biggs, 2002) and is preferred for visibility measurements in turbid water. The main reason is to avoid interference due to shadowing of the sight path by the viewer in very turbid water (~ 20–100 mm).

Table 3 – Black disk sizes for different visibility ranges

To keep the apparent size of the disk near-constant in the ‘optically large’ range of 1-10° of arc.

Disk size (diameter)	Visibility range
200 mm	> 1.5 m
60 mm	> 0.5–1.5 m
20 mm	0.1–0.5 m
SHMAK tube (20 mm diam.)	0.02–0.5 m

3.3.2.1 Black Disk Measurement

Choose a site in a run area with wadeable depths and velocities less than 1 m/s. Pools should be avoided because of very slow currents and the likelihood of dead zones, but if a pool is used (e.g. so as to have sufficient path of sight in small rivers at low flow), extra care should be taken to avoid bed disturbance plumes. Water velocities should preferably exceed 0.1 m/s, to ensure that disturbed fines flow out of the viewing area reasonably quickly. Take care to avoid shadows (e.g. from bridges, trees, observers) and ensure that there are no interfering objects behind the disk (e.g. rocks) to a distance of at least 50% of the black disk distance.

The following procedure is preferably carried out by two people. Measurement can be taken by a single person provided the disk can be fixed to a stake or other thin structure that does not distort the background light field in the water.

1. The disk is either held or set in place, submerged just below the water surface.
2. The observer pulls the tape measure taut and waits for any disturbed sediment to flush from the path of sight (see Figure 4).
3. The disk is surveyed with the top of the viewer box snug against the observer’s face and allowing time for the eyes to adjust to the ambient lighting in the river.
4. When the disk is in view against the water background (i.e. not the river bank for example), the observer moves the disk until it just disappears. The distance from disk to viewer window is recorded as y_1 .

5. The observer then moves slowly back towards the disk until it just reappears and the distance from disk to viewer window is recorded as y_2 .
6. The average of the disappearance and reappearance distances is the horizontal visibility or horizontal black disk sighting range, $(y_1 + y_2)/2$.
7. The observer takes a second measurement or changes places with the second person so that they take an independent second measurement.
8. The measurement value to be reported is the average of the two measurements. If the difference between the two average measurements is greater than 10%, measurements should be repeated until better agreement is achieved.

Measurements shall be recorded to a resolution of 1%. For example, a visual clarity measurement around 1 m should be recorded to the nearest cm (e.g. 0.93 m or 1.13 m) but for measurements > 10 m recording to the nearest decimeter is sufficient (e.g. 9.3 m or 11.3 m). Measurements < 1m should be recorded to the nearest mm (e.g. 0.093 m or 0.113 m).

Note: Visual observations by two or more field staff can provide a useful internal quality assurance check to decrease the risk of bias (e.g. from sediment disturbance plumes, or inadvertent shadowing across the path of sight – particularly under the partial shade of riparian trees during clear sunny conditions).

Equipment and maintenance specifications for black disk are outlined in Annex F. These include an annual check of the condition of the black disk viewer against a reference viewer.

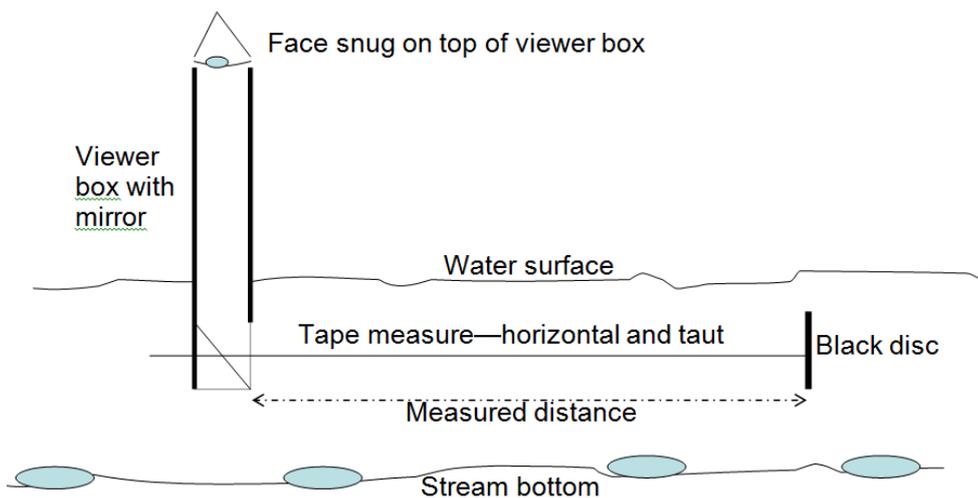


Figure 4 – Schematic showing equipment arrangement for correct measurement of horizontal black disk visual clarity

3.3.2.2 Clarity Tube Measurement

A clarity tube (commonly referred to as a Stream Habitat Monitoring Assessment Kit (SHMAK) tube) can be regarded as a mesocosm of the in situ black disk observation – at least for visibilities less than about 0.6 m, in which range the

SHMAK and in situ measurements give statistically identical results (Kilroy & Biggs, 2002). As with black disk observations, the light path should be uniformly lit, so take care to avoid shadows falling on the clarity tube during measurements; for example, from trees or observers.

The following procedure is easier when carried out by two people, although a single team member can perform all the tasks with care and some practice.

1. Obtain a 2 L water sample from a run area at the site and fill and cap the tube. A few 100 mL can be used for a pre-rinse if there is any concern about carry-over of water from the last use of the tube.
2. Orient the tube horizontally, with assistance of another team member or by resting on a suitable surface such as a fence post or vehicle roof (Figure 5). The aquarium magnets are deployed so that the magnet with mounted black disk is on the inside of the tube and its magnet pair is on the outside of the tube. The black target should be facing the viewing window (at the end) of the tube.
3. The black target is viewed while being moved slowly away towards the extinction point by shifting the outside magnet paired to that inside the tube.
4. The disappearance distance for the disk is noted and then the reappearance distance. The tube visual clarity measurement shall be recorded as the average of these two distances.



Figure 5 – Measuring visual clarity through a SHMAK tube

Photograph: Source: Rebecca Stott.

After use, the magnets should be stored safely within the protective sleeve for the SHMAK tube, but outside the tube (to avoid damage, particularly to the end window).

At extremely low visual clarity (e.g. < 0.1 m as may occur in a flood), tube measurements can be performed following the same procedure, but on a volumetrically diluted sample. This will require diluent water (e.g. municipal tap water) and plastic labware (a 2 L cylinder and 250 mL cylinder kept clean and dust free in large plastic bags) to prepare the diluted sample. Alternatively, turbid water samples can be taken back to the office or laboratory where dilutions for the clarity tube measurements are easier to carry out.

Note: Visual clarity measurements on volumetrically diluted samples represent best practice rather than a requirement of this Standard. Municipal tap water, with a typical visual clarity of 10 m or more, is usually suitable for performing dilutions. For example, the true visual clarity of river water in high flood could be calculated as 3.1 mm (0.0031 m) from a measured visual range of 0.154 m on a water sample diluted 50-fold with tap water contained within a SHMAK tube.

3.3.2.3 Beam Transmissometry Measurement

Deployment of a green light beam transmissometer can substitute for direct measurement of visual clarity by black disk and can also be used to verify the visual observations. This is because the green light LED (peak emission about 530 nm) is closely interconvertible with human measurements of visual clarity (human eyes have peak sensitivity at about 550 nm in the green range) (Zanevald & Pegau, 2003).

While beam transmissometry can provide more precise measurements, these instruments have a fixed path length which limits their dynamic range. For example, a common 250 nm path beam transmissometer sensor can measure beam attenuation in the range 0.2 to 12 m⁻¹ (equivalent visibility is in the range 0.4 to 24 m), a 60-fold range. 'Dirtier' waters need to be sampled and diluted to be in range. Beam attenuation is inter-convertible with black disk visual range:

$$y_{BD} = 4.8/c(550)$$

Visual clarity estimated as 4.8/c (where c is beam attenuation calculated from the transmissometry) should agree with visual clarity measured by black disk within 10% (Zanevald & Pegau, 2003).

3.3.3 Colour

The colour of water has three main dimensions: hue, brightness and colour purity. Research suggests that hue (Figure 6) is the strongest dimension for water colours (Davies-Colley et al., 1997). Colour (hue) measured in the field can be formalised with the use of Munsell colour standards to an accuracy of ± 2.5 Munsell hue units. Colour is best observed free of interfering surface reflections, using a black disk viewer in a horizontal direction (see subsection 3.3.2.1), eliminating any bottom effects should the riverbed be visible.

The sky conditions and percentage cloud cover should be recorded at the time of measurement.

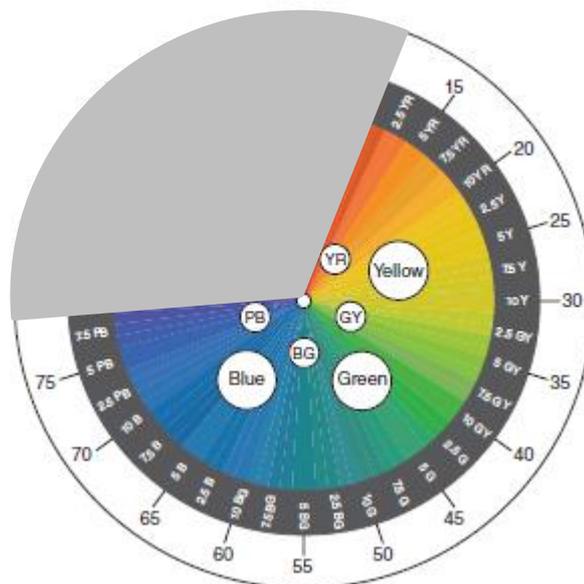


Figure 6 – Illustration of the colour hue range expected for natural waters, from exceptionally clear, purple blue waters (5 PB) to humic stained rivers (2.5 YR)

Pure water is about 7.5 PB.

Source: Modified from West et al. (2016).

Research is currently underway to maximise the use of camera photography in recording water colour and converting RGB images to Munsell standards. It is recommended that a photograph of water colour is also taken looking down the viewing tube. This should assist with method development and standardisation of techniques. As camera sensors improve and use on a variety of platforms (e.g. camera, drones) develops, spatial and temporal changes in water colour are expected to become an important tool in water quality monitoring. This will complement remote sensing of water colour from space and expand capabilities in resolution and at times of cloud cover when surface expression is blocked.

3.3.4 Discharge Measurement

Discharge is useful for interpretation of long-term water quality data, including for flow adjustment in trend detection and for calculation of material fluxes; for example, annual contaminant loads (e.g. WMO 2013). Discharge at the time of sampling ('flow stamping') is most important but a continuous record of flow may also assist with interpreting water quality (because antecedent flow influences water quality) and is needed for load estimation.

Discharge at the time of sampling may be determined from a nearby continuous flow recorder site, carrying out a gauging at the time of sampling, or from reading water level at a staff gauge close to the monitoring site that has an established stage-discharge rating to convert water levels to approximate flows.

Further guidance on flow measurements is provided in:

- NEMS *Water Level*, and
- NEMS *Open Channel Flow*.

Overall, further guidance is needed around 'flow stamping' to support water quality interpretation, including the use of model-simulated flows in non-gauged catchments. Generally speaking, an estimate of flow in the order of $\pm 20\%$ should be sufficient for 'flow stamping' purposes. Greater precision may be necessary for load estimation purposes.

4 Water Sample Collection

In This Section

This section focuses on the collection of river water samples. It outlines sample collection methods, bottle filling, sample filtering, and sample transport and handling.

4.1 Sampling Platform

A range of platforms may be used for sampling, including wading (preferred), bankside, bridges, automatic sampling stations and boats (see subsection 2.3).

4.1.1 Sampling Point

Water samples shall be collected in open water so that they are representative of the river reach (see subsection 2.1). Samples shall also be collected upstream of the monitoring platform to avoid contamination or sediment re-suspension (see subsection 2.3). If you need to sample somewhere different from usual, take particular care to avoid local influences on water quality such as backwater eddies, road run-off from bridges, tributary inflows, and point sources, etc. Details of any sampling that occurs in a non-standard way (e.g. water samples taken from bridge during a high-flow event instead of by wading at the regular sampling location) shall be recorded on the field form.

When sampling from a boat, if possible, take the water sample from a point ahead of the bow of the boat as it moves into the current to minimise any possible contamination.

4.2 Sampling Method

River water samples collected under this Standard shall be near-surface samples (defined in this Standard as 0.2 m below the water surface) collected by hand, or a pole, bucket or automatic sampler.

4.2.1 By Hand

Water samples shall be collected by hand 0.2 m below the water surface wherever practical (Figure 7). Avoid touching the inside of sample bottles or lids.



Figure 7 – In-river wading and water sample collection by hand

Photograph: Juliet Milne.

4.2.2 Sampling Pole

Water samples collected by a fixed-length or – preferably – telescopic pole from a bank shall be collected a sufficient distance from the bank to ensure the sample is collected in open, flowing water (Figure 8). The sample bottle is placed face up in the pole's 'gripper', uncapped and then the sampler reaches out with the pole (already extended to the appropriate length) the desired distance from the bank. The pole and sample bottle are gently plunged straight down into the water 0.2 m below the water surface and then turned into the direction of the current to allow air to escape and the bottle to fill (subsection 4.3).



Figure 8 – Water sample collection using a telescopic pole from the river bank

Photograph: Juliet Milne.

4.2.3 Bucket

Rinse the bucket in the river at least three times before use. If sampling from bridges (Figure 9), lower the bucket from the upstream side of the bridge to avoid potential contamination sources from run-off associated with the bridge, or birds and wildlife roosting or living in or under the bridge structure. A small weight on one side of the bucket will help to ensure that it dips below the water's surface.

If sub-sampling from a bucket, water should be decanted from the bucket (ensure constant mixing) into the sample bottles to avoid sample contamination.



Figure 9 – Water sample collection from a bridge using a bucket

Photographs taken at base flow conditions for illustrative purposes. Bucket sampling from a bridge should be limited to when this is the only safe option for sampling (e.g. a river in high flood conditions).

Photographs: Juliet Milne.

4.2.4 Automatic Sampler

In extreme cases, where other conditions prevent sampling by hand, telescopic pole or a bucket, samples may be obtained by triggering an automatic sampler if one is located on site. It is beyond the scope of this NEMS to document the use of these instruments.

4.2.5 Sample Bottle Filling and Labelling

Sample bottle, volume and filling requirements depend on the water quality variables of interest (see Table 4 in subsection 5.4). General bottle filling requirements are outlined below. Ensure that sample bottle caps are tightly sealed after filling.

An air pocket facilitates mixing before sub-sampling and is crucial for testing some variables but not others; for example, if pH is to be measured in the laboratory, complete filling is needed to prevent shift of pH with shift of the carbonate equilibria.

Although 500 mL bottles are probably suitable for most physico-chemical tests in routine river quality monitoring, some particulate variables (e.g. TSS) require relatively large volumes (potentially up to 5 L) in clear waters.

Where multiple bottles are supplied for multiple related tests (e.g. soluble and total nutrients), the bottles should be filled from one large water sample. This minimises sample 'partitioning' during the transfer/sub-sampling exercise.

Note: Sub-sampling into smaller bottles should include keeping the main sample well mixed and preferably half filling each smaller bottle from this sample before going back to top each up.

Unpreserved bottles

Rinse at least two 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.

Unpreserved sterile bottles (for microbiological testing)

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 from another larger unpreserved collection bottle (or bucket) that has been rinsed at least twice in the water to be sampled. Decant the required sample volume from the larger bottle into the smaller bottle containing the preservative. 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.

4.2.6 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.

4.2.7 General Bottle Filling Procedure

When filling sample bottles, avoid any surface microlayer that is potentially present and may not be visible by collecting river water samples at about 0.2 m depth. Surface microlayers may include bacteria and nutrients, as well as hydrophobic compounds, foams and floatable scums, concentrated at the water surface. Ensure that sample bottle caps are tightly sealed after filling.

The following procedure shall be used for filling all unpreserved water sample bottles collected by wading/hand (illustrated in Figure 10) or use of a sampling pole:

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 bulk (unpreserved) sample bottle after rinsing at least twice with river water.

3. Submerge the bottle with the opening pointing straight down.
4. At the desired depth (~ 0.2 m), gently tip the bottle up into the flow, allowing air to escape and water to enter the bottle.
5. Secure the bottle cap under water then remove to an iced container for storage.

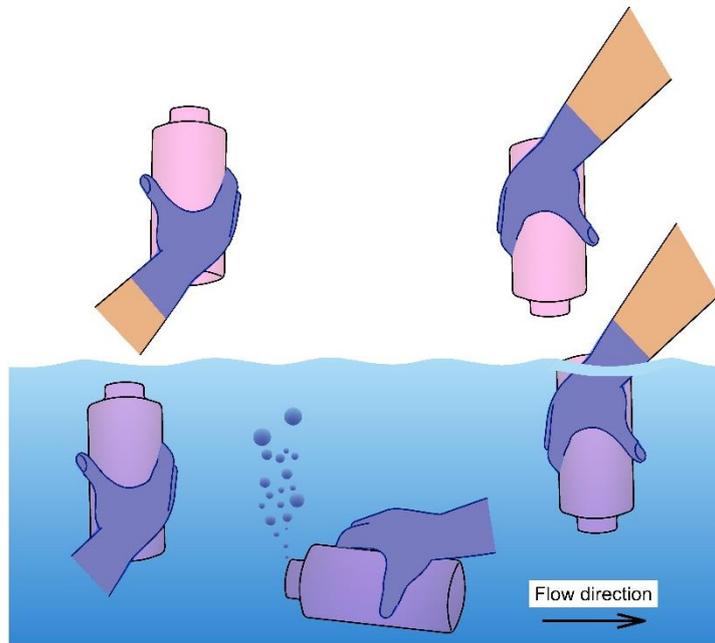


Figure 10 – Sampling technique for unpreserved sample bottles

The sample bottle is gently dipped upside down into the water to about 0.2 m depth. Turn towards the flow. Hold for 3 seconds. Turn upwards and lift out of the water.

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

Take extreme care to avoid disturbing bottom sediments during sample collection. A different (pre-rinsed and unpreserved) sampling bottle may assist in taking these samples if the river or stream is very shallow. In conditions of extreme low flow, when it may be necessary to sample from near stagnant residual pools, a pump sampler could be used with care to avoid both surface microlayers and bottom sediments.

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

4.2.8 Field Filtering

If field filtering is necessary (see subsection 1.9), this should be performed using a plastic (polyethylene, polypropylene or similar, 50–100 mL capacity) syringe and 0.45 µm filter, as follows:

1. Rinse the syringe in the river before filling with a sub-sample from the bulk unpreserved sample bottle.

2. Attach a clean filter on the end of the syringe, avoiding contamination of the syringe and filter outlets from fingers, and discharge a few drops of the sample from the syringe needle.
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.

Water samples from some soft-bottomed or glacial-fed rivers, and many rivers in high state of flow, may contain high concentrations of particulate material. Such samples may require pre-filtering using a series of progressively larger filter sizes or a larger surface area cartridge type filter (Figure 11).

If the syringe must be refilled or the 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.

Record on both the field record form and Chain of Custody form if a water sample has been filtered in the field.



Figure 11 - Examples of different filters used for filtering river water samples

Photographs: Environment Southland.

4.3 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, especially for microbial samples) 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 pads 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 12).

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



Figure 12 – 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 pads and bubble wrap.

Photographs: Andrew Yuill.

4.4 Chain of Custody

A Chain of Custody (CoC) form (Annex C) 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; for example, for dissolved forms of nutrients
- the laboratory tests required (if not already pre-printed on the form)
- anything unusual about the samples, if relevant (e.g. possible saline influence or likelihood of high faecal indicator bacteria content), 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 that accompanied the samples and prompt (same day) return of this 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), 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, dissolved metals), 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 4. These can be considered minimum detection limits; for nutrients, anions and cations, lower (ultra-trace) detection limits may be desirable for some 'very clean' (i.e. oligotrophic or microtrophic) river waters.

All laboratory measurements are accompanied by an uncertainty factor (Figure 13). 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.

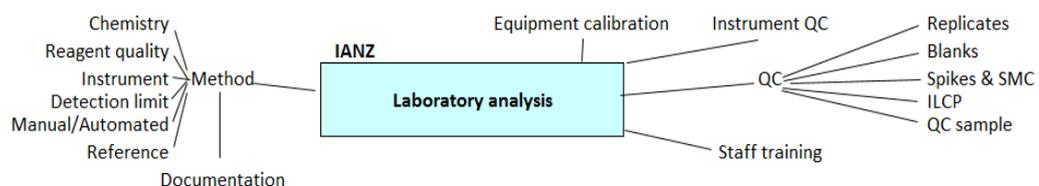


Figure 13 – Common laboratory-specific uncertainties in the water measurement process

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 4 sets out the test methods that shall be performed on river water samples collected under this Standard. For many variables, there are multiple test methods available but the method(s) specified has been determined as the most appropriate for long-term (e.g. SoE) river water 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 seven 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 4: Sample bottle and filling requirements and laboratory test method details for river water quality variables under this Standard

Note: This table assumes filtering of samples, where required, occurs at the laboratory. 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 36 hours of collection, preferably sooner. * Measurement resolution and not MDL.
Specific Conductivity (SpC)	µS/cm at 25°C			APHA 2510 B, conductivity meter, 25°C	0.1*	* Measurement resolution and not MDL.
Turbidity (Turb)	FNU			ISO 7027, near-infrared light turbidity meter	0.05	Should be measured within 36 hours of collection, preferably sooner.
Total Suspended Solids (TSS)	mg/L	Unpreserved, filled to the top	2000	APHA 2540 D	1	A 5L sample is required for a MDL of 0.5 mg/L. A 1L sample only equates to a MDL of 3 mg/L.
Absorbance (Absorb) • at 340 nm • at 440 nm • at 780 nm	m ⁻¹	Unpreserved	100	APHA 5910 B, spectrophotometry	0.002	Sample should be filtered, and ideally measured, on day of sample receipt. Spectrophotometric absorbance of the filtrate is used to estimate absorption coefficients for calculation of CDOM.

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Variable	Units	Bottle type, preservative and filling	Recommended minimum sample volume (mL)	Method(s) and description	Method detection limit (MDL)	Method modifications and comments
<i>Nutrients</i>						
Nitrate Nitrogen (NO ₃ -N)	mg/L	Unpreserved, no head space	100	APHA 4500 B-NO ₃ I, flow injection analyser	0.002	Calculated (NNN – NO ₂ -N).
Nitrite Nitrogen (NO ₂ -N)						Filter sample on day of receipt. APHA 4110 B may be considered when samples are being tested for a wider anion suite (see Part 1 <i>Groundwater</i>).
Nitrite-Nitrate Nitrogen (NNN)				APHA 4500-NH ₃ H, flow injection analyser	0.005	
Ammoniacal Nitrogen (NH ₄ -N)						
Total Nitrogen – Direct (TN-A)						

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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 Nitrogen – Indirect (TN-K) ¹	mg/L	Sulphuric acid preserved (for TKN component)	100	Calculated from the measurement of Total Kjeldahl Nitrogen (TKN, measured via APHA 4500-N _{org} D) + NNN.	0.11	TN-K is not eligible for QC 600 and is not suitable for microtrophic river waters with very low nitrogen concentrations. However, this method may be preferred where TSS concentrations are typically > 20 mg/L and an existing record of TN-indirect measurements exists. Duplicate testing will reduce MDL to 0.05 mg/L.
Dissolved Reactive Phosphorus (DRP)		Unpreserved, no head space	100	APHA 4500-P G, flow injection analyser	0.001	
Total Phosphorus (TP)				APHA 4500-P B 5 or J acid persulphate digestion then analysis by APHA 4500-P G	0.002	APHA 4500-P B 5 and this Standard allow for digestion using either potassium persulphate or ammonium persulphate.
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).

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Variable	Units	Bottle type, preservative and filling	Recommended minimum sample volume (mL)	Method(s) and description	Method detection limit (MDL)	Method modifications and comments
<i>Anions and cations (dissolved)</i>						
Bicarbonate (HCO ₃ diss)	mg/L CaCO ₃	Unpreserved, no head space	500	APHA 4500-CO ₂ D OR APHA 2320 B titration	1.0 at 25°C	Filtered sample. Filtering represents a modification of method APHA 2320 B.
Bromide (Br diss)	mg/L			APHA 4110 B, ion chromatography	0.05	Filtered sample.
Calcium (Ca diss)				APHA 3120 B, ICP-OES OR APHA 3125 B ICP-MS		Filtered sample.
Carbonate (CO ₃ diss)	mg/L CaCO ₃			APHA 4500-CO ₂ D OR APHA 2320 B titration	1.0 at 25°C	Filtered sample. Filtering represents a modification of method APHA 2320 B.
Chloride (Cl diss)	mg/L			APHA 4110 B, ion chromatography	0.05	Filtered sample.
Fluoride (F diss)				APHA 4110 B, ion chromatography OR APHA 4500-F C or G, ion selective electrode	0.05	

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Variable	Units	Bottle type, preservative and filling	Recommended minimum sample volume (mL)	Method(s) and description	Method detection limit (MDL)	Method modifications and comments	
Iron (Fe diss)	mg/L	Unpreserved, no head space	500	APHA 3120 B, ICP-OES OR APHA 3125 B ICP-MS	0.02	Filtered sample. Where APHA 3125 B is used for Mg, K or Na, this will represent a method modification (Mg, K and Na are not specifically covered by this test method). * Method resolution and not MDL	
Magnesium (Mg diss)					0.005		
Manganese (Mn diss)					0.05		
Potassium (K diss)				APHA 4500-SiO ₂ -F OR APHA 3120 B	0.1		
Silica (SiO ₂ diss reactive)					APHA 3120 B, ICP-OES OR APHA 3125 B ICP-MS		0.02
Sodium (Na diss)							0.5
Sulphate (SO ₄ diss)					APHA 4110 B, ion chromatography		1* at 25°C
Total Alkalinity (Alkt)	mg/L CaCO ₃	APHA 2320 B, auto titration					

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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	Unpreserved, no head space	500	APHA 1030 E, calculation	0.1*	* Method resolution and not MDL
Total Hardness (Hard)	mg/L CaCO ₃	OR where acid preservative is used		APHA 2340 B, calculation	1	Filtered sample. Calculated from dissolved calcium and dissolved magnesium.
<i>Metals and metalloids (dissolved)</i>						
Aluminium (Al diss)	mg/L	Unpreserved, no head space	100	APHA 3125 B (ICP-MS)	0.005	Analysis performed on a 0.45 µm (laboratory) filtered sample preserved with nitric acid.
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	

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Variable	Units	Bottle type, preservative and filling	Recommended minimum sample volume (mL)	Method(s) and description	Method detection limit (MDL)	Method modifications and comments
<i>Metals and metalloids (total)</i>						
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	
<i>Microbial</i>						
Faecal Coliforms (FC)	cfu/100 mL	Sterile, filled with small head space left	100	APHA 9222 D, membrane filtration	1	A single larger 400 mL sterile bottle can be used where more than one indicator bacteria are to be tested.
<i>E. coli</i> (EC)	MPN/100 mL			APHA 9223 B, Colilert		
Enterococci (Ent)	MPN/100 mL			APHA 9230 D b, Enterolert		

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Variable	Units	Bottle type, preservative and filling	Recommended minimum sample volume (mL)	Method(s) and description	Method detection limit (MDL)	Method modifications and comments
Chlorophyll <i>a</i> (CHLA) and Phaeophytin (Phaeo)	mg/L	Unpreserved, opaque bottle	1000	APHA 10200 H and fluorometry	0.0002	Laboratory filtration promptly on receipt of sample. Acetone extraction. Use spectrometry on samples where CHLA concentrations exceed 0.005 mg/L (conventional fluorometry may be unreliable for samples with moderate to high chlorophyll <i>b</i> concentrations).
			500	APHA 10200 H and spectrophotometry	0.003	

5.4.3.1 pH

This Standard recommends that pH is measured on an airtight river water sample submitted to the laboratory (refer subsection 1.7). Measurements made in the field and laboratory shall be considered as separate variables (pH – field and pH, respectively). This is because it is typically very difficult to reconcile field and laboratory pH measurements, even where both measurements are reported as pH at 25°C (a requirement of this Standard).

5.4.3.2 Turbidity

Both white light (APHA 2130 B) and near infra-red light (ISO 7027) turbidity test methods are available but there is not necessarily a numerical correspondence or even a close correlation between the two. The ISO 7027 method is required under this Standard for consistency with the NEMS *Turbidity* (continuous in situ measurements) and discrete measurements of turbidity in the field (subsection 3.1.5).

5.4.3.3 Suspended Sediment

Suspended sediment can be measured as total suspended solids (TSS) or as suspended sediment concentration (SSC). The test methods for these variables both involve gravimetric filtration but differ in that TSS is performed on a volumetric sub-sample whereas SSC is performed by filtering the entire sample. The TSS test was originally developed for wastewater monitoring where suspended matter is relatively uniform and composed largely of neutrally buoyant organic matter. The SSC test is more reliable for capture of rapidly settling sand-sized sediment particles present in water samples from rivers and other natural waters (e.g. Gray et al. 2000, Selbig & Bannerman 2011) and is the recommended method for use in all catchment or storm sediment load assessments. For environmental waters, TSS is best restricted to ‘clear water’ samples collected at base or low flows and should not be measured to estimate sediment concentrations in storm-flow event samples.

TSS and SSC will only produce comparable results if rapidly settling sand particles are not present in a sample. In clear waters, a reliable measurement at low levels via either method requires a relatively large (up to 5 L; e.g. Davies-Colley et al., 2014) sample volume.

Specific guidance on SSC measurement is being addressed in the NEMS *Suspended Sediment* (in preparation). The recommended test method specifications will be included in a future iteration of this NEMS.

5.4.3.4 Total Nitrogen

There are two different test methods for total nitrogen in New Zealand at present (Table 4):

- Direct measurement via APHA 4500-NO₃ I, denoted in this Standard as TN-A and

- Indirect measurement by summation from the determination of total Kjeldahl nitrogen (TKN) and nitrite-nitrate nitrogen (NNN).

Recent analysis of an extensive river water quality data set from the Wellington Region by Davies-Colley and McBride (2016) found that the two methods often produce differing results, particularly when water samples contain suspended particulate matter. For this reason, total nitrogen by each method shall be treated as separate variables under this Standard.

Overall, because the TN-A method is a direct measurement and offers a much lower detection limit that is more desirable for long-term monitoring programmes in low nutrient river waters, this method shall be used under this Standard. There are limitations to using this method on samples that contain high TSS (> 20 mg/L) where total nitrogen may be under-estimated. Organisations with long-term monitoring records obtained using TN-K need may wish to retain this test method. Alternatively, at the very least, water samples shall be tested using both methods for a minimum of 12 months (see subsection 5.7).

In terms of quality coding under this Standard:

- only river water samples analysed as TN-A shall be eligible for assignment of the highest quality code (QC 600), and
- river water samples analysed as TN-K shall only be eligible for assignment of a maximum quality code of QC 500.

5.4.3.5 Total Phosphorus

Either APHA-4500-P B 5 or J is recommended for the digestion of water samples prior to total phosphorus determination. Method APHA-4500-P J is a potassium persulphate digestion that has the added benefit of enabling a simultaneous digestion for total nitrogen analysis (i.e. both total phosphorus and total nitrogen (as TN-A) can be analysed from the same digested water sample). In contrast, APHA 4500-P B 5 allows for digestion using either potassium persulphate or ammonium persulphate.

Note: Recent laboratory trials comparing persulphate and potassium persulphate digestions are summarised in Milne and Robinson (2019).

At present in New Zealand, some laboratories supply sulphuric acid-preserved sample bottles for total phosphorus determination while others add this preservative upon sample receipt at the laboratory. The results of a recent national interlaboratory comparison performed on acid preserved and unpreserved river, lake and coastal water samples have indicated that there is no clear evidence of any impact on sample integrity or MDLs from the use of acid preservatives (Milne & Robinson, 2019). This Standard therefore recommends that laboratories supply monitoring agencies with unpreserved sample bottles for the collection of river water samples.

Note: In future, sample analysis by ICPMS may offer improved MDLs.

5.4.3.6 Faecal Coliforms, *E. coli* and Enterococci

Multiple test methods exist for microbial indicator bacteria. This Standard requires the methods specified in Table 4 to be used. In the case of *E. coli*, the Colilert enzyme substrate method (APHA 9223 B) is recommended because, although less precise than membrane filtration methods (e.g. APHA 9222 G):

- Colilert represents newer technology and is a superior method based on biochemistry
- Measurement up to 2419 *E. coli* per 100mL is possible without sample dilution
- Colilert has less chance for error or failure, and
- 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'.

Note: Colilert is also the current method of choice for measurement of E. coli in recreational waters (MfE/MoH 2003) and potable waters (MoH 2008), providing for cost efficiencies where river waters are sampled for both SoE and human health purposes.

Sample dilutions should be performed where a river water sample is expected to render an *E. coli* count >2419 MPN per 100mL (e.g. samples collected in wet weather from catchments under urban or rural land use).

Colilert and membrane filtration test methods work by different processes and therefore do not necessarily produce equivalent results. For this reason, the use of membrane filtration or other alternative test methods to Colilert shall not be eligible for a quality coding rating higher than QC 500. If a membrane filtration method is used, a minimum of two and preferably three, sample dilutions should be performed on each river water sample to ensure a conclusive result can be obtained.

5.4.3.7 Anions and Cations

At present in New Zealand, some laboratories supply acid-preserved sample bottles for cation determination while others add this preservative upon sample receipt at the laboratory. The results of a recent national interlaboratory comparison performed on acid preserved and unpreserved river, lake and coastal water samples indicate that there is no clear evidence of any impact on sample integrity or MDLs from the use of acid preservatives (Milne & Robinson, 2019). This Standard therefore recommends that laboratory supply monitoring agencies with unpreserved sample bottles for the collection of river water samples for anion and cation determination.

There are also several 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 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 $\pm 5\%$. 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 $\pm 7\%$. Unrounded data should be used in anion-cation balance calculations.

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

And the typical criteria for acceptance are as follows:

Anion sum meg/L	Acceptable difference
0 – 3.0	± 0.2 meq/L
3.0 – 10.0	$\pm 2\%$
10.0 – 800	$\pm 5\%$

5.4.3.8 Chlorophyll *a*

Water samples shall be analysed for chlorophyll *a* using APHA 10200 H by fluorometry, with acetone as the solvent. The exception is for water samples collected from rivers that are classified as eutrophic or worse (defined in this Standard as having an annual median chlorophyll *a* concentration of greater than 0.005 mg/L). For samples from eutrophic rivers, the use of the less sensitive test method, APHA 10200 H by spectrophotometry, is acceptable.

*Note1: Conventional fluorometry is not recommended for use on water samples containing high concentrations of chlorophyll *a* (e.g. >0.020 mg/L), owing to being prone to spectral interferences (see Milne and Robinson, 2019).*

Note2: The APHA 10200 H method also provides for determination by spectrophotometry and high-performance liquid chromatography (HPLC). The HPLC method is not currently available for routine monitoring in New Zealand but is a superior method that could be investigated for adoption in the future. This method is capable of reporting different chlorophyll pigments and may offer a slightly improved detection limit.

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. TP ≥ DRP).

Note1: Laboratories can provide a QC report on request (usually for a charge).

Note2: There is currently no ILCP available in New Zealand for nutrient or chlorophyll a analyses at the concentrations typically measured in oligotrophic rivers (see Milne and Robinson, 2019).

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 QA

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 2.2), which are specific to the site location and may change with time but generally not on each site visit,
- visit metadata (subsection 2.6), which are specific observations made about where and when field measurements and water samples were collected, and
- water quality data, which generally consist of both field measurements and laboratory measurements made on one or more water samples.

All three 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 2.2.

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 2.6, 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:

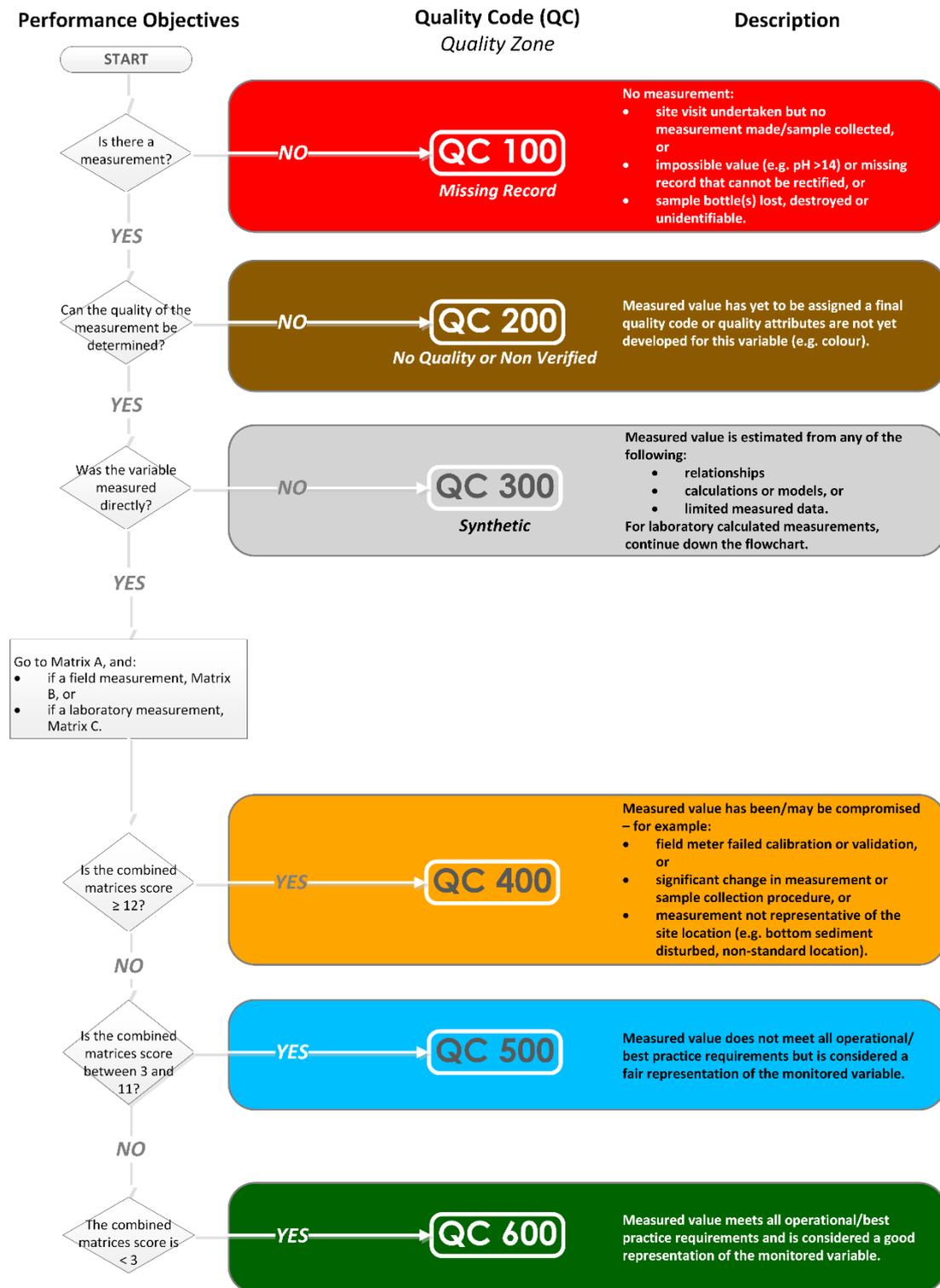
- its associated measurement date, time and units
- field instrumentation (make, model and number) or laboratory name, location and test method (whichever is applicable)
- clear reference to its associated form (dissolved, total, reactive, etc.), where applicable (e.g. nutrients and metals)
- all relevant visit-related metadata, including the name(s) of personnel conducting field measurements and sampling (subsection 2.6)
- relevant laboratory comments (subsection 5.5) where applicable, and
- its associated quality code (subsection 6.2.1).

6.2 Data Processing

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. 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.



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. In accordance with the NEMS Dissolved Oxygen, dissolved oxygen measurements of > 100% saturation shall also obtain a maximum of QC 500.

Note 3: Quality considerations for beam transmissometry and colour field measurements require further development. Measurements of these variables shall be coded QC 200 in the interim.

Note 4: Child codes (e.g. QC 510 or QC 550) 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 <i>(subsection 1.1)</i>	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 <i>(subsection 2.2)</i>		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 <i>(subsection 2.1)</i>		Different field measurement/ water sample location		Field measurement/water sample location consistency maintained

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Criteria	12 points	3 Points	1 Point	0 Points
Visit Metadata <i>(subsections 1.4 & 2.6)</i>	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: <ul style="list-style-type: none"> • an identifier for the actual field meter(s) used, or • for visual clarity, disk size/measuring apparatus details 		Visit metadata recorded on a field form in accordance with the Standard, including: <ul style="list-style-type: none"> • measurement date, time and units • for visual clarity, disk size/measuring apparatus • field meter(s) make, model and ID number, and • the environmental conditions under which measurements/ water samples were collected
Representativeness <i>(subsection 2.1)</i>	Field measurement/water sample not representative of the site and compromised; for example, sediment disturbance, backwater	Field measurement / water sample not fully representative of the site		Field measurement/water sample representative of the site, taken in flowing water and away from any immediate contamination sources; for example, dead animal carcass
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 <i>(subsection 3.1)</i> [Applies to Temp, DO % Sat, DO, SpC – field, pH – field, and Turb – field]	Sensor accuracy does not meet that specified in the Standard for the variable in question and is also outside the relevant criteria listed under the adjacent ‘1 point’ and ‘3 points’ columns, and/OR for Turb – field, the sensor does not conform to ISO 7027 and/OR for DO% Sat and DO, an electrochemical (i.e. membrane-based) sensor is used without a mechanical stirrer.	Sensor accuracy deviates from that specified in the Standard for the variable in question but meets the following criteria: <ul style="list-style-type: none"> Temp: $\pm 0.5^{\circ}\text{C}$ and/OR for DO% Sat and DO, an electrochemical (i.e. membrane-based) sensor is used with a mechanical stirrer to ensure the velocity of water past the sensor exceeds 0.3 m/s.	Sensor accuracy meets: <ul style="list-style-type: none"> Turb – field: ± 1 FNU and $\pm 5\%$ at >1000 FNU 	Sensor accuracy meets the requirements of the Standard for the variable in question

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Criteria	12 points	3 Points	1 Point	0 Points
Field Meter Validation and Calibration <i>(subsection 3.1)</i> [Applies to Temp, DO % Sat, DO, SpC – field, pH – field and Turb – field]	Validation and/or calibration failed or not performed – or no records available OR An alternative validation method under Annex E 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 E) validation and/or calibration meet the requirements of the Standard but: <ul style="list-style-type: none"> • end-of-day (post sampling run if using Annex E) validation (for SpC and pH only) failed/not performed, and/or • supporting information missing (e.g. pH – mV; 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 <i>(subsection 3.3)</i>	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 <i>(subsection 3.3)</i>	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: <ul style="list-style-type: none"> • dissolved oxygen is corrected for barometric pressure • pH and SpC are reported at a reference temperature of 25°C

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Criteria	12 points	3 Points	1 Point	0 Points
Black disk visual clarity				
Equipment Specifications <i>(subsection 3.3.2)</i>	The viewer and/or mirror were dirty or scratched on the day of use, OR Large areas of paint are missing from some equipment surfaces	Some of the equipment showed signs of wear on the day of use and required maintenance; for example, cleaning, repainting	All measuring equipment, including disks and the viewer are maintained in accordance with the Standard, with the exception of checks of the viewer against a reference viewer	All measuring equipment, including disks and the viewer, are maintained in accordance with the Standard, with: <ul style="list-style-type: none"> • annual verification of the viewer's integrity using a reference viewer against, and • confirmation that the viewer window and mirror were clean and free of scratches on the day of use
Visual Clarity Measurement <i>(subsection 3.3.2)</i>	A viewer was not used to obtain the measurements, OR A sediment plume affected observations	Only one visual clarity measurement was made, OR An incorrect sized disk was used, OR A sediment plume was created by river bed disturbance that may potentially have affected observations	Only one of disk disappearance distance and disk re-appearance distance was measured	Measurement was made in accordance with the Standard, including the use of a viewer, the correct sized disk and recording of both the disk disappearance and reappearance distances.
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 <i>(subsection 5.1)</i>	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 <i>(subsections 1.11 & 4.4)</i>	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 <i>(subsection 5.2.1)</i>	Samples received > 48 hours after collection		Samples received within 48 hours of collection	Samples received within 24 hours of collection (to enable processing within 36 hours of collection)

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Criteria	12 points	3 Points	1 Point	0 Points
Sample Temperature on Arrival <i>(subsection 5.2.2)</i>	Samples arrive at or above 10°C* * OR greater than the sample collection temperature where samples are delivered within 2 hours of collection <i>Note: If microbial samples arrive frozen or with evidence of ice crystals, then code QC 100 ('no result').</i>			Samples arrive <10°C* and the microbial sample was not subject to freezing, in whole or part, * OR less than the sample collection temperature where samples are delivered within 2 hours of collection
Sample Bottles and Condition <i>(subsections 4.3 & 5.2.2)</i>	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		Sample bottle used for the variable is consistent with the requirements of the Standard and no anomalies are identified by the laboratory in the condition of the bottle or sample
Test Method <i>(subsection 5.4.3)</i>		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

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Criteria	12 points	3 Points	1 Point	0 Points
Soluble and Total Nutrient Ratios <i>(subsection 5.6)</i> [Applies to nutrients only]	The soluble measurement value is greater than its corresponding total measurement value, with no overlap in the UoM values for the two measurements			The soluble nutrient measurement value is less than or equal to its corresponding total measurement value, taking into account Uncertainty of Measurement (UoM) values for both measurement values (e.g. $DRP \leq TP$ or $NO_3-N \leq TN-A$) OR N/A (i.e. all other variables)
Anion and Cation Balance Check <i>(subsection 5.4.3.7)</i> [Applies to anions and cations only]	The calculated anion-cation balance does not agree within $\pm 5\%$, or, where the river water is of low ionic strength (i.e. at an anion sum of 3 meq/L), the balance is outside of $\pm 7\%$			The calculated anion-cation balance agrees within $\pm 5\%$, or, where the river water is of low ionic strength (i.e. at an anion sum of 3 meq/L), the balance is within $\pm 7\%$
Measurement Units, Detection Limit and Resolution <i>(subsection 5.4.3)</i>	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				

6.3 Quality Coding

6.3.1.1 Performance

All water quality data shall be quality coded in accordance with the NEMS *Quality Code Schema*. A quality code shall be assigned to individual measurements for each water quality variable.

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.

6.3.1.2 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 D)
- field record form (subsections 1.4 and 2.6, and Annex B)
- completed Chain of Custody form (subsections 1.11 and 4.4, and Annex C), and
- laboratory report (subsection 5.5).

Site metadata (subsection 2.2) and QA (subsection 1.2) 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), and
Note: Pre-population of historical measurement ranges for water quality variables measured in the field on the field 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; for example, anion-cation balance.
Note: Scatterplots are a useful way of inspecting the data. For example, a plot of visual clarity versus turbidity can assist with identifying inconsistent measurements and prompting further checks or investigation.

6.3.1.3 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.

6.3.1.4 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.

6.4 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.

6.4.1 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.

6.4.2 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.

6.4.3 Data Archiving

The archiving procedures, policies and systems shall consider:

- future data-format changes
- off-site duplication of records, and
- disaster recovery.

6.5 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.

6.5.1.1 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.

6.5.2 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.

6.5.2.1 Catchment 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 water body and catchment

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- 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.

6.5.2.2 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.

6.5.3 Other Requirements

6.5.3.1 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.

6.5.3.2 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

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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.

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Annex B – Example Field Record Form

Note: This form is a guide only and can be modified as appropriate to include additional information (e.g. periphyton and deposited sediment cover observations). Customising the form on a monitoring site basis is recommended, including listing the expected range of field measurement values based on historical monitoring (see subsection 6.2.1.2).

Field Record Form: Rivers

Programme Name _____
Site Name & No. _____
GPS Location Easting _____ Northing _____
Sample Run Name _____ (leave blank if N/A)
Date _____
Field Personnel _____

Visit Metadata

Weather Fine Overcast Drizzle Rain Rain in last 24 hours? Y N
 Wind Direction NW N NE SE S SW Digital Photo Y N
 Wind Speed Calm Light Moderate Strong
 River Level (stage) Low Normal High Other _____ m
 Time (NZST) Arrival on site _____ **Official visit time** _____ Departure from site _____

Comments (e.g. stock on banks/in water, river discoloured, scums, wildfowl, local bank erosion, new hazards, etc.)

Field Measurements

Black Disk _____ m (Measurement 1) Measurement method Black disk Clarity Tube
 _____ m (Measurement 2) Disk Size 20 mm (<0.5 m) 60 mm (0.5 - 1.5 m)
 _____ m Final measurement 200 mm (> 1.5 m) N/A
 Colour _____ Munsell card Light conditions Sun Shade
 _____ Meter make, model & number

Water Temperature _____ °C _____
 Dissolved Oxygen _____ mg/L _____
 Dissolved Oxygen _____ % sat. _____
 Specific Conductivity _____ μS/cm _____
 pH _____ pH _____
 Turbidity _____ FNU _____
 Chlorophyll *a* _____ RFU _____
 Water flow _____ m³/s Rated Gauged Estimated

Water Samples

Sample No/ID _____ QA/QC Sample Details _____
 Total No. of Bottles _____ Field Filtered Y (No. of filters _____) N
 Collection Method Wading Grab pole Other _____
 Sample Appearance Colourless Clear Turbid Humic Other _____
 Odour Y N

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

Annex C – 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	<input type="radio"/> Room temperature <input type="radio"/> Chilled <input type="radio"/> Frozen Temperature _____ °C Comments (e.g. appropriate bottle used, headspace requirements met) _____ _____ _____	
Job. No.	_____	

Sample Details *(Client to complete)*

Type Groundwater River / Stream Lake Estuarine / Coastal
 Have samples been field filtered? Y N Details _____

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

Annex D – 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 Y 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 Y 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? (120 - 175 μS/cm)
_____	_____	_____ μS/cm	_____ °C	<input type="radio"/> Y <input type="radio"/> N
<i>pH</i> (pH 7)		_____ pH	_____ °C	Passed Validation? (6.7 - 7.3 pH) <input type="radio"/> Y <input type="radio"/> N
<i>ORP</i>		_____ mV	_____ °C	Passed Validation? (200 - 280 mV) <input type="radio"/> Y <input type="radio"/> N

Comments

Annex E – 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.

Annex F – Black Disk Equipment

The equipment required for black disk measurements includes:

- underwater periscope (black disk viewer) – kept covered by a sleeve, when not in use, to reduce scratching of windows
- 45° angle mirror (that fits into the black disk viewer)
- black disks of appropriate size (200 mm, 60 mm and 20 mm diameter disks)
- tape measure (20 m), and
- disk holder(s), such as a black pole or stake with a means of attaching the black disk targets at suitable heights. The holder can be held by a field assistant or driven into the streambed,
- a SHMAK clarity tube (with paired aquarium magnets on one of which is mounted a 20 mm diameter black disk), and
- a clean container (e.g. 2 L sample bottle) for containing the water sample for measurement using the SHMAK clarity tube (about 1.5 L volume).

All equipment deployed close to the black disk targets in sight of the observer should be sprayed matt black.

Equipment maintenance

The disk targets should be sprayed with matt black paint as should any surfaces that might affect the measurement; for example, retaining bolts and hooks, stakes, tripods, and other disk holding devices. These surfaces should be checked ahead of each deployment and resprayed if necessary.

The window and 45° mirror of the underwater periscope must be clean and not scratched. Glass windows and mirrors are preferable to polycarbonate or other plastics in being harder and less vulnerable to scratching, but with the disadvantage of being more fragile and heavier.

Viewer windows should be kept covered by a sleeve of neoprene or inside a large plastic bag to protect from dust and abrasion and mechanical damage. Likewise, the SHMAK clarity tube (acrylic plastic) should be kept in a sleeve or cover to protect against scratching. The 45° mirror should be stored separate from the viewer (not inside the viewer) so that relative movement of mirror and viewer does not cause abrasion or other damage.

Measuring tapes may stretch over time and this should be checked and the tape replaced before bias exceeds 1 part in 100 (1%).

