5. Physico-chemical monitoring methods

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Introduction

Overview of this chapter

Chapter 5 assists you to undertake physico-chemical monitoring of freshwater rivers and streams by providing guidance on methods for monitoring ten selected physico-chemical indicators. The technical information in this chapter will assist you to:

- understand the physical and chemical components of your waterway
- understand each physico-chemical indicator, including what it is and why it is important
- choose a monitoring method (for each indicator) that is right for your needs
- carry out your chosen monitoring method for each indicator
- interpret your data to evaluate the physical and chemical condition of your waterway.

Why this chapter is important

This chapter will help you understand the value of physico-chemical monitoring and determine whether it is an appropriate tool to answer your monitoring objectives. Monitoring the physico-chemical conditions at a site can give a direct insight into the condition of the water body at a point in time. By measuring and recording the physical and chemical characteristics of water, judgments can be made about a range of important issues such as the suitability of the waterway for a range of potential uses, the condition and health of the waterway, the effect of human activities on the waterway (both positive and negative), changes through time and space, and catchment conditions and function.

This chapter will also illustrate how to undertake physico-chemical monitoring. The methods guides within this chapter provide a summary of various monitoring methods for each indicator and the data quality that can be produced using each method. It is important to be aware of the data quality that your project requires and to select an appropriate method that will produce data of sufficient quality to answer your monitoring objectives. It is important that the monitoring method you choose is suitably matched to the quality of data required to meet your project objectives.

How to use this chapter

Chapter 5 supports Question 9 in the development of a monitoring plan (see Table 5–1). Use this chapter as a planning tool and a reference guide for physico-chemical monitoring methods.

The overview section provides information on the physical and chemical properties of water, monitoring methods and equipment, sampling procedures, laboratory and colorimetry analysis, data confidence, and safety considerations.

The remaining sections provide specific information on physical and chemical monitoring methods for the following indicators:

- dissolved oxygen
- electrical conductivity
- water flow—velocity and discharge
- pH
- water temperature
- transparency
- total suspended solids
- turbidity
- nitrogen
- phosphorus.

For each indicator, information is provided on its features and importance, specific monitoring methods and equipment, data confidence procedures, and how to interpret results.

The physico-chemical record sheet template is provided in Chapter 10.

Table 5–1 Steps in developing a monitoring plan

Key steps	Monitoring plan questions
Set monitoring objectives	Q1 Why are you monitoring? Q2 Who will use your data? Q3 How will the data be used? Q4 What data quality do you require?
Develop a study design	Q5 What is your study type? Q6 What will you monitor? Q7 Where will you monitor? Q8 When and how often will you monitor?
Choose monitoring methods and procedures	Q9 What methods will you use?
Plan data management, interpretation, reporting and communication	Q10 Who will be involved and how? Q11 How will the data be managed and reported? Q12 How will you ensure confidence in your data?

Overview of physico-chemical monitoring methods

Measuring physical and chemical properties of water

Water quality is never static, and always differs between any two locations and between any two times. This inherent variability makes measuring and interpreting water quality a rewarding, challenging and, at times, frustrating exercise.

The concept of water quality is an abstract one, as it cannot be defined by any one measurement or indicator. Water quality is the net effect of all influences on and interactions within a body of water, including cumulative effects and their interactions. These effects are sometimes so varied and complex that it is not possible to define them all. To solve this problem, water quality is described in terms of its measurable physical and chemical characteristics, or indicators.

When developing your project, you should consider study design principles. Before selecting appropriate methods, you need to thoroughly consider:

- what indicators you will monitor
- where you will monitor—the spatial scope of your project and where sites should be placed within your area to meet your objectives
- when and at what frequency you are going to monitor, including sampling dates and times of day
- representativeness—the extent to which a proposed monitoring site is indicative of the type of conditions you are attempting to monitor
- comparability—the extent to which the measurements taken at one site are comparable to similar measurements taken at another site
- health and safety—the risks involved with the sites and methods selected. If the risks cannot be managed, the site must be classified as unsuitable.

For further information on designing your study, refer to Chapter 4 of this manual.

Choosing your monitoring methods

Once you have decided what, where and when to monitor, you will need to decide which methods to use. For many indicators, several possible methods may be used. The method chosen should suit the needs of your project and be within your available resources. This is likely to depend upon factors such as:

- what your reasons for monitoring (objectives) are
- how the data will be used
- what data quality is required
- how much time and money is available
- what kind of knowledge and skills are required for the method.

The method chosen must be suitably matched to the quality of data required to meet your project objectives. To assist in this process, a methods guide is provided for each indicator. The methods guides provide an overview of the range of different monitoring methods and their resultant data quality. If the method you intend to use will not produce the data quality required to meet your objectives, there is a high chance that your project will fail to meet your desired outcomes. If you cannot achieve the required data quality, you may need to reconsider your objectives or change the methods you intend to use to ones that will meet the quality requirements.

Once a method has been determined for an indicator, it may be referred to as a parameter. A parameter is an indicator with a specified method of measurement.

When specifying your methods you will need to consider each of the following:

- the units you will use to record your results
- the type of equipment you will use
- the tolerable error range (TER)
- processes for calibrating equipment (if relevant)
- any relevant quality assurance and quality control procedures
- the level of competency required to make the measurements
- additional considerations such as health and safety issues.

All the sampling and storage techniques used throughout this chapter are written in accordance with the Standards Australia & Standards New Zealand document AS/NZS 5667.1:1998 (1998). This standard 'provides general principles to be applied in sampling for physical, chemical, microbiological or radiological analysis of waters and waste waters, including bottom sediment and sludges, for the purposes of process control, quality characterisation, identification of sources of pollution and the monitoring of background levels.'

Methods guides

Specific to chapters 5, 6 and 7 is the use of methods guide tables. The methods guide aims to assist you to select an appropriate monitoring method for a water quality indicator. The table provides an overview of several methods for each water quality indicator, and within each method is the option to produce data of analytical, indicative or demonstrative quality. Your selection of method should take the level of data quality and resource requirements (skill, knowledge, time and cost involved in the method) into consideration, as well as the objectives of your monitoring project.

Three levels of data quality are used within the methods guide: demonstrative, indicative and analytical. Each level is based on reasons for monitoring, how the data will be used and who will use the data. Your required level of data quality will be dictated by your monitoring plan objectives. See Table 5–2 for details on the three levels of data quality.

For physico-chemical monitoring, the TER is an important consideration in choosing your level of data quality. Table 5–2 lists general TERs for each level of data quality; however, these values are merely a guide. Physico-chemical parameters have a broad range of possible values that can be measured using a variety of units of measurement. Due to the difference in the normal range of possible values for each parameter, TERs for each parameter will vary. Examples of indicator-specific TERs are given for each monitoring method.

Resource requirements for each monitoring method in terms of knowledge, skills, time and cost will differ according to the methods chosen. One method may be time consuming but cheap, whereas another method may be quick but expensive. The requirements for each resource have been estimated and included in this chapter to assist you when selecting the most appropriate method within your resources. The values were created based on feedback from laboratory suppliers, people experienced in monitoring methods, and literature.

Knowledge and skills

This value estimates the level of awareness and experience required to successfully carry out the method. The values used include:

- beginner—little or no experience is required to successfully carry out the method. Method is straightforward
- some experience—method is suitable for people with some previous experience, or possibly for some beginners (under supervision of an experienced person)
- expert advice—method is complex and requires expert advice or training to successfully perform.

Time

This value estimates the labour time needed to undertake the method. Depending on the method used, this may include the time taken for laboratory analysis to be conducted.

Cost

This value estimates the financial cost of carrying out the method. This may refer to the cost of equipment, or the cost of a laboratory analysis per sample. Be aware that these values are estimates only.

For an example of the method tables used throughout Chapter 5, and steps for how to use each table, refer to Table 5–3.

Table 5–2 Data quality categories for community-based waterway monitoring

Details of categories	Data quality categories		
	Demonstrative	**Indicative**	**Analytical**
Accuracy and precision of data	Lower level	Medium level	Higher level
Tolerable error range (TER)*	High (e.g. > ±50% for physico-chemical monitoring)	Medium (e.g. ±10–50% for physico-chemical monitoring)	Low (e.g. ±10% for physico-chemical monitoring)
Data uses	Demonstrate basic waterway conditions Raise community or school students' awareness about waterway health concepts and issues Conduct training in general waterway monitoring techniques	Provide a general indication of waterway conditions Undertake background studies	Contribute to State of the Environment reporting Assist government agencies to refine or develop water quality guidelines Assist with academic research activities

* Note that the TER specified here is a generalisation, and users should refer to monitoring methods for further details on relevant TERs.

Table 5–3 Example methods guide for physico-chemical indicators

	Method 1			Method 2			Method 3		
Data quality	**Knowledge and skills**	**Time (hours)**	**Cost ($)**	**Knowledge and skills**	**Time (hours)**	**Cost ($)**	**Knowledge and skills**	**Time (hours)**	**Cost ($)**
Analytical							Expert advice	> 5	> 500
Indicative	Beginner	< 1	> 500	Some experience	> 5	< 500	Some experience	< 1	> 500
Demonstrative	Beginner	< 1	< 200						

Step 1: Decide what data quality you require. Select the row that corresponds to your selection.

Step 2: Scan the resource requirements for each method (knowledge, skills, time and cost). Consider the time and amount of money you have to undertake the method and whether you have experience in the method. Select the appropriate method based on these available resources—for example, if you have no time constraints, a budget of $500 and a little experience in waterway monitoring, you would select Method 2.

Step 3: Refer to the detailed information on the selected method to attain your required level of data quality. Information includes:

- method summary
- monitoring method
- equipment
- quality control procedures
- participant competency
- calibration
- maintenance
- quality control checks.

Monitoring equipment

Parameter-specific monitoring equipment is detailed within the section of this chapter on that parameter. However, all methods require a common set of equipment. When monitoring physical and chemical waterway parameters, you are likely to need:

- a boat (beware of safety risks and insurance issues associated with boats)
- waders or waterproof boots (always wear appropriate footwear and beware of safety risks associated with waders)
- a hat, sunscreen and sunglasses
- safety equipment as required—for example, hard hats, flotation devices, protective clothing and mobile telephones
- a sampling pole and bottles
- a clean sampling bucket with sealing lid and thin cable (< 5 mm diameter)
- clean containers for samples—see the sections on laboratory analysis for selecting the right containers for each analysis
- plastic disposable gloves and safety glasses
- an esky or fridge to keep samples cool, where necessary
- equipment to take measurements—for example, a watch, tape measure and thermometer
- reagents and standard solutions
- field data sheets and labels
- relevant documents—for example, technical reference manual, instruction manuals, and calibration and maintenance documents
- pens, pencils or waterproof markers
- a first aid kit
- containers for solid and liquid waste.

All equipment must be suitably cleaned, stored and maintained to ensure reliability. Be aware of expiry dates on perishable items such as reagents and safety equipment. For further details regarding health and safety equipment refer to the *Health and safety guidelines for community-based waterway monitoring* (Department of Natural Resources and Water 2006).

Units of measurement

The result for any indicator can be expressed in a range of different units. Prior to monitoring, you should determine which units of measurement will best meet your needs. The units of measurement used should always be clearly recorded when collecting data.

Conversion is usually possible between one unit and another. For example, concentrations of a solute are generally expressed as milligrams per litre (mg/L), but may also be expressed as micrograms per litre (µg/L), parts per thousand (ppt) or parts per million (ppm).

Conversion is:
1 mg/L = 1000 µg/L = 1 ppm = 0.001 ppt

Specific information on units of measurement for each indicator is provided in the sections of this chapter relating to that indicator.

Capturing a representative water sample

The representativeness of your water sample will depend on how and where you take the water sample, and how you use sampling containers and water quality instruments.

Note: Additional precautions need to be taken when sampling for nutrient analyses. The following information is relevant to all nutrient sampling, though each sampling method can have its own specific procedures. See the individual sections on each nutrient for the specific steps involved in sampling for that nutrient.

How to take a water sample

The way you collect a sample of water can have a large influence on the accuracy of your results. Accordingly, it is important that you document the methods used to collect your samples, and that the procedures themselves do not affect the parameter you are measuring. For example, if you are collecting a sample to test for turbidity, you need to be especially careful not to stir up bed sediments in the vicinity of your sample.

The physico-chemical conditions within most waterways are naturally highly variable, so monitoring methods must be designed to minimise further variability associated with the monitoring procedures used. Variations associated with the monitoring process are referred to as *artefacts* and can become quite misleading if not adequately dealt with. Some simple procedures to help minimise artefacts associated with your sampling procedure include:

- labelling bottles before they are used, by recording the site, date, time, person and analysis required
- monitoring from the same place on each occasion
- monitoring at approximately the same time of day
- consistently using the same methods to sample
- managing and investigating the data in the same way
- replicating at an appropriate spatial and temporal scale—for example, collecting all samples from catchment headquarters during summer.

Where to take a sample

Whenever you take a sample, you should try to ensure that the sample you collect is representative of the waterway at the time of monitoring. Some ways to help improve the representativeness of your sample include:

- monitoring in flowing waters whenever possible rather than in areas of still water
- capturing your water sample away from the stream bank, the stream bed and other physical structures such as walls or pylons
- where possible, trying to take a water sample from the middle of the stream. The safest way of doing this is by using a sampling bottle attached to a pole. Using buckets attached to ropes or sampling from a boat is dangerous and needs to be done with caution
- taking your water sample approximately 10–30 centimetres (cm) below the surface of the water whenever possible. This avoids surface effects such as altered temperature or dissolved oxygen concentration associated with climatic conditions.

Every time you take a measurement or collect a water sample, you should record your method and, if applicable, the result on a field data sheet. These sheets help you record all the essential information associated with where, when and how the data was collected and by whom. Field data sheets should also allow you to record additional information about relevant conditions at the time of sampling—for example, climatic conditions, flow or particular disturbances relevant to the indicator. For more information on field sheets and field sheet templates, see Chapter 10.

Using a sample container

Taking a water sample directly into a sample bottle is recommended, as it avoids any unnecessary double-handling of the water sample. An extension pole is ideal for holding sample bottles, and enables you to collect a more representative sample away from possible sources of contamination. Alternatively, a bucket with an airtight lid may be used, with subsamples decanted to appropriate containers (this method should be avoided when sampling for nutrients, whenever possible).

If decanting the sample to other containers, particularly when using a bucket, never submerge the subsample bottle into the bucket. Always pour water from the original container into the subsample container once it has been rinsed three times. It is important that the sample in the bucket be fully stirred, with particulates kept in suspension prior to decanting into the subsample container. Take care to avoid contact with foreign bodies—in particular, your hands.

If using a bucket, consider the following:

- Use caution if deploying into fast-flowing water, particularly when sampling from bridges using ropes.
- Keep the airtight lid on the bucket at all times when it is not in use.
- Do not use the bucket for any other purpose than the collection of water samples.
- A lanyard cord or rope may be attached to the bucket for ease of handling. To avoid potential contamination from water dripping into the sample, the cord should be the smallest diameter practical (< 5 mm) and be of a non-permeable material such as nylon.

Using a water quality instrument

Water quality probes come in a variety of configurations and types. This section considers both in situ probes and instruments requiring a water sample.

In situ probes, such as multi-probes and handheld probes with sufficiently long cabling to access representative water, are those that can be deployed directly into the water body. The deployment procedure for in situ probes is as follows:

1. Remove any protective storage or transport casings.
2. Ensure that the equipment is calibrated and functioning correctly.
3. Deploy the probe into representative section of water (see 'Where to take a sample').
4. Allow the reading to stabilise.
5. Record the reading and complete the remainder of the field sheet.

Other instruments such as probes with short cables and field colorimeters/nephelometers require a water sample for deployment. The deployment procedure for such instruments is as follows:

1. Capture a representative water sample (see 'Using a sample container').
2. Remove any protective storage or transport casings from the instrument.
3. Ensure that the equipment is calibrated and functioning correctly.
4. Deploy the instrument into a suitable container. To avoid potential contamination, only ever place a probe into a sample from which no further readings will be taken. Take required subsamples first, and only deploy one probe into one subsample.
5. Allow the reading to stabilise.
6. Record the reading and complete the remainder of the field sheet.

For both types of probe, it is important that you closely follow the manufacturer's instructions.

Data confidence procedures

Follow these data confidence procedures to help you gain maximum value from your monitoring effort:

- **Document your actions**. Assessing the suitability or quality of data is impossible without adequate documentation. Always use standard forms such as field data sheets and calibration sheets. If you see something you feel may be important, document it.
- **Use standard procedures.** Develop a set of standard procedures and follow them each time you take a measurement. This will greatly increase the comparability of your data and provide the necessary documentation to demonstrate data confidence.
- **Calibrate equipment**. Calibrate each time you use the equipment, against good quality standard solutions. Use this as an opportunity to carry out routine checks for wear and tear, and maintenance. Document all calibrations and maintenance.
- **Maintain equipment**. Maintain all of your equipment to keep it in working order. You never know when you might need it.
- **Ensure training and competency**. Ensure that participants in your monitoring are adequately trained to undertake the monitoring activity; this also includes health and safety risk assessment and training activities. Document their competency and training requirements.
- **Use quality controls** such as field blanks, equipment blanks and shadow testing. These are very powerful tools for determining data quality and troubleshooting potential problems.

Specific data confidence procedures are listed in the sections on each water quality parameter. See Chapter 3 for further details on data confidence.

Containers, treatments, preservation and storage

The physical and chemical characteristics of a water sample can and will start to change from the moment the water sample is taken. When samples are to be analysed at a laboratory, actions must be taken to minimise these changes during transport and storage.

Appropriate sample containers vary depending on the substance you are testing (also known as the *analyte*). While plastic (PTFE or PET) bottles are appropriate for many analytes, borosilicate glass is required for others. In addition, consideration must be given to the volume of water required for a given analyte. Too small a sample may lead to inaccurate results or no results, while too large a sample may increase the costs of laboratory analysis.

To enhance the accuracy of your analysis, treatment activities—such as filtering to remove micro-particulates using a 45 µm filter, and acid preservation—should be carried out whenever appropriate. Often, it is important to conduct treatment activities in the field immediately after sample capture to minimise potential changes in water quality during handling and storage. Preservation and storage procedures aim to minimise changes during transport and storage at the laboratory. Techniques include acidification, refrigeration and freezing.

Laboratory analyses

The aim of laboratory analysis is to obtain accurate and precise data in a controlled environment (ANZECC & ARMCANZ 2000a). Laboratory analysis tends to be more accurate than field analysis and can provide a far greater range of tests and parameters than field methods. When choosing a laboratory to analyse your samples, you should consider not only practical factors such as cost and proximity, but also technical factors such as quality assurance protocols and capacity. National Association of Testing Authorities (NATA) accreditation is the most important consideration when selecting a laboratory to conduct your analysis. A laboratory that is NATA-accredited has been formally recognised as being competent in specific types of testing, measurement, inspection and calibration.

ANZECC and ARMCANZ (2000a) recommend considering the following questions when choosing a laboratory:

- Does the laboratory have appropriate equipment to undertake the analytical methods chosen?
- Are the laboratory facilities suitable for the planned analyses?
- Do laboratory staff have the expertise, training and competence to undertake the planned analyses?
- Has a laboratory data management system been established?
- Does the documentation provided by the laboratory meet your needs?
- Has a laboratory quality assurance plan been developed?
- Are protocols for preparing and analysing samples written and validated?
- Are standard methods being used?
- Have the accuracy, bias and precision of analytical methods been established?
- Do operation procedures specify instrument optimisation and calibration methods?
- What quality assurance or quality control procedures and activities does the laboratory undertake?
- Have all reasonable steps been taken to protect the health and safety of laboratory staff?

Ask as many questions as you need to when selecting a laboratory, to ensure that you know exactly what services and data quality the laboratory can provide and that this will meet your needs. For further details, see ANZECC and ARMCANZ (2000a).

Colorimetry

One of the main methods of measuring the concentration of a chemical substance in a water sample is called *colorimetry*. In colorimetry, chemicals react with the analyte in question to produce a coloured reaction, which is then measured with colorimetric equipment to return a result. The concentration of an element in a water sample is proportional to the intensity of colour produced by the test chemicals (for example, azo dye). This photochemical reaction can be measured using various grades of equipment, which include comparators, photometers and spectrophotometers. All three types operate on the principal of measuring the intensity of colour developed using the test chemicals. The following sections explain some important differences between equipment types.

Comparators

Comparators use the operator's visual perception to determine the intensity of colour produced. The concentration of the analyte is estimated by best matching the colour produced to a colour wheel or colour chart for predetermined concentrations. This kind of measurement is subjective, considering that many people have varying degrees of colour-blindness. Another shortcoming of colour comparators is the choice of only one chemical methodology to test for the parameter. The advantage of comparators is their reasonably low equipment cost compared to photometers and spectrophotometers. When used correctly, comparators provide a simple and low-cost means of roughly indicating analyte levels.

Comparators are appropriate for identifying polluted sites in the waterway—for example, stormwater run-off in urban streams, and wastewater treatment outfalls. A comparator is useful for identifying high concentrations. To increase resolution, some manufacturers provide long glass tubes to hold the treated sample; this has the effect of intensifying the colour present when looking through the length of the tube and allows lower concentrations to be measured. Groups can use this method in the field to obtain an indicative measure of the analyte present in the water sample.

Photometers

Photometers operate by focusing light through a lens, a coloured filter and the water sample, then onto a detector. The detector converts light intensity into an electrical current, which is displayed as the concentration of chemical in solution. The photometer removes human error associated with a comparator and usually comes with filters capable of measuring various wavelengths. This means that photometers usually have the capacity to test a sample using more than one chemical methodology and may cover a range of parameters. The ability to measure at different wavelengths is limited by the types of filter provided by the manufacturer. Instrument specifications should be consulted before purchasing a photometer to determine whether the filters provided will cover the wavelengths required to measure a particular parameter. The cost of a photometer falls between that of a comparator and a spectrophotometer. When used correctly, photometers provide a simple and low-cost means of indicating analyte levels.

Spectrophotometers

Spectrophotometers are the same as photometers except that they employ a glass prism or grate (rather than filter) that can produce and measure across the full light spectrum. The required wavelength is obtained by using a moveable slit between the prism and the sample. This means that a spectrophotometer has the flexibility to measure a greater range of parameters using more than one chemical methodology. However, spectrophotometers are more expensive than comparators or photometers and are usually less robust. Spectrophotometers are generally used in analytical laboratories.

Photometers and spectrophotometers are more fragile than colour comparators and are therefore more at risk of breaking in the field. They must be carefully maintained and must be calibrated with a reagent blank before each sample run and, if you are doing many tests, between each sampling.

Interpreting your results

To interpret your results, you need to be aware of how the data you obtained relates to the range of possible results. Consider:

- whether your results fall within the range of acceptable results
- the nature of the water being tested
- the monitoring question being asked.

Example

A pH result of 8.2 means little without an understanding of the pH scale, which ranges from 0.1 (highly acidic) through 7.0 (neutral) to 14.0 (highly alkaline).

Whether 8.2 is a good or bad result depends on the question being asked. If the pH at the site is normally below 7.1, this may be a negative result. Alternatively, if you are assessing the possible impact on aquatic ecosystem health, the ANZECC guidelines (2000b) suggest limited likelihood of harmful impacts on waterway health.

Information on interpreting the results of each parameter is provided in the section of this chapter relating to that parameter.

Safety considerations

Personal safety while monitoring water quality is based on managing potential risks. A risk assessment should be completed before and during any activity that a monitoring group is undertaking. Hazards must be identified and pointed out to all team members, and all risk control measures must be documented and explained on the project risk assessment form. A risk assessment process must be completed for each new site or for every change in activities taking place. Remember that personal safety comes first; no task is so important that safety should be compromised.

Health and safety requirements specific to certain monitoring methods are listed in the 'Health and safety' sections for individual parameters. For a more comprehensive review of health and safety risk management, refer to the *Health and safety guidelines for community-based waterway monitoring* (Department of Natural Resources and Water 2006).

Dissolved oxygen

Importance of dissolved oxygen

Dissolved oxygen (DO) is the amount of oxygen that is held (dissolved) in water. Aquatic animals and micro-organisms require oxygen for respiration (breathing). Maintenance of healthy and diverse aquatic ecosystems depends on oxygen being maintained at sufficient levels. Reductions in DO levels may result in the decline or absence of some aquatic species. At very low levels, only a few tolerant species may be present; however, the number of individuals of the tolerant species can be high.

DO is a useful general indicator of water quality. It can reveal how metabolic processes are operating within a water body and it can indicate the presence of certain pollutants, particularly organic matter from plants and animals such as fallen leaves, animal manure or sewage effluent.

DO levels may be expressed as milligrams per litre (mg/L) or as a per cent saturation (% sat.). Milligrams per litre relate to the physical quantity of oxygen dissolved in the water, while per cent saturation relates to the proportion of oxygen dissolved in the water compared to the theoretical level of DO capable of being held in pure, still water. Levels can exceed 100% during periods of high photosynthesis, such as during an algal bloom.

Per cent saturation is considered to be a better measure of the availability of oxygen to aquatic organisms than milligrams per litre and also allows direct comparisons between DO results from sites with different salinity and temperature values.

Factors affecting dissolved oxygen

DO levels in natural waters vary depending on several factors including:

- how fast the oxygen can get into the water
- how fast the oxygen is used up
- photosynthesis by plants and algae.

The speed at which oxygen can enter and mix through a water body depends on the surface area, and the rate and extent to which the water mixes—that is, how turbulent the water is. For these reasons, shallow, fast-flowing streams running over cobbles or rocks have high oxygen levels (Figure 5–1) while still, slow-flowing or deeper pools may have reduced oxygen levels, particularly at deeper levels (Figure 5–2).

Oxygen is used up through the respiration (breathing) of animals and bacteria. The most important users of oxygen are bacteria, which break down organic matter. The more organic matter there is in a stream, the greater the bacterial population. High levels of bacteria lead to increased oxygen use and hence, lower DO levels. For example, deep, murky lowland rivers contain more organic matter than upland streams and are therefore likely to have lower oxygen levels. Streams in urban catchments may experience consistently lower-than-expected DO levels due to continuous input of organic matter from urban drains.

Aquatic plants and algae release large amounts of oxygen back into the water during daylight hours as a by-product of photosynthesis. During the evening, these same plants use oxygen as part of the respiration process. Bacteria, macro-invertebrates, fish and other water life also use oxygen at varying rates during the day and night. Oxygen levels therefore vary over the 24-hour daily cycle based on production levels and demand. Peak DO levels usually occur in the early afternoon and minimum levels just before sunrise (Figure 5–3). The extent of DO variation depends on the amount of algae and plants in the water and the degree to which shading reduces available light for the photosynthesising process. Large amounts of algae and aquatic plants can cause the water to become temporarily supersaturated (oxygen levels greater than 100% saturation) during the day. Supersaturation can be harmful to fish because it causes the oxygen concentration in fishes' blood to rise, and then when the fish move to water that has less DO, bubbles of oxygen quickly form in their blood, harming circulation.

Monitoring considerations

It is recommended that DO be determined on site rather than in the laboratory. Results may be measured either directly within the water body or from a representative sample. Whichever method you use, take particular care to avoid unduly agitating the water surface or disturbing sediments during sampling.

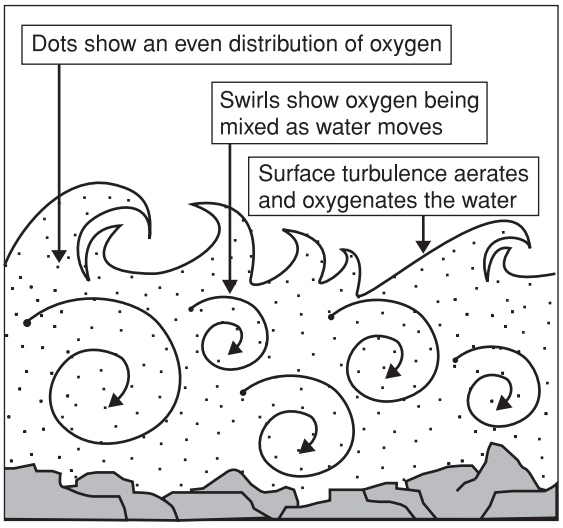


Figure 5–1 Oxygen entering shallow, flowing water

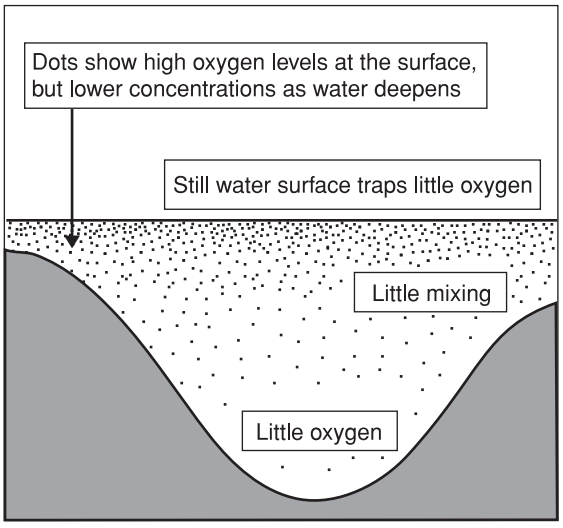


Figure 5–2 Oxygen in deep, still water

Time of day and season

Increases in water temperature reduce the solubility of oxygen in water and increase oxygen diffusion out of water into the atmosphere. Water temperatures show seasonal as well as daily patterns of fluctuation, with water temperatures tending to be lowest before sunrise and highest in the mid-afternoon. DO levels will be highest in the afternoon and lowest just before sunrise each day regardless of temperatures.

Recording the time of day on your results sheet when you test for DO is important, since levels change depending on the time of day as well as water temperatures (Figure 5–4). Try to collect samples at the same time each day to allow easier comparison of data collected on different days. When measuring DO, be sure to take a temperature reading because this will enable you to calculate per cent saturation figures later on.

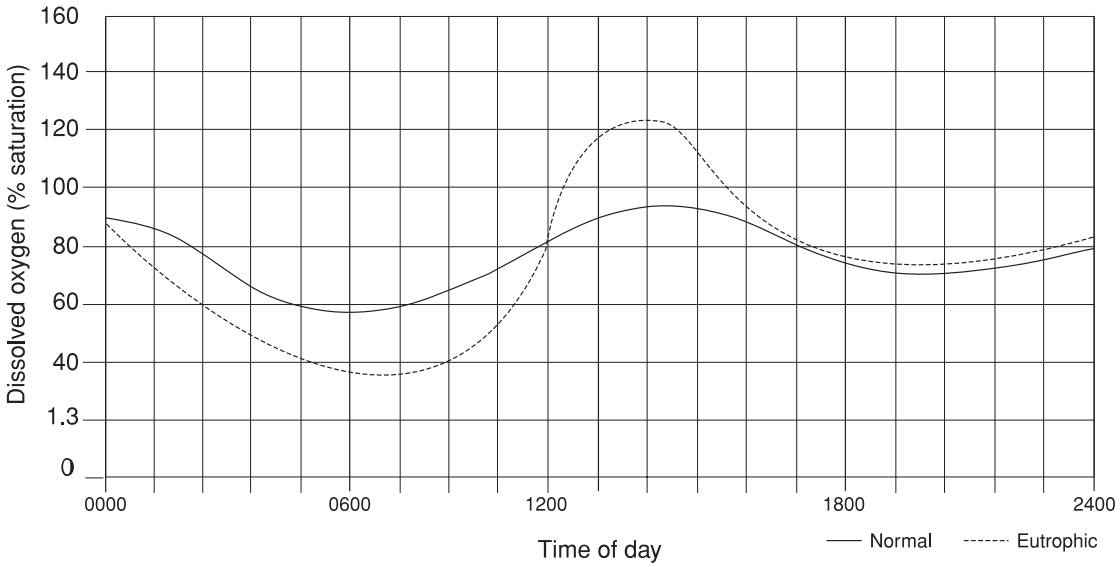


Figure 5–3 Dissolved oxygen levels over 24 hours in a normal and a eutrophic waterway
(Waterwatch Australia Steering Committee 2002)

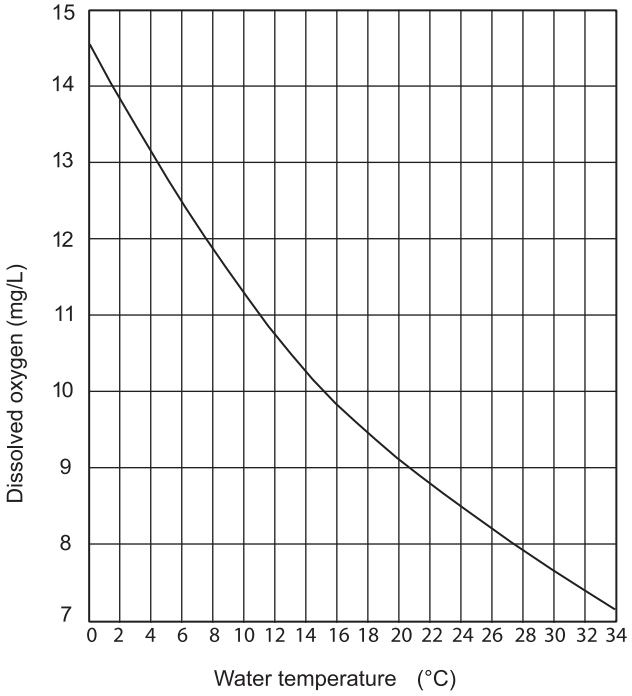


Figure 5–4 Dissolved oxygen per litre of water, at different temperatures at sea level
(Waterwatch Australia Steering Committee 2002)

Salinity level

Saline waters hold less oxygen than fresh water, therefore the salinity of a waterway should be considered when measuring DO levels. Increases in salinity reduce the maximum DO concentrations in water. For example, fresh water at 20 °C is only 80% saturated if it contains 7.3 mg/L of DO, but sea water is 100% saturated.

Be sure to take a salinity reading (by measuring electrical conductivity) if you wish to calculate per cent saturation from DO concentration. The majority of modern DO meters will provide a per cent saturation reading. If testing in estuaries, be aware that tidal flow may influence oxygen concentrations in a number of different ways due to the changing mix of sea and fresh water.

Altitude

At high altitudes, the lower atmospheric pressure leads to lower DO concentrations. For example, at 1850 metres (m) above sea level, the amount of DO in the water (in absolute terms—mg/L) will be only 80% of the amount at sea level in otherwise identical conditions.

Water depth

In lakes and large, deep rivers, DO levels are most likely to vary according to depth in the water column. In general, when taking water samples, submerge your arm to wrist level and ensure that the mouth of the sampling bottle is away from any surface contaminants.

Water discharge points

When organic wastes enter the river from point sources such as sewage treatment plants and animal feedlots, bacterial activity increases and oxygen levels are reduced. The effect of these inputs is best assessed by comparing DO at sites upstream and downstream from the point source (Figure 5–5).

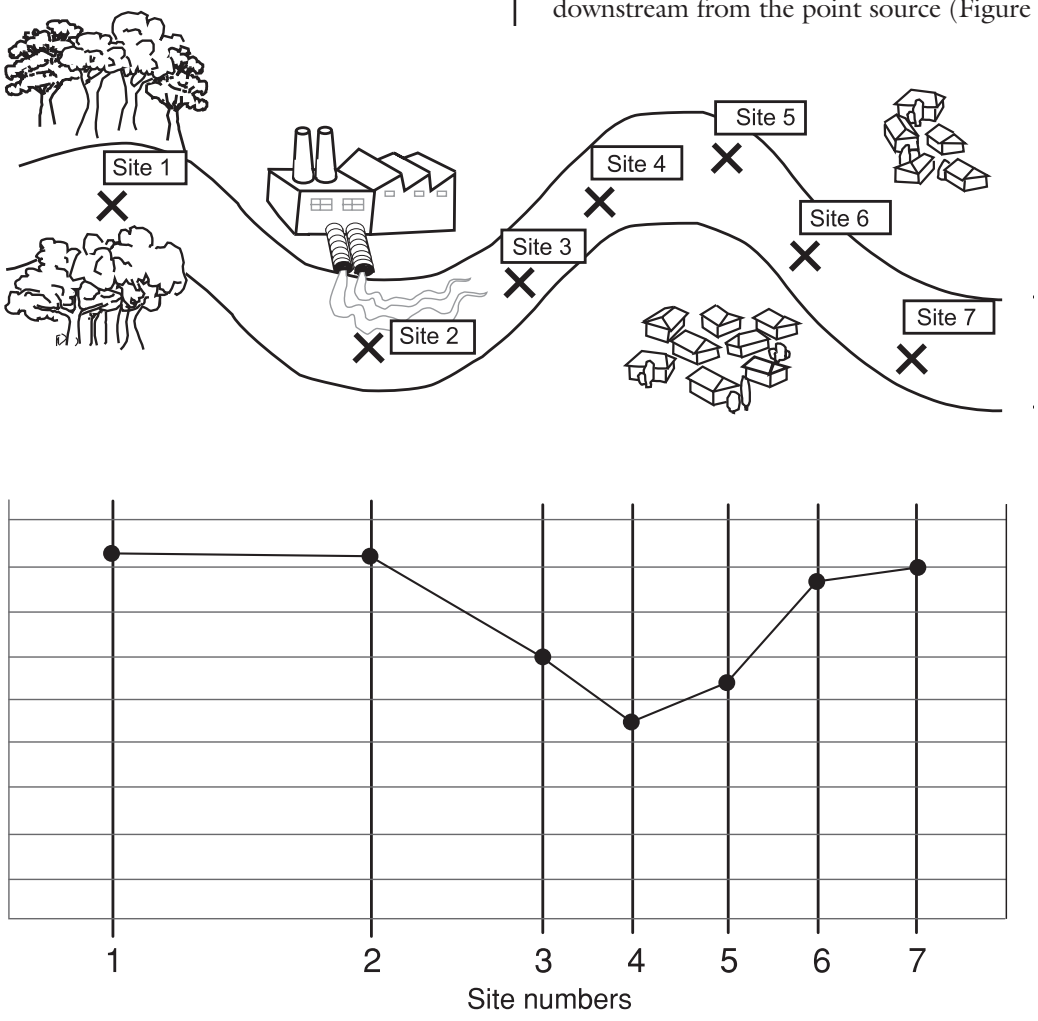


Figure 5–5 Comparison of dissolved oxygen levels at sites upstream and downstream of suspected sources of pollution (Foster 1994)

Excess algal growth

Nutrient pollution causes increased algal growth. This changes the 24-hour DO cycle (Figure 5–3), giving higher maximum and lower minimum DO values. Measuring the difference between dawn and mid-afternoon values may provide a measure of the amount of algal activity, and any critical fluctuations in DO levels that may adversely affect aquatic biota.

Since minimum levels occur at dawn, measurements of DO at this time are a good indicator of the maximum stress to aquatic biota. In addition, monitoring DO levels mid-afternoon will indicate whether supersaturation is occurring. As DO levels are critical to fish, a good place to sample is in the pools that fish tend to favour or in the spawning areas that they use.

Flow effects

Streams with a reasonable amount of flow can be expected to have high levels of DO. Under very low flow conditions, streams become stagnant and lower DO levels are likely to occur. During flood events DO levels may be high, but once flood flows recede the bacterial breakdown of organic matter carried by the flood can lower DO levels for days or even weeks following heavy rain. Land uses in a catchment affect the amount of organic matter entering streams during storm events. Thus, post-storm DO concentrations in waterways in disturbed catchments may fall to lower values than those in less disturbed catchments.

The DO levels in and below riffle areas, waterfalls or dam spillways are typically higher than those in pools and slow-moving stretches. If you wish to measure the effect of a dam, you should sample for DO behind the dam, immediately below the spillway and upstream of the dam.

Monitoring methods

DO can be determined by titration, colorimetry and DO meter (electrode). Titrations use chemical reactions to provide a coloured endpoint that can be interpreted visually. Colorimetry relies on measuring the intensity of colour development, which is proportional to the concentration of an analyte in the water. DO meters essentially monitor the changes in potential (voltage) caused by differing concentrations of oxygen dissolved in the water.

Titration

Titration refers to the use of a measurable volume of chemicals that react with oxygen to produce a colour change (endpoint). The volume of chemicals used is proportional to a DO value. Titrations can be conducted in a drop-wise manner, using a pipette and manually titrating, or using equipment that carries out the titration automatically.

The Winkler titration technique is the most commonly employed DO titration method. It is important to determine the manufacturer's specifications to ensure that the accuracy, resolution and range of the test kit meets monitoring requirements.

Although titrations can produce accurate results, the process is time-consuming compared to the meter method for DO analysis. It is therefore not suitable for multiple or time series (such as 24-hour variation) data.

Colorimetry

Colorimetry uses a chemical reaction between a water sample and an iodine or chloroform-iodine solution to measure DO levels. The iodine solution (the reagent) reacts with oxygen in the sample (the analyte) to produce a yellow (iodine) or purple (chloroform-iodine) colour change. The intensity of the colour change corresponds with the amount of DO present in the sample. The intensity of the colour change is read by an electronic colorimeter that displays the DO concentration. Colorimetry can produce high quality data; however, this method can be time-consuming compared to the use of a DO meter.

Dissolved oxygen meter

DO meters measure the change in potential (voltage) caused by differing oxygen concentrations by using a sensing and a reference electrode. The use of a DO meter is the most effective method for collecting quantitative data due to the fact that it is able to collect high-resolution readings accurately over a wide range. DO meters provide readings quickly and easily with minimal extra time or effort required for duplicate or multiple sets of readings, and can be used to easily collect time series data. DO meters can usually calculate and display readings in milligrams per litre (mg/L) or per cent saturation (% sat.).

If you plan to use a DO meter, consider that they need to be calibrated regularly—daily when in use, or more frequently if working at locations of differing altitudes or changeable atmospheric conditions (affecting barometric pressure). They can be quite expensive to purchase, and their limited shelf life means that they may need to be replaced or rejuvenated periodically.

Interpreting your results

Depending on the units your equipment measures, it is possible to convert between milligrams per litre and per cent saturation, as outlined below.

Referring to Figure 5–6, follow these steps to calculate per cent saturation DO for fresh water (less than 1000 mg/L salinity):

1. Plot temperature on the upper scale.
2. Plot oxygen concentration on the lower scale.
3. Hold a ruler between the two points. The point where the ruler crosses the middle scale is the per cent saturation reading.
4. Record this result on the water quality results sheet (see Chapter 10 for record sheets).

To calculate per cent saturation DO for saline water (more than 1000 mg/L salinity), you need to know:

- the measured salinity (conductivity) in milligrams per litre
- the water temperature in degrees Celsius
- the measured DO in milligrams per litre.

1. Use Table 5–4 to establish the potential DO. Locate the nearest level of salinity across the top, and the nearest temperature on the left hand side. Where they cross registers the potential DO for the water in milligrams per litre.
2. Divide the measured DO by the potential DO.
3. Multiply this by 100. This is the result in per cent saturation.

How you interpret your results will depend on your monitoring objectives. See Chapter 8 of this manual for advice on data interpretation for a range of monitoring objectives. If you are conducting routine monitoring and wish to determine the health of your waterway, or its suitability for different water uses, you will need to compare your data to the relevant guideline values.

If you are monitoring for the purpose of protecting aquatic ecosystems, the DO concentration should not fall below the 20th percentile of values typical for a waterway in your region (ANZECC & ARMCANZ 2000b). A DO concentration of 2 mg/L will not support fish, and DO concentrations below 3 mg/L are stressful to most aquatic animals. At least 5 to 6 mg/L are required for fish growth and activity. Daytime concentrations of 6 mg/L could be cause for concern, as high daytime levels could mean low night-time levels.

For ecosystem protection, the optimal DO level for a site depends on a number of factors, including what region you are monitoring in and the water body type. *The Queensland water quality guidelines* (Environmental Protection Agency 2006) provide DO values for ecosystem protection for three regions and a range of water body types (Table 5–5). The relevant guideline value is determined by where in Queensland you are and what type of water body you are monitoring. Refer to the *Queensland water quality guidelines* (Environmental Protection Agency 2006) for advice of the boundaries of the water quality regions and for definitions of the water body types.

Table 5–4 Effect of conductivity and temperature on potential dissolved oxygen concentrations (mg/L) in waters at sea level (adapted from Waterwatch Australia Steering Committee 2002)

Temperature in °C	Conductivity in µS/cm (salinity in mg/L)				
	0 (0)	**14 400 (9000)**	**28 800 (18 000)**	**43 200 (27 000)**	**57 800 (36 000)**
0	14.6	13.7	12.9	12.1	11.4
5	12.8	12.0	11.3	10.7	10.1
10	11.3	10.7	10.1	9.5	9.0
15	10.1	9.5	9.0	8.5	8.1
20	9.1	8.6	8.2	7.7	7.3
25	8.2	7.8	7.4	7.1	6.7
30	7.5	7.2	6.8	6.5	6.2
35	6.9	6.6	6.3	6.0	5.7

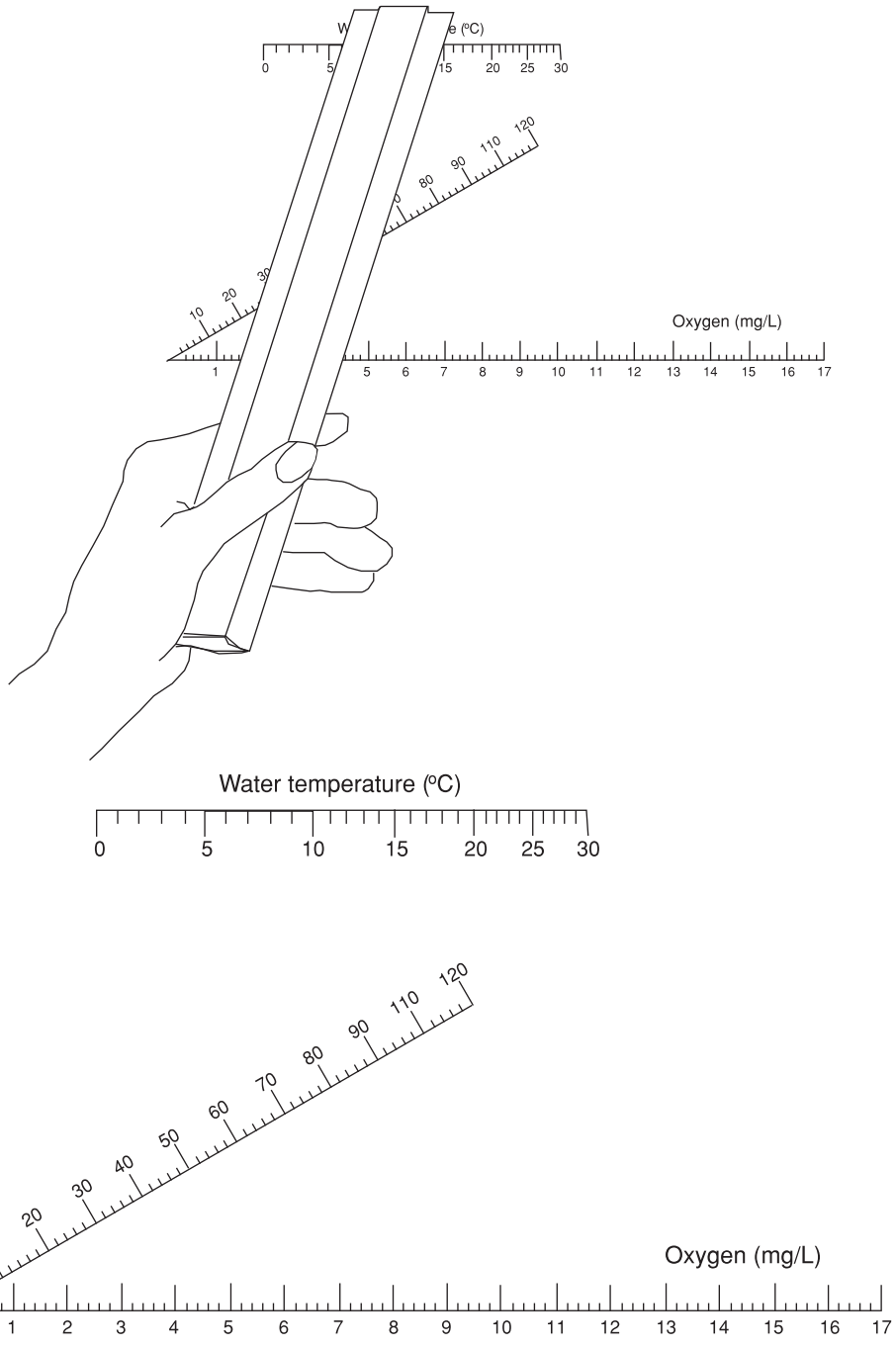


Figure 5–6 Determining per cent saturation dissolved oxygen (fresh water) (Cassidy 2003)

Table 5–5 Guideline dissolved oxygen values for fresh waters in Queensland (adapted from Environmental Protection Agency 2006; ANZECC & ARMCANZ 2000a)

Protection of aquatic ecosystems			
Water body type	**Region**	**Guideline DO range**	**Comments**
Upland streams	South East Qld	90–110% sat.	Lower after storms
	Central Coast	90–110% sat.	
	Wet Tropics	90–100% sat.	
Lowland streams	South East Qld	85–110% sat.	Lower after storms
	Central Coast	85–110% sat.	
	Wet Tropics	85–120% sat.	
Freshwater lakes or reservoirs	South East Qld	90–110% sat.	Australia-wide minimum 70% sat. at the surface (no guideline for deeper)
	Central Coast	90–110% sat.	
	Wet Tropics	90–120% sat.	
Wetlands	South-eastern Australia	–	See ANZECC and ARMCANZ (2000a) for region boundaries
	Tropical Australia	90–120% sat.	
Other uses			
Water use	**Sub-use**	**Guideline DO range**	**Comments**
Drinking water	No health-based guideline but low concentrations allow growth of nuisance micro-organisms (iron-, manganese-, sulfate- and nitrate-reducing bacteria) and cause taste and odour problems, staining, and corrosion		
Recreation	Visual amenity		Guidelines for protection of aquatic ecosystems should apply
Agriculture	Tropical aquaculture	> 4 mg/L	Optimal levels vary for individual fish species

The *Queensland water quality guidelines* also outline more specialised subregional guidelines for water bodies in the Douglas, Gold Coast hinterland, Fraser Island and North Stradbroke Island catchments.

Where subregional or regional guidelines are unavailable (such as for Eastern Cape York, Gulf Rivers, Lake Eyre and Murray–Darling), refer to the *Australian and New Zealand guidelines for fresh and marine water quality* (ANZECC & ARMCANZ 2000b). When this is the case, you should always keep in mind the natural variations described earlier, and collect some reference values from unpolluted local water bodies. For most purposes, a level of 85% saturation is considered acceptable for surface waters in Queensland.

For advice on developing your own guideline values and comparing your results with guideline values, see Chapter 8.

Guidelines exist for other monitoring objectives, such as assessing the quality of water for agricultrual uses or for drinking. See the guideline references section at the back of this chapter for a list of available guidelines to suit your monitoring objectives.

Health and safety

Be aware of health and safety issues when monitoring for DO. Examples of such issues include the following:

- The Winkler titration test uses a number of potentially hazardous chemicals. Take care that the chemicals are not flicked into eyes or spilled onto skin or clothes, and always wear safety glasses and rubber gloves. When testing, place the liquid waste bottle, paper towels and squirt-bottle of deionised water nearby.
- Manganous sulfate can irritate eyes and skin, so avoid all direct contact.
- Alkaline potassium iodide azide can cause severe burns and is poisonous if swallowed.
- Direct contact with sulfuric acid will cause severe burns, inhalation can cause coughing and chest problems, and ingestion may be fatal.
- Take care when using glassware. Handle all glass carefully to avoid breaking or smashing, and never use cracked or damaged glassware.

Refer to the *Health and safety guidelines for community-based waterway monitoring* (Department of Natural Resources and Water 2006) for further information.

Table 5–6 Methods guide for dissolved oxygen

	Winkler titration			Colorimetry			DO meter/electrode		
Data quality	**Knowledge and skills**	**Time (mins)**	**Cost ($)**	**Knowledge and skills**	**Time (mins)**	**Cost ($)**	**Knowledge and skills**	**Time (mins)**	**Cost ($)**
Analytical	Expert advice	20–40	90–160	Expert advice	15–35	2600–3000	Some experience	3–5	850–1500
Indicative	Expert advice	20–40	90–160	Expert advice	15–35	2000–2600	Some experience	3–5	850–1500
Demonstrative	Some experience	10–25	40–60	Beginner	10–20	30–70	Beginner	> 3	300–400

Winkler titration method

Summary

This method:

- determines DO in milligrams per litre (mg/L)
- uses chemicals that react with oxygen to produce a colour change. The volume of chemical used is proportional to the DO value
- is the most commonly used DO titration method
- is an accepted option in the AS/NZS 5667.1:1998 standard (Standards Australia & Standards New Zealand 1998) for water and wastewater treatment.

Equipment

You will need:

- a DO field kit and instructions
- ample reagents for the number of tests being conducted.

To produce **indicative** data:

- suggested instrument test range is 0–20 mg/L
- suggested test resolution is at least 0.5 mg/L
- suggested instrument test accuracy is ±0.5 mg/L.

To produce **analytical** data:

- suggested instrument test range is 0–20 mg/L
- suggested test resolution is at least 0.1 mg/L
- suggested instrument test accuracy is ±0.2 mg/L.

Monitoring method

1. Capture a representative water sample in a 250 or 300 mL bottle.
2. Add 1 mL of manganous sulfate and 1 mL of iodide azide.
3. Mix by inverting the bottle until a precipitate forms and settles.
4. When half the bottle volume is occupied by clear liquid above the precipitate, add 1 mL of sulfuric acid.
5. Re-stopper the bottle and invert it several times until the precipitation has all dissolved. The sample will turn a yellow-brown colour, as free iodine has been released in it.
6. Titrate the sample by adding sodium sulfate until a pale straw colour appears.
7. Add a starch indicator and continue to titrate until the blue colour first appears.

Quality control procedures

- Ensure that the accuracy, resolution and range of the test kit meet monitoring requirements—check the manufacturer's specifications.
- Follow the instructions in the kit you have purchased.
- Renew sodium thiosulfate every 12 months.
- Rinse sample containers and ensure that they are free of contaminants prior to sampling in water being tested.
- Conduct tests immediately in the field, directly from the waterway.

Participant competency

To produce **demonstrative** data, no prior experience in using the equipment is required. To produce **indicative** or **analytical** data, strong experience and/or expert training in the use of the equipment is required. For analytical data, inter-operator comparisons are recommended.

Calibration

Not applicable to the Winkler titration method.

Maintenance

- Ensure that reagents are within the expiry date and are not contaminated. Replace sulfate reagents every twelve months.
- Clean glassware after each test by rinsing with deionised water and drying before storing.

Quality control checks

For **indicative** data:

- conduct a replicate test on 10% of the samples. The results should fall within the designated TER (for example, ±0.5 mg/L)
- conduct twice-yearly tests on a known saturated DO sample. This test will reveal any deterioration of the reagents over time
- test a saturated DO sample any time a reagent is replaced. Compare the results with those from a calibrated DO meter
- confirm each reading by having two people read the level of titrant in the syringe.

For **analytical** data:

- conduct a replicate test on 10% of the samples. The results should fall within the designated TER (for example, ±0.3 mg/L)
- have a duplicate sample tested by a professional water quality officer during the initial stages of the project. The difference between the values of the duplicate samples needs to be within the TER

- continue external periodical checks by participating in shadow-testing workshops.
- conduct twice-yearly tests on a known saturated DO sample. This test will reveal any deterioration of the reagents over time
- test a saturated DO sample any time a reagent is replaced. Compare the results with a calibrated DO meter
- confirm each reading by having two people read the level of titrant in the syringe.

Colorimetry

Summary

In this method:

- DO is determined in milligrams per litre
- chemicals react with oxygen to produce a coloured solution that is measurable with colorimetric equipment.

Note: A colorimeter can by used to analyse other parameters such as phosphorus and nitrogen.

Equipment

You will need:

- water sampling equipment
- a colorimeter (for example, a spectrophotometer, photometer or comparator) and reagents
- manufacturer's instructions.

To produce **indicative** data:

- suggested instrument test range is 0–20 mg/L
- suggested test resolution is at least 0.5 mg/L
- suggested instrument test accuracy is ±0.5 mg/L.

To produce **analytical** data:

- suggested instrument test range is 0–20 mg/L
- suggested test resolution is at least 0.1 mg/L
- suggested instrument test accuracy is ±0.2 mg/L.

Monitoring method

Capture a water sample (follow the sampling procedure on page 5–9). Follow the manufacturer's instructions.

Quality control procedures

- Rinse the bottle in the water being tested, three times prior to sampling.
- Ensure that no air bubbles are in the captured sample.
- Collect the water directly from the water body being tested.
- Conduct the test in the field to reduce the effect of bacteria on the reading.

Participant competency

To produce **indicative** or **analytical** data, strong experience and/or expert training in the use of the equipment is required. For **analytical** data, annual inter-operator comparisons are recommended.

Calibration

For **indicative** and **analytical** data, complete:

- monthly calibration and TER checks
- equipment-specific maintenance and calibration records.

Maintenance

- Keep colorimetric equipment clean by following the manufacturer's instructions.
- Clean all sampling containers and eskies without using detergents.
- Keep maintenance logs for all colorimetric equipment.
- Ensure that reagents have not expired and replace when necessary.

Quality control checks

For **demonstrative** data, calibrate the meter according to the manufacturer's instructions.

For **indicative** data:

- conduct a replicate test on 5% of the samples. The results should fall within the designated TER (for example, ±0.5 mg/L)
- calibrate the meter according to the manufacturer's instructions prior to each use.

For **analytical** data:

- conduct a replicate test on 10% of the samples. The results should fall within the designated TER (for example, ±0.3 mg/L)
- have a duplicate sample tested by a professional water quality officer during the initial stages of the project. The difference between the values of the duplicate samples needs to be within the TER
- continue external periodical checks by participating in shadow-testing workshops
- calibrate the meter according to the manufacturer's instructions prior to each use.

Dissolved oxygen meter

Summary

This method:

- determines DO in milligrams per litre (mg/L) or per cent saturation (% sat.)
- uses sensing and reference electrodes to monitor changes in potential (voltage) caused by differing oxygen concentrations
- is quick and easy
- allows for multiple and duplicate readings to be taken
- can be used for time series data collection.

Note: DO meters are the most effective method for collecting quantitative data.

Equipment

You will need:

- a DO meter
- a potentiometric (polarographic) electrode or Galvanic electrode
- the manufacturer's instruction manual
- extra membranes and electrolyte solution for the probe
- water sampling equipment (for instruments that require a captured water sample for deployment).

To produce **indicative** data:

- suggested instrument test range is 0–20 mg/L
- suggested test resolution is at least 0.5 mg/L
- suggested instrument test accuracy is ±0.5 mg/L.

To produce **analytical** data:

- suggested instrument test range is 0–20 mg/L
- suggested test resolution is at least 0.1 mg/L
- suggested instrument test accuracy is ±0.2 mg/L.

Monitoring method

1. Deploy in situ meters as per the manufacturer's instructions. For meters that require a captured water sample, follow the sampling procedure on page 5–9. Take readings as per the manufacturer's instructions.
2. Account for temperature differences. Changes in temperature will affect the accuracy of the DO meter due to diffusion speed. Many meters have automatic temperature compensation to deal with this interference. Alternatively, you can perform calculations manually.
3. Account for water movement. The way in which a DO meter operates results in the consumption of DO at the membrane surface. This means that, in still waters, the reading will slowly decrease until it is well below the actual DO concentration of the water sample. If your meter does not have an in-built stirrer that provides a constant flow of new water over the membrane surface or a rapid pulse system that compensates for a lack of flow, you must manually stir the electrode to increase flow across the surface. Stirring technique and speed must be consistent from day to day and between operators.

Quality control procedures

- Conduct the test immediately in the field to achieve maximum accuracy.
- Take your sample upstream of where you are standing, in undisturbed water.
- To address oxygen depletion at the membrane, move the electrode when measuring.

Participant competency

To produce **demonstrative** data, no prior experience in the use of the equipment is required. To produce **indicative** and **analytical** data, some prior experience and training in the use of the equipment is required. For **analytical** data, annual inter-operator comparisons are recommended.

Calibration

For **indicative** data, calibrate the meter prior to each use or monitoring session according to the manufacturer's instructions. Results can also checked against readings from the Winkler method.

For **analytical** data, calibrate the meter before each use, according to the manufacturer's instructions. For example:

1. Surround the probe with moist air.
2. Wait at least ten minutes for the temperature to stabilise.
3. Select an appropriate DO range and set the salinity compensation control to zero.
4. Adjust the calibration setting until the meter displays the calibration value.
5. Wait two minutes to verify calibration stability. Readjust if necessary.

Maintenance

- Inspect the membrane daily when in use for cuts, punctures and air bubbles.
- Replace the membrane if damaged and ensure that the electrolyte inside the probe is kept at the correct level. Refer to the manufacturer's instructions.

Quality control checks

For **indicative** data:

- conduct a replicate test every ten samples. The results should fall within the designated TER (for example, ±0.5 mg/L)
- test a blind sample every six months.

For **analytical** data:

- conduct a replicate test every ten samples. The results should fall within the designated TER (for example, ±0.3 mg/L)
- test a blind sample every three months
- have a duplicate sample tested by a professional water quality officer during the initial stages of the project. The difference between the values of the duplicate samples needs to be within the TER
- continue external periodical checks by participating in shadow-testing workshops.

Electrical conductivity

Importance of electrical conductivity

Electrical conductivity (EC) is a measure of the capacity of a sample of water to conduct an electrical current. This is primarily determined by the number of ions in the solution. Ions are charged particles dissolved in the water to form a solution and are commonly known as salts. The more salts present in the water, the greater the capacity of the solution to conduct a current. Therefore, EC can be used as an effective measure of the saltiness (salinity) of a solution. The types of ions associated with salinity are chlorides, sulfates, carbonates, sodium, magnesium, calcium and potassium.

EC is usually expressed as microsiemens per centimetre (µS/cm), but may also be reported using millisiemens (mS/cm) or decisiemens (dS/cm).

1000 µS/cm = 1 mS/cm

1000 mS/cm = 1 dS/cm

Appropriate salt concentrations, along with several related physical and chemical processes, are vital for aquatic plants and animals. Salinity beyond the normal range can damage ecosystem health and function, and cause high numbers of aquatic plant and animal fatalities. Salinity levels outside the normal range can also have an impact on human uses, rendering the water unsuitable for domestic and agricultural consumption.

High levels of salt can affect the nutrient uptake capacity of plant roots by blocking chemical transfer processes.

Very high salt concentrations may increase clarity of a water body through a process known as *flocculation*. The charged salt ions cause suspended particles to clump together, increasing their density and causing them to fall out of suspension.

Salty water is denser than fresh water, which causes the fresh water to float on the denser salt water. This physical separation of the water bodies, known as a *halocline*, occurs in poorly mixed water bodies such as deep pools and dams. This process can severely affect non-mobile, bottom-dwelling organisms.

Factors affecting electrical conductivity

Factors that are likely to influence EC include:

- those that determine the ionic composition of the water body—for example, geology, soils and land use
- those that introduce additional ions into the water body—for example, discharge of salty water from irrigation, industrial discharge, sewage treatment, urban run-off and groundwater
- dilution or concentration effects—for example, rainfall and run-off generally dilute, whereas evaporation concentrates ions and hence increases salinity and EC.

Monitoring considerations

EC is measured by immersing a conductivity meter (electrode) in water. The meter measures the water's capacity to conduct an electric current across a known distance. This capacity depends on the number of ions (salts) in the solution; the more ions (salts), the greater the charge that can be conducted.

Different electrodes are available for fresh, brackish and sea water. Use an electrode that matches the expected conductivity range of the waterway.

Sampling considerations for EC are reasonably limited. As the ions can move quite freely in solution, issues associated with poor mixing are less apparent than with other parameters. Accordingly, the standard sampling considerations outlined in the overview of this chapter are generally sufficient to ensure a representative sample. Water temperature should be recorded even when using a temperature-compensated probe.

Water temperature

Ions in solution become more active as water temperature rises. Increased ion activity increases the capacity of a water sample to conduct an electrical current. Therefore, as water temperature increases, EC increases. The influence of water temperature needs to be considered, and compensated for, when measuring EC.

Most EC meters have built-in temperature compensation, which converts any reading to a standardised water temperature (25 °C). When reporting the data, temperature compensation needs to be expressed. For instance, the units in this case would be µS/cm at 25 °C.

Be aware of whether the equipment you are using is temperature-compensated. If it is not temperature-compensated, comparing readings taken at different places and times is more difficult. A generalised conversion factor of a 2% increase in conductivity per degree Celsius can be used to convert non-compensated readings for the purpose of comparison. This should only be used as a rough rule of thumb, because the extent of temperature-related variation would depend on the types of ions present in each water sample.

Calibrations and maintenance

Most electrodes require routine calibration using solutions of a known conductivity (standard solutions). Electrodes may be classified as single-point or multi-point. Multi-point probes can be calibrated against two or more standard solutions, adjusting the relationship (slope) between concentrations if required, whereas single-point calibrations do not allow for variation of the slope and should be calibrated against a standard solution that is closely matched to the expected EC of the sample. For these reasons, multi-point probes are preferable.

EC probes are generally robust, with maintenance limited to cleaning the electrodes using methylated spirits (or similar) to remove foreign particles and algal growth. Always follow manufacturer's instructions when calibrating or cleaning equipment.

Interpreting your results

Water bodies tend to have a predictable pattern of EC values, which, once known, can be used as a baseline to compare readings against. EC tends to increase gradually during dry spells due to evapo-concentration and a greater influence associated with (saltier) groundwater. Rainfall generally dilutes salt, except for localised saline run-off, and will result in decreased EC within the waterway. A sudden change in EC not associated with climatic factors may indicate human impacts such as regulation of flow or discharge of waters into the waterway.

The salinity of Australian streams varies widely across the country, with many local exceptions to general patterns. Accordingly, establishing guidelines can be difficult. In general, adverse biological effects may be anticipated in waters with an EC above 1500 µS/cm at 25 °C (ANZECC 1992).

How you should interpret your EC data depends on your monitoring objectives. If you are conducting routine monitoring for waterway health or assessing the suitability for a water use, you will need to compare your data with the relevant guideline values. Refer to Chapter 8 of this manual for further advice on interpreting your results for a range of monitoring objectives and how to compare your data to guideline values.

Guidelines have been established for protection of aquatic ecosystems in freshwater streams in Queensland based on statistical analysis of state agency data (Table 5–7). The correct guideline value to compare your results with will depend on where in Queensland you are sampling. Refer to Appendix G of the *Queensland water quality guidelines* (Environmental Protection Agency 2006) for definitions of each region. These values were established by taking the 75th percentile of the data for each catchment. Catchments with comparable EC were combined. See Chapter 8 for information on calculating percentiles.

Table 5–7 Guideline electrical conductivity values for fresh waters in Queensland (adapted from Environmental Protection Agency 2006; Cassidy 2003)

Protection of aquatic ecosystems			
Catchments	**Guideline EC (75th percentile)**	**Catchments**	**Guideline EC (75th percentile)**
Cape York	125 µS/cm	Callide, Upper Burnett	760 µS/cm
Wet Tropics	92 µS/cm	Southern Coastal	520 µS/cm
Burdekin–Bowen	271 µS/cm	Sandy Coastal	626 µS/cm
Belyando–Suttor	168 µS/cm	Southern Divide	1 120 µS/cm
Don	680 µS/cm	Condamine, MacIntyre	500 µS/cm
Central Coast North	375 µS/cm	Maranoa–Balonne–Border Rivers	325 µS/cm
Central Coast South	970 µS/cm	Western Murray–Darling Basin	169 µS/cm
Fitzroy North	720 µS/cm	Lake Eyre	200 µS/cm
Fitzroy Central	340 µS/cm	Gulf of Carpentaria	500 µS/cm
Other uses			
Water use	**Sub-use**	**Guideline EC range**	**Comments**
Drinking water		< 800 (desired)	If > 50% change in levels, action should be taken
Agriculture	Tropical aquaculture	0–5 ppt	Optimal levels vary for individual fish species
Irrigation	All crops	0–650 µS/cm	
	Excluding very low tolerance crops	650–1300 µS/cm	
	Medium and high tolerance crops only	1300–3000 µS/cm	
	High tolerance crops only	3000–5000 µS/cm	
	Extremely tolerant crops	5000–8000 µS/cm	
	Too saline for irrigation	> 8000 µS/cm	

Table 5–8 Indicative electrical conductivity for Australian water bodies (Suttar 1990)

Water body type	Conductivity (µS/cm at 25 °C)
Pure rainwater	< 15
Freshwater rivers	0–800
Marginal river water	800–1600
Brackish water	1600–4800
Saline water	> 4800
Sea water	51 000

More specialised subregional guidelines for protection of aquatic ecosystems in Fraser Island and North Stradbroke Island water bodies are also available in the Queensland water quality guidelines (Environmental Protection Agency 2006).

If Queensland guidelines are unavailable, use the *Australian and New Zealand guidelines for fresh and marine water quality* (ANZECC & ARMCANZ 2000b). If no appropriate guidelines are available, it is worth comparing your results to the average conductivity ranges for the water body type you are assessing (Table 5–8). Results within the listed ranges would be considered acceptable in the absence of established guidelines.

If data is collected on a regular basis, you can develop your own guideline values, specific to your monitoring objectives. For information and advice on developing your own guidelines and comparing your data to guideline values, see Chapter 8.

Guidelines also exist for other monitoring objectives such as the assessment of water quality for agricultural uses or drinking water (Table 5–7). See the guideline references list at the back of this chapter for available guidelines to suit your monitoring objectives.

Health and safety

Refer to the *Health and safety guidelines for community-based waterway monitoring* (Department of Natural Resources and Water 2006) for further information.

Table 5–9 Methods guide for electrical conductivity

	Conductivity meter			Lab analysis		
Data quality	**Knowledge and skills**	**Time (mins)**	**Cost ($)**	**Knowledge and skills**	**Time (working days)**	**Cost ($)**
Analytical	Some experience	20–40	850–1200	Some sampling experience	5–20	7–10
Indicative	Some experience	20–40	90–170			
Demonstrative	Beginner	10–25	75–100			

Conductivity meter

Summary

A conductivity meter measures the capacity of water to conduct an electric current across a known distance (µS/cm at 25 °C, µS/cm, mS/cm).

The capacity of water to conduct current depends on the amount of ions (salts) in solution. The more ions (salts), the greater the charge that can be conducted.

Equipment

You will need:
- a conductivity meter
- the manufacturer's instruction manual
- water sampling equipment for instruments that require a captured water sample for deployment.

To produce **indicative** data:
- the suggested test resolution is 1 µS/cm
- the suggested test accuracy ±5%.

To produce **analytical** data:
- the suggested test resolution is 1 µS/cm
- the suggested test accuracy is ±2%.

Monitoring method

Deploy in situ meters as per the manufacturer's instructions. For meters that require a captured water sample, follow the sampling procedure on page 5–9 and take readings as per the manufacturer's instructions.

Quality control procedures

- Ensure adequate movement of water past electrodes using a gentle swirling motion.
- Conduct the test immediately in the field to increase the level of accuracy.

Participant competency

For **demonstrative** data, no prior experience in the use of the equipment is required. For **indicative** and **analytical** data, some prior experience and training in the use of the equipment is required. For **analytical** data, annual inter-operator comparisons are recommended.

Calibration

For **indicative** data:
- calibrate prior to each monitoring session
- refer the manufacturer's instructions for calibration details.

For **analytical** data:
- perform multi-point calibration at 25 °C on a weekly basis, or prior to each monitoring session
- refer to the manufacturer's instructions for calibration details.

Maintenance

Conductivity changes by 2% for every degree Celsius change in temperature. Most meters have a temperature compensation facility which should give a reading equivalent to 25 °C.
- Assess the accuracy of the temperature compensation every six months by testing the calibration solution at different temperatures.
- Wash the electrodes after testing with deionised water to keep free from contaminants.
- Periodically soak electrodes for 10–15 minutes in alcohol, and then rinse with deionised water.

Quality control checks

For **indicative** data:
- test a field replicate test every ten samples. Results should fall within the designated TER (for example, ±30%)
- test a blind sample every six months.

For **analytical** data
- conduct a field replicate test every ten samples. Results should fall within the designated TER (for example, ±10%)
- test a blind sample every three months
- have a duplicate sample tested by a professional water quality officer or laboratory in the initial stages of the project. The difference between the values of the duplicate samples need to be within the TER
- at the end of a sampling run, ensure that the meter has maintained its calibration. If the meter has lost its calibration, the data needs to be discarded.

Laboratory analysis

Summary

In this method, EC is measured by:

- collecting a water sample and transporting it to a NATA-accredited laboratory
- analysing the sample to determine the EC (µS/cm at 25 °C, µS/cm, mS/cm).

Equipment

You will need:

- field sampling equipment (refer to page 5–9)
- an esky with ice or refrigerator to keep samples cool.

The laboratory must be NATA-accredited for EC analysis.

Monitoring method

1. Follow the sampling procedure on page 5–9.
2. Store the sample in an esky or refrigerator.
3. Deliver the sample to laboratory for analysis within a month of the sample being captured.

Quality control procedures

In the field:

- field data sheets must provide details of the date and time of collection, environmental and climatic conditions, nature of pre-treatment, preservation technique, location of site, sample type being collected, person undertaking the sampling and any other conditions that may influence the sample
- sample containers should be labelled clearly and adequately. Include the date of sample, name of sampler, location and site details, preservation technique and type of parameter to be analysed.

In the laboratory:

- quality control procedures must be performed on at least 40% of all samples submitted. These measures include duplicates, calibration standards, reference materials, replicates, spikes and blanks
- a split sample should be sent to a separate laboratory annually (or at the beginning and completion of each project) to measure analysis accuracy
- a field blank must be taken and analysed annually (or at the beginning and completion of each project)
- results must state the procedure used, the units of measurement, and any other relevant information about the results.

Participant competency

Specific training in nutrient collection, storage and preservation protocols is recommended for all field monitors.

Calibration

The laboratory is responsible for calibration of analysis equipment to appropriate standards.

Maintenance

All field sampling equipment and safety gear should be kept in good condition and maintained as required. Detergent must not be used to clean these items. The laboratory is responsible for maintaining analysis equipment.

Quality control checks

Appropriate acceptance criteria need to be established and should be supported by the use of a quality control chart.

Water flow—velocity and discharge

Importance of water flow

Stream velocity and discharge are among the most important of physical conditions. The amount of water and the rate at which it moves affects both ambient water quality and its downstream impacts.

Velocity is the rate at which water moves, measured as the distance that water travels over a given period of time. Velocity is generally expressed in terms of metres per second (m/s).

Discharge is the amount or volume of water moving past a given point for a given period of time. Discharge may be measured using a variety of units (for example, cubic metres per second) depending on the scale of the stream, the time period of interest, and the monitoring project type.

The flow rate and discharge volumes of a stream can affect water quality and stream condition through a range of processes including dilution, concentration, scouring, mixing and settling.

During periods of rainfall, a large proportion of stream flow comes directly from the landscape of the catchment. This water has high energy, causing erosion of soils and streams, increasing turbidity and nutrient concentrations, reducing clarity and altering pH. The rapidly moving water mixes well, creating uniform, high concentrations of dissolved oxygen and altering water temperature.

Factors affecting flow

Stream discharge is a measure of the amount of water moving out of a catchment via the stream channel. It is greatly influenced by the weather, increasing during periods of rainfall and decreasing during dry periods. Flow is also influenced by evaporation rates and groundwater interception. Flow patterns are highly variable, but tend to demonstrate seasonal and longer-term patterns based on climate variability.

Human activities have the potential to dramatically alter stream flows. In particular, building dams and other structures has the potential to alter flow volumes, rates and timing. In an effort to reduce these impacts, many dams now release environmental water to help sustain vital ecosystem functions downstream; however, the impact of dams on flow remains significant. Other human activities that influence flow are water extraction—for a variety of purposes including direct consumption (drinking water), domestic supply, agriculture and industry—and physical alteration of catchments and streams such as the clearing of vegetation, flood plain works, and the modification of the stream channel itself.

Monitoring considerations

Accurately measuring discharge is a difficult and time-consuming process; however, because of the significant influence that flow has on water quality, it is an important consideration for many monitoring programs. Due to the difficulty of measuring flow, it is recommended that you obtain discharge data from your local water authority or from the relevant state government authority (in Queensland, this is the Department of Environment and Resource Management). These organisations monitor flow on a routine basis and have networks of flow-gauging stations along most major streams.

Measuring stream velocity is a more simple exercise and may be used for rough comparisons of stream flow conditions.

Monitoring methods

Two methods for monitoring flow are:

- the float method—a float is timed as it passes through a known distance to establish the velocity at which it is moving
- the head rod method—the *head* (gravitational potential of water flowing in the stream) is calculated and then converted back to a measure of velocity.

Another useful measure when assessing the influence of flow is the cross-sectional area of the stream, which needs to be known in order to calculate discharge.

Equipment required for the above methods—such as tape measures and measuring rods—is easy to use and is readily available to most community groups. More complex equipment—such as current meters that use fans and acoustic Doppler techniques—is available, but is generally beyond the requirements and capabilities of most community monitoring activities. If such equipment is being considered, please consult the manufacturer, a research organisation or the relevant government agencies for support and assistance.

Float method

Choose a 10 m section of stream that is relatively straight, uniform and free from snags, vegetation and other obstacles. Avoid structures such as culverts or bridges if the water is speeding up or slowing down as it passes these structures, as this will exaggerate the average velocity for the reach. If the flow is very low, or if a satisfactory 10 m reach is not available, use a shorter length reach, (for example, 5 m).

Divide the distance travelled (in metres) by the time taken (in seconds) to calculate the water velocity in metres per second (m/s). Then multiply this by a correction factor of 0.9 to compensate for the variability in water velocity associated with depth and across the channel; water flows more quickly in the centre of the channel, and more quickly at the surface than near the bottom.

Example

Distance travelled	= 10 m
Average time taken	= 18 s
Correction factor	= 0.9
Calculated stream velocity	= (10 ÷ 18) × 0.9
	= 0.555 × 0.9
	= 0.5 m/s

Head rod method

The head rod is a quick and potentially more accurate measure than the float method for shallow streams with a velocity not less than about 0.3 m/s.

Head rods are difficult to use in deeper streams or when velocities exceed about 2.5 m/s.

A head rod is a one-metre stainless steel ruler, approximately 40 mm wide, marked in 1 mm (or similar) intervals. The base should comprise a flat disc to prevent it from sinking into the stream bed during measurements (refer to Figure 5–7). The method involves wading across the stream and taking five to ten measurements at approximately equal intervals.

This method involves recording the height of the water column with the thin edge of the rod facing upstream and then rotating the rod 90° so that the rod is then perpendicular to the direction of flow. As the water flows into the head rod, resistance creates a standing wave. Record the new height of the water column from the top of the head rod. The difference between the two measures is the head. The procedure is repeated at five to ten more points and the average head is calculated. Using the following formula, the average stream velocity, in metres per second, can be determined:

Average stream velocity = $\sqrt{(2gh)}$

Where: g is the gravitational constant of 9.81 and

h is the average stream head for the cross section

Example

Average stream head	= 0.1 m
Average stream velocity	= $\sqrt{(2 \times 9.81 \times 0.1)}$
	= $\sqrt{(1.962)}$ = 1.40 m/s

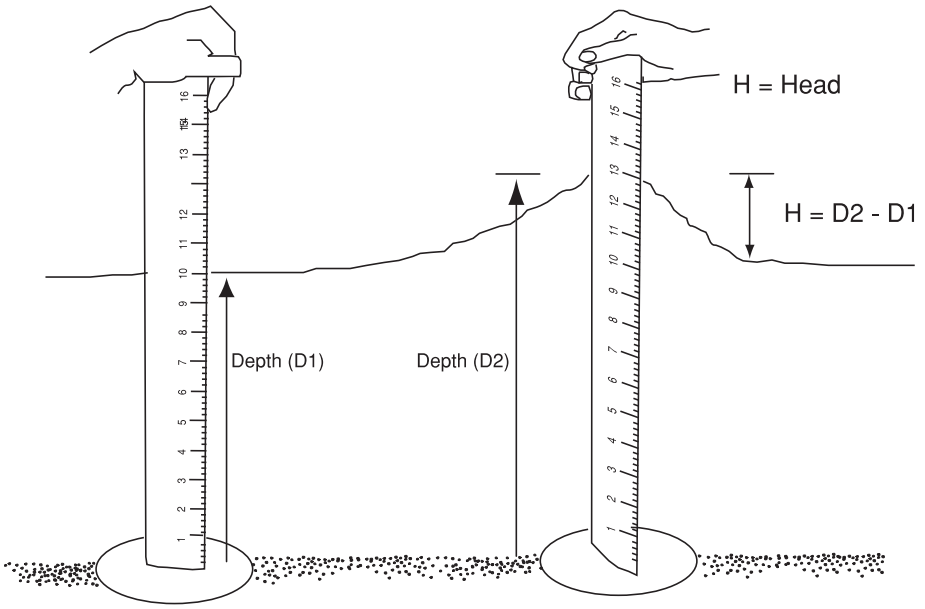


Figure 5–7 Using the head rod method (Waterwatch Australia Steering Committee 2002)

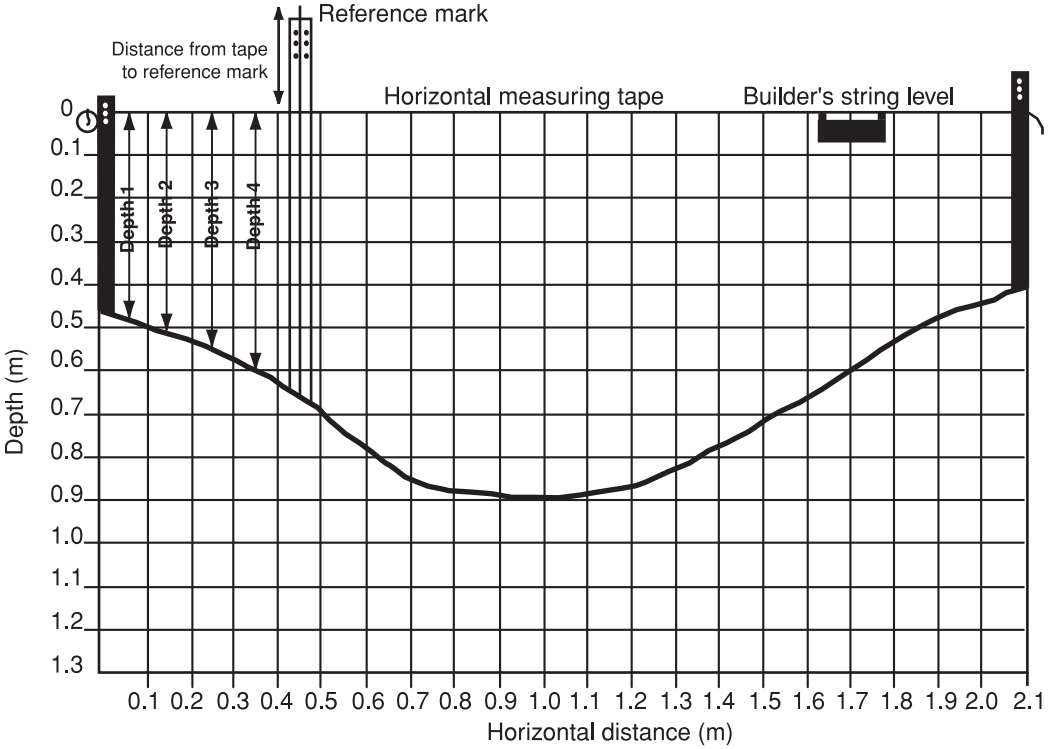


Figure 5–8 Example of a plot illustrating stream bed depth

Stream cross-section

Calculating the cross-sectional area of a stream provides a range of useful information including wetted perimeter, depth, areas of stream energy, and connectivity to the flood plain. The cross-sectional area needs to be known to calculate discharge and loads; however, care is required to avoid compounding errors when calculating discharges and loads.

Using a permanent benchmark will enable the stream to be resurveyed, allowing changes in stream cross-section (due to erosion or deposition) to be measured. Choose and clearly mark a permanent, easily located structure—such as a large rock, tree, star-picket or peg—about 1 m above the water level. Clearly mark the structure with permanent paint or a tag and keep location details with other site information.

To calculate the cross-sectional area of a stream, refer to the monitoring method on page 5–41.

Calculating your results

Once you have taken these measurements, use the following steps to calculate the cross-sectional area of the stream:

1. On graph paper, plot the depth from the horizontal tape to the stream bed (Figure 5–8).
2. Count the number of squares between the line indicating the stream bed and the top of the graph. This is the cross-sectional area in square metres (m^2). See Figure 5–9 for an example.
3. Prepare a second graph of vertical distance (m) from the reference mark to the water surface and cross-sectional area (m^2) (see Table 5–10 and Figure 5–10).

Table 5–10 Measurements of vertical distance from the reference mark to the water surface and cross-sectional areas (Cassidy 2003)

Depth (m) from the mark	Area (m^2)
1.3	0
1.2	0.055
1.1	0.145
1.0	0.265
0.9	0.425
0.8	0.615

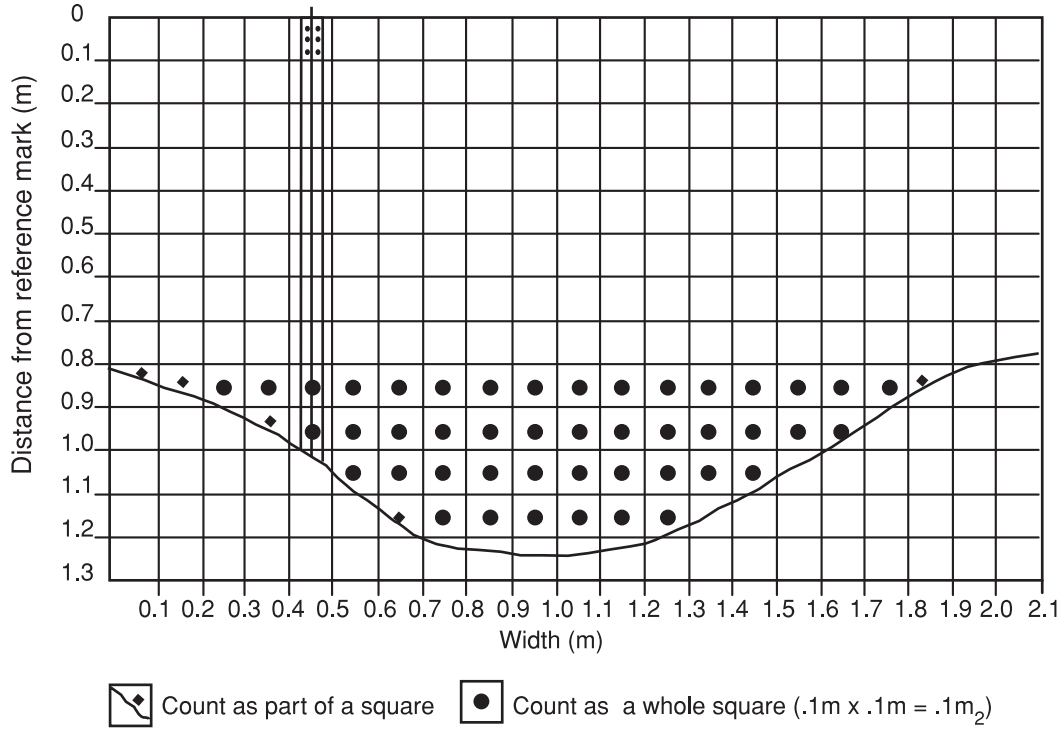


Figure 5–9 Calculating the area in the cross-section (Cassidy 2003)

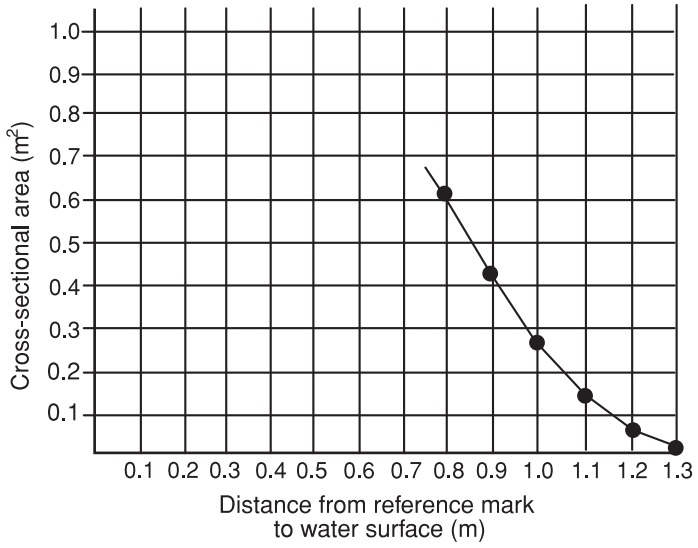


Figure 5–10 Vertical distance (m) from the reference mark to the water surface and cross-sectional area (m²) (Waterwatch South Australia 1996; image from Cassidy 2003)

Interpreting your results

How you interpret your results will depend on your reasons for monitoring. If you are conducting routine monitoring to assess waterway condition, or you are determining the suitability of the water for specific uses, you should compare your results to the relevant guideline values. See Chapter 8 of this manual for more information and advice on interpreting results for a range of monitoring objectives.

Discharge

To estimate the discharge at your site, multiply the stream velocity by the stream cross-sectional area of water at the site.

Formula:	Discharge (m^3/s) = velocity (m/s) × cross-sectional area (m^2)
Remember:	1000 litres (L) = 1 cubic metre (m^3)
	1 000 000 litres = 1 megalitre (ML)

Stream discharge is commonly referred to in terms of megalitres per day (ML/day); however, it is important to remember that any recording of discharge is only an instantaneous estimate of the current discharge, so multiplying the values up to daily (or greater) time increments will introduce further inaccuracies. Minimum flow levels have been established for some regulated rivers in Queensland under water resource plans and resource operations plans, and can be assessed in compliance monitoring programs. These plans are available on the Department of Environment and Resource Management website <www.derm.qld.gov.au>.

Pollutant loads

Loads of phosphate, nitrate, salt and soil transported by the stream from the catchment can be estimated. By measuring, for example, the amount of phosphate in the water, the amount of phosphate lost each hour can be calculated. Then, by estimating the catchment area using a contour map, the amount of phosphate lost from each hectare during rain events can be calculated. The following example calculates the phosphate loss rate for a subcatchment of 63 ha, with load of 0.06 mg/L phosphate measured and a stream discharge of 260 m^3/s.

Formula

Discharge (m^3/s) = cross-sectional area (m^2) x velocity (m/s)

Formula

To convert litres per second to megalitres per day, multiply by 0.0864

$$1 \text{ L/s} = \frac{60 \text{ s} \times 60 \text{ min} \times 24 \text{ hr}}{1{,}000{,}000}$$

$$= 0.0864 \text{ ML/day}$$

Example

Cross-sectional area = $0.16 m^2$

Velocity = 0.3m/s

Discharge = $0.6 m^2$ x 0.3 m/s
= $0.18 m^3/s$
= 180 L/s

Discharge (megalitres/day) = 180 L/s x 0.0864
= 15.6 ML/day

The *Queensland water quality guidelines* (Environmental Protection Agency 2006) and the *Australian and New Zealand guidelines for fresh and marine water quality* (ANZECC & ARMCANZ 2000b) do not provide guideline values suitable for interpreting loads results. Future versions of the Queensland guidelines will consider this issue further. It is possible to develop your own event-based guidelines; however, there are important issues you should consider. See section 4 of the Queensland guidelines for further information on load-based guidelines.

Chapter 8 also includes information on developing your own guidelines and comparing your results to guideline values.

Health and safety

Measuring flow is potentially dangerous, as it involves working outdoors and around water. Exercise extreme caution if you need to enter the water. Only those participants that are competent swimmers should ever enter the water. Always be careful when retrieving the float.

Refer to the *Health and safety guidelines for community-based waterway monitoring* (Department of Natural Resources and Water 2006) for further information.

Formula

$$\text{Loss rate (mg/ha/hr)} = \frac{\text{concentration (mg/L) x discharge (L/hr)}}{\text{catchment area (ha)}}$$

Example

Steps

1. Measured phosphate concentration mg/L is: 0.06 mg/L phosphates as P
2. Measured stream discharge is: 260 m^3/s
3. Convert dishcarge in m^3/second to litres/hour. Multiply by 3 600 000 to get litres/hour (60 x 60 x 1000): 260 x 3 600 000 = 936 000 000 L/hr
4. Estimate the surface area of your catchment in hectares: 63 ha
5. Loss rate is:

$$\frac{0.06 \times 936\,000\,000}{63}$$

= 891 428.57 mg/hr/ha

= 0.89142857 kg/hr/ha

= 0.89 kg/hr/ha

(Cassidy 2003)

Float method

Summary

This method measures stream velocity in metres per second (m/s) by determining the average time required for a float to travel a known distance.

Equipment

You will need:
- a float (any buoyant object that is visible at the water surface)
- a 10 m tape measure
- a stopwatch
- a hand net to retrieve the float.

Monitoring method

1. Measure and mark out a 10 m reach using a tape measure and surveyor's tape (or similar). Use a straight stretch with a uniform flow pattern.
2. Place the float into the water a few metres upstream of the reach. This will allow time for the float to reach the same velocity as the water around it.
3. Start timing when the float enters the beginning of the marked reach.
4. Stop timing when the float reaches the end of the reach.
5. If the float gets caught along the way, start again.
6. Use a hand net to capture the float at the end of the reach.
7. Repeat the procedure at least five times to derive an average time recording.

Quality control procedures

Always:
- ensure that the time and distance are measured accurately
- ensure that the float is clean and in good condition
- start again if the float becomes caught in backwater or in vegetation.

To produce **demonstrative** data:
- use a suitable float
- repeat the process at least five times to derive an average.

To produce **indicative** data:
- use the same float for all measurements
- use a spotter at both the start and end of the timed distance
- repeat the process at least eight times to derive an average.

Participant competency

The minimum competency required is familiarity with use of equipment, sampling methods and documentation.

Calibration

Calibration does not apply to this method.

Maintenance

Check condition of float and tape measure.

Quality control checks

Quality control checks do not apply to this method.

Table 5–11 Methods guide for water flow

Data quality	Float method			Head rod			Stream cross-section		
	Knowledge and skills	Time (mins)	Cost ($)	Knowledge and skills	Time (mins)	Cost ($)	Knowledge and skills	Time (mins)	Cost ($)
Analytical									
Indicative	Beginner	20–30	25–40	Some experience	5–10	20–50	Some experience	15–30	20–40
Demonstrative	Beginner	< 3	25–40						

Head rod method

Summary

This method calculates the 'head' (gravitational potential of water flowing in the stream) and converts this to a measure of velocity in metres per second (m/s).

The head rod method is suitable for shallow streams with a velocity not less than about 0.3 m/s. It is difficult to use in deeper streams or when velocities exceed about 2.5 m/s.

Equipment

You will need a head rod.

Monitoring method

1. Place the rod into the waterway a small distance from the water edge, where there is a discernable flow. Record the height of the water column with the thin edge of the rod facing upstream (that is, parallel to the direction of flow).
2. Rotate the rod 90° so that the rod is now perpendicular to the direction of flow. This should create a standing wave. Record the new height of the water column from the top of the head rod. The difference between the two measurements (in metres; 1 mm = 0.001 m) is the head.
3. Repeat the procedure at five to ten more points across the stream.
4. Calculate the average head (h) for the cross-section by adding the measurement values and then dividing the total by the number of readings.
5. Calculate the average stream velocity (m/s) using the following formula:

   Average stream velocity = $\sqrt{(2gh)}$

   Where: g is the gravitational constant of 9.81 and h is the average stream head (m) for the cross section

Quality control procedures

Repeat all readings 5 to 10 times to increase data confidence.

Participant competency

Some experience and training is required in the use of equipment and calculation.

Calibration

No calibration is required.

Maintenance

Ensure that the rod is kept clean and in good condition.

Quality control checks

Compare velocity measurements from the head rod with readings from a gauging station. Results should be within 30% of the gauging station measurements.

Stream cross-section

Summary

This method determines the cross-sectional area of a stream in square metres (m^2) using a hand-held lineal (not surveyed) measure.

Equipment

You will need:

- a 50 m or 100 m plastic measuring tape
- a hammer and pegs
- a surveyor's staff or similar—that is, a pole with accurate length measurements
- a spirit level.

Monitoring method

1. Hammer a peg into each bank above the maximum height you wish to measure.
2. Stretch your measuring tape across the stream from one peg to the other. It is important that the tape is both taut and level. Use your spirit level to ensure that the tape is horizontal.
3. Record the height of the tape relative to the benchmark. Ideally, you would measure from the benchmark itself. If this cannot be done, position your pegs so that the tape is in line with the benchmark.
4. Starting at the peg on the left bank (looking downstream), measure the vertical distance (height) from the tape to the stream bed. Record this distance, as well as the horizontal distance from the left bank peg at which the measurement was taken. Also record the vertical distance between the tape and the surface of the water.
5. Repeat this process at 15 to 20 equally spaced points across the stream.
6. On graph paper, or similar, plot each vertical distance against the horizontal distance at which the measurement was taken.
7. Join each dot to indicate the profile of the cross-section.
8. From this profile, you can estimate the cross-sectional area of the stream channel for the recorded water level. To do this, calculate the area under the curve.

Quality control procedures

Ensure that the tape measure has not stretched.

Participant competency

Some experience and training is required in the use of equipment and calculation.

Calibration

No calibration is required for this method.

Maintenance

Ensure that the equipment is kept clean and in good condition.

Quality control checks

No quality control checks are required for this method.

pH

Importance of pH

pH is an abbreviation of 'pondus hydrogenii' and is the measure of the proportion of hydronium ions (H_3O^+) to hydroxide ions (OH^-) in a substance or, more simply, a measure of the relative acidity or alkalinity of a substance. pH values range from 0.1 (highly acidic) to 14 (highly alkaline). Generally, pH values will range between 4 and 10 in rivers and streams. When a substance has no net alkalinity or acidity, it is said to be neutral and has a pH of 7 (Figure 5–11).

pH is measured on a logarithmic scale, so that each pH unit represents a tenfold change from the previous unit. For example, a water body with a pH of 5.0 is ten times more acidic than one with a pH of 6.0, and a water body of pH 4.0 is 100 times more acidic than one with a pH of 6.0.

All aquatic animals and plants are adapted to a certain pH range, and most freshwater biota fall into the range 6.5 to 8.0. Changes in pH outside the normal range of a water body may have direct impacts on stream biota such as physical stress and increased susceptibility to disease or death, or indirect effects. Many compounds are more soluble in acidic waters than in alkaline waters. The pH of the wet area around roots affects nutrient uptake by plants. pH affects the solubility of heavy metals and ions in water, and hence total dissolved solids.

At a broad scale, stream pH may be used as an indicator of gross pollution problems. Waterways with unusually high or low pH values can be flagged for future investigations into any potential issues that affect pH. At a finer scale, pH can be used to monitor the trend of waterway health and the effect that interactions such as seasonality, algal blooms, bottom sediments and flow events have on pH.

Factors affecting pH

Respiration and photosynthesis

Respiration and photosynthesis of aquatic plants and algae can cause large changes in pH. Carbon dioxide (CO_2) is produced during respiration by animals 24 hours a day, and is consumed by plants during photosynthesis in the daylight hours. This carbon dioxide dissolves in water to form carbonic acid (H_2CO_3). Carbonic acid is a weak acid. Some of its molecules ionise to make free hydrogen ions (H^+), which further reduces the pH.

Adding more carbon dioxide to water—for example, by respiration—will increase the number of hydrogen ions and lower the pH. On the other hand, removing carbon dioxide—for example, by photosynthesis—will increase the pH. Accordingly, increased alkalinity in a water body may be indicative of an algal bloom.

A cyclic pattern of addition and removal of carbon dioxide takes place over a 24-hour period due to photosynthesis occurring only during the daylight hours. The highest pH values usually occur during mid-afternoon (Figure 5–12).

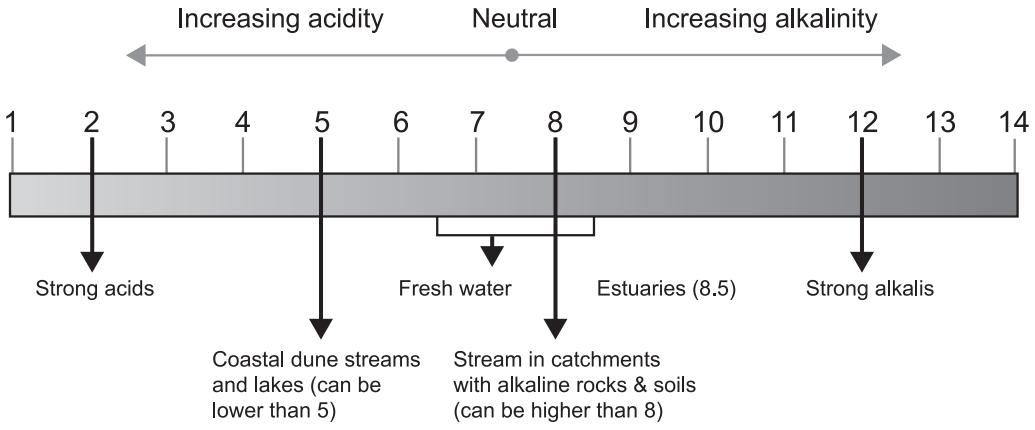


Figure 5–11 pH scale (Waterwatch Queensland 2003)

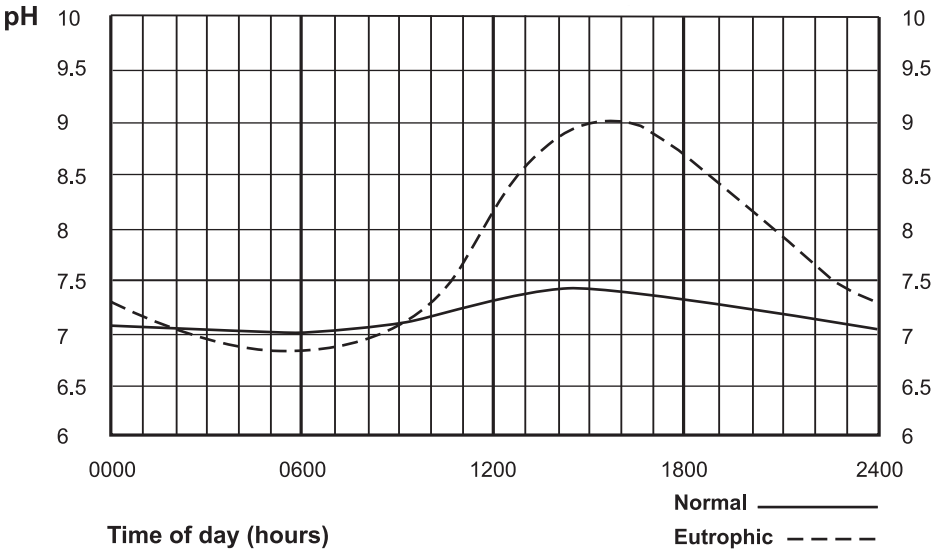


Figure 5–12 Daily variation of pH for normal and eutrophic waters (Cassidy 2003)

Buffering capacity

Buffering capacity is the ability of a water body to cope with the addition of acid (H^+) or base (OH^-) without changing its overall pH.

Water containing low concentrations of ions such as calcium, magnesium, sodium, chloride, sulfate and carbonate tend to be poorly buffered. The more of these ions present in the waterway, the better the water body is able to accept acidic or basic inputs with little change to the overall pH. This is because the various ions bind with the added H^+ or OH^- to neutralise their effects.

Poorly buffered waters (in general, low-salinity waters) are more likely to have larger fluctuations in measured pH than more strongly buffered waters. In general, small streams in pristine areas tend to be poorly buffered, while larger lowland rivers are normally well-buffered. Large variations in pH readings may not necessarily indicate problems with the testing procedure, but rather may reflect the normal variation at that site.

Catchment variations

Wide variations in pH can occur because of the differing buffering capacity of differing catchment geology and soil types.

Terrestrial vegetation types also influences the pH. Tannin-rich plants such as eucalypts and ti-trees break down in water to form humic acids, which decrease pH. Billabongs and coastal dune lakes may have low (acidic) pH values, sometimes less than 5.0, due to the presence of humic acids.

Increasing salinity causes an increase in pH due to the higher capacity of the water to buffer acids. In a typical estuary, pH would rise in line with increasing salinity levels from values from 6.5 to 7.5 in the upstream freshwater reaches, to between 8 and 8.5 in downstream, fully saline coastal areas.

Human influences

Human activities can influence stream pH in a number of ways. These may include direct effects of land management activities and direct discharge pollution, or indirect effects such as algal blooms caused by nutrient enrichment.

One of the more common causes of unnatural changes to pH occurs in catchments where acid sulfate soils have been disturbed and exposed to the atmosphere. Such disturbance may be the result of mining, agricultural practice or urban development. Exposure of these soils to atmospheric oxygen causes acids to be formed. During rain events, these acids are washed into streams where they cause short-lived, but sometimes quite large, falls in pH. pH levels as low as 2.5 have been recorded as a result of acid sulfate soils. Fish and other aquatic animals suffer from skin irritations, tumours, ulcers and impaired gill functioning in such acidic water. Detection of these low pH events requires sampling during or soon after rain events, because the acid water is soon flushed away and pH returns to normal values through natural stream processes.

Some industrial wastes have pH values outside the normal range and thus have the potential to affect pH in receiving waters. However, in Australia, discharge of highly acidic or alkaline waste water is rarely, if ever, permitted. Such wastes are required to have pre-treatment to correct the pH balance before discharge is allowed.

Changes in pH can be caused by atmospheric deposition (acid rain or dry particle deposition) and fossil fuels burned by cars, factories and smelters.

Monitoring considerations

Measurements of pH can provide information about the natural condition of a water body as well as how it is affected by pollution from human activities.

Because photosynthetic plants and algae can cause significant natural changes in pH, you should always sample at the same time of day.

Monitor upstream and downstream of suspected pollution sources. You should monitor pH from a suspected point source of contamination at your test sites and two independent reference sites.

Note the geology and soils of the catchment in which you are monitoring pH, to help you interpret pH changes from one site to another. If you wish to apply these methods to estuary monitoring, note the state of the tide and also record conductivity readings before attempting to interpret pH.

Take particular care to avoid disturbing sediments or scums during sampling.

Monitoring methods

pH may be measured using a variety of methods, including:

- a pH meter
- colorimetry
- pH test strips
- titration.

pH may be measured in the laboratory; however, samples need to be refrigerated immediately after capture and analysed as soon as possible, preferably within six hours, to ensure representativeness of in-stream conditions.

pH meter

Generally speaking, electronic pH meters prove to be the most appropriate approach. They are able to give instantaneous, in situ results for a reasonable cost. When purchasing a pH meter, consider whether the meter has:

- automatic temperature compensation. pH meters use a formula to convert potential (voltage) into a pH value. A component of this formula is temperature, which is set at a default of 25 °C. When waters tested for pH are approximately 25 °C, there will be no error in the pH reading; however, when the water temperature is significantly higher or lower than 25 °C, pH readings will be inaccurate. Some pH meters test temperature and incorporate real temperature data into the formula before displaying pH readings. This capability is known as automatic temperature compensation. Meters with this capability are less likely to produce a temperature-orientated error and are preferable for quantitative data collection
- a separate or combination electrode. Separate pH and reference electrodes are used for the highest precision and research measurements. Combination pH electrodes are much more practical to use and therefore most pH electrodes on the market are the combination type
- a single- or double-junction electrode. Single- or double-junction electrodes are suitable for monitoring normal environmental waters. A double junction prevents heavy metals, sulfides, proteins and other materials from precipitating at the electrode junction; however, double junctions increase the response time of the equipment. Refer to the manufacturer's specific instructions
- a refillable or sealed electrode. Refillable or sealed electrodes are suitable for monitoring normal environmental waters. Refillable electrodes have stoppers that allow the reference chamber to be refilled with reference solution, making them economical and long-lasting. Sealed electrodes are heavy-duty in comparison and require virtually no maintenance or refilling; however, they must be replaced when the fill solution is low.

Colorimetry

Colorimetry is best performed on-site. However, this approach is time-consuming and may not be suitable due to compromises associated with working in the field. Colorimetry can be performed using a comparator, photometer or spectrophotometer.

pH test strips

pH test strips provide a cheaper alternative to pH meters and colorimetry, but lack accuracy and are only suitable for indicative measurements.

Titration

Titrations are best performed on-site. However, they are time consuming and may not be suitable due to compromises associated with working in the field.

Interpreting your results

When interpreting pH data, be aware of the potential effect on pH of diurnal variations in pH associated with the photosynthesis of aquatic plants. Unnaturally high (alkaline) waters during the afternoon indicate eutrophic conditions, which can result in an algal bloom. It is important to be aware of baseline conditions for each site. How to interpret your results will depend on your monitoring objectives. See Chapter 8 for information and advice on how to interpret your data for a range of monitoring objectives.

For baseline monitoring, interpreting pH values requires some knowledge of the natural ranges likely to be found in the catchment. A pH of 6.5 might be normal in some streams, but, if found in a limestone catchment, would indicate a possible problem (as limestone makes waters more basic).

If you are conducting routine monitoring of waterway health or assessing the water's suitability for specific uses, you should compare your results to the relevant water quality guidelines. Guideline values for pH have been developed for the protection of Queensland aquatic ecosystems for different water body types in three regions (Table 5–12). Which values you should compare your data to will depend on where, and in what sort of water body, you are monitoring. The *Queensland water quality guidelines* (Environmental Protection Agency 2006) define the region and water body types used. The Queensland guidelines also outline more specialised subregional guidelines for water bodies in the Douglas, Gold Coast hinterland, Fraser Island and North Stradbroke Island catchments.

If there are no Queensland guidelines that are suitable for your region (such as for Eastern Cape York, Gulf Rivers, Lake Eyre and Murray–Darling), use the *Australian and New Zealand guidelines for fresh and marine water quality* (ANZECC & ARMCANZ 2000b). These national guidelines suggest a default range between 6.5 and 8.0 for south-east Australia, and 6.0 and 8.0 for tropical areas. Changes of more than 0.5 pH units from

Table 5–12 Guideline pH values for fresh waters in Queensland (adapted from Environmental Protection Agency 2006)

Protection of aquatic ecosystems			
Water body type	**South East Queensland**	**Central Coast**	**Wet Tropics**
Lowland streams	6.5–8.0	6.5–8.0	6.0–8.0
Upland streams	6.5–8.2	6.5–7.5	6.0–7.5
Lakes and reservoirs	6.5–8.0	6.5–8.0	6.0–8.0
Wetlands	–	–	–
Other uses			
Water use	**Sub-use**	**Guideline pH range**	**Comments**
Agriculture	Tropical aquaculture	6.8–9.5	Optimal levels vary for individual fish species

the natural seasonal maximum or minimum in fresh water should be treated as a potential risk. See Chapter 8 for detailed information about comparing your results with guideline values.

With enough data, you can develop your own guidelines. Refer to Chapter 8 of this manual for information and advice on developing your own guidelines.

For guidelines aligned with monitoring objectives other than ecosystem health, see the guideline references list at the back of this chapter.

Health and safety

The titration method carries the following specific health and safety considerations:

- Titration tests use a number of potentially hazardous chemicals, so always wear safety glasses and rubber gloves and take care that the chemicals are not flicked into eyes or spilled onto skin or clothes. When testing, place the liquid waste bottle, paper towels and squirt-bottle of deionised water nearby.
- Titration chemicals can irritate eyes and cause burns to skin, and are poisonous if swallowed.

See the *Health and safety guidelines for community-based waterway monitoring* (Department of Natural Resources and Water 2006) for further information.

Table 5–13 Methods guide for pH

	pH meter			Colorimetry			pH test strips			Titration		
Data quality	**Knowledge and skills**	**Time (mins)**	**Cost ($)**	**Knowledge and skills**	**Time (mins)**	**Cost ($)**	**Knowledge and skills**	**Time (mins)**	**Cost ($)**	**Knowledge and skills**	**Time (mins)**	**Cost ($)**
Analytical	Some experience	< 10	120–260	Expert advice	20–40	1700–3000				Expert advice		90–160
Indicative	Some experience	< 5	120–260	Expert advice	15–35	1500–2000				Expert advice		90–160
Demonstrative	Beginner	< 3	90–120	Beginner	15–30	100–150	Beginner	< 5	20–35	Beginner		40–60

pH meter

Summary

This method measures pH by monitoring change in potential (voltage) caused by differing H^+ (hydrogen) concentrations using sensing and reference electrodes.

Equipment

You will need:
- a pH meter
- the manufacturer's instruction manual
- sampling equipment for meters that require a captured sample
- calibration solutions and containers.

To produce **indicative** data:
- the suggested instrument test range is pH 0.1 to 14
- the suggested test resolution is 0.2 pH units
- the suggested instrument test accuracy is ±0.5 pH units.

To produce **analytical** data:
- the suggested instrument test range covers the complete pH scale (0.1 to 14)
- the suggested test resolution is 0.1 pH units
- the suggested instrument test accuracy is ±0.1 pH units.

Monitoring methods

1. Deploy in situ meters as per manufacturer's instructions. For meters that require a captured sample, follow the steps on page 5–9 and take the reading as per the manufacturer's instructions.
2. Rinse the electrode well with deionised water.
3. Take temperature readings if your meter does not have automatic temperature compensation.
4. Periodically measure the pH of the calibration solution to test accuracy. If it has drifted, recalibrate. Do not reuse buffer solutions.

Quality control procedures

- Observe the maximum shelf life for standard solutions.
- Conduct the test immediately in the field to increase the level of accuracy.

Participant competency

To produce **indicative** and **analytical** data, some experience or training in the use of the equipment is required. For **analytical** data, inter-operator comparisons are recommended.

Calibration

For **indicative** data:
- conduct calibration prior to each monitoring session
- recalibrate if the error exceeds 0.5 pH units
- calibrate at pH 7.0 and either 4.0 or 10.0 depending on whether the waterway being tested is likely to be acidic or alkaline.

For **analytical** data:
- ensure that certified standards are not more than three months old
- conduct calibration fortnightly or prior to each monitoring session
- recalibrate if the error exceeds 0.2 pH units
- calibrate at pH 7.0 and either 4.0 or 10.0 depending on whether the waterway being tested is likely to be acidic or alkaline.

Maintenance

- Inspect the meter for damage daily when in use.
- Clean and maintain electrodes regularly.
- Wipe the glass probe with methylated spirits, then rinse with deionised water.
- Add paper wadding dampened with tap water to the cap to prevent the probe from drying.

Quality control checks

For **indicative** data:
- test a field replicate every 10 samples. Results should fall within the designated TER (for example, ±0.5 pH units)
- test a blind sample every six months.

For **analytical** data:
- test a field replicate every ten samples. Results should fall within the designated TER (for example, ±0.2 pH units)
- test a blind sample every three months
- have a duplicate sample tested by a professional water quality officer during the initial stages of the project. The difference between the values of the duplicate samples needs to be within the TER
- continue external checks periodically through shadow-testing workshops.

Colorimetry—pH

Summary

This method measures pH by using chemicals that react with H^+ (hydrogen) to produce a coloured solution that is proportional to the pH and is measurable using colorimetric equipment.

A colorimeter can be used to analyse other parameters such as phosphorus and nitrogen.

Equipment

You will need:
- water sampling equipment
- a colorimeter (for example, a photometer, spectrophotometer or comparator) and reagents
- the manufacturer's instructions.

To produce **indicative** data:
- the suggested instrument test range is pH 0.1 to 14
- the suggested test resolution is at least 0.2 pH units
- the suggested instrument test accuracy is ±0.5 pH units.

To produce **analytical** data:
- the suggested instrument test range is pH 0.1 to 14
- the suggested test resolution is at least 0.1 pH units
- the suggested instrument test accuracy is ±0.2 pH units.

Monitoring method

Capture a water sample follow the sampling procedure on page 5–9. Follow the manufacturer's instructions to carry out colorimetry.

Quality control procedures

- Rinse sampling containers three times in the water being tested, prior to sampling.
- Ensure that there are no air bubbles in the captured sample.
- Collect the water directly from the water body being tested.
- Conduct the test in the field to increase the accuracy of the reading.

Participant competency

For **indicative** and **analytical** data, strong experience and or expert training in the use of the equipment is required. For **analytical** data, annual inter-operator comparisons are recommended.

Calibration

For **indicative** and **analytical** data:
- conduct monthly calibration and TER checks
- keep equipment-specific maintenance and calibration records.

Maintenance

- Keep colorimetric equipment clean by following the manufacturer's instructions.
- Keep sampling containers clean without the use of detergents.
- Keep maintenance logs for all colorimetric equipment.
- Ensure that reagents have not expired, and replace when necessary.

Quality control checks

For **indicative** data:
- conduct a replicate test on 5% of the samples. The results should fall within the designated TER (for example, ±0.5 pH units)
- calibrate the meter according to the manufacturer's instructions prior to each use.

For **analytical** data:
- conduct a replicate test on 10% of the samples. The results should fall within the designated TER (for example, ±0.2 pH units)
- calibrate the meter according to the manufacturer's instructions prior to each use.
- continue external periodical checks by participating in shadow-testing workshops.

pH test strips

Summary

This method:

- is simple and easy to use
- can determine pH in small volumes of water
- involves chemically impregnated paper reacting with H^+ (hydrogen) to produce a colour indicating pH level.

Note: Wide-range pH strips cover all or almost all of the pH scale, but suffer in precision and accuracy due to this coverage. Narrow-range pH strips cover a narrower range (between 2 and 3 pH units) but have increased accuracy and precision within this range.

Equipment

You will need:

- a pH test kit
- a sample bottle, washed in phosphate-free detergent and rinsed three times with tap water and three times with deionised water
- deionised water.

Monitoring method

1. Rinse the pH tube with sample water.
2. Tear off a piece of indicator strip that is slightly longer than the tube. Leave half a centimetre of the strip protruding from the top when the tube is recapped. This enables the indicator strip to be easily removed when the test is complete.
3. Fill the tube with sample water, put the cap on and swirl the water around the indicator paper.
4. Wait for one minute for the colour to develop fully.
5. Place the tube on the black strip running through the middle of the pH colour indicator levels on the inside lid of the pH test box.
6. Compare the colour on the indicator paper with the pH colours on the lid to find the pH reading.

Quality control procedures

- Minimise damage or staining by storing the pH kit in dry, dark conditions.
- Analyse immediately in the field to increase the accuracy of the test.

Participant competency

No prior experience in the use of the equipment is required.

Calibration

pH strips cannot be calibrated. Prolonged storage may make the paper less accurate.

Maintenance

- Pour the water into a liquid waste bottle and place the pH paper in a solid waste container.
- Wash the sample bottle with phosphate-free detergent and rinse three times with tap water and three times with deionised water.

Quality control checks

- Check pH strips against known reference solutions.
- Test results from pH strips against those from a calibrated pH meter.

Titration—pH

Summary

This method:

- measures pH (in pH units) with chemicals that react with H^+ (hydrogen) to produce a colour change. The volume of chemical used is proportional to the pH value
- can collect quantitative data.

Equipment

You will need:

- a pH field kit and instructions
- ample reagents for the number of tests being conducted.

To produce **indicative** data:

- the suggested instrument test range is pH 0.1 to 14
- the suggested test resolution is at least 0.2 pH units
- the suggested instrument test accuracy is ±0.5 pH units.

To produce **analytical** data:

- the suggested instrument test range is pH 0.1 to 14
- the suggested test resolution is at least 0.1 pH units
- the suggested instrument test accuracy is ±0.1 pH units.

Monitoring method

1. Capture a representative water sample in a 250 mL or 300 mL bottle.
2. Add 1 mL of manganous sulfate and 1 mL of iodide azide.
3. Mix by inverting the bottle until a precipitate forms and settles.
4. When half the bottle volume is occupied by clear liquid above the precipitate, add 1 mL of sulfuric acid.
5. Re-stopper the bottle and invert it several times until the precipitate has all dissolved. The sample will turn a yellow-brown colour, as free iodine has been released in it.
6. Titrate the sample by adding sodium sulfate until a pale straw colour appears.
7. Add a starch indicator and continue to titrate until the blue colour first appears.

Quality control procedures

- Check manufacturer's specifications to ensure that the accuracy, resolution and range of the test kit meet monitoring requirements.
- Follow the instructions in the kit you have purchased.
- Renew sodium thiosulfate every twelve months.
- Ensure that the sample container is free of contaminants, and rinsed in the water being tested prior to sampling.
- Conduct the test immediately in the field, directly from the waterway.

Participant competency

To achieve **demonstrative** data, no prior experience in the use of the equipment is required. To achieve **indicative** and **analytical** data, strong experience or expert training in the use of the equipment and sampling is required. For **analytical** data, inter-operator comparisons are recommended.

Calibration

Calibration does not apply to titration methods.

Maintenance

- Ensure that reagents are within the expiry date and are not contaminated. Replace sulfate reagents every twelve months.
- Clean glassware after each test by rinsing with deionised water and drying before storage.
- Confirm each reading by having two people read the level of titrant in the syringe.

Quality control checks

For **indicative** data:

- conduct a replicate test on 10% of the samples. The results should fall within the designated TER (for example, ±0.5 pH units)
- conduct twice-yearly tests on a known standardised pH sample. This test will reveal any deterioration of the reagents over time
- test a sample any time a reagent has been replaced. Compare the results with a calibrated pH meter.

For **analytical** data:

- conduct a replicate test on 10% of the samples. The results should fall within the designated TER (for example, ±0.2 pH units)
- have a duplicate sample tested by a professional water quality officer during the initial stages of the project. The difference between the values of the duplicate samples needs to be within the TER
- continue external periodical checks through participating in shadow-testing workshops
- conduct twice-yearly tests on a sample with a known pH. This test will reveal any deterioration of the reagents over time
- test a sample any time a reagent has been replaced. Compare the results with those from a calibrated pH meter.

Water temperature

Importance of water temperature

Temperature is a measure of how hot or cold a substance is. Water temperature in Queensland is normally measured in degrees Celsius (°C). Water temperature is important because it affects the rate of many biological and chemical processes in waterways, and the amount of oxygen that can dissolve in the water. The change in temperature within a waterway is largely controlled by the effect that the sun has on the earth. The capacity of the sun to change water temperature is influenced by the Earth's rotational pattern (season, latitude and time of day), air circulation, cloud cover, vegetation cover, flow rate, water depth and altitude. Temperature affects physical, chemical and biological processes within a body of water and therefore influences many water quality parameters.

The wellbeing of all aquatic life, from bacteria to fish and mammals, is influenced by water temperature. Temperature directly affects the metabolic rate of plants and animals. Aquatic species have evolved to live in water of specific temperature ranges. If water temperatures change beyond the normal ranges, organisms do not function as effectively and may become more susceptible to toxic wastes, parasites or diseases. With extreme temperature changes, many organisms in an ecosystem will die. Changes in long-term temperature patterns may result in a different species composition of an ecosystem.

Fish spawning (mating and laying eggs) success also depends on temperature, as each species has a preferred spawning temperature range. Macro-invertebrates, an essential component of the aquatic food chain, are also temperature-sensitive, as are the adults of several fish species.

Changes in water temperature may affect:

- the dissolved oxygen (DO) content of water. Warmer water holds less oxygen than cooler water, decreasing the amount of oxygen for the animals to breathe
- the rate of photosynthesis by aquatic plants
- the metabolic rate of animals (the rate at which they process food)
- the rate of decay by bacteria
- reproductive success
- sensitivity of animals to toxic wastes, parasites and diseases.

Factors affecting water temperature

Water temperature may be influenced by:

- air temperature
- type, depth and flow of the water body
- exposure to sunlight
- turbidity or murkiness of the water body
- groundwater inflows
- cold or warm water discharges
- stormwater run-off
- vegetation.

Surface water tends to be warmer than deeper water. Shaded areas near the bank and shaded reaches tend to be cooler than exposed reaches on sunny days. The magnitude of this variation increases with the size and depth of the water body.

Small upland streams tend to have a more consistent water temperature profile than larger rivers. In larger, deeper rivers, the water temperature is more likely to vary throughout the river and throughout the water column due to the waters not mixing uniformly. Smaller upland streams also tend to be cooler due to altitudinal effects and increased levels of shading by riparian (river bank) vegetation relative to their size.

The water temperature of streams changes through time. Daily changes may be significant in smaller streams (as much as 20 °C), with the warmest temperatures in the mid- to late afternoon and the coolest in the early morning, around sunrise.

Streams that are deep, spring-fed or shaded do not heat up as quickly as shallow, unshaded streams. The overall temperature of large streams does not change rapidly because of the larger volume of water that must be heated.

In lakes, dams and ponds, the temperature of the surface water is often several degrees warmer than the water near the bottom. This occurs because warmer surface water is less dense than cold water and therefore floats on top of the colder water. This creates a distinct body of warm water. The two bodies of water are said to be separated by a *thermocline*, which may be disturbed by strong winds or through seasonal variations in air temperature.

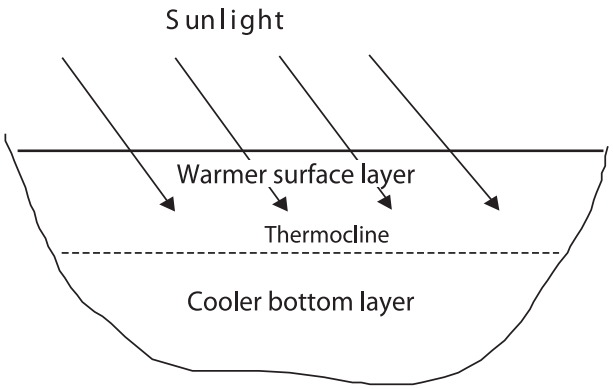
A temperature versus depth profile of a lake or dam will often show a sharp change in temperature at the thermocline, where the warm layer meets the colder bottom layer. Under stable climatic and flow conditions, a water temperature difference of 3 °C is sufficient to sustain a thermocline.

Because of the lack of mixing at the thermocline, oxygen diffuses slowly from the upper layer into the lower layer. As bacteria, animals and chemical processes in the bottom layer consume DO, oxygen levels may drop to near zero (anoxic conditions). Under anoxic conditions, several chemical reactions can commence, including the release of biologically available phosphorus from the sediment to the water, and the production of hydrogen sulfide (rotten egg gas).

In groundwater, the temperature at any one site may vary only slowly, but there can be relatively large temperature differences between surface water and groundwater bodies at differing depths.

Human effects on water temperature

Human activities may raise or lower the temperatures of streams and rivers. This is known as thermal pollution. Factors that raise water temperature are most critical during summer, when low flows and higher temperatures place



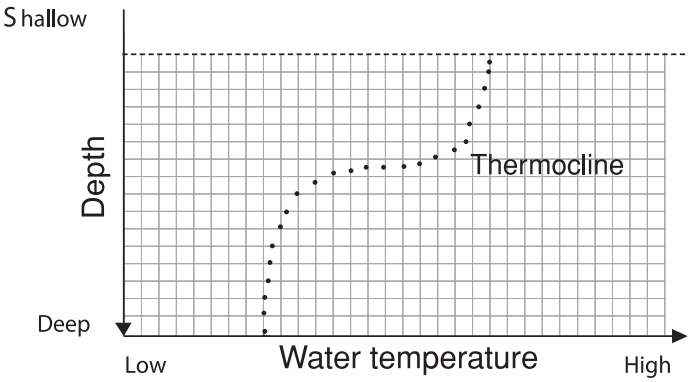


Figure 5–13 Temperature versus depth profile in a water body (Cassidy 2003)

more stress on the aquatic life. Human activities that lead to altered water temperatures include:

- removing trees and other bank vegetation, which allows more sunlight to penetrate and heat the water
- widening streams. Clearing vegetation from catchments can cause (often unintentional) widening of streams due to increased run-off volumes and velocity scouring out riverbanks. Widened streams are usually shallower than non-widened streams, and water in shallow streams is more readily heated than water in deeper streams
- discharging warmed water from industry and power plants.

Other sources of thermal pollution from human activities include:

- urban stormwater that has absorbed heat from paved surfaces such as streets and parking areas before it runs into the stream
- impoundments such as dams, which release cold waters from the bottom of the water column
- erosion, which increases the number of particles suspended in the water. These particles absorb and reflect heat from the sun and therefore prevent solar penetration, particularly in slow-flowing, poorly mixed streams.

Monitoring considerations

Water temperature should be measured as part of any monitoring work, and is best done at the same time of day each monitoring session. If you wish to measure DO levels, you will also need to measure temperature. Water temperature is also required for determining electrical conductivity and pH.

In deep areas or lakes, several measurements from the top to the bottom of the water column can be taken, to create a temperature profile.

If you suspect that point-source discharges into the stream are raising the temperature, take two measurements upstream of the discharge, one immediately downstream, then two more at further distances downstream. If there is an impact, the temperature immediately downstream of the discharge should be greater than those of the upstream sites. Temperatures further downstream should show a recovery, with temperatures gradually returning to lower levels. Take the same monitoring strategies if you believe that a constructed water body such as a dam is reducing the water temperature downstream. Make sure that the water sample is representative; be aware of temperature variations, particularly at the surface and the water edge.

Monitoring methods

Temperature can be determined by an expansion–contraction thermometer or digital temperature probe.

Thermometer

It is preferable to use alcohol-filled rather than mercury-filled thermometers, as alcohol thermometers are less hazardous if broken. Armoured thermometers are also more practical for field use than unprotected glass thermometers, and are worth the additional expense. The level of data quality you can produce will depend on the accuracy of the thermometer—for example, whether the thermometer is accurate to 0.1 °C or 0.5 °C.

Digital temperature probe

Be aware that some pH or DO meters may also measure temperature, so it may not be necessary to purchase a separate temperature probe. Some meters have components that require care around water. Batteries are required for the digital temperature probe.

Interpreting your results

Aquatic organisms may experience stress where a temperature change exceeds 2 °C over a 24-hour period. As a guideline, the increase in water temperature from heated effluent should be less than 2 °C (ANZECC 1992).

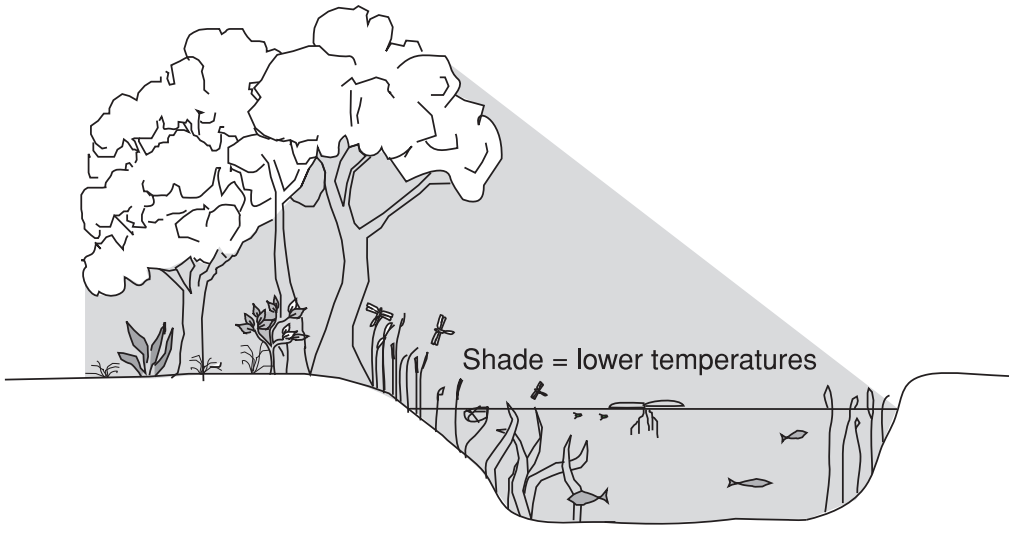


Figure 5–14 Riparian vegetation shades waterways during part of the day

Table 5–14 Guideline water temperature values for Queensland (adapted from Environmental Protection Agency 2006)

Protection of aquatic ecosystems			
Define local upper and lower guidelines using 80th and 20th percentiles, respectively, of temperatures (°C) measured in suitable local water bodies			
Other uses			
Water use	**Sub-use**	**Guideline temperature range**	**Comments**
Agriculture	Tropical aquaculture	21–32 °C	Optimal levels vary for individual fish species

Temperature is an important consideration when interpreting DO and dissolved phosphate (PO_4) data. The amount of oxygen dissolved in water decreases as the temperature rises. Very warm temperatures are thus a problem for many aquatic organisms that take their oxygen from the water because, as the temperature rises, so too does their metabolic rate and demand for oxygen. However, the amount of oxygen available in the water is less due to the higher temperature, which further increases the shortfall in oxygen supplies for the organisms.

How you interpret your temperature data will depend on the aims of your monitoring project. If your objectives are to conduct routine assessments of waterway health or to assess water suitability for specific uses, you should compare your results with the appropriate guideline values. See Chapter 8 for further information on comparing your results to guidelines, and on interpreting your results for a range on monitoring objectives.

To protect aquatic ecosystems, the *Queensland water quality guidelines* (Environmental Protection Agency 2006) do not provide regional guidelines for water temperature, as this indicator is highly site-specific. They recommend developing local temperature guidelines for daily maximum temperature and daily variation in temperature. This should be done by calculating the 80th and 20th percentiles of existing water temperature data (Table 5–14) from nearby streams in reference (good) condition that have similar stream geomorphology. The 80th percentile provides the maximum acceptable temperature and the 20th percentile the minimum. Any temperatures that fall between these two values fall within the acceptable range. See Chapter 8 for information on calculating percentiles.

The *Australian and New Zealand guidelines for fresh and marine water quality* (ANZECC & ARMCANZ 2000b) also provide information on trigger values (values that should trigger a specified management action or change in condition) that can assist you in determining whether temperature ranges and fluctuations are posing a problem for aquatic organisms in the waterway.

Where guidelines have not been established, interpreting temperature readings requires information about the natural range of temperatures expected for that site. Over a series of measurements through the year, build up a picture of the temperatures at your sampling site, noting the time of day. Observe any temperature that is unusually high or low. See Chapter 8 of this manual for information and advice on developing your own set of guidelines and comparing your results to guideline values.

For monitoring objectives not listed in Table 5–14, refer to the guideline references section at the back of this chapter to identify any existing suitable guidelines.

Health and safety

When monitoring temperature with a glass thermometer, there is the potential for glass stick injuries to occur.

See the *Health and safety guidelines for community-based waterway monitoring* (Department of Natural Resources and Water 2006) for further information.

Table 5–15 Methods guide for water temperature

	Expansion–contraction thermometer			Digital temperature probe		
Data quality	**Knowledge and skills**	**Time (mins)**	**Cost ($)**	**Knowledge and skills**	**Time (mins)**	**Cost ($)**
Analytical	Beginner	< 15	25–40	Beginner	< 15	60–190
Indicative	Beginner	< 15	5–25	Beginner	< 15	40–60
Demonstrative	Beginner	< 15	5–10	Beginner	< 15	40–60

Expansion–contraction thermometer

Summary

This method measures temperature in degrees Celsius (°C) by immersing an expansion–contraction thermometer in water until the temperature reading stabilises.

Equipment

You will need an expansion–contraction thermometer that covers the expected temperature range (for example, 0 °C to 50 °C).

To produce **demonstrative** data:
- the suggested instrument resolution is at least ±0.5 °C
- the suggested instrument accuracy is at least ±0.5 °C.

To produce **indicative** data:
- the suggested instrument resolution is at least ±0.2 °C
- the suggested instrument accuracy is at least ±0.2 °C.

To produce **analytical** data:
- the suggested instrument resolution is at least ±0.1 °C
- the suggested instrument accuracy is at least ±0.1 °C.

Monitoring method

1. Place the thermometer into the waterway or into the water sample as soon as it has been collected.
2. Wait approximately one minute, or until the reading stabilises.
3. Read the temperature to the nearest marking while the thermometer bulb is still immersed in water. View the reading at as close as possible to eye level.
4. Repeat these steps at least three times. If results are variable, take up to ten measurements.
5. Record results on water quality results sheet.
6. Note any temperature variation that is unusually high or low.

Quality control procedures

- Follow the use and maintenance instructions for the equipment.
- Conduct shadow testing whenever possible.

Participant competency

Little or no experience is required, although familiarity with using the equipment is beneficial.

Calibration

No calibration procedures are available for this method.

Maintenance

- Check the thermometer regularly for defects such as cracks.
- After use, rinse the thermometer with clean water, dry it and return it to its protective container.

Quality control checks

For **indicative** and **analytical** data:
- test a field replicate every ten samples. Results should fall within the designated TER (for example, ±0.5 °C for indicative data or ±0.2 °C for analytical data)
- before initial use and every six months thereafter, check instrument readings against those from a precision thermometer that reads in 0.1 °C increments. Compare the readings at 0 °C and 25 °C. If they are not within the TER, the thermometer will need to be replaced.

For **analytical data**, have a duplicate sample tested by a professional water quality officer during the initial stages of the project. The difference between the values of the duplicate samples needs to be within the TER.

Digital temperature probe

Summary

This method:

- measures temperature in degrees Celsius (°C)
- is performed by immersing a digital temperature probe in water until the temperature reading stabilises
- is a quick and easy method for taking multiple temperature readings.

Equipment

You will need a digital temperature probe that covers the expected temperature range (for example, 0 °C to 100 °C).

To produce **demonstrative** data:

- the suggested instrument resolution is at least ±0.5 °C
- the suggested instrument accuracy is at least ±0.5 °C.

To produce **indicative** data:

- the suggested instrument resolution is at least ±0.2 °C
- the suggested instrument accuracy is at least ±0.2 °C.

To produce **analytical** data:

- the suggested instrument resolution is at least ±0.1 °C
- the suggested instrument accuracy is at least ±0.1 °C.

Monitoring method

1. Place the probe into the waterway or into the water sample as soon as it has been collected.
2. Wait approximately one minute, or until the reading stabilises.
3. Record the result on the water quality results sheet.
4. Repeat at least three times. If results are variable, take up to ten measurements.
5. Note any temperature variation that is unusually high or low.

Quality control procedures

- Check equipment prior to each sampling run for condition (including battery condition) and damage.
- Follow the use and maintenance instruction manual for the equipment.
- Conduct shadow testing whenever possible.

Participant competency

Little to no experience is required, although familiarity with the use of equipment is beneficial.

Calibration

Temperature probes come pre-calibrated. Subsequent calibration is not possible.

Maintenance

- After use, rinse the probe with clean water, dry it and return to protective container. Keep free from dirt or other contaminants.
- Check the probe for damage such as cracks on a regular basis.

Quality control checks

For **indicative** and **analytical** data:

- test a field replicate every ten samples. Results should fall within the designated TER (for example, ±0.5 °C for indicative data or ±0.2 °C for analytical data
- before initial use, and every six months thereafter, check the instrument reading against those from a precision thermometer that reads in 0.1 °C increments. Compare the readings at 0 °C and 25 °C. If they are not within the TER, the thermometer needs to be replaced.

For **analytical** data:

- have a duplicate sample tested by a professional water quality officer during the initial stages of the project. The difference between the values of the duplicate samples needs to be within the TER.

Transparency

Importance of transparency

Transparency, also known as visual water clarity, is a measure of how far visible light is able to pass through water. Measuring transparency provides information on the amount of light being transmitted through the water.

Reduced light levels may affect several important ecological and management processes including:

- the photosynthetic capacity of plants and algae. Reduced photosynthetic capacity of plants and algae can affect water quality parameters such as dissolved oxygen, pH and transparency. This can have major effects on aquatic food webs as well as habitat structure and composition
- visual range. A reduction in visual clarity can affect predator–prey relationships, mating, and spawning. This can lead to a change in species distribution and composition
- solar radiation. Reduced transparency reduces the depth of solar penetration into a waterway, which may affect a range of physical, chemical and biological processes.

Reduction of visual range also has significant effects on human perceptions of the aesthetic qualities of waterways.

Factors affecting transparency

Transparency is affected by many materials and processes, such as turbidity from suspended materials entering the water through natural or human-caused run-off or as a result of biological or chemical activity in the waterway. These processes include:

- hill-slope and gully erosion
- waste discharges
- run-off from urban areas
- erosion of river banks and beds
- bottom feeders, such as carp, stirring up bottom sediments
- biological growth such as algal blooms, diatom blooms and plankton
- physical disturbance to the river channel or banks, such as gravel removal or dredging
- physical disturbance to the surrounding land including logging, cultivation, grazing, development, road construction, road drainage, excavation for buildings, and mineral extraction
- water colouration from tannin, iron-containing sediments and similar.

Monitoring considerations

Transparency is determined using equipment that measures the distance to the point at which reflected light is no longer visible.

Methods for monitoring transparency are quick, easy and cheap; however, their usefulness may be limited in waterways that:

- are fast-flowing
- are shallow and highly transparent
- have surface waves
- have surface scums or biological blooms
- are highly turbid.

By using both a transparency tube and a Secchi disc, transparency should be measurable under all but the most highly turbid conditions.

Monitoring methods

The most commonly used pieces of equipment for monitoring transparency are transparency tubes and Secchi discs.

Transparency tube

A transparency tube is a hollow, transparent cylinder into which water is poured to derive a measure of transparency. Water is poured into the tube until the markings at its base are no longer distinguishable—this is known as the *light extinction point*. Transparency tubes are not suitable for use in highly turbid waters, which make determination of the point of light extinction difficult to accurately determine. It should be noted that the end point (when the lines are barely visible) is highly subjective and likely to vary between operators. This equipment can only be used in water with a transparency less than the length of the tube.

Secchi disc

A Secchi disc is a round, flat disc marked with alternating quarters of white and black. The disc is attached to a weighted rope and lowered into the water until the black quarters are no longer visible. The depth at which this occurs is called the Secchi depth and is used to calculate transparency. Measures of transparency using a Secchi disc are successful in relatively clear waters. However, in highly turbid waters (high suspended solid content) use of this equipment is impaired due to the narrowness of the band between the disc being fully visible and fully invisible.

Secchi discs are not suitable for deployment under a range of circumstances that include:

- shallow water where the bottom is clearly visible
- fast-flowing water where the disc cannot be deployed vertically in the water column
- water affected by surface waves
- water with surface scums or biological blooms.

Interpreting your results

How you interpret your results will depend on your monitoring objectives. See Chapter 8 of this manual for advice and information on data interpretation for a range of monitoring objectives.

Measurements of transparency are generally used to explore the health and functions of aquatic ecosystems. However, there are no established water transparency guidelines for the protection of freshwater ecosystems in Queensland with which you can compare your results. Guideline values for transparency (measured as Secchi depth) have only been developed for estuarine and marine waters in Queensland (Environmental Protection Agency 2006). This is because turbidity is considered to be a more suitable indicator for longer-term investigations of water quality trends in fresh waters.

For objectives other than the protection of aquatic ecosystems, check the guideline references section at the end of this chapter for any available guidelines suitable for your monitoring objectives. Although official guidelines are not well-established for transparency, you can devise your own specific guidelines if you have enough data. Refer to Chapter 8 for information and advice on developing your own guideline values, and on comparing data with established guidelines.

Health and safety

See the *Health and safety guidelines for community-based waterway monitoring* (Department of Natural Resources and Water 2006) for further information.

Table 5–16 Methods guide for transparency

	Transparency tube			Secchi disc		
Data quality	**Knowledge and skills**	**Time (mins)**	**Cost ($)**	**Knowledge and skills**	**Time (mins)**	**Cost ($)**
Analytical				Some experience	< 5	50–70
Indicative	Beginner	< 3	30–60	Beginner	< 5	50–70
Demonstrative	Beginner	< 3	30–60	Beginner	< 5	50–70

Transparency tube

Summary

This method measures transparency in millimetres (mm). A representative sample of water is poured into the tube until the bottom of the tube is no longer visible. The height of the water is then measured.

Equipment

You will need:

- a transparency tube
- water sampling equipment.

Monitoring method

1. Capture a representative water sample (see page 5–9). Ensure that the sample is well-mixed before testing.
2. Hold the tube out of direct sunlight. Gradually pour the sample into the turbidity tube while looking vertically down the tube. A white tile or piece of paper beneath the tube may increase visibility.
3. Stop pouring at the point where you can barely see the lines on the bottom.
4. Using an accurate ruler or tape measure, measure the height of the water column from the bottom of the meniscus (the curved water surface). Use less than (<) and greater than (>) symbols if values are out of range.

Quality control procedures

- Only allow a person with good vision (with glasses, if necessary) to use the transparency tube method.
- Ensure that sediments are not disturbed in the water while collecting the sample.
- Conduct tests in appropriate light conditions (shade).

Participant competency

No prior experience in using the equipment is required; however, prior use of equipment and sampling experience is beneficial.

Calibration

No calibration is required.

Maintenance

Wash the transparency tube thoroughly with tap-water and ensure that the tube is kept clean, scratch-free and free from contamination.

Quality control checks

For **indicative** data, compare the results with Secchi disc results periodically. The results should fall within the designated TER (for example, ±50%).

Secchi disc

Summary

This method:

- determines transparency in centimetres (cm) by measuring the distance that light passes through water. A black and white disc attached to a long tape measure or cord is lowered in the water until barely visible. Depth of the disc at this point is recorded as the transparency measurement
- is cheap and easy to use
- is a good method for deep, clear waterways—i.e. less than 10 nephelometric turbidity units (NTU).

Equipment

To produce **analytical** data, follow Australian Standard 3550.7-1993 (Standards Australia 1993) for construction and use of a Secchi disc.

To produce **indicative** or **demonstrative** data, use any form of Secchi disc.

Monitoring method

1. Lower the disc until it just disappears from view. Record the depth of the disc from the water surface.
2. Raise the disc until it just reappears into view. Record the depth of the disc from the water surface.
3. The midpoint of the two readings is the Secchi disc depth. Use less than (<) and greater than (>) symbols if values are out of range.

Quality control procedures

- Only allow a person with good vision (with glasses, if necessary) to use the transparency tube method.
- Conduct tests in appropriate light conditions (shade), stream flow conditions and weather conditions
- Ensure that the Secchi disc is clean.
- Check the accuracy of markings on the disc cord.
- Ensure that sediments are not disturbed in the water while taking a reading.

Participant competency

To produce **analytical** data, some experience and training in the use of equipment is recommended. To produce **indicative** and **demonstrative** data, no prior experience in the use of the equipment is required, but may be beneficial.

Calibration

No calibration is required.

Maintenance

- Ensure that the Secchi disc is cleaned after use.
- Check for condition, accuracy of markings and cord stretch.

Quality control checks

For **indicative** data, test a field replicate every ten samples. The results should fall within the designated TER (for example, ±50%).

For **analytical** data:

- test a field replicate every ten samples. The results should fall within the designated TER (for example, ±20%)
- conduct inter-operator comparisons on an annual basis.

Total suspended solids

Importance of suspended solids

Total suspended solids (TSS) is a measure of the amount of solid particles held in suspension within a water sample. It is expressed as the total weight of solids present for a given volume of water, usually milligrams per litre (mg/L). Due to limitations associated with the filtering process, this measure does not include dissolved solids or solids of less than 2.0 microns (1 micron = 1/1000 millimetre).

TSS is an important indicator of the sources and amount of sediment entering and being transported in a waterway. Sediment loads can be calculated by multiplying TSS concentrations by discharge (total flow over a given period of time, usually litres per day). Sediment loads are very useful in quantifying rates of soil loss from a catchment or exploring or the amount of sediment transported to the sea.

Sometimes TSS concentrations may be elevated due to the impact of a single source, such as run-off from a work site. On other occasions, TSS can indicate a long-term imbalance in ecological health of the entire catchment. TSS can be measured to assess the impact of erosion and deposition over time and distance. The findings of recent studies conducted in Queensland river systems indicate a relationship between TSS and total phosphorus (TP) as well as TSS and total nitrogen (TN). Therefore, TSS could be used in the future as a surrogate measurement for TP and TN on a regional basis (R Packett 2006, pers. comm., 10 August).

The amount of TSS in a stream can impact on a range of ecological and management activities.

Ecological processes

High levels of TSS reduce water clarity and increase turbidity, contributing to:

- altered water temperatures, which affect biological, physical and chemical processes
- reduced light and clarity, which impacts on biological processes such as predation, mating, spawning and photosynthesis
- increased sediment deposition, which leads to the smothering of benthic (stream bed) structures and the biological organisms that use them.

Suspended particles often provide a source of attached pollutants such as nutrients, toxic materials and harmful bacteria, which can impact on biological communities.

High levels of suspended solids generally indicate excess levels of erosion and bank instability within a catchment. Unstable banks tend to be poorly vegetated and provide limited habitat value for aquatic plants and animals.

Management issues

High concentrations of sediment will damage pumps and clog filters, irrigation pipes and sprinkler systems. They indicate poor land and vegetation management practices.

Visual amenity is often associated with sediment concentrations. Waters with high sediment levels are considered unattractive and undesirable.

High sediment concentrations increase sedimentation rates in water storages such as dams and weirs, and other locations where flow rates are reduced.

Factors affecting total suspended solids

Natural (or background) TSS levels in waterways vary from low levels in mountain streams to high levels in lowland rivers during rainfall events.

The capacity of a waterway to hold sediments in suspension is influenced by:

- stream velocity—rapidly flowing water has greater energy and can hold far greater amounts of sediment in suspension than slower-flowing or still water. Additionally, increased stream velocities increase bank erosion, which is usually a major contributor of suspended solids during flow events
- sources of sediment such as run-off and discharge from human activities. These may include construction, agricultural practices, logging activity, industrial discharges, stormwater or dredging
- sediment types—smaller sediments and charged particles will stay in suspension longer than other types.

Salinity, as occurs in estuaries, can affect the TSS in a water body. At higher salinities, particles present in the water body tend to clump together (flocculate) and settle out of the water column, forming mud banks.

Total suspended solid concentrations in the water column are affected by:

- geology, soil type and topography
- stream type, shape and structure (geomorphology)
- rainfall intensity and catchment run-off
- hill-slope and gully erosion
- stream bed and bank erosion
- agricultural and industrial activities
- stream bed disturbance—for example, by bottom feeders such as carp, and anoxic gases
- direct discharge of waste material
- stormwater run-off
- the condition and extent of riparian vegetation
- flood plain and wetland retention and deposition
- flow rate and velocity
- salinity concentrations.

Monitoring considerations

Regularly monitoring TSS at a number of sites throughout a catchment can help detect spatial patterns and longer-term trends of sediment transport throughout the catchment.

To measure point-source impacts (those originating from a distinct point), monitor upstream and downstream of the source—particularly before, during and immediately after rain events.

Sediment loads can be calculated by multiplying TSS by river discharge rates. If you wish to do these calculations, consider locating your sites close to a stream-gauging station.

Monitoring methods

Monitoring total suspended solid concentrations involves collecting a representative sample for laboratory analysis. Generally, 1 L is a sufficient amount, though more volume may be required for very low levels of suspended solids.

When collecting a sample for TSS analysis, it is important not to use subsamples poured from a bucket. During events when stream velocities are high, particulates are held in suspension. When the water is decanted from a bucket to subsample containers, larger particles can drop out, causing inaccurate results. Therefore, it is recommended that a complete sample be taken in a 1 L bottle at the site.

The laboratory will filter a known volume of water through a weighed filter, dry the filter and sediment at 105 °C, and then weigh the filter and the retained solids.

TSS = weight of dried filter and retained solids – dry weight of filter

Interpreting your results

Natural TSS concentrations are highly variable, depending on stream type and prevailing conditions. How you should interpret your data depends on your monitoring objectives. If you are conducting routine monitoring to assess waterway health, or monitoring to determine the suitability of the water for specific uses, you should compare your results to guideline values. For information and advice on interpreting data for a range of monitoring objectives, and on comparing your results to guidelines, refer to Chapter 8 of this manual.

The Environmental Protection Agency developed limited ecosystem protection guidelines for sediment concentrations in Queensland waterways (Table 5–17), so interpretation currently should be based on changes to expected values. If you are using the Queensland guidelines, it is important to identify the region and type of water body in which you are monitoring because of the natural variability in sediment concentrations throughout the state. The *Queensland water quality guidelines* (Environmental Protection Agency 2006) provide definitions of the regional boundaries and water body types they use.

Table 5–17 Guideline total suspended solids values for fresh waters in Queensland (adapted from Environmental Protection Agency 2006)

Protection of aquatic ecosystems		
Water body type	**South East Queensland**	**Central Coast**
Lowland streams	6 mg/L	10 mg/L
Upland streams	6 mg/L	–
Other uses		
Water use	**Guideline TSS range**	**Comments**
Drinking water	< 25 mg/L	Used by South East Queensland Water

Where Queensland guidelines are unavailable (such as for Wet Tropics, Eastern Cape York, Gulf Rivers, Lake Eyre and Murray–Darling), use the *Australian and New Zealand guidelines for fresh and marine water quality* (ANZECC & ARMCANZ 2000b). If no suitable guidelines are available, you can establish your own specific guidelines if you have enough data. Refer to Chapter 8 for information and advice on developing your own guideline values.

For monitoring objectives other than ecosystem protection, compare your results to relevant guidelines.

Health and safety

See the *Health and safety guidelines for community-based waterway monitoring* (Department of Natural Resources and Water 2006) for further information.

Table 5–18 Methods guide for total suspended solids

	Laboratory analysis		
Data quality	**Knowledge and skills**	**Time (working days)**	**Cost ($)**
Analytical	Some experience	5–20	12–17
Indicative			
Demonstrative			

Laboratory analysis —TSS at 105 °C

Summary

This method calculates suspended solids in milligrams per litre (mg/L). A known volume of sampled water is filtered through a pre-weighed filter paper. The filter paper and retained sediment is then oven-dried at 105 °C for one hour, cooled to room temperature in a desiccator, then weighed.

The drying, desiccation and weighing steps are then repeated to give an average final weight (filter paper plus retained sediment) based on two measurements. A final concentration (mg/L) is calculated by subtracting the initial weight of the paper from the final weight (filter paper plus retained sediment), and dividing by the volume of water that was filtered.

Equipment

For fieldwork, you will need:
- a clean sampling container
- water sampling equipment.

For laboratory work, you will need:
- scales (balance) able to weigh to 0.1 mg
- desiccator—used to keep filter paper dry between use and weighing
- glass-fibre filter paper capable of filtering solids greater than 0.2 microns in diameter
- drying oven capable of operating between 103 and 105 °C.

Monitoring method

1. Rinse the sampling container (normally plastic, 1 L) three times in water to be sampled.
2. Capture a representative water sample in the container. Ensure that sediments are not disturbed in the water while collecting the sample.
3. Place the sample in an esky or fridge. Samples may be stored in a dark, cool environment for several days before filtration if necessary.
4. Send the sample to the laboratory for analysis.

Quality control procedures

- Ensure that the sample is stirred before filtration.
- Ensure that laboratory work follows Australian Standard 3550.4-1990 (Standards Australia 1990).
- Document laboratory quality assurance and quality control procedures.

Participant competency

Some experience or training in sampling methods is required.

Calibration

The laboratory is responsible for calibrating equipment (including scales, filter paper and oven) within acceptable tolerances.

Maintenance

Ensure that all sampling equipment is clean and in good condition.

Quality control checks

- Use a blank for every sampled batch.
- Schedule a replicate for every ten samples for each operator.

Turbidity

Importance of turbidity

Turbidity is a measure of water clarity. To the naked eye, turbid water appears cloudy or muddy, as suspended particles such as clay, silt, sand, algae, plankton, micro-organisms and other substances scatter the passage of light through the water. Turbidity differs from colour; water can have high colour and low turbidity. Tannin-rich waters that flow through peaty areas, such as in wallum swamps or flood plain billabongs and wetlands, generally have low levels of turbidity.

Turbidity is most commonly recorded in nephelometric turbidity units (NTU). This is an open-ended scale commencing at zero for clear (filtered) water. Natural (or background) turbidity levels in waterways vary from less than 1 NTU in mountain streams to more than 1000 NTU in some lakes and lowland rivers during rainfall events. In Queensland, upland rivers commonly have higher NTU readings during floods than lowland rivers.

Turbidity is caused by materials entering the water via natural or human-induced processes, through run-off and erosion or as a result of physical, chemical or biological activity within the waterway. It can indicate a range of issues in the aquatic ecosystem. Potential sources of turbidity include:

- hill-slope and gully erosion
- waste discharges
- run-off from urban areas
- eroding river banks and beds
- bottom feeders, such as carp, stirring up bottom sediments
- biological growth such as algal blooms, diatom blooms and plankton
- physical disturbance to the river channel or banks, such as gravel removal or dredging
- physical disturbance to the surrounding land including logging, cultivating, grazing, development, road construction, road drainage, excavation for buildings, and mineral extraction.

Turbidity often increases sharply during and after a rainfall because the energy of falling and flowing water is the primary way that sediment becomes dislodged and carried into rivers.

Turbidity levels may influence water temperature. Under some circumstances, higher turbidity can raise water temperature due to increased thermal mass, reducing dissolved oxygen levels. In other cases, increased turbidity may reduce solar penetration, thus reducing water temperatures.

Turbidity levels may influence light penetration and optical properties of water. High turbidity may reduce the amount of light passing through water. Reduced light levels may reduce the rate of photosynthesis among aquatic plants and algae, therefore reducing dissolved oxygen levels. Reduced light penetration may alter optical properties, affecting predation, reproduction and photosynthesis of organisms.

The suspended materials causing turbidity can cause smothering problems. As particles settle out of suspension, they can:

- clog fish gills, which reduces their resistance to disease, lowers growth rates, and affects egg and larval development
- settle into the stream bed and spaces between the rocks on the bottom, reducing the amount and type of habitat available.

Suspended particles also provide a place for harmful bacteria to breed, and can transport attached pollutants such as nutrients and toxic materials.

In the examples above, the problem is not turbidity, but rather the presence of suspended particles within the water column, of which turbidity is a measure. Turbidity is an indirect measure relative to arbitrary standards. Though not an exact measure, turbidity can be used as an indirect indicator of:

- transparency—related to aesthetic values or habitat quality for predators to see their prey
- total suspended solids (TSS), as an indication of the amount of suspended sediment or the benthic effects of sedimentation.

Turbidity is a measure that is used when the direct measures of transparency or TSS are not logistically, financially or statistically appropriate.

Factors affecting turbidity

Turbidity may increase due to increased stream velocity, sediment run-off from urban and agricultural practices, logging activity, industrial discharges, stormwater and other sources.

Salinity concentrations can affect turbidity, particularly in estuaries. At higher salinity concentrations, suspended particles tend to clump together (flocculate) and settle out of the water column, forming (in the case of estuaries) mud banks.

Turbidity is affected by:

- geology, soils and topography
- stream type, shape and structure (geomorphology)
- rainfall and catchment run-off
- hill-slope and gully erosion
- stream bed and bank erosion
- agricultural and industrial activities
- stream bed disturbance—for example, by bottom feeders such as carp, or anoxic gases
- direct discharge of waste material
- stormwater run-off
- excessive algal, diatom or plankton growth
- riparian vegetation condition and extent
- flood plain and wetland retention and deposition
- flow rate and velocity
- salinity concentrations.

Monitoring considerations

Regularly monitoring turbidity at a number of sites throughout a catchment can help detect longer-term trends such as increasing erosion in the catchment.

Turbidity can be measured in either the field or the laboratory. Field measurements are preferable, providing that data quality can be met, as this limits handling and storage considerations such as sediment settling or adhering to the sample container.

Take particular care to avoid disturbing sediments during sampling.

To measure point-source impacts (those originating from a distinct point), monitor two sites above and two below the source, particularly before, during and immediately after rain events. Turbidity is affected by river discharge and velocity, so be sure to consider these when you collect your sample.

Although they are very simple to use, turbidity tubes tend to overestimate turbidity in samples that are highly coloured and underestimate turbidity in samples containing very fine particulates such as clay.

Monitoring methods

Turbidity can be measured with:

- a turbidity meter, sometimes referred to as a nephelometer
- a turbidity tube.

Turbidity meter (nephelometer)

A turbidity meter is an instrument which measures the amount of light passing through a water sample. The light is reflected off suspended particulates within the water; the more particulates present, the more light is reflected and the higher the turbidity.

Turbidity tube

Turbidity tubes do not directly measure turbidity, but water clarity (transparency). The turbidity tube scale is non-linear (logarithmic) and there are gaps between numbers. When the water level is between two numbers, record the value as less than (<) the next number above the water level. The end point (when lines are barely visible) is highly subjective and is likely to vary between operators.

This measure of clarity is then converted to a measure of turbidity, based on a standard equation derived by measuring the transparency of known turbidity standards. This is an inexpensive and easy way to obtain a relative measure of turbidity. However, transparency is not turbidity and the use of a standard equation does not take into account the differing reflective properties from one sample of water to the next. For these reasons, a turbidity tube cannot provide a highly accurate measure of turbidity, but indicates relative turbidity.

Table 5–19 Guideline turbidity values for fresh waters in Queensland (adapted from Environmental Protection Agency 2006)

Protection of aquatic ecosystems			
Water body type	**South East Queensland**	**Central Coast**	**Wet Tropics**
Lowland streams	50 NTU	50 NTU	15 NTU
Upland streams	25 NTU	25 NTU	6 NTU
Lakes and reservoirs	1–20 NTU	1–20 NTU	2–200 NTU
Wetlands	–	–	2–200 NTU
Other uses			
Water use	**Sub-use**	**Guideline turbidity range**	**Comments**
Drinking water	–	< 25 NTU	From South East Queensland Water
Agriculture	Tropical aquaculture	< 80 NTU	Optimal levels vary for individual fish species

Interpreting your results

Natural turbidity levels in waterways vary from less than 1 NTU in mountain streams to hundreds or even thousands of NTU during rainfall events or in naturally turbid waters.

How you should interpret your data depends on your monitoring objectives. Refer to Chapter 8 of this manual for advice on interpretation techniques for a range of objectives. Interpreting turbidity readings requires information about the natural turbidity in your area. There are large variations in turbidity in Australian river systems; inland rivers tend to be naturally more turbid than coastal rivers. Find out the normal range in your catchment from your catchment coordinator, natural resource management agency or local council.

If your objectives include conducting routine assessments of waterway health or water suitability for other specified uses, you should compare your data with the relevant guidelines for these objectives. For ecosystem protection, the Environmental Protection Agency (2006) developed limited turbidity guidelines for some water body types in three Queensland regions (Table 5–19). These guidelines may be used with care in the designated regions and water bodies. Definitions of the regional boundaries and water body types can be found in the Queensland water quality guidelines (Environmental Protection Agency 2006).

If your objectives do not involve ecosystem protection, refer to the 'other uses' section of Table 5–19, or check the guideline references section at the end of this chapter for available guidelines that match your monitoring objectives.

The *Queensland water quality guidelines* (Environmental Protection Agency 2006) also outline more specialised subregional guidelines for water bodies in the Douglas and North Stradbroke Island catchments. If there are no Queensland guidelines suitable for your region (such as for Eastern Cape York, Gulf Rivers, Lake Eyre and Murray–Darling), refer to the *Australian and New Zealand guidelines for fresh and marine water quality* (ANZECC & ARMCANZ 2000b). The national guidelines provide default turbidity trigger values relevant to Queensland (Table 5–20). Chapter 8 contains information on how to compare your results with guidelines values.

Table 5–20 Default turbidity trigger values (NTU) for ecosystem protection (ANZECC & ARMCANZ 2000b)

Ecosystem type	South-east Australia	Tropical Australia
Upland rivers	2–25	2–15
Lowland rivers	6–50	2–15
Lakes and reservoirs	1–20	2–200
Estuarine and marine	0.5–10	1–20

It is possible to develop your own specific guidelines if you have enough data of suitable quality. For information and advice on developing your own guidelines, see Chapter 8.

If your objectives do not involve ecosystem protection, refer to the 'other uses' section of Table 5–19, or check the guideline references section at the end of this chapter for available guidelines that match your monitoring objectives.

Comparing transparency, suspended solids and turbidity

Transparency, TSS and turbidity all measure similar characteristics of water but differ enough to warrant caution when comparing one measurement with another. Turbidity measurements can act as a surrogate for TSS concentrations provided that a suitable number of TSS samples are collected. For example, a turbidity logger can collect data at short intervals over a given period. This data can be related to TSS values collected at similar intervals. If a good relationship exists, a conversion from turbidity data to TSS data can take place. Understanding the relationships between turbidity, TSS and transparency will give you a much better understanding of the functions and processes within your waterway.

Health and safety

Formazin (a derivative of formaldehyde and hydrazine) chemical standards used to calibrate turbidity meters are considered carcinogenic and must be handled with extreme care.

See the *Health and safety guidelines for community-based waterway monitoring* (Department of Natural Resources and Water 2006) for further information.

Table 5–21 Methods guide for turbidity

Data quality	Turbidity meter (nephelometer)						Turbidity tube		
	Field			Laboratory testing					
	Knowledge and skills	Time (mins)	Cost ($)	Knowledge and skills	Time (working days)	Cost ($)	Knowledge and skills	Time (mins)	Cost ($)
Analytical	Some experience	5–10	1200–2600	Some sampling experience	5–20	8–14			
Indicative	Some experience	< 5	1200–1600						
Demonstrative	Beginner	< 5	700–1200				Beginner	< 3	25–60

Turbidity meter

Summary

Turbidity is a measure of water clarity. Turbidity meters measure the intensity of light scattered by particles in the water.

This method measures turbidity in nephelometric turbidity units (NTU) and can measure a wide range of values, from 0 to 1000 NTU.

Equipment

You will need:
- a turbidity meter (nephelometer)
- water sampling equipment for instruments that require a captured water sample for deployment
- the manufacturer's instruction manual.

Use any form of turbidity meter to produce **demonstrative** data.

To produce **indicative** data, you will need a turbidity meter capable of measuring the scattered light at 90° to the light beam that measures NTU. Instrument accuracy needs to be at least ±5%.

To produce **analytical** data, you will need:
- a turbidity meter capable of measuring the scattered light at 90° to the light beam that measures NTU. Instrument accuracy must be at least ±2%
- appropriate sampling and storage equipment for laboratory analysis (for example, 250 mL sampling container and esky).

Monitoring method

- For in situ instruments, deploy as per the manufacturer's instructions.
- For meters that require a captured water sample, follow the sampling procedure on page 5–9. Take readings as per the manufacturer's instructions.
- For laboratory analysis, follow the sampling procedure on page 5–12.

Quality control procedures

- Ensure that turbidity is not increased through physical disturbance while collecting the sample or taking a reading.
- Stir, but do not shake the sample before testing to resuspend particles and avoid adding air bubbles.
- Analyse the sample on site as close to the time of sampling as possible.
- For a laboratory analysis, the sample must be stored in chilled, dark environment.

Participant competency

For indicative and analytical data, some experience and training is required in the use of equipment and sampling methods.

Calibration

Formazin calibration standards need to be inverted several times before use. Do not shake, as this will introduce tiny air bubbles that affect optical properties and therefore the turbidity value.

For **indicative** data, calibrate the instrument on a monthly basis and prior to use.

For **analytical** data, calibrate the instrument on a weekly basis and prior to use.

Maintenance

Check the instrument for damage after use. Damaged meters must be repaired to the manufacturer's specifications.

Quality control checks

For **indicative** data:
- conduct a replicate every ten samples. The results should fall within the designated TER (for example, ±5 NTU or 10%)
- conduct shadow testing or blind sample tests annually.

For **analytical** data:
- conduct a replicate every ten samples. The results should fall within the designated TER (for example, ±2 NTU or 5 %)
- conduct shadow testing or blind sample tests quarterly
- have a duplicate sample tested by a professional water quality officer during the initial stages of the project. The difference between the values of the duplicate samples needs to be within the TER
- continue external periodical checks through shadow-testing workshops.

Turbidity tube

Summary

This method:

- measures turbidity in nephelometric turbidity units (NTU)
- is performed by pouring water into the plastic turbidity tube until the lines on the bottom of the tube are barely visible. The measurement is taken from a scale on the tube
- is very simple to use and gives good comparative measures.

Equipment

You will need:

- a turbidity tube
- water sampling equipment.

Monitoring method

1. Capture a representative water sample (see page 5–9).
2. Ensure that the sample is well-mixed before testing.
3. Hold the tube out of direct sunlight. Gradually pour the sample into the turbidity tube while looking vertically down the tube. A white tile or piece of paper beneath the tube may increase visibility.
4. Stop pouring at the point where you can barely see the lines on the bottom.
5. Note the reading from the scale on the side of the tube. If the reading is above 200, record as > 200 NTU. If you fill the turbidity tube to the top or past the last reading and the black lines are still visible, take the reading as less than the last number—that is, < 10 NTU.
6. Record the reading as NTU on a water quality record sheet.

Quality control procedures

- Only allow a person with good vision (with glasses, if necessary) to use the turbidity tube method.
- Ensure that the turbidity of the water is not increased while collecting the sample.
- Read the tube measurement out of direct sunlight.
- Analyse as soon as possible. The sample may be kept for up to 24 hours, and must be stored in a dark, chilled environment.
- Stir but do not shake the sample before testing to resuspend particles and avoid adding air bubbles.

Participant competency

- At a minimum, users should be familiar with use of equipment, sampling methods and documentation.
- Be aware of variability between operators and perform inter-operator comparisons.

Calibration

No calibration is required.

Maintenance

Wash the turbidity tube thoroughly with tap-water and ensure that the tube is kept clean, scratch-free and free from contamination.

Quality control checks

Compare the results with turbidity meter readings periodically.

Nutrients

The remainder of this chapter provides information on monitoring nutrients, with a focus on nitrogen and phosphorus. Nitrogen and phosphorus are essential to life on earth. Nitrogen makes up approximately 78% of the earth's atmosphere, while phosphorus makes up approximately 0.1% of the earth's crust (ANZECC & ARMCANZ 2000b). Like all nutrients, both nitrogen and phosphorus are crucial to ecosystem health at certain concentrations; however, excess levels of either can have negative implications for a waterway ecosystem. Monitoring nutrients can provide valuable insights into the condition of a waterway ecosystem.

Accurately monitoring the nutrients of a waterway is a challenging exercise. Sample contamination and analysis inaccuracies can occur without appropriate data confidence measures in place. To ensure an accurate analysis of waterway nutrients, the following data confidence procedures need to be carried out for all nutrient monitoring.

The following section provides information that should be referred to when undertaking phosphorus and nitrogen sampling (adapted from Standards Australia & Standards New Zealand 1998; Wruck & Ferris 1997; ANZECC & ARMCANZ 2000a).

Nutrient sampling procedure

1. Remove the lid from the grab sample bottle or bucket, taking care not to touch the inside of the lid, bottle or bucket. Contact with fingers can contaminate the sample so it is recommended that gloves be worn.
2. If necessary, clear any surface scum or floating matter carefully using the underside of the sample container (the sample must be representative of the waterway, not the scum or floating matter).
3. Invert the container as it enters the water. Air pressure in the container prevents non-representative surface waters from entering the container.
4. Once you reach the desired depth, turn the bottle opening upstream and allow the container to fill completely.
5. Use only one hand to take the sample. Keep your hands away from the opening of the sample container.
6. Rinse the lid in sample water, replace it, and then shake the container.
7. Reopen the container and discard the contents downstream.
8. Complete this rinsing process three times before taking a final grab sample ready for sample extraction.

If you plan to transfer the sample to other containers, ensure that these containers have also been rinsed three times with sample water.

To transfer water from one container to another, always pour the sample from the sampling container into the receiving container. Never submerge a receiving container into the sample bucket, as this will cause contamination.

Using a syringe filter

1. Once the sample container has been rinsed three times and the grab sample is taken, remove water from the sample container using the syringe, taking care to keep fingers away from the syringe tip.
2. Rinse the syringe three times, ensuring that the water in the syringe is not discarded back into the sample container.
3. Use the syringe to take a 60–100 mL sample (an aliquot) of water from the container.
4. Remove the protective cover from the single-use 0.45 µm filter and place the filter on the end of the syringe, taking care not to touch the ends of the filter with your fingers. When sample waters have a high suspended solids content, a glass fibre pre-filter can be added between the 0.45 µm filter and the syringe to slow clogging of the 0.45 µm filter with sediments.
5. Deliver a 10 mL portion of filtered water into the 150 mL filtered nutrient bottle. Replace the lid, and then shake the bottle to rinse.
6. The rinse water is then discarded and the remaining 50–90 mL portion of filtered water from the syringe is delivered to the 150 mL filtered nutrient bottle. If the filters clog up before the 50 mL sample is delivered into the bottle, a new set of filters must be placed on the syringe before continuing. This is to ensure that a large enough sample is collected for the laboratory to use in the analysis.
7. Replace the lid on the filtered nutrients bottle, screwing it down as hard as possible. If the lid is not tightly secured, water may contaminate the sample by entering the sample bottle.

8. Place the sample in an esky under crushed ice. As ice cools the bottle, it will contract, creating the potential for water to be drawn into the bottle and contaminate the sample if the lid is not tightly secured.
9. Discard the leftover water in the grab sample bucket and replace the bucket's lid, ready for reuse.
10. Remove and discard the filter from the end of the syringe, taking care not to contaminate the end of the syringe with fingers.

After sampling

Once all the samples are collected, the nutrient bottles should be stored in ice slurry and frozen within 24 hours. Leave at least 25 mm of air space in the sample container to allow for the water to expand when frozen. The freezer should only hold nutrient samples, to minimise cross-contamination from food products in the freezer.

The recommended time for samples to be stored prior to analysis is up to one month.

Do not store nutrient samples with those collected for metal analyses. The preservative used for metal analysis contains nitric acid, which may contaminate nutrient samples.

Data confidence for nutrient laboratory analysis

Quality control procedures

The following quality control procedures must be observed in the field:

- Field sampling needs to be conducted in accordance with AS/NZ 5667.1:1998 (Standards Australia & Standards New Zealand 1998). The nutrient sampling procedure on page 5–73 can be used as a guide for nutrient sampling and collection.
- Field data sheets must provide details of the date and time of collection, environmental and climatic conditions, nature of pre-treatment, preservation technique, location of site, sample type being collected, person undertaking the sampling, and any other conditions that may influence the sample.
- Sample containers must be labelled clearly and adequately. Include the date of sample, name of sampler, location and site details, preservation technique, and type of parameter to be analysed.

The following quality control procedures must be observed for laboratory analysis:

- The laboratory must be NATA-accredited for laboratory analysis. The scope of accreditation must reflect the nutrient species (molecular type within each nutrient class), concentration and the water body being sampled.
- Laboratory-based quality control procedures—such as duplicates, calibration standards, reference materials, replicates, spikes and blanks—should be performed on all of the samples submitted.
- A split sample should be sent to a separate laboratory annually (or at the beginning and completion of each project). The results from these laboratories should conform to either one of these criteria:
  - The difference between the results is less than ±0.002 mg/L.
  - The relative per cent difference is less than 5%.
- The laboratory in question should be informed if they do not conform to at least one of these criteria to explain the origin of the discrepancy.
- A field blank should be taken and analysed annually (or at the beginning and completion of each project). If the result is greater than ±0.002 mg/L, the origin of the contamination must be determined and rectified.
- Laboratory reports must provide details about the results, including the procedure used and the units of measurement.

Participant competency required for sampling

Specific training in nutrient collection, storage and preservation protocols is recommended for all field monitors. Training can be justified due to the high cost of laboratory analysis and the potential for data loss and corruption of samples.

Calibration

The laboratory is responsible for calibrating and maintaining equipment to appropriate standards.

Maintenance

All field sampling equipment and safety gear is to be maintained as required and kept in good condition. Do not use detergent to clean these items.

Quality control checks

Establish appropriate acceptance criteria and support these with the use of a quality control chart.

Data confidence for nutrient colorimetry test kits

Quality control procedures

- Follow to the nutrient sampling procedure on page 5–73 to collect a sample.
- Ensure that field data sheets provide details of the date and time of collection, general environmental and climatic conditions, nature of pre-treatment, preservation technique, location of site, sample type being collected, person undertaking the sampling, and any other conditions that may have affected the sample.
- Check whether the results fall within the required range. State the action taken if results are out of the required range and describe how the data is tagged to make the data user aware of this.
- Document all procedures and results using field sheets, calibration and maintenance logs.
- Include at least one check sample to verify that equipment and reagents are working within the specified limits. The check sample needs to reflect the concentration and water body type being analysed.

Participant competency

For **indicative** data, the coordinator and samplers should complete formal training in nutrient collection, storage and preservation protocols.

For **demonstrative** data, only the coordinator is required to undertake informal or formal training in nutrient collection, storage and preservation protocols.

Calibration

Field kits are factory-calibrated. Calibration checks need to be conducted to ensure that equipment is operating effectively and that reagents are not off. For **indicative** data, check for contamination by calibrating sample bottles with a reagent blank (deionised water) in the colorimeter before each sampling run.

Check or calibrate equipment every time on use against:

- a blank—the error for the blank should be no more than ±0.015 mg/L
- a low-range standard—the error for the low-range standard should be no more than ±0.05 mg/L
- high-range standard—the error for the high-range standard should be no more than ±10%
- equipment-specific maintenance and calibration records.

For **demonstrative** data, perform a quarterly check of colorimetric equipment against blank, low-range and high-range standards if possible. There is no set TER.

Maintenance

- Keep colorimetric equipment clean by following manufacturer's instructions.
- Maintain colorimetric equipment as necessary and keep maintenance logs.
- Keep all field sampling equipment and safety gear in good condition, and maintain as required.
- Keep sampling buckets, bottles, filtering equipment and eskies clean. Do not use detergent to clean these items, as it can be a source of contamination.

Quality control checks

Establish appropriate acceptance criteria and support these with the use of a quality control chart where appropriate.

For **indicative** data:

- conduct a replicate test on 10% of the samples. The results should fall within the designated TER (for example, ±50%)
- have a duplicate sample tested by a professional water quality officer or laboratory early in the monitoring program. The difference between the values of the duplicate samples needs to be within the TER
- continue periodic external checks by participating in shadow-testing workshops.
- undertake inter-operator comparisons during each sampling event.

Nitrogen

Importance of nitrogen

Nitrogen makes up about 78% of the atmospheric volume as the inert N_2 gas. Nitrogen is the fourth most common element found within living organisms—after carbon, hydrogen and oxygen—and is crucial for many biological processes. The inert (stable) nature of the N_2 molecule results in little atmospheric nitrogen becoming available in a form that is useable for biological uptake within waterways, where it is essential for biological growth.

Forms of nitrogen that can be taken up for biological activity include nitrate (NO_3), nitrite (NO_2) and ammonium (NH_3 and NH_4). Nitrate and ammonium are the most bio-available forms of nitrogen found in waterways. As nitrates and ammonium do not evaporate, they are likely to remain in the waterway until consumed by biota. Therefore both nitrates and ammonium are often responsible for nuisance plant growth.

Most nitrogenous materials that occur in natural waterways tend to be converted to nitrate, so all sources of combined nitrogen (including organic nitrogen and ammonium) should be considered potential sources of nitrate.

Nitrite, like nitrate, does not evaporate and tends to remain in a waterway until consumed by plants or animals. High concentrations of nitrite are potentially toxic to humans and animals

Ammonium is a product of the decomposition of organic waste. It can be used as an indicator of the amount of organic matter within a waterway. Ammonia (NH_3) is toxic to aquatic biota at high levels, and increases in concentration when dissolved oxygen concentrations are low. However, when pH levels are high, NH_3 concentrations increase. Ammonium (NH_4) is the form of nitrogen most readily assimilated by plants but is potentially toxic to aquatic animals. When pH levels are low, NH_4 levels increase.

Natural entry of these biologically significant forms of nitrogen into a waterway includes:

- weathering of nitrogen-rich minerals
- nitrogen fixation by bacteria and cyanobacteria
- lightning reacting with atmospheric nitrogen precipitated in rain.

Unnatural entry of biologically significant forms of nitrogen into a waterway includes:

- manure from livestock
- sewage discharge.

Monitoring nitrogen and phosphorus provides insight into whether there are risks of algal blooms occuring. Nitrogen, along with phosphorus and carbon, is an essential element for organism growth—in particular, aquatic algae and plants. Under natural conditions, populations are regulated by the limited supply of nitrogen available. However, if nitrogen within a waterway exceeds natural levels, algal blooms and nuisance plant growth may be triggered.

Water quality impacts associated with algal blooms include:

- an initial increase in dissolved oxygen due to additional photosynthesis, then dramatic decreases as the bloom eventually breaks down and is consumed by bacteria
- altered pH
- altered water temperature
- increased turbidity (reduced water clarity)
- changed flow characteristics.

Unlike phosphorus, nitrogen readily dissolves into water and does not bind easily to soils. Ammonium in particular is very soluble, but often undergoes oxidisation and becomes nitrate. Nitrates can pose contamination problems in groundwater and, in very high concentrations, can contribute to methaemoglobinaemia in infants. Methaemoglobinaemia is a blood disorder characterised by the presence of a higher-than-normal level of methaemoglobin (a form of haemoglobin that does not bind oxygen) in the blood. Nitrates accelerate the rate of methaemoglobin formation, which is how very high nitrate levels can induce the disease.

For this reason, a limit of 11.29 mg/L as nitrogen has been set on drinking water (NHMRC & NRMMC 2004). Nitrite (NO_2) is known to form carcinogenic compounds (nitrosamines) when in acidic conditions.

Another difference between nitrogen and phosphorus is that nitrogen does not follow a one-way path to the endpoint of flow (usually the ocean) as phosphorus does. Instead, it cycles between a variety of forms within the waterway. Nitrite, the ammonium ion and ammonia (NH_3) can be nitrified back to nitrate, which, in turn, can be denitrified and volatilised back into the atmosphere as N_2 gas. Please refer to Figure 5–15 for an explanation of the nitrogen cycle.

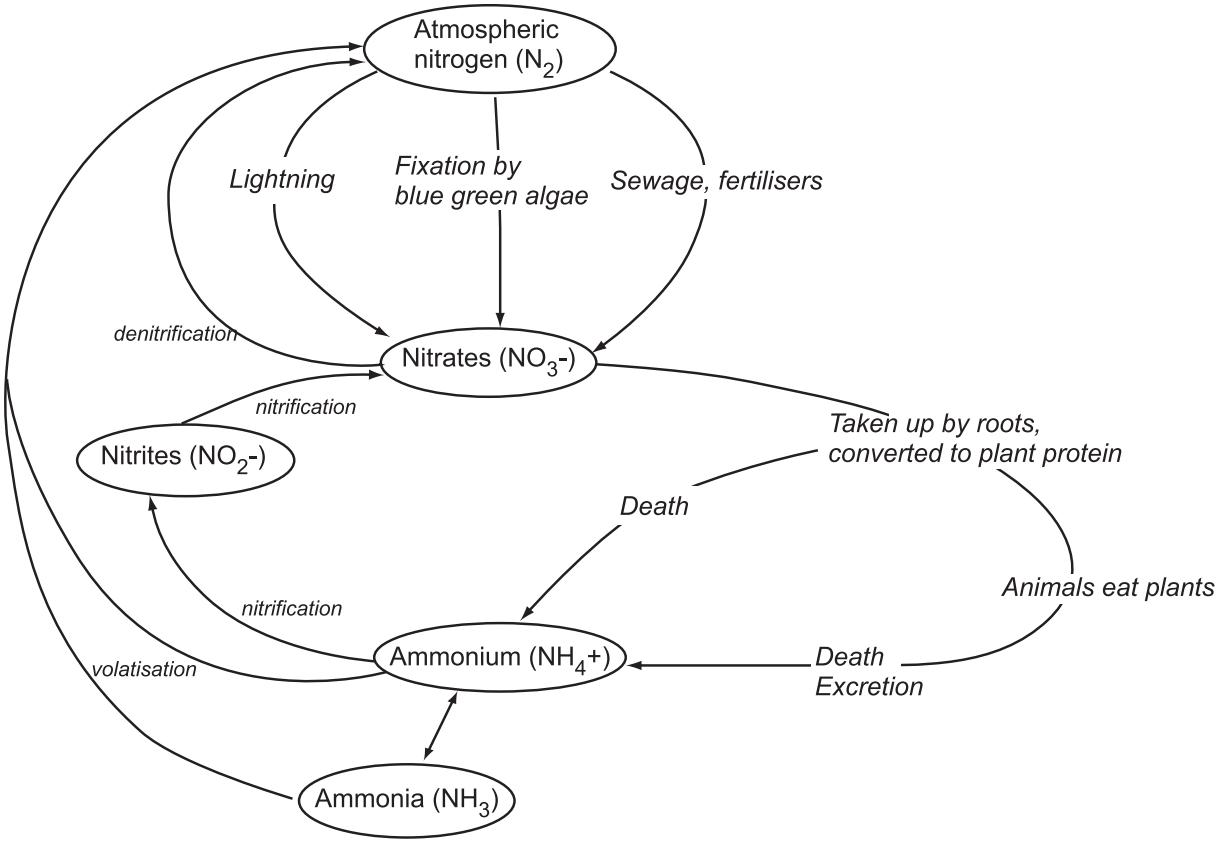


Figure 5–15 The nitrogen cycle (Cassidy 2003)

Factors affecting nitrogen

Normal levels of nitrogen are vital to maintain a natural population of aquatic organisms inhabiting a water body. Factors influencing these concentrations include:

- rock type and geology
- soil types
- vegetation
- climatic and seasonal factors
- organic decomposition.

However, concentrations are often increased due to human activities. Activities that accelerate the entry of nitrogen into a waterway include:

- soil disturbance through farming and urbanisation
- fertiliser application
- industrial discharges
- automobile emissions
- fossil fuel burning
- wastewater treatment release
- manure from livestock and urban pets.

Monitoring considerations

Many everyday items are high in nitrogen. Food, cigarettes, detergents and sunscreens are examples of such items. Care should be taken not to transfer contaminants from hands to a test sample. Never touch the water sample, and use buckets, bottles and vials that are both cleaned and rinsed. To avoid contamination, use the following procedures for monitoring and equipment:

- When cleaning buckets, bottles and vials, never use detergents.
- Never store food or fish products near samples that are to undergo nitrogen analysis.
- Rinse sample buckets with the sample water at least three times before taking a grab sample.
- Clean and rinse containers used to store water samples (for laboratory analysis) as per the laboratory's specifications.
- Dedicate all glassware and sampling containers to the analysis of a particular parameter—for example, ammonium. This reduces the risk of cross-contamination, and minimises the need for extra rinsing and the use of reagents.

Table 5–22 Summary of the common measurable forms of nitrogen

Form of nitrogen	Information and steps for measurement
Nitrite NO_2	Can be measured directly using cadmium reduction (minus the reduction step), colorimetric (reddish-purple azo dye) and UV direct methods.
Nitrate NO_3	Nitrate is usually determined by subtracting the nitrite test result from the NO_x test result. Therefore a NO_x test and one of the nitrite tests are required to determine nitrate.
Oxides of nitrogen (NO_x)	Sum of nitrite and nitrate. Can be measured directly using dimethylphenol, nitrate electrode, cadmium reduction and chromotropic acid methods. Many test kits often refer to their NO_x kits as nitrate kits. In most environmental situations, oxygen is in excess; hence the majority of NO_x will be NO_3. Nitrate and Nitrite readily interchange in the natural environment. Therefore, a NO_x test is a good test method for reporting nitrogen directly available for biological uptake.
Ammonia (NH_3)	Ammonia is produced primarily through the breakdown of animal and vegetable wastes. It can be measured directly using salicylate, Nessler, phenate and ammonia selective electrode methods.
Total Kjeldahl nitrogen (TKN)	Total Kjeldahl nitrogen is the sum of organic nitrogen plus ammonia in a water body. Kjeldahl nitrogen can be determined by conducting the macro-Kjeldahl or semi-micro-Kjeldahl method.
Organic nitrogen	Analytically, organic nitrogen can be determined by conducting a Kjeldahl nitrogen test and an ammonia test and then subtracting the ammonia test result from the Kjeldahl nitrogen test result.
Total nitrogen (TN)	Total nitrogen can be determined by oxidising all forms of nitrogen to nitrate using the simultaneous persulfate digestion method. In theory, conducting a TKN and NO_x test and adding the results can also determine total nitrogen; however, this practice is not recommended due to the compounding of errors and interferences when running multiple sets of analyses. Total nitrogen is the test required for the calculation of load-based estimates.

Samples of soluble nutrients need to be filtered in order to remove particulate matter and minimise the adsorption and biological uptake of biologically available nitrogen from the sample. Filtration should occur when testing for ammonia, nitrite and nitrate for both field kits and lab samples. If water is not filtered, speciation (the formation of different nitrogen-containing compounds) cannot occur. Unfiltered nitrogen samples are only suitable for the analysis of total nitrogen. Refer to the nutrient sampling procedure on page 5–73 for further details on water sampling.

Different tests have been developed to react with different forms of nitrogen. Table 5–22 provides information on the different forms of nitrogen and the steps required to measure each form.

Of the above forms, oxides of nitrogen (NO_x), ammonia (NH_3) and total nitrogen (TN) are the most relevant forms of nitrogen for community-based waterway monitoring.

NO_x can be used to indicate the level of nitrogen directly available to biological activity in a waterway, and as an environmental health indicator concerning the illness of methaemoglobinaemia.

Ammonia can be used to indicate the level of nitrogen directly available for biological activity, and is especially useful in indicating the success of sewage treatment plants.

Total nitrogen indicates the total nitrogen potentially available in a water sample. Total nitrogen is the form typically used for determining total load-based estimates in flowing waterways.

Monitoring methods

Monitoring nitrogen can be difficult, as it usually involves measuring very low concentrations, down to 0.01 mg/L or lower. Changes at very low concentrations of nitrogen—for example, from 0.01 to 0.02 mg/L—can still have a significant impact on waterways.

When monitoring nitrogen, you should direct special attention towards the unit of measurement being used, particularly when comparing data to guideline values. For example, a large number of nutrient test kits measure all nitrogen oxides (NO_x) as NO_x, while the *Queensland water quality guidelines* and ANZECC and ARMCANZ (2000b) record values of NO_x as N (nitrogen) in their guidelines. To compare NO_x as NO_x values with NO_x as N values, the data needs to be converted to the same unit of measurement. Similar precautions need to be taken when testing for ammonia. Be aware of whether your values are in milligrams per litre (mg/L) or micrograms per litre (µg/L). Again, it is inappropriate to compare values of differing units of measurement, so you must convert all values to the same unit of measurement. To be certain of your units of measurement when using a field test kit, refer to the manufacturer's instructions. For details on how to convert different units of measurement, refer to the conversion advice below.

1 mg/L of (NO_3) nitrate as nitrogen (N)
= 4.43 mg/L of nitrate as nitrate

1 mg/L of (NO_2) nitrite as nitrogen (N)
= 3.29 mg/L of nitrite as nitrite

1 mg/L of (NH_3) ammonia as nitrogen (N)
= 1.21 mg/L of ammonia as ammonia

1 mg/L of (NH_4) ammonium as nitrogen (N)
= 1.29 mg/L of ammonium as ammonium

1 mg/L = 1000 µg/L

Which monitoring equipment you need depends on whether you will be:

- undertaking field colorimetry (using a comparator, photometer or spectrophotometer) or
- undertaking the analyses in a laboratory.

Colorimetry

Potentially, field colorimetric kits can collect intermediate water quality data for oxides of nitrogen (NO_x) and ammonia (NH_3). For field colorimetry, samples should be filtered before analysis to reduce interferences from turbid or coloured water. In some instances, a background correction may be effective on unfiltered samples. Higher-quality data requires the use of a laboratory when measuring these forms of nitrogen.

Total nitrogen should be determined in the laboratory, as samples require digestion in order to oxidise hydrolysis samples to NH_4 or NO_3.

Interpreting your results

The right way to interpret your data depends on the objectives of your monitoring program. Chapter 8 of this manual provides information and advice on data interpretation for a range of common monitoring objectives.

If you are conducting routine monitoring to assess waterway health, or you want to determine the suitability of the water for a specific use, your results should be compared with the relevant guidelines. See Chapter 8 for information on how to compare your results with guideline values.

Guidelines have been established to suit a range of different monitoring objectives. The *Queensland water quality guidelines* (Environmental Protection 2006) and the *Australian and New Zealand guidelines for fresh and marine water quality* (ANZECC and ARMCANZ 2000b) include guideline values for the protection of aquatic ecosystems. Table 5–23 shows the regional nitrogen guideline values, from the Queensland guidelines, for aquatic ecosystem protection and aquaculture. Before using these guidelines it is essential to consider the region and type of water body in which you are monitoring. Definitions of the regional boundaries and water body types are contained in the guidelines.

Table 5–23 Guideline nitrogen values for fresh waters in Queensland (adapted from Environmental Protection Agency 2006)

For protection of aquatic ecosystems					
Water body type	**Region**	**NH_4 (mg N/L)**	**NO_x (mg N/L)**	**Organic nitrogen (mg N/L)**	**TN (mg N/L)**
Lowland streams	South East Qld	0.02	0.06	0.42	0.5
	Central Coast	0.02	0.06	0.42	0.5
	Wet Tropics	0.01	0.03	0.2	0.24
Upland streams	South East Qld	0.01	0.04	0.2	0.25
	Central Coast	0.01	0.015	0.225	0.25
	Wet Tropics	0.006	0.03	0.125	0.15
Lakes and reservoirs	South East Qld	0.01	0.01	0.33	0.35
	Central Coast	0.01	0.01	0.33	0.35
	Wet Tropics	0.01	0.01	0.33	0.35

Other uses						
Water use	**Sub-use**	**Total ammonia**	**NH_3**	**NO_3**	**NO_2**	**Comments**
Agriculture	Tropical aquaculture	< 1.0 mg N/L	< 0.1 mg N/L	1–100 mg N/L	< 0.1 mg N/L	Optimal levels vary for individual fish species

Table 5–24 Nitrogen trigger values (mg N/L) for ecosystem protection (ANZECC & ARMCANZ 2000b)

	South-east Australia			Tropical Australia		
Ecosystem type	**TN**	**NO_x**	**NH_4**	**TN**	**NO_x**	**NH_4**
Upland rivers	0.25	0.015	0.013	0.15	0.03	0.006
Lowland rivers	0.50	0.04	0.02	0.2–0.3	0.01	0.01
Freshwater lakes	0.35	0.01	0.01	0.35	0.01	0.01
Wetlands	No data			0.35–1.20	0.01	0.01
Estuaries	0.30	0.015	0.015	0.25	0.03	0.015

The *Queensland water quality guidelines* (Environmental Protection Agency 2006) also outline more specialised subregional guidelines for water bodies in the Douglas, Gold Coast hinterland, Fraser Island and North Stradbroke Island catchments. Where subregional or regional guidelines are unavailable (such as for Eastern Cape York, Gulf Rivers, Lake Eyre and Murray–Darling), refer to the *Australian and New Zealand guidelines for fresh and marine water quality* (ANZECC & ARMCANZ 2000b). The ANZECC and ARMCANZ nitrogen trigger values for ecosystem protection are shown in Table 5–24. Trigger values are provided for total nitrogen (TN), oxides of nitrogen (NO_x) and ammonium (NH_4) concentrations.

You can also develop your own local guideline values using the information provided in Chapter 8.

For other monitoring objectives, refer to the guideline references section at the end of this chapter for the relevant guidelines.

Health and safety

The following health and safety requirements are specific to methods for monitoring nitrogen:

- Take some clean water with you for washing down chemical spills on your skin and clothes.
- Have a squirt-bottle ready to wash down eyes in case of chemical exposure.
- Use methods that minimise your possible contact with chemicals.
- To avoid contamination and contact with possible toxic chemicals, never put your thumb over the test tubes when you shake or swirl them.
- Never pipette with your mouth; always use a pipette bulb.
- Use goggles and gloves when handling reagents.
- Hold all test bottles over a wide-mouthed liquid waste bottle while adding the liquid and powder reagents.
- After each piece of used equipment has been rinsed with distilled water, pour the rinse water into the liquid waste bottle.

See the *Health and safety guidelines for community-based waterway monitoring* (Department of Natural Resources and Water 2006) for further information.

Table 5–25 Methods guide for nitrogen

	Oxides of nitrogen (NO_x)						Ammonia (NH_3)						Total nitrogen (TN)					
	Laboratory analysis			Colorimetry			Laboratory analysis			Colorimetry			Laboratory digestion and analysis			Colorimetry		
Data quality	K and S	Time (days)	Cost ($)	K and S	Time (days)	Cost ($)	K and S	Time (days)	Cost ($)	K and S	Time (days)	Cost ($)	K and S	Time (days)	Cost ($)	K and S	Time (days)	Cost ($)
Analytical	Expert advice	5–20	14–20				Expert advice	5–20	14-30				Expert advice	5–20	27–55			
Indicative				Expert advice	20–40	1700–3000				Expert advice	20-40 mins	1700–3000				Expert advice	40–60	700–3000
Demonstrative				Some exp.	15–35	$100-130				Some exp.	15-35 mins	100–130				Some exp.	25–50	100–130

Colorimetry (spectrophotometer/ photometer/comparator) —NO_x

Summary

In this method:

- oxides of nitrogen (NO_x) are measured (mg/L as nitrogen)
- reagents react with the water sample to form a red colour, which represents the amount of NO_x present
- the colour is matched against a spectrum to determine the concentration of nitrogen oxides.

Spectrophotometers and photometers measure the amount of light transmitted or absorbed at a nominated wavelength. They are best used at sites where the expected concentrations of NO_x are relatively low (down to 0.02 mg/L).

Comparators are appropriate for monitoring sites with expected high concentrations of NO_x (greater than 0.1mg/L), including stormwater, run-off in urban streams and waste water treatment outfalls.

A NO_x test is a good test method for reporting nitrogen directly available for biological uptake, as nitrite and nitrate readily interchange in the natural environment.

Equipment

You will need:

- field sampling equipment as listed in the overview section of this chapter
- a 100 mL plastic bottle (washed in water only, not detergent) if samples are not to be analysed in the field
- an esky with ice or a refrigerator to keep samples cool if samples are not to be analysed in the field.

To produce **indicative** data, you will need a photometer or spectrophotometer capable of measuring oxides of nitrogen using a chemical methodology suitable for the water being tested. The instrument accuracy should be ±0.02 mg/L.

To produce **demonstrative** data, you will need a comparator, photometer or spectrophotometer capable of measuring NO_x using a chemical methodology suitable for the water being tested.

Note: Many test kits often refer to their NO_x kits as nitrate kits.

Monitoring method

1. Follow the nutrient sampling procedure on page 5–73. Take the sample in a 100 mL plastic bottle that has not been washed in detergent. Refrigerate immediately.
2. To perform colorimetry, follow the manufacturer's instructions.
3. Calculate the sum of nitrite and nitrate. This can be measured directly using dimethylphenol, nitrate electrode, cadmium reduction and chromotropic acid methods.

Data confidence procedures

Refer to the section 'Data confidence for nutrient colorimetry analysis'.

Laboratory analysis—NO_x

Summary

In this method:

- oxides of nitrogen (NO_x) are determined (mg/L as nitrogen)
- a water sample is collected and transported to a NATA-accredited laboratory for analysis following AS/NZS 5667.1:1998 procedure (Standards Australia & Standards New Zealand 1998)
- the sample is analysed by the laboratory.

A NO_x test is a good method for reporting nitrogen directly available for biological uptake, as nitrite and nitrate readily interchange in the natural environment.

Equipment

You will need:

- field sampling equipment as per the list on page 5–9
- a 100 mL plastic bottle washed in water only, not detergent
- an esky with ice or a refrigerator to keep samples cool.

The laboratory must be NATA-accredited for nitrogen analysis. The chemical methods used must be suitable for the water being tested.

Monitoring method

1. Follow the nutrient sampling procedure on page 5–73.
2. Refrigerate samples immediately and freeze within 24 hours. Frozen samples may be stored for up to one month prior to analysis.
3. Calculate the sum of nitrite and nitrate. This can be measured directly using the dimethylphenol, nitrate electrode, cadmium reduction or chromatographic methods.

Data confidence procedures

Refer to the section 'Data confidence for nutrient laboratory analysis'.

Laboratory analysis—NH_3

Summary

In this method:

- ammonia (NH_3) is measured (mg/L as nitrogen)
- a water sample is collected and transported to a NATA-accredited laboratory for analysis following AS/NZS 5667.1:1998 (Standards Australia & Standards New Zealand 1998) procedure
- the sample is analysed by the laboratory.

Ammonia is produced primarily through the breakdown of animal and vegetable waste, and adsorb to (collects on the surface of) soil particles readily. Ammonia can be measured directly using salicylate, Nessler, phenate and ammonia selective electrode methods.

Equipment

You will need:

- field sampling equipment as listed in the overview section of this chapter
- a 100 mL plastic bottle washed in water only, not detergent
- 0.2 or 0.45 micron membrane filter apparatus (if filtering the sample)
- an esky with ice or a refrigerator to keep samples cool.

The laboratory must be NATA-accredited for nitrogen analysis. The chemical method used must be suitable for the water being tested.

Monitoring method

1. Follow the nutrient sampling procedure on page 5–73. Collect the sample in a 100 mL plastic bottle that has not been washed in detergent.
2. Refrigerate immediately, and freeze for up to one month.
3. Send to the laboratory for analysis.

Data confidence procedures

Refer to the section 'Data confidence for nutrient laboratory analysis'.

Colorimetry (spectrophotometer/ photometer/comparator) —NH_3

Summary

In this method:

- reagents react with the water sample to form a blue colour, which represents the amount of nitrogen present
- the colour is matched against the spectrum to determine ammonia in milligrams per litre (mg/L) of nitrogen.

Spectrophotometers and photometers measure the amount of light transmitted or absorbed at a nominated wavelength. They are best used at sites where the expected concentrations of ammonia are relatively low (down to 0.02 mg/L).

Comparators are appropriate for monitoring sites with expected high concentrations of ammonia (greater than 0.1 mg/L), including stormwater, run-off in urban streams, and waste water treatment outfalls.

Ammonia is produced primarily through the breakdown of animal and vegetable waste and adsorbs to (collects on the surface of) soil particles readily. It can be measured directly using salicylate, Nessler, phenate and ammonia selective electrode methods.

Equipment

You will need:

- field sampling equipment as listed in the overview section of this chapter
- a 100 mL plastic bottle (washed in water only, not detergent) if samples are not to be analysed in the field
- a 0.2 or 0.45 micron membrane filter apparatus
- an esky with ice or refrigerator to keep samples cool if samples are not to be analysed in the field.

To produce **indicative** data, you will need a photometer or spectrophotometer capable of measuring ammonia using a chemical methodology suitable for the waters being tested. The instrument accuracy should be ±0.02 mg/L.

To produce **demonstrative** data, you will need a comparator, photometer or spectrophotometer capable of measuring ammonia using a chemical methodology suitable for the waters being tested.

Monitoring methods

1. Follow the nutrient sampling procedure on page 5–73. Take the sample in the 100 mL plastic bottle.
2. Use a 0.2 or 0.45 micron membrane filter apparatus.
3. Refrigerate the sample immediately. Freeze for up to one month.
4. Follow the manufacturer's instructions to perform colorimetry.

Data confidence procedures

Refer to the section 'Data confidence for nutrient colorimetry analysis'.

Colorimetry (spectrophotometer/ photometer/comparator) —TN

Summary

In this method:

- total nitrogen is measured in milligrams per litre (mg/L)
- reagents react with water sample to form a blue colour, which represents the amount of nitrogen present. The colour is matched against the spectrum to determine mg/L of nitrogen.

Spectrophotometers and photometers measure the amount of light transmitted or absorbed at a nominated wavelength. They are best used at sites where the expected concentrations of total nitrogen are relatively low (down to 0.02 mg/L).

Comparators are appropriate for monitoring sites with expected high concentrations of total nitrogen (greater than 0.1 mg/L), including stormwater, run-off in urban streams and waste water treatment outfalls.

Total nitrogen is the test required for calculating load-based estimates.

Equipment

You will need:
- field sampling equipment as listed in the overview section of this chapter
- 250 mL plastic bottle (washed in water only, not detergent) if samples are not to be analysed in the field
- an esky with ice or a refrigerator to keep samples cool if samples are not to be analysed in the field.

To produce **indicative** data, you will need a photometer or spectrophotometer capable of measuring total nitrogen using a chemical methodology suitable for the waters being tested. The instrument accuracy should be ±0.2 mg/L.

To produce **demonstrative** data, you will need a comparator, photometer or spectrophotometer capable of measuring total nitrogen using a chemical methodology suitable for the waters being tested.

Monitoring methods

1. Follow the nutrient sampling procedure on page 5–73. Collect the sample in the 250 mL plastic bottle and refrigerate immediately.
2. Follow the manufacturer's instructions to perform colorimetry. Total nitrogen can be determined by completing digestion of all forms of nitrogen to nitrite using the simultaneous persulfate digestion or oxidation method.

In theory, conducting a TKN and NO_x test and adding the results can also determine total nitrogen. This practice is not recommended, however, due to the compounding of errors and interferences caused by running multiple sets of tests.

Data confidence procedures

Refer to the section 'Data confidence for nutrient colorimetry analysis'.

Laboratory analysis—TN

Summary

In this method:
- total nitrogen is measured in milligrams per litre (mg/L)
- a water sample is collected and transported to a NATA-accredited laboratory for analysis following AS/NZS 5667.1:1998 procedure
- the sample is analysed by the laboratory.

Total nitrogen is the test required for calculating load-based estimates.

Equipment

You will need:
- field sampling equipment as listed in the overview section of this chapter
- a 250 mL plastic bottle washed in water only, not detergents
- an esky with ice or refrigerator to keep samples cool.

The laboratory performing the tests must be NATA-accredited for nitrogen analysis. The chemical methodology used must be suitable for the water being tested.

Monitoring methods

1. Follow the nutrient sampling procedure on page 5–73. Collect the sample in the 250 mL plastic bottle and refrigerate immediately. Freeze for up to one month.
2. Send the sample to the laboratory for analysis.

Total nitrogen can be determined by completing digestion of all forms of nitrogen to nitrite using the simultaneous persulfate digestion or oxidation method.

In theory, conducting both the total Kjeldahl nitrogen (TKN) and NO_x tests and adding the results can also determine total nitrogen. This practice is not recommended, however, due to the compounding of errors and interferences caused by running multiple sets of tests.

Data confidence procedures

Refer to the section 'Data confidence for nutrient laboratory analysis'.

Phosphorus

Importance of phosphorus

Phosphorus is a nutrient that is widely distributed in many rocks, soils and living organisms. Its relative scarcity in the aquatic environment is a result of its low solubility and the tendency for dissolved phosphorus to bind with soil particles suspended in the water column. When the particles settle, the phosphorus bound to the suspended soil is buried in bottom sediments, leaving the water relatively devoid of phosphorus. This tends to limit the growth of algae and other biological organisms that require phosphorus for function and growth.

Unlike nitrogen and carbon, phosphorus has no gaseous form present in the atmosphere. Therefore, entry of phosphorus into the water column is via phosphorus-bearing sediments, animal wastes or decomposing organic material falling, washing or blowing into the waterway. It is also re-released into the water column from bottom sediments due to disturbances such as high flows or anoxic conditions.

Pure, 'elemental' phosphorus (P) is rare in nature. The phosphorus found in surface and groundwater is usually phosphate (PO_4^{3-}). Phosphate types include:

- orthophosphates (inorganic phosphates)—the simplest form of phosphate, with a chemical symbol of PO_4^{3-}. As orthophosphate is not bound to any carbon molecules or to other phosphates in the form of a condensed phosphate, it is immediately available for biological uptake. Orthophosphates are found in detergents and fertilisers, and are in the form required by plants and algae for growth
- organic phosphates, which are bound to carbon molecules. Organic phosphates can be found in the tissue of plants and animals. As a result of being bound to carbon molecules, organic phosphates are not directly available for biological uptake; however, they can be broken down through bacterial decomposition and through chemical digestion
- condensed phosphates—chains of two or more orthophosphate groups that are linked together. Forms include metaphosphate, pyrophosphate and polyphosphate. Condensed phosphates are found in laundry and cleaning agents, and can be rapidly hydrolysed (broken up) into orthophosphate, which is then available for immediate biological uptake.

The large number of phosphate sources and the variety of routes that phosphate takes to a waterway make it difficult to pinpoint and manage sources of phosphate enrichment. Natural sources of phosphorus include:

- soil
- phosphate-containing rocks
- animal wastes
- decomposing plants.

Effects on water quality

In pristine water bodies, naturally low levels of phosphate limit the growth of aquatic plants. A sudden increase in phosphorus can stimulate great increases in aquatic plants (macrophytes) and algae.

An algal bloom may cause an initial increase in dissolved oxygen (due to increased photosynthesis), reduction in water clarity or increase in pH. Once the available phosphorous has been consumed, the algae die and are consumed by bacteria, ultimately decreasing levels of dissolved oxygen available to other organisms in the river system.

Increased phosphate levels may stimulate blue-green algal blooms, which lead to decreased clarity, pH changes, unpleasant odours and, potentially, the production of toxins. Consumption of these toxins may lead to death of stock or birth defects, and can inhibit the immune and nervous systems. Australia's largest recorded blue-green algal bloom occurred in the Darling River in 1991–92 and covered approximately 1000 km^2.

The addition of phosphate, particularly in warm climates, can lead to watercourses becoming choked with aquatic weeds. This impedes flow—which elevates temperature and changes other river characteristics—and causes physical disturbances. As with algae, the subsequent death and decay of nuisance plants leads to dramatically reduced oxygen concentrations and the further release of phosphates into the sediments. Rivers in this condition are described as *eutrophic*; the process of nutrient enrichment is *eutrophication*.

Increased nutrients in a river system can eventually affect receiving lakes, dams and even the ocean. Lakes are particularly susceptible to the effects of increased nutrient inputs, as the nutrients are not removed from the system. This may cause large increases in weed growth, lower oxygen levels or eutrophic conditions.

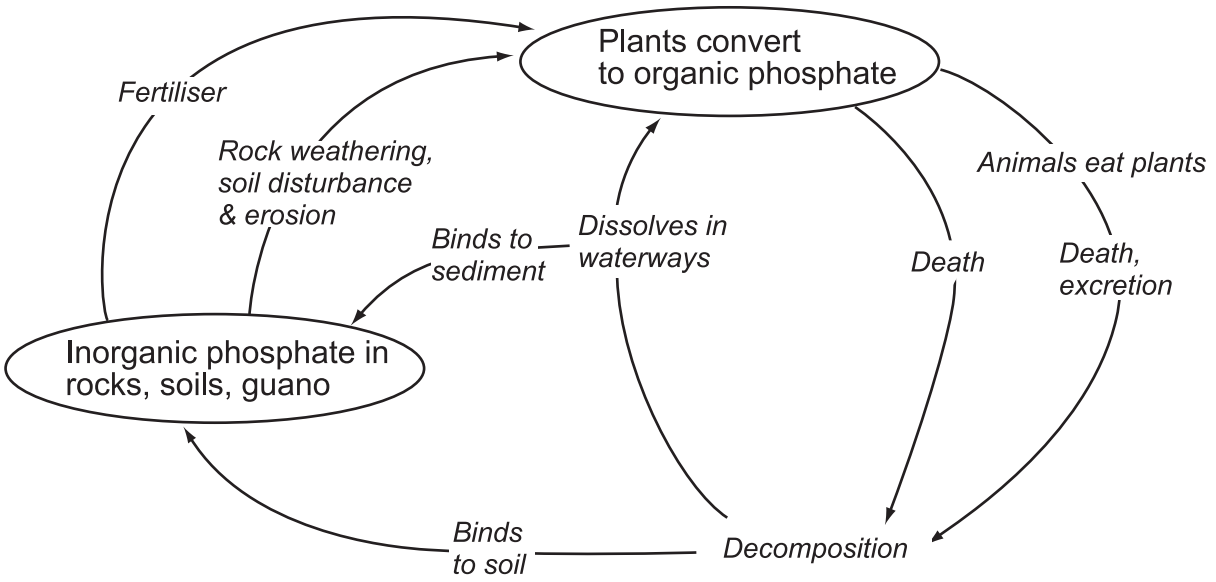


Figure 5–16 The phosphorus cycle (adapted from Behar 1997)

Phosphate concentrations generally do not pose a direct human or animal health risk unless they are present in very high concentrations, whereby they may interfere with digestion. Accordingly, phosphate concentrations are not directly regulated for drinking water.

Phosphorus cycles through the environment, changing form throughout. Aquatic plants take in inorganic phosphate and convert it to organic phosphate in their leaves and stems. Aquatic animals obtain organic phosphate by eating aquatic plants, animals, or decomposing plant and animal material.

When plants and animals excrete wastes or die, the organic phosphate that they contain sinks to the bottom of the water column. Bacterial decay converts the organic phosphate back to inorganic phosphate, which then moves back into the water column when the bottom is stirred up by animals, human activity, chemical interactions or water currents. It is again taken up by plants, and the cycle begins again (see Figure 5–16).

In a river system, phosphate tends to move downstream as the current carries decomposing plant and animal tissue and suspended phosphate. It becomes stationary only when it is taken up by plants or is bound to particles that settle to the bottom of the water column.

Factors affecting phosphorus

Factors that are likely to affect phosphorus concentrations include:

- rock type and geology
- soil types
- rates of erosion (bank, gully and rill erosion)
- climatic factors such as precipitation and wind
- flow rates and water levels
- human and animal wastes
- phosphate-containing fertilisers
- discharge from sewage treatment plants
- urban run-off.

Phosphate also comes from many human sources including human wastes, fertilisers and detergents, and landscape processes.

Organic phosphate from animal wastes can enter the river system in run-off from manure, storage areas, feedlots and farmyards. The main sources of organic phosphate in human waste are sewage treatment facilities, leaking septic systems or systems that are not properly maintained. Unless sewage treatment plants are specifically designed to completely remove phosphate, only a portion of the phosphate entering them is removed. Many sewage treatment plants have agreed limits as to how much phosphate can be discharged. Some industrial wastes that flow

through the plant with the sewage can interfere with phosphate removal. Storm activity can lead to phosphates entering waterways via raw sewage that may be discharged directly into waterways by overloaded treatment plants.

Phosphate-rich fertilisers enter waterways through run-off from fertilised lawns and cropland. Nearly all fertilisers contain orthophosphate. Most detergents and commercial cleaning preparations contain condensed phosphates. Water supply and boiler water treatment may also contribute condensed phosphates to the water cycle. In time, these condensed phosphates break down to orthophosphates. An increasing number of detergents have reduced phosphate content (0% to 10% phosphorus by weight).

Phosphate occurs naturally in the soil in dissolved and suspended forms bound to soil particles. Soil erosion from disturbed land introduces phosphate to the water when soil enters the river. Wetlands that are drained for development release phosphate that has accumulated in the sediment over time.

Due to the tendency of phosphorus to bind to sediments, it enters waterways in the same way as sediments. As a result, factors that influence erosion and suspended solid concentrations are also likely to influence phosphate concentrations. This capacity to bind with sediments also contributes to the general non-availability of phosphorus for biological processes and its dropping out of suspension and binding with bottom sediments.

If disturbed, however, these bottom sediments may contribute phosphorus back into the water column. Causes of disturbance include:

- high flow velocities, particularly associated with dam and weir operation
- physical and mechanical disturbance of bottom sediments—for example, by stock access, burrowing animals and human activities
- frequent variations in water height, such as in a dam or weir pool, where the effect of wave lapping leads to resuspension of sediments
- the production and release of sulfur dioxide among active bacteria within bottom sediments, which occurs under highly eutrophic conditions. This causes physical disturbance of sediments as the gas is released to the surface and creates the rotten gas smell associated with highly eutrophic waters
- stratification in water bodies, which can indirectly influence phosphate levels in the water by lowering pH and dissolved oxygen levels. Under these conditions, phosphate release from sediments increases
- the presence of high levels of some other chemicals, namely iron and manganese, which can also enhance the release of phosphate from sediments.

Monitoring considerations

Phosphorus can occur as a range of salts and other compounds. Orthophosphate (PO_4^{3-}) is formed by the combination of one atom of phosphorus and four atoms of oxygen and is the molecule that all phosphorus tests react with to produce a measurable coloured reaction in colorimetry.

Two measures of phosphorus are used on a regular basis. All test methods measure orthophosphate but allow different forms of phosphorus present in the water sample to be distinguished from each other. The different methods measure *filterable reactive phosphate* (FRP) or *total phosphorus* (TP).

Methods measuring FRP are the most accurate method for estimating phosphate concentrations available for biological uptake, and are recommended over those measuring *total reactive phosphorus* (TRP). The FRP test will provide a result on the amount of orthophosphate in a sample. However, due to the chemicals used to produce the colorimetric reaction, a small fraction of condensed phosphates are hydrolysed during the reaction. Data must therefore be expressed as FRP and not orthophosphate.

Filtering the water sample before analysis drastically reduces the overestimation associated with TRP. Another advantage of the filtration process is that the filtered sample is left virtually colourless (except in the case of tannin-stained water), so colorimetric instrument readings are less hampered by background colour readings.

The use of a 0.45 micron pore filter allows consistent separation of particle sizes but does not separate all suspended material from dissolved forms of phosphorus. The filter removes particulate matter from the sample, minimising sorption/adsorption and biological uptake from the sample. This reduces the overestimation of orthophosphate in the sample. The 0.45 micron membrane filters cost approximately $1.00 to $2.00 each and must be replaced after each sample to avoid

cross-contamination, or more frequently to avoid clogging when sampling highly turbid waters.

Undertaking a TP test indicates the total amount of inorganic, organic and particulate phosphorus in a water sample, both suspended and dissolved in the water. This is useful for characterising the water body and assessing catchment condition. TP values can be used in conjunction with flow rates to provide load-based estimates of phosphorus being transported downstream, but do not indicate the fraction of phosphorus that is available for direct biological uptake. This limits the value of TP as an indicator of ecological risk. TP concentrations are often many times higher than orthophosphate as P in the same sample.

The TP test involves digesting the sample using heat and acid to break down all phosphorus forms to orthophosphate. Because the sample is not filtered, the procedure measures both dissolved and particulate orthophosphate. Because of the digestion step, measuring TP is not easily carried out under field conditions. Because of the extra equipment, use of acid and much longer time required to complete a TP test, it should be considered appropriate for external laboratory analysis only. Take extreme caution when carrying out the TP test and disposing of waste from the reactions.

Many everyday items such as food and laundry detergent contain high concentrations of orthophosphate. When collecting and testing waters for phosphorus analysis, be aware of potential contamination from hands and fingers, and take care not to transfer contaminants to a test sample. Never directly touch the water sample or the buckets, bottles and vials that are to be used. Never store food or fish products near samples that are intended for phosphorus analysis.

Never use detergents when cleaning buckets, bottle and vials; they contain phosphorus, which will readily adhere to the sides of containers. Use the following procedures:

- Rinse sample buckets with the sample water at least three times before taking a grab sample.
- Clean and rinse containers used to store water samples ready for laboratory analysis as per the laboratory specifications.
- Rinse glassware that is used for in situ colorimetric analysis with tap-water three times. Next, rinse it with hydrochloric acid (1 to 2 molar in strength), and then rinse again with sample water three times before being filled with the water sample being tested. This process must be done before every new sample is tested.

Monitoring methods

Monitoring phosphate is challenging because it usually involves measuring very low concentrations, down to 0.01 mg/L or lower. Changes at very low concentrations of phosphate—for example, from 0.01 to 0.02 mg/L—can still have a significant impact on waterways.

You should first consider your reasons for testing for phosphate, and the levels that are likely to be found. For example, if you are monitoring for changes in phosphate concentrations in a catchment with background concentrations of 0.02 mg/L, an environmentally significant increase (2 mg/L) may not be detectable if the instrument you are using is not capable of taking readings at low levels.

Colorimetry

As a guide, a field colorimeter should have a minimum detection level of 0.05 mg/L and accuracy of within 50% of the true value. However, for many rivers, lakes and estuaries in near-natural catchments, environmentally significant changes in phosphate levels are very low. Low levels can be measured by sending a sample to a commercial laboratory for testing.

There are three major chemical methodologies used for measuring orthophosphate in a water sample:

- the vanadomolybdophosphoric acid colorimetric method
- the stannous chloride method
- the ascorbic acid method.

Test kit manufacturers will often modify these chemical methodologies slightly and each product should be examined carefully to gain a better understanding of the specific reactions and associated interferences of the kit. It is important to understand the typical range for each different chemical methodology. This will ensure that the right test can be chosen, taking into account the natural conditions of your local waterway.

Many ions, including salts, interfere with the vanadomolybdophosphoric acid colorimetric method and stannous chloride method. The ascorbic acid chemical methodology is recommended as the test of choice for most situations. However, you should be aware of the low range restrictions and colour interferences for this test.

All phosphorus tests use colorimetry to measure the proportion of phosphorus in a water sample. Therefore, turbid or coloured water has the potential to affect the accuracy of results. The effect of turbid water can be minimised by filtering the sample before analysis as with the FRP test.

Interpreting your results

The data interpretation procedure you should use depends on the objectives of your monitoring program. Chapter 8 of this manual contains information and advice on how to interpret your results for a range of monitoring objectives.

Units of expression

Before you interpret your results, it is important to be aware of the units your results are expressed in. Different colorimeters report results in different units, either the weight per litre of orthophosphate (PO_4^{3-}) or elemental phosphorus (P). Most orthophosphate test kits provide results as orthophosphate; however, some test kits and most scientific reports and papers report results as the weight per litre of the elemental phosphorus component of the sample. This is also particularly the case for Queensland and national guideline values. It is important to record the units that the test equipment displays and convert your results to a different unit if necessary.

If the phosphorus test kit displays the result as orthophosphate and a conversion to elemental phosphorus is necessary, simply multiply the result by 0.33. If the phosphorus test kit displays the result as elemental phosphorus and a conversion to orthophosphate is necessary, simply multiply the result by 3.066. Examples are given below.

Conversion from orthophosphate to elemental phosphorus (P)

Test kit result—orthophosphate	Conversion factor	Conversion to elemental phosphorus (P)
10 mg PO_4^{3-}/L	× 0.33	= 3.3 mg P/L

Conversion from elemental phosphorus to orthophosphate

Test kit result—phosphorus	Conversion factor	Conversion to orthophosphate
10 mg P/L	× 3.066	= 30.66 mg PO_4^{3-}/L

Guidelines for ecosystem protection and other uses

If you are conducting routine monitoring to assess waterway health, or if you are determining whether the water is suitable for a specific use, you should compare your results to the relevant guidelines. There is a list of existing guidelines at the end of this chapter, and Chapter 8 provides information on how to compare your results to guideline values.

When monitoring for the protection of aquatic ecosystems, you should compare your results to the *Queensland water quality guidelines* (Environmental Protection Agency 2006). The main ecological concern associated with phosphorus concentrations in streams is the likelihood of algal blooms and nuisance plant growth. The Queensland guidelines provide guideline values for TP and FRP concentrations for three regions of Queensland, shown in Table 5–26.

When using the *Queensland water quality guidelines* (Environmental Protection Agency 2006), you need to consider the region you are monitoring in and what type of water body you are monitoring. Definitions of the regions and water body types are contained in the guidelines.

The Queensland guidelines also outline more specialised subregional guidelines for water bodies in the Douglas, Gold Coast hinterland, Fraser Island and North Stradbroke Island catchments. Where subregional or regional guidelines are unavailable (such as for Eastern Cape York, Gulf Rivers, Lake Eyre and Murray–Darling), refer to the Australian and New Zealand guidelines for fresh and marine water quality (ANZECC & ARMCANZ 2000b). The ANZECC and ARMCANZ nitrogen trigger values for ecosystem protection are also shown in Table 5–26.

Table 5–26 Phosphorus guideline and trigger values for ecosystem protection (adapted from ANZECC & ARMCANZ 2000b; Environmental Protection Agency 2006)

Environmental Protection Agency guideline values (mg P/L)			
Water body type	**Region**	**FRP**	**TP**
Lowland streams	South East Qld	0.02	0.05
	Central Coast	0.02	0.05
	Wet Tropics	0.004	0.01
Upland streams	South East Qld	0.015	0.03
	Central Coast	0.015	0.03
	Wet Tropics	0.005	0.01
Lakes and reservoirs	South East Qld	0.005	0.01
	Central Coast	0.005	0.01
	Wet Tropics	0.005	0.01

ANZECC and ARMCANZ trigger values (mg P/L)				
Ecosystem type	**South-east Australia**		**Tropical Australia**	
	TP	**FRP**	**TP**	**FRP**
Upland river	0.02	0.015	0.01	0.005
Lowland river	0.05	0.02	0.01	0.004
Freshwater lakes	0.01	0.005	0.01	0.005
Wetlands	–	0.01–0.05	0.005–0.025	–

If no suitable guidelines are available, you can establish your own local guidelines. See Chapter 8 for information on how to establish your own guideline values and compare your results to existing guideline values.

For monitoring objectives other than the protection of ecosystems, compare your results to any relevant guidelines. See the guideline references section at the end of this chapter for a list of available guidelines for different monitoring objectives.

Health and safety

The following health and safety requirements apply to the digestion and colorimetry method for monitoring TP:

- Safety glasses and gloves must be worn at all times.
- Sulfuric acid and phosphate acid reagent are strong acids and can cause severe burns. The first aid procedure for acid on skin is to flush it with plenty of water.
- Ammonium persulfate is harmful if swallowed. Avoid contact with eyes and skin.
- Sodium hydroxide causes severe burns.
- Phosphate reducing reagent is an irritant.

See the *Health and safety guidelines for community-based waterway monitoring* (Department of Natural Resources and Water 2006) for further information.

Table 5–27 Methods guide for phosphorus

	Filterable reactive phosphate (FRP)						Total phosphorus (TP)					
	Laboratory analysis			Colorimetry			Laboratory digestion and analysis			Digestion and colorimetry		
Data quality	K and S	Time (days)	Cost ($)	K and S	Time (mins)	Cost ($)	K and S	Time (days)	Cost ($)	K and S	Time (mins)	Cost ($)
Analytical	Some exp.	5–20	14–20				Some exp.	5–20	22–30			
Indicative				Some exp.	20–40	1700–3000				Expert advice	35–60	1700–3000
Demonstrative				Some exp.	15–35	120–150				Some exp.	25–60	120–150

Note: Laboratory prices are given as costs per sample. Field colorimetry prices are given as the cost of equipment.

Colorimetry (spectrophotometer/ photometer/comparator) —FRP

Summary

In this method, reagents react with the water sample to form a blue colour, which is then matched against the spectrum to determine the amount of phosphorus present (mg/L).

Spectrophotometers and photometers measure the amount of light transmitted or absorbed at a nominated wavelength. They are best used at sites where the expected concentrations of phosphates are relatively low (down to 0.02 mg/L).

Comparators are appropriate for monitoring sites with expected high concentrations of phosphates (greater than 0.1 mg/L), including stormwater, run-off in urban streams and waste water treatment outfalls.

FRP provides an excellent indication of the amount of phosphorus available for direct biological uptake. FRP may be used as an estimate of orthophosphate concentrations present.

Equipment

You will need:

- field sampling equipment as listed in the overview section of this chapter
- a 100 mL plastic bottle (washed in water only, not detergents) if samples are not to be analysed in the field
- a 0.2 or 0.45 micron membrane filter apparatus
- an esky with ice or a refrigerator to keep samples cool if they are not to be analysed in the field.

To produce **indicative** data, you will need a photometer or spectrophotometer capable of measuring orthophosphate using a chemical methodology suitable for the waters being tested. Instrument accuracy should be:

- ±0.02 mg/L for low-range orthophosphate tests
- ±0.01 mg/L for high-range orthophosphate tests.

To produce **demonstrative** data, you will need a comparator, photometer or spectrophotometer capable of measuring orthophosphate using a chemical methodology suitable for the waters being tested.

Monitoring methods

1. Follow the nutrient sampling procedure on page 5–73 when carrying out field work. To handle samples, use a 100 mL plastic bottle that has not been washed in detergent. Refrigerate the sample immediately and freeze for up to one month.
2. Follow the manufacturer's instructions to carry out colorimetry.

Note: Chemicals in reaction hydrolyse a small part of bound phosphates, resulting in slight overestimation of orthophosphates in sample. Results must therefore be expressed as FRP, not orthophosphate.

Data confidence procedures

Refer to the section 'Data confidence for nutrient colorimetry analysis'.

Laboratory analysis—FRP

Summary

In this method:

- FRP is measured in milligrams per litre (mg/L)
- the water sample is collected and transported to a NATA-accredited laboratory for analysis following AS/NZS 5667.1:1998 procedure (Standards Australia & Standards New Zealand 1998)
- the sample is analysed by the laboratory.

FRP provides an excellent indication of the amount of phosphorus available for direct biological uptake. FRP may be used as an estimate of orthophosphate concentrations present.

Equipment

You will need:

- field sampling equipment as listed in the overview section of this chapter
- a 100 mL plastic bottle washed in water only, not detergent
- a 0.2 or 0.45 micron membrane filter apparatus
- an esky with ice or a refrigerator to keep samples cool.

The laboratory must be NATA-accredited for phosphorus analysis. The chemical methodology used must be suitable for the water being tested.

Monitoring methods

1. Follow the nutrient sampling procedure on page 5–73 to carry out field work. To handle samples, use a 100 mL plastic bottle that has not been washed in detergent. Refrigerate immediately and freeze for up to one month.
2. Send to the laboratory for analysis.

Note: Chemicals in reaction hydrolyse a small part of bound phosphates, resulting in slight overestimation of orthophosphates in the sample. Results must therefore be expressed as FRP, not orthophosphate.

Data confidence procedures

Refer to the section 'Data confidence for nutrient laboratory analysis'.

Laboratory digestion and analysis—TP

Summary

In this method:

- TP is measured in milligrams per litre
- the water sample is collected and transported to a NATA-accredited laboratory for analysis following AS/NZS 5667.1:1998 procedure (Standards Australia & Standards New Zealand 1998)
- the sample is digested and analysed by the laboratory.

Equipment

You will need:

- field sampling equipment as listed in the overview section of this chapter
- a 250 mL plastic bottle that has not been washed in detergent
- an esky with ice or a refrigerator to keep samples cool.

The laboratory must be NATA-accredited for phosphorus analysis. The chemical methodology used must be suitable for the water being tested.

Monitoring methods

To carry out field work, follow the nutrient sampling procedure on page 5–73. When handling samples, use a 250 mL plastic bottle that has not been washed in detergent Refrigerate immediately and freeze for up to one month.

Consider the following:

- The TP test measures the immediately and bio-available forms of phosphorus in the sample. TP concentrations in the sample are often many times higher than orthophosphate concentrations.
- This method may be used in conjunction with flow rates to provide load-based estimates of phosphorus being transported downstream.
- This method does not indicate the fraction of phosphorus available for direct biological uptake, but may be used as an estimate of potential available phosphorus in the aquatic system.
- Samples must be digested.
- Laboratory costs are quite high compared to field analysis.

Data confidence procedures

Refer to the section 'Data confidence for nutrient laboratory analysis'.

Digestion and colorimetry (spectrophotometer/ photometer/comparator) —TP

Summary

In this method, reagents react with water samples to form a blue colour. The colour is matched against a spectrum to determine the amount of phosphorus present (mg/L).

Spectrophotometers and photometers measure the amount of light transmitted or absorbed at a nominated wavelength. They are best used at sites where the expected concentrations of phosphates are relatively low (down to 0.02 mg/L).

Comparators are appropriate for monitoring sites with expected high concentrations of phosphates (greater than 0.1 mg/L), including stormwater, run-off in urban streams and waste water treatment outfalls.

Equipment

You will need:

- field sampling equipment as listed in the overview section of this chapter
- a 250 mL plastic bottle (washed in water only, not detergent) if samples are not to be analysed in the field
- an esky with ice or a refrigerator to keep samples cool if samples are not to be analysed in the field.

To produce **indicative** data, you will need a photometer or spectrophotometer capable of measuring orthophosphate using a chemical methodology suitable for the waters being tested. The instrument accuracy should be:

- ±0.1 mg/L for low-range orthophosphate tests
- ±0.2 mg/L for high-range orthophosphate tests.

To produce **demonstrative** data, you will need:

- a comparator, photometer or spectrophotometer capable of measuring orthophosphate using a chemical methodology suitable for the waters being tested
- a TP digestion field kit.

Monitoring methods

1. To carry out field work, follow the nutrient sampling procedure on page 5–73. Store samples in 250 mL plastic bottles and refrigerate immediately. Bottles must not have been washed in detergent.
2. Follow the manufacturer's instructions for 'cooking' (digesting), neutralising the sample, and colorimetry. Because of the digestion step, measurement of TP is very difficult to complete under field conditions. Extreme caution must be taken when carrying out the TP test. Also take care when disposing of waste from the reactions.

Data confidence procedures

Refer to the section 'Data confidence for nutrient colorimetry analysis'.

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Guideline references

Objective type	Available guidelines
Aquatic ecosystems	Environmental Protection Agency 2006; ANZECC & ARMCANZ 2000a; 2000b
Protection of the human consumer	Food Standards Australia New Zealand 2007, *Australia New Zealand food standards code*, ANSTAT Pty Ltd, Canberra, viewed 8 March 2007, <http://www.foodstandards.gov.au>
Recreation	National Health and Medical Research Council 2005, *Guidelines for managing risk in recreational waters*, Australian Government, Canberra, viewed 8 March 2007, <http://www.nhmrc.gov.au>
Visual amenity	ANZECC & ARMCANZ 2000b
Aquaculture	ANZECC & ARMCANZ 2000b
	Department of Primary Industries and Fisheries 2005, *Site identification for aquaculture—assessment of chemical contamination in site selection* (formerly *Water quality in aquaculture*, DPI notes April 2004), Queensland Government, Brisbane, viewed 8 March 2007, <http://www2.dpi.qld.gov.au/fishweb/17950.html>
	Food Standards Australia New Zealand 2007, Australia New Zealand Food Standards Code, ANSTAT Pty Ltd, Canberra, viewed 8 March 2007, <http://www.foodstandards.gov.au>
Irrigation, stock watering and farm use	ANZECC & ARMCANZ 2000b
Drinking water (including supply)	NHMRC & NRMMC 2004