WATERWATCH AUSTRALIA NATIONAL TECHNICAL MANUAL

module 4

Physical and Chemical Parameters

Module 4 – Physical and Chemical Parameters
Waterwatch Australia National Technical Manual
by the Waterwatch Australia Steering Committee

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Preface

The Waterwatch Australia National Technical Manual was prepared by the Waterwatch Australia Steering Committee to provide guidance and technical support to the Waterwatch community monitoring network throughout Australia. The content has been gathered from a range of publications, including the existing State Waterwatch Technical Manuals. The guidelines and information reproduced in this Manual have been agreed by the members of the committee based on their knowledge and experience in coordinating community monitoring programs in Australia with advice from the scientific community.

The Manual has been published as a series of modules. Each module is a stand-alone document addressing an important aspect of community waterway monitoring. The following modules are available in the Manual:

1. Background
2. Getting Started: the team, monitoring plan and site
3. Biological Parameters
4. Physical and Chemical Parameters (this module)
5. Data... Information... Action!
6. Waterwatch and Schools
7. Estuarine Monitoring
8. Groundwater Monitoring

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Before you begin

This section contains information and tips that you need to know before you go into the field or laboratory. It discusses sampling methods and equipment in a general sense, how to select sampling sites, how to record information about samples and how to make sure you get good results. It also discusses important safety considerations as well as reagents and waste disposal.

Please read this section before you proceed with the second section and before you go into the field or laboratory.

Scope of this module

One way that Waterwatchers can assess the health of catchments and waterways is by examining the water's quality. We do this by measuring various physical and chemical characteristics (or parameters) of the water, such as temperature, salinity and turbidity.

This module outlines the water quality characteristics and how they behave in a range of conditions. It describes methods of measuring them and gives hints to help interpret the measurements. The module also describes how to collect, store and analyse a water sample. It gives reminders about safety when sampling, and lists the nationally-adopted methods and equipment.

Details on how to use the equipment commonly used by Waterwatch groups can be obtained from your Waterwatch State facilitator or regional coordinator. A field for each of the parameters described in this module has been included in the Waterwatch Database program (see module 5, Data... Information... Action!).

About water

Water has some remarkable features:

- Water is known as a universal solvent because it can dissolve many substances, both solid and gaseous, that come into contact with it.
- Water is the only natural substance that exists as solid, liquid and gas within normal earth temperatures.
- The temperature of water affects how quickly substances dissolve in it and, in some cases, the quantity that can be dissolved: for example, warm water holds less dissolved oxygen than colder water, but it holds more of most solids. Temperature also has a major effect on living things within the water. Compared to air or soil, bodies of water change temperature slowly, so aquatic life is generally not exposed to sudden fluctuations of temperature.
- Water that contains dissolved salts is a good conductor of electricity — the basis of the technique for measuring the level of salt in the water (salinity).
- Moving water and ice are powerful agents of erosion, removing particles from unprotected soil surfaces, river-banks and rock faces, resulting in water muddy with extraneous matter (turbidity).
- Water has surface tension, which causes it to form drops and to have a 'skin' strong enough to support the weight of some aquatic insects.
- Water also sticks to other surfaces, enabling the capillary action of water in fine tubes, such as soil pores.

The properties of water vary naturally depending on the surrounding environment, so data collected about water quality must be interpreted in the context of the waterbody's particular environment and position in the catchment.

With our existing knowledge no-one can list 'normal' temperature, turbidity, salinity and so on for every part of every waterbody in Australia. The 'normal' characteristics of a waterbody can best be discovered by measuring them over a period of time that is long enough to encompass a range of normal situations.

Ideally, each group that cares about a waterbody will make regular measurements of its characteristics to determine patterns that are usual for that waterbody in wet, dry and 'normal' years.

Tests, methods and equipment

By measuring the physical and chemical characteristics of our local waterbodies we can determine the health of our water and therefore its ability to sustain life. Several of the physical and chemical characteristics of a waterway or waterbody can be measured by more than one method. Methods can range from simple to complex. Some are accessible to primary school children; others require greater skill, and a few methods have to be used in analytical laboratories on samples that Waterwatchers have collected.

The results of the measurements can also range considerably in usefulness, depending on how much attention is given to detail during the measuring. Results may merely indicate the condition of the waterbody, or they may give very accurate data that can be used to identify matters significant for the waterbody's ecology and health.

In all methods, quality control is important so the measurements are as credible and meaningful as possible. The greater the quality control, the more useful are the data.

To choose a method, first check your group's monitoring plan (see module 2) to identify why you are monitoring. Is it to:

- educate or raise awareness?
- identify major trouble spots?
- identify the effect of contamination and contamination control activities and for reporting to government agencies?
- determine the precise severity of contamination problems and to rank sites on the waterway or waterbody?
- identify whether waterways or waterbodies are clean enough for their designated uses?
- identify significant water quality trends?
- select sites for remedial action?
- support government agency monitoring efforts?

- encourage the community to have ownership of their environment and to take suitable actions to maintain and enhance the environment?

The quality and quantity of data you collect will depend on your reason for monitoring and on who will be using your data. For example, the data may be of value to teachers, students, the general public, land-owners, natural resource managers, government agencies, and catchment and rivercare groups. For some of these groups, only the highest quality data will do, while others will be satisfied with intermediate or low data confidence. Your choice of method may also be affected by the accessibility of your selected sampling sites and your frequency of monitoring.

How often your group monitors will depend on the questions you want to answer. For example, baseline monitoring should take place regularly during baseflow conditions (weekly to monthly); contamination effect monitoring should take place at the time of discharge or the time of use of the waterway (e.g. for swimming).

Monitoring consists of more than just taking measurements or samples on the spot. It also entails recording the results (including date and time and weather conditions) in a standard format and storing them in the Waterwatch database or forwarding them to the regional coordinator for storage.

If your observations show that a contamination incident has occurred, it is important to report it immediately to the Waterwatch coordinator, for advice on appropriate action.

Selecting sites

The way in which you choose a site will depend on the type of waterbody and your reasons for monitoring it (see also module 2).

- Use your catchment map to select sites that appear to meet your needs.
- Get permission to enter private land.
- Go to each site and check that it is accessible and safe to work at, that it is representative of conditions in the waterway and suitable to your needs.
- Photograph each site at the sample collection point and record directions to the site for future visits. Place the directions and photographs in a looseleaf binder and store with your monitoring plan and catchment map.
- Mark site locations on your catchment map.
- Record details of the site location in your monitoring plan (see module 2, question 7).
- List all the sites selected, along with your reasons for choosing them (see module 2, question 7).
- Describe the precise location of the sampling point for others to do repeat sampling, e.g. 'at overhanging rock on left bank 10 m upstream of bridge'.
- Register the site with your Waterwatch coordinator.

Collecting water samples

The way you collect and treat your samples can have a huge effect on your results. For accuracy and precision you should aim always to sample:

- from the same location, and
- at the same time each day;

and you should:

- handle, test and analyse in the same way, and
- ensure your sample container and collection methods are appropriate for the characteristic you are testing.

Your choices of methods for collecting samples should be guided by the purpose of your monitoring program and the quality of data you need.

Where to sample

Generally sample:

- in the middle of the stream, or as far away from the edge as possible;
- about 20 cm below the surface;
- in the main current; and
- upstream from where you are standing.

Avoid sampling surface water or stagnant water, non-flowing water near the stream edge or surface, or water near the stream bottom, unless you specifically intend to examine these situations.

Choosing a sample type

Some natural variation in water quality within a waterbody is to be expected. The effect that this variation can have on the data can be quite large. Different sample types — grab or composite — can be used to account for this variability. Grab samples are collected in separate bottles and kept as single entities throughout the measurement stage. Composite samples are taken separately and then bulked with others before the measurement stage.

Grab samples are the type commonly used by Waterwatch groups, as they are simple. The type of sample you take is not as important as ensuring consistency in the time you monitor and the way in which you monitor.

Sampling equipment

For a large waterbody you may need a boat. Alternatively, an extension (long-handled) sampling pole enables you to collect water from wide or deep streams or pools. Rubber boots or waders will give you access to small and shallow streams or pools (but, for safety, don't wear waders in a boat).

You will also need:

- clean containers for the samples (see Choosing containers below)
- boxes to carry samples in
- plastic disposable gloves and safety glasses
- an esky to keep the samples cool, where necessary
- equipment for making the measurements, such as thermometers, tape measures, and so on
- reagents
- electronic meters
- record sheets (see pages 47 to 52 of this module)
- instruction manuals
- pens
- first aid kit
- containers for solid and liquid wastes

And so on. The list will depend on your objective and methods.

Choosing containers

For most basic water quality tests a plastic or glass bottle will suffice. The most important consideration is to make sure your container is clean. It used to be said that household detergents should never be used for washing sample bottles, because phosphate molecules that used to occur in detergents have a tendency to attach (adsorb) to the inside surfaces of sample containers and bottles, contaminating the samples you take. Nowadays, however, detergents are all, or almost all, phosphate-free (read the label). If a phosphate-free detergent is not available, your containers must be acid-washed in a laboratory, to remove possible adsorbed phosphate before they are used in the field.

The bottles you use must be able to withstand repeated contact with hydrochloric acid. Plastic bottles — high-density polyethylene or polypropylene — are preferable to glass because they will better withstand breakage. If factory-sealed disposable Whirl-pak® bags are used for sampling, no preparation is needed. If other containers are to be used they will need to be prepared for sampling. If you are collecting water samples or sediments for pesticides, heavy metals or bacterial analysis by a laboratory, ask the laboratory to provide the required containers.

To prepare your own containers for sampling, follow the instructions for cleaning containers in this section.

Cleaning your sample containers

All sample containers and glassware, whether new or reused, must be clean.

- In a laboratory, wash each bottle and cap with a brush and phosphate-free detergent.
- Rinse three times with tap water.
- Rinse with 10% nitric acid — check with laboratory staff to be sure you have the right acid.
- Rinse three times with deionised water.
- Drain upside down on a rack.
- When clean and dry, replace the cap.
- Store in a clean and dry place until required.

How to sample

There are a few things to remember when you are collecting water samples:

1. If you are wading, approach the sampling spot from downstream. Try not to disturb the bottom sediment. Collect the water sample on your upstream side.
2. If you are in a boat, approach the sampling spot from downstream. Carefully reach over the side and collect the water sample from the upstream side of the boat.
3. Remove the cap from the sample bottle just before sampling. Do not touch the inside of the bottle or the cap as this may contaminate the sample.
4. Hold the bottle near its base and plunge it (opening downward) below the water surface. If you are using an extension pole, remove the cap, turn the bottle upside down and plunge it into the water. Air pressure within the bottle will stop surface scum and water entering the bottle. Hold it about 20 cm beneath the surface or, if the water is shallow, mid-way between the surface and the bottom.

Using an extension pole to hold a sample bottle

When you extend the handle, leave 10 cm unextended, for strength.

Have a coworker hold on to you when you are using the extended pole.

When retrieving the bottle and water sample, hold the pole slightly downwards pointing away from you to avoid being wetted by water from inside the long arm.

Do not lift or carry the pole above your head in case it touches power lines — the metal arm would conduct electricity to you and electrocute you.

5. Turn the bottle underwater into the current and away from you. In a slow-moving river, push the bottle underneath the surface and away from you in an upstream direction.
6. Empty the bottle downstream of you, or use the first sample for turbidity measurements. Then repeat steps 4 and 5. (The idea is to remove any material left over from washing the container that could modify a chemical measurement on the sample.)
7. Fill the bottle completely and recap the bottle carefully. Remember, do not touch the inside.
8. If transporting the bottle to a laboratory, write details of the sample on the water quality result sheet (see page 51) and on the bottle label. Be sure to label each sample bottle clearly and distinctively.
9. Be aware of the standard methods and times for preserving the quality of the samples you collect (see Table 4.1).

Information about your samples

Every time you collect and label a sample, you should also record its details on the water quality result sheet (see pages 51–52). These details will be useful when you analyse your results.

- It is important to note details that accurately identify the site and the sampling point; and the date, time of day, weather and flow conditions, because these factors can affect nutrient concentrations.
- Your interpretation of the sample result may depend on the methods used to measure it, so it's sensible to note your method and any variations to it on the result sheet, as well as any information which may affect the results of the analysis, such as any preparatory-treatments you may make to the sample.
- In case you need to discuss the sample later, you also should record the name of the sampling person, and the preservation method used, if any.

Table 4.1: Standard preservation methods and holding times for key parameters

Parameter	Preservation method	Maximum holding time	Comments
pH	Refrigeration	24 hours	Fill sample bottle completely to exclude air. Preferably tested in the field.
Conductivity	None required	24 hours	Fill sample bottle completely to exclude air. Preferably tested in the field if samples have low EC <20 µS/cm.
	Refrigeration	1 month	
Turbidity	None required	24 hours	Preferably tested in the field
Suspended solids	Refrigerate	24 hours	
Nitrate	Refrigeration	24 hours	Unfiltered sample.
	Filter on site and freeze	1 month	
Phosphate, dissolved	Filter on site and refrigerate	24 hours	
	Filter on site and freeze	1 month	
Phosphate, total	Refrigerate	24 hours	
	Freeze	1 month	
Dissolved oxygen	None required Fix oxygen in the field and store in the dark	24 hours	Determine on site. Avoid excessive turbulence to sample. Fix as described in chosen method.
Temperature	Not applicable	Not applicable	Must be analysed on site.
Pesticides, heavy metals, faecal coliforms	Contact analytical lab for details.		

* Source: *Water quality — Sampling. Part 1.* AS/NZS 5667.2: 1998. Australian/New Zealand Standard.

The physical and chemical characteristics of a water sample can change during transport and storage. Careful packaging can prevent damage to the containers and loss of the sample. Preservation methods only slow chemical and biological changes that inevitably occur after collecting your sample. Some parameters change more quickly than others, and so need to be analysed on site. In general, the shorter the time between collection and analysis, the more reliable your results will be. Table 4.1 outlines recommended standard holding times and preservation techniques for ensuring high quality data.

Some hints to help you get good results

Calibrate

To maintain your equipment in good working order and get high quality results, you should regularly inspect and calibrate each piece of test equipment, and record the calibration results in a table; see the Waterwatch equipment maintenance and calibration record sheet on page 48.

- In all cases, calibrate all kits or instruments against appropriate standard solutions (which contain known amounts of the substance to be tested), and adjust them as necessary.

Avoid contamination

- To avoid contamination and contact with possibly toxic chemicals, never put your thumb over test tubes when you shake or swirl them.
- Do not empty excess reagents back into their original containers. Instead, put them into a special waste container that you can dispose of safely at the laboratory.
- Do not wet dispensing spoons or allow them to touch the inside of a test bottle or tube. Dry the spoons thoroughly if they do become wet. After a spoon has been used, tap the spoon on the rim of the test bottle or tube to dislodge any remaining particles and, if necessary, wipe the spoon with a paper towel. Immediately place the paper into the solid waste container.
- Do not allow droppers to touch the test bottles or tubes — this will contaminate the droppers.

Be careful when using chemical reagents

- For safety, never pipette with your mouth; always use a pipette bulb.
- Hold reagent droppers vertically above the test bottles, not at an angle. The droppers have been specially calibrated to deliver exact amounts of solution when they are held vertically. If they are held at an angle, they will deliver less solution.
- Wash all glassware with deionised or distilled water after each use. Both distilled water and deionised water are available from chemical suppliers and supermarkets or you can purchase a kit to produce your own.
- Always use fresh standard solutions for chemical tests. For example, commercially prepared sodium thiosulfate solution has a shelf-life of 1 year but if you make your own it only lasts about three weeks, so make a fresh solution as needed.

Make 'internal' quality control checks

- Test one or two field replicates every 10 samples to check for precision of sampling and analysis.
- Where appropriate, test a Waterwatch mystery solution every six months to check for problems with equipment, method or reagent.

Field replicates

A field replicate is a sample taken at the same time and place as another and treated identically, or a measurement made immediately after another at the same spot and in the same way.

Waterwatch mystery solutions

Mystery solutions, available from Waterwatch coordinators, are solutions that have been analysed by experienced analysts. Test these solutions yourself, and then compare your own test results with the original analysis. This will help you assess the accuracy of your techniques and of your equipment.

Consider using external checks

For external checks, send 10% of your samples to a separate laboratory elsewhere to be analysed, and then compare their results with your own for the same samples.

You can increase the quality of your data with your current equipment simply by always using the hints and checks above. If the extra results obtained by internal and external checks do not exactly agree with your own results, calculate by how much the results differ. This can be expressed as a percentage. For example, if an external result reports a turbidity reading of 100 units and your result is 110, you can record an 'error' or variation of +10% for all your turbidity meter results (but not for results of other parameters, such as pH — they must be tested separately). The smaller the percentage variation between your results and the external ones, the more confidently you and others can use your results to help solve the problems in your waterway.

Safety

In general, if proper safety precautions are followed, the tests in this module do not present significant health or safety risks. There are, however, some basic precautions you should take to ensure your own safety and that of those working with you.

- Let someone know where you are going and when you will return.
- Do not work alone.
- Use methods that minimise your possible contact with chemicals.
- Use goggles and gloves when handling reagents.
- Read material safety data sheets that come with reagents and keep material safety data sheets accessible during testing for directions on how to handle exposure in case of accident or ingestion.
- Make sure you have safe and easy access to the waterway. Beware of slippery rocks and banks.
- Be wary of passing traffic if you are sampling near a road or from a bridge.
- Be able to swim in case you fall in.
- Avoid contact with contaminated water. Use gloves while sampling, but take them off as soon as you've finished. Don't touch your skin with wet gloves.
- Keep a fully-stocked first aid kit handy.
- Wear sturdy waterproof shoes with a good grip.
- Wear suitable clothes including a hat and shirt.
- Don't forget the sunblock.
- 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.
- To avoid contamination and contact with possibly toxic chemicals, never put your thumb over the test tubes when you shake or swirl them. Use something inert instead.
- Never pipette with your mouth; always use a pipette bulb.
- Hold all test bottles over a wide-mouthed liquid waste bottle while adding the liquid and powder reagents.

Material safety data sheets

Material safety data sheets are fact sheets the manufacturer includes with each chemical used for water quality tests. They are to ensure all water quality monitors know about the hazards of chemicals produced or used. The data sheets contain usage, storage, first aid and disposal information for hazardous products.

- Place all used gloves, used paper towels, empty reagent packaging and any other rubbish from testing into a plastic garbage bag with no tears in it, and take it with you when you leave the field site. Try to leave the site cleaner than you found it.
- After each piece of used equipment has been rinsed with distilled water, pour the rinse water into the liquid waste bottle. Consult your Waterwatch coordinator about disposing of liquid waste.
- Do not put solid waste into the liquid waste bottle.

Do not allow children to test in the field without adult supervision — students must be fully supervised by their teacher in accordance with Education Department guidelines.

Reagents

A reagent is a substance which, on account of the reactions it causes, is used in chemical analysis. For accurate results, reagents need to be kept in good condition and used before their expiry date.

Keeping reagents in good condition

Many reagents in test kits can become contaminated and degrade quickly under field conditions. The inevitable result is inaccurate measurements of water quality, extra expense and a lot of wasted time. By checking the condition of the reagents and taking a few simple precautions, you can avoid these problems.

Check the appearance of reagents and look for any changes such as colour, cloudiness and formation of solids. If in doubt over the condition of reagents, test a water sample with reagents and compare your result from a test carried out with another kit, or with fresh reagents, or with a meter. Replace any reagents that have been degraded.

Reagents degrade more quickly at high temperatures, so store and transport them away from heat and sunlight.

Many reagents react with oxygen or carbon dioxide in the air so keep bottles tightly capped when not in use.

Contamination of reagents with foreign matter or other chemicals will cause degradation. Use dedicated spoons and droppers for each reagent to avoid cross contamination.

How to determine the expiry date of reagents

Replacing reagents is a major ongoing expense for Waterwatch groups. However, avoiding expired reagents is important for all groups particularly where data quality is important.

Reagents have a limited life span from the date of manufacture, e.g. sodium thiosulfate (1 year) and starch indicator (1.5 years), and it makes little sense to continue using

them after expiry. The manufacturer will tell you the life span of each reagent.

You should record the date of manufacture and write the date of expiry on the label of each reagent bottle. To do this, look for a series of numbers usually at the bottom left corner of any reagent label. The first two digits indicate the week of manufacture and the third digit indicates the year. For example, a sodium thiosulfate reagent bottle with the numbers 0382341 would have been made in week 3 (January) of 1998. Since sodium thiosulfate has a one-year life-span, the expiry date is week 3 of January 1999.

Waste disposal

Leave the site cleaner and tidier than you found it — pick up and transport out all rubbish you generate as well as other people's rubbish, if possible.

Solid waste container

Place all used gloves, used paper towels, empty reagent packaging and any other rubbish from testing into an intact and secure plastic garbage bag and take it with you when you leave.

Toxic waste

Be very careful if you are testing nitrate with the cadmium reduction method. Cadmium is present in the reagent powder and drops to the bottom of the test tube at the end of the test. Waste from this test should not be poured down the drain but stored separately in a hazardous waste jar labelled 'toxic waste'. This jar must be disposed of as 'special waste', along with other such wastes from your organisation or school.

Liquid waste bottle

Hold all test bottles over a wide-mouthed liquid waste bottle while adding the liquid and powder reagents from the following tests: pH, dissolved oxygen, phosphate and nitrate.

After each piece of used equipment has been rinsed with distilled water, pour the rinse water into the liquid waste bottle.

Do not put solid waste into the liquid waste bottle.

Consult your Waterwatch coordinator about disposing of the liquid waste.

Methods

This section contains information about tests you can conduct; what they are for; and how to do them.

Some physical and chemical characteristics of water quality can be measured more simply and quickly than others. There are three levels of difficulty — only the first two levels are described in this module.

The first (the 'very simple' level) includes flow, pH, salinity (total dissolved solids), turbidity (total suspended solids), temperature and dissolved oxygen. These can all be measured by anyone in the community including students at all levels of schooling.

The second — measuring concentrations of phosphate and nitrate — even though relatively easy to do, is suitable only for members of the community and for students in upper primary and secondary school.

The third — measuring levels of chlorophyll-a, faecal coliform bacteria (using filtration and culture equipment), pesticides and heavy metals — are not included in this module, but information about them will be available from your Waterwatch coordinator. It is recommended that only upper secondary school students (particularly those studying science) and trained members of the community be involved.

Flow

What is it and why does it matter?

Flow: the volume of fluid (in this case, water) that passes through a passage of any given section in a unit of time

The water generally comes from surface run-off and from water that has passed through the soil and out into the waterway.

The amount of any particular substance carried in the water is known as the load. The faster and bigger the flow of the water, the stronger the current, and the heavier the load it can carry.

When there is little water in the waterway (low flow) most of the water entering the stream will be from underground seepage, and the flow rate is slow. Sediment settles quickly to the bottom, sections of the stream will become semi-stagnant resulting in low dissolved oxygen concentrations, algal growth will increase if there is adequate light, leading to algal blooms, and salinity and water temperature may increase to values that affect the biota in the waterway.

Moderate flows ensure good mixing of oxygen with water, and dilution and flushing of contaminants.

After heavy rainfall the water level rises or floods (high flow) because run-off rushes into the waterway increasing turbidity and the load of contaminants. During flooding, the concentrations of oxygen, turbidity, pH, salinity and nutrients can be expected to fluctuate.

For the purposes of measurement, flow is the velocity of water multiplied by the cross-sectional area of the stream. These two quantities must be measured as accurately as possible to avoid compounding errors when calculating flow.

What factors affect flow?

Flow is modified by conditions along and around the waterway, such as:

- structures, such as dams and weirs, in the waterway
- removal (diversion) of water for use in irrigation, industry and households
- rainfall, snow melt, and water releases from dams and power stations
- entry of groundwater
- evaporation
- the leakiness of the river bed and banks

The size of a waterway and its flow rate affect its water quality. For example, discharges containing contaminants will have less effect on large swiftly flowing rivers than on small slow streams. This is one reason for measuring flow — to work out the load of contaminants and sediment the waterway is carrying.

Because velocity and flow have a significant effect on water quality, it is important that you record them at the time of sampling and, if possible, during the previous few days. It is particularly valuable to know if flows are at low, moderate or high level and if the level is rising or falling. This is because the concentrations of nutrients, turbidity and contaminants tend to be higher when the stream level is rising than when it is falling.

Suggested methods, equipment and reporting

There are three ways to measure water velocity. A simple method is to see how fast a floating object travels downstream over a chosen distance. This is called the float method, and it is described on page 11.

Secondly, flow data can be obtained from the local water authority, if your site is near a gauging station. The local water authority measures and keeps records of flow on a regular basis at gauging stations spaced out along all main waterways.

Thirdly, the head rod method can be used (see page 11). Note, however, that head rods are limited to relatively shallow streams with medium velocities.

Float method for determining water velocity

The float method is easy to understand and something most of us have done as children. You simply float an object on the water and measure the time it takes to travel a set distance.

Equipment

The equipment you will need for this method includes:

- tennis ball, apple or orange
- net to catch the ball or fruit
- 10 metre tape or rope
- stopwatch

Procedure

1. Mark out a 10-metre length of the waterway, upstream of your sampling site. Choose a section of the waterway that is relatively straight and free of vegetation or obstacles. Avoid areas with a culvert or bridge because those structures will modify the true flow. If the flow is very slow, mark out a shorter distance.
2. Position a person at each end of the 10-metre section.
3. Place the ball on the surface near the middle of the waterway at least 2 metres upstream of the end of the tape so it has time to come up to water speed.
4. When the ball is in line with the beginning of the tape, start the stopwatch.
5. Stop the watch when the ball gets to the end of the 10-metre section.
6. Repeat the procedure at least three times at this site and average the results.

To calculate the water velocity, divide the distance travelled in metres by the time taken in seconds. Then multiply by a correction factor of 0.9 to compensate for the variability in velocity with depth and across the channel, i.e. water will flow more slowly at the edges than in the middle, and more slowly near the bottom than near the surface. For example:

distance travelled = 10 metres
average time taken = 18 seconds
correction factor = 0.9
∴ stream velocity = (10 x 0.9) ÷ 18 = 0.5 metres per second

Head rod method for determining water velocity

The head rod method is quick and possibly more accurate than the float method for shallow streams.

Head rods are limited to use in relatively shallow streams. Also, they may be difficult to read for velocities of less than 0.5 metres per second and they are hard to handle in velocities greater than about 2.5 metres per second.

The method involves wading across the stream, and measuring the water depth at approximately equal intervals across the stream, including the deepest part. Five to ten measurements are recommended, and the more you take the more accurate your estimate will be.

Equipment

The equipment you will need for this method includes:

- a head rod
- waders or tall rubber boots

A head rod

A head rod is a 1 metre stainless steel ruler about 40 mm wide, or a wooden ruler with a bevelled edge. The bottom end should sit on a small flat disk to prevent it from sinking into the stream bed during use. The width can vary within the normal range of ruler widths.

Procedure

1. Place the rod in the waterway, a small distance from the edge (up to 0.5 metre in larger streams) where there is measurable flow. Measure the depth of the stream in metres with the thin edge of the head rod facing into the flow. Record the height (m) of the water against the rod (depth 1).
2. Rotate the head rod 90° so the flat side faces the flow, creating a standing wave or 'head' (see Figure 4.1). Record the new height of the water (in m) at the top of the standing wave (depth 2). The difference between depth 1 and depth 2 in metres is the head. Record this in your data sheets.
3. Repeat these measurements at 5 to 10 different points across the stream.
4. Calculate the average head (h) in metres from these measurements.
5. Calculate the average velocity of the stream in metres per second (m/s) using the formula below.

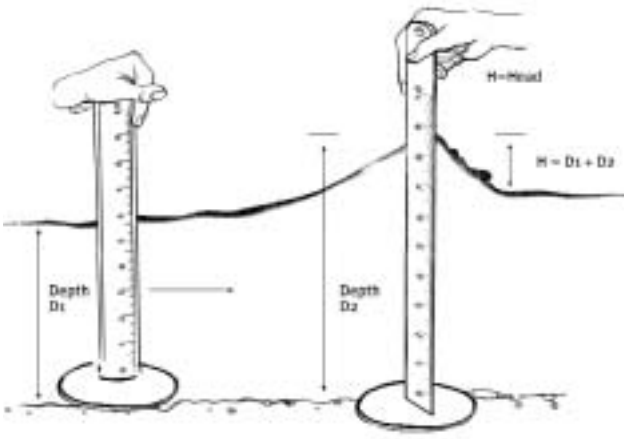
Average velocity (m/s) = $\sqrt{(2gh)}$,
where g is the gravitational constant of 9.81*

e.g. If the average head height is 0.5 m, the average velocity is $\sqrt{(2 \times 9.81 \times 0.5)} = 3.13$ m/s.

If the average head height is 1 m, then the average velocity would be $\sqrt{(2 \times 9.81 \times 1)} = 4.42$ m/s.

* *The gravitational constant is not significantly affected by height above sea level*

Figure 4.1: Using a head rod



Method for determining stream cross-section

The cross section is determined by measuring the width and depth of the waterway, and multiplying these measurements together (see Figure 4.2). The depth will vary across the waterway and so the width and depth should be measured in small intervals and aggregated to determine the total area.

Use two posts or similar to stretch your measuring string (marked at 0.1 m intervals) across the waterway at the water surface.

Measure and record the depth of the water at each interval.

Multiply each depth reading by 0.1 m and add the results together to determine your cross-sectional area in square metres (m^2).

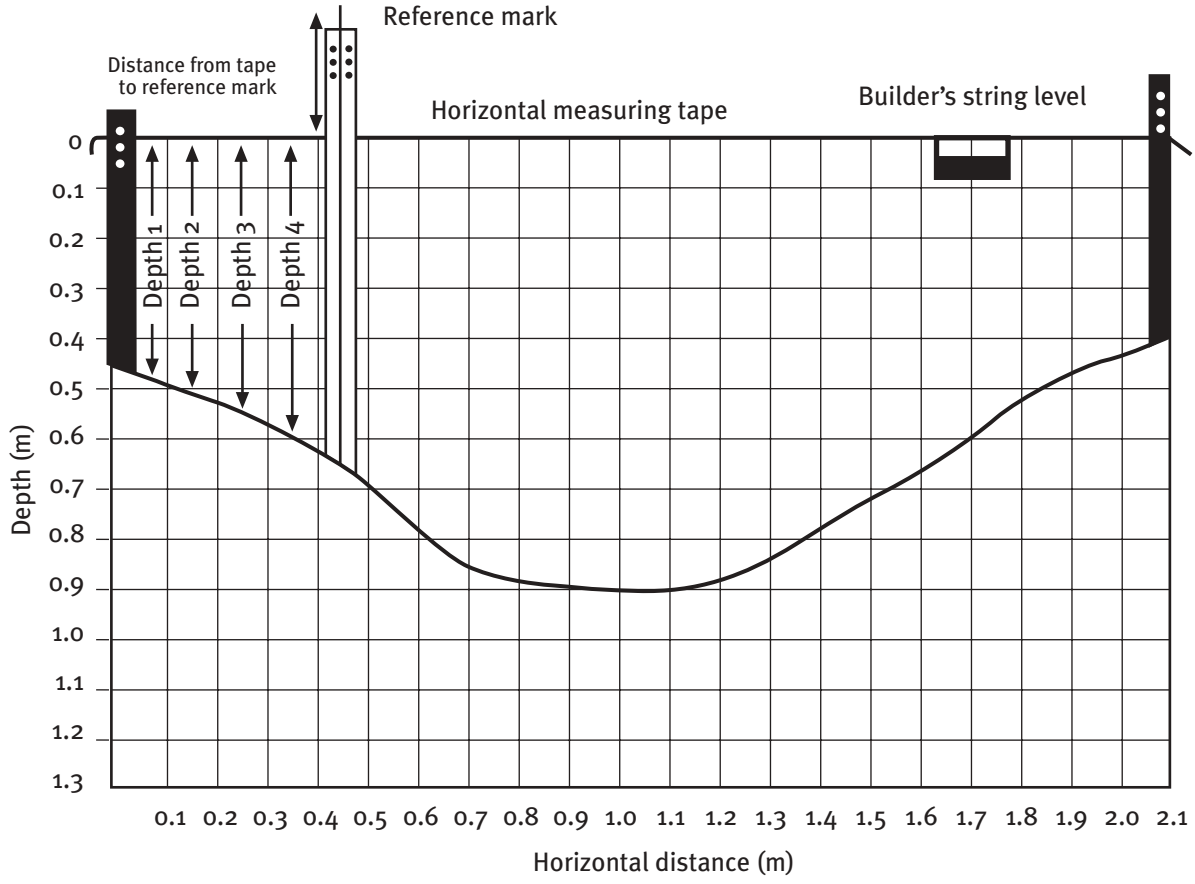
At a culvert, the cross-section is usually either circular or rectangular. Simply measure the width or diameter of the pipe. On graph paper, make a scale drawing of the shape of the culvert and count the number of squares to find the cross-sectional area.

Equipment

The equipment you will need for this method includes:

- 50 metre or 100 metre plastic tape
- 5 metre metal tape, long wooden or metal ruler or weighted string (perhaps with a disk on the bottom to stop it sinking into the mud at the bottom)
- a spirit level — ideally one that hangs on a string line
- clipboard, pen, paper, pencils, erasers, short ruler
- gum-boots, or wetsuit boots or waders

Figure 4.2: Plotting the stream channel on graph paper



- optional peg or star post/picket (steel fencing-post) and hammer or star post driver
- graph paper

Procedure

1. Secure a marker peg or post, such as a star picket, in the stream bed. This will mark your measuring section and be your reference marker. Place it where it will be accessible when the stream is flowing but not so it obstructs flow. Set the reference marker up so it is above the deepest water height you expect to measure.
2. Use star pickets (preferable) or tomato stakes or survey pegs or similar to hold your measuring tape across the stream adjacent to the reference marker and use a spirit level to ensure the tape is horizontal.
3. Prepare a table with column headings for horizontal distance, depth and area (see Figure 4.2).
4. Measure from the horizontal tape to the top of the reference post.
5. Record this value.
6. Take depth measurements from the horizontal tape to the bottom of the creek at 0.1 metre intervals, as described earlier.
7. Add the value recorded in Step 5 to each depth.
8. Enter this value in the depth column.
9. Record the horizontal distance from your starting point and depth in this way as you work your way across the stream at each interval.
10. From your recorded measurements draw the stream cross-section on graph paper and calculate the total area from the sum of the areas of the 0.1 metre intervals.

Reference markers

Establishing reference markers can make determining the cross-sectional area much simpler when you are sampling at sites on a regular basis. By setting up a reference marker in your waterway and developing a cross-sectional area graph you can simply read a depth level off the reference marker and determine cross-sectional area from the graph. After storm events or flooding, the waterway channel may change in shape and size; if so, you will need to recalibrate the cross-sectional area graph.

This use of reference markers is best for small streams, culverts, V-notch weirs, or sites located at bridges. You may be able to measure depth of slow-flowing rivers by carefully taking the measurements from a boat.

Data confidence

To make sure the flow data you collect are of good quality, repeat the velocity measurements (by float or head rod methods) 5–10 times each, and make 20 measurements of water depth. Once you have enough measurements over time, it is possible to make a flow rating curve (see Figure 4.3 on page 15). Subsequent calculations of flow can be compared with that, to check they are within the normal range.

Interpreting your results

Velocity is relatively easy to work out and, by itself, provides a rough measure of the likely effect of contamination on water quality in the stream. By comparing the results of measurements at different times at your site you will be able to identify low, normal and high flows. You may find corresponding changes in other water quality results. For example, you may find that turbidity tends to increase as velocity increases.

By combining your flow measurements (velocity and cross-sectional area) with your corresponding measurements of, say, phosphorus concentrations, you can estimate the loss of phosphorus per hectare of catchment, along your waterway. Your results are only a guide to what is happening in the catchment at a particular time. The final result depends on the accuracy of both the water quality test and flow measurements, so you can expect errors in load estimates of up to 50%.

You can have more confidence in your data if they are for a range of flows. For example, if you sample only moderate flows, you are possibly under-estimating the loads lost from the catchment during the whole year because the highest loads are carried in floods. On the other hand, if you only sampled high flow conditions, the estimated loads are probably over-estimated.

Nevertheless, load estimates provide an interesting picture of what is happening in your catchment and allow you to identify some possible causes of problems, particularly when put together with other results and information.

How to calculate load estimates

You need to know the flow in your waterway to estimate how much of any particular substance is being washed downstream. For example, you may wish to know how much phosphorus (P) is moved by your waterway in an hour or a day. This sort of quantity is called the instantaneous load.

Instantaneous load of P = flow x phosphorus concentration

If your water monitoring gives a phosphorus reading of 3 mg/L and your flow is 37.5 L/s, then

instantaneous load of P = 37.5 L/s x 3 mg/L = 112.5 mg/s.

Multiply this by 3600/1000 to calculate grams of phosphorus per hour, and then by 24/1000 to calculate kilograms of phosphorus per day.

So, 112.5 mg/s x 3600 s/h = 405,000 mg/h = 405 g/h, and

405 g/h x 24 h/d = 9720 g/d = 9.72 kg/d — even though the initial P concentration seemed quite low!

Only small amounts of phosphorus naturally come from the soil. Most of the 10 kilograms of phosphorus calculated above would be the result of land use practices in the catchment. It could be due to fertilising in the area or direct dumping of wastes into the water.

If the phosphorus is leaching in from the soil we can calculate the loss rate of P, which is the rate of loss of phosphorus from the land into the water for a given unit of time. We usually think of loss rate in terms of hours.

Loss rate = instantaneous load (kg/h) ÷ catchment area (hectares)

So, for a 400 hectare (ha) catchment, loss rate = 405 g/h ÷ 400 ha = 1.0125 g/ha/h.

How to calculate the flow of water passing through your site

The flow (discharge rate) is the volume of water — in cubic metres (m^3) or litres (L) — that flows past a specific site every second. We can express the flow in cubic metres per second (m^3/s) or megalitres per day (ML/d).

Remember that 1 m^3 of water = 1000 L.

To calculate the flow, multiply the cross-sectional area of the stream underwater at your site by the stream velocity.

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

Example:

Cross-sectional area	= 0.6 m^2
Velocity	= 0.3 m/s
Flow	= 0.6 m^2 x 0.3 m/s
	= 0.18 m^3/s
	= 180 L/s

Record your results on a water quality results sheet (see pages 51–52).

Safety considerations when measuring flow

Let someone know where you are going and when you will return.

Do not work alone.

Students must be fully supervised by their teacher in accordance with Education Department guidelines.

Ensure safe and easy access. Beware of slippery rocks and ground.

If sampling near a road or from a bridge, be wary of passing traffic.

Be able to swim if you fall in.

Avoid contact with contaminated water. Use gloves while sampling, but take them off as soon as you've finished. Don't touch your skin with wet gloves.

Keep a first aid kit available.

Feet should be covered; remember sunblock, hat, t-shirt.

The flow rating (discharge) curve

If you have been calculating stream cross-sectional area and velocity at your own site, you can establish your own flow rating curve to make it easier to estimate future flows. The curve will also allow you to identify possible errors made in measuring velocity and cross-sectional area of your site.

When you have measured discharge for a range of water levels (e.g. Table 4.2), you can plot a graph which will allow you to estimate discharge by simply measuring down from your reference mark to the water surface.

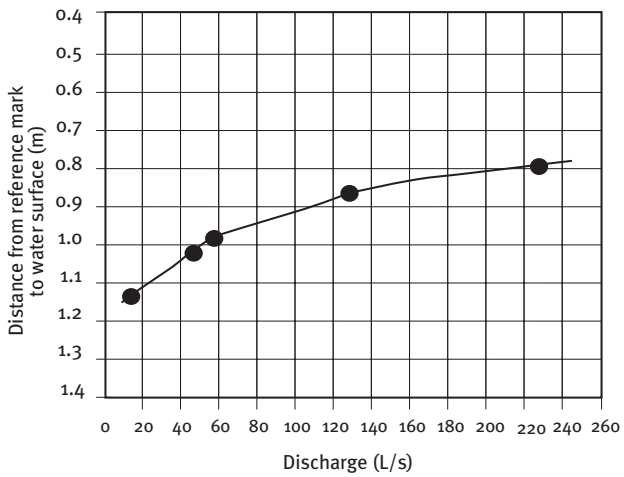
To prepare a graph, as shown in Figure 4.3, plot your measured discharge values (flow) against the distance from the reference marker for each measurement.

Draw a smooth curve of best fit through the points.

As new measurements become available, add the values and adjust the curve as necessary.

Ideally, the points should fall on a smooth curve. However, this depends on the channel shape at your monitoring site. The accuracy of your flow estimates will be better at sites that are relatively regular in shape, such as an irrigation ditch, with straight smooth sides and a profile of the channel that follows the same contours both above and below the water.

Figure 4.3: Flow rating curve for a stream monitoring site



Your flow estimates for low to moderate flows should fall within 10% to 15% of a line forming a smooth curve.

Table 4.2: Example of discharge data

Date	Time	Distance travelled by float (m)	Time in seconds (s)	Velocity (m/s)	Corrected velocity (m/s)	Distance (m) of reference mark to water surface	Cross-sectional area (m^2)	Discharge (L/s)
		6	23	0.26	0.23	1.04	0.20	46.0
		15	45	0.33	0.30	0.88	0.43	129.0
		10	62	0.16	0.14	0.11	0.11	15.4
		10	40	0.25	0.23	0.25	0.25	57.5
		10	24	0.42	0.38	0.59	0.59	224.2

Temperature

What is it and why does it matter?

Temperature: how hot or cold a substance is.

The temperature of a waterbody directly affects many physical, biological and chemical characteristics. Warm waters are more susceptible to eutrophication — a build-up of nutrients and possible algal blooms — because photosynthesis and bacterial decomposition both work faster at higher temperatures. Oxygen is less soluble in warmer water and this can affect aquatic life. By contrast, salts are more soluble in warmer water, so temperature can affect the water's salinity.

Temperature directly affects the metabolic rate of plants and animals. Aquatic species have evolved to live in water of specific temperatures. If the water becomes colder or warmer, the organisms do not function as effectively, and become more susceptible to toxic wastes, parasites and diseases. With extreme temperature change, many organisms will die. Changes in long-term temperature average may cause differences in the species that are present in the ecosystem.

What factors affect temperature?

Water temperature varies in response to:

- air temperature
- exposure to sunlight and amount of shade
- turbidity of the water, which is often a result of erosion in the catchment
- groundwater inflows to the waterbody
- discharge of warmed water from industry and power plants, or cold water from dams
- vegetation
- type, depth and flow of waterbody

Small upland streams have a more consistent temperature than do large rivers, due to the churning and relatively uniform mixing of the water. In slow-moving deep rivers, the non-turbulent water does not mix well, so the temperature can vary across the river and from the top to the bottom of the water column. The large volume of water in large streams also prevents rapid changes in temperature.

Riparian (river-bank) vegetation provides shade and traps sediment particles that would otherwise enter the waterway and absorb heat from sunlight. The shade and clarity of the water help to keep the water cool and well oxygenated.

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

Suggested methods, equipment and reporting

Water temperature is measured in degrees Celsius (°C), with a glass thermometer or a digital meter. It must be measured in the field. Thermometers filled with alcohol are preferred over those filled with mercury because they are less hazardous if broken. Armoured thermometers for field use can withstand more than unprotected glass thermometers and are worth the additional expense. Meters designed for other tests, such as pH or dissolved oxygen, may also measure temperature and can therefore be used instead of a thermometer.

Equipment

The equipment you will need for this method is a glass thermometer or digital meter. Before using a glass thermometer, check it for cracks, and also check the alcohol or mercury column for breaks.

Procedure

If materials entering the waterbody from isolated sources (point sources) such as pipes are thought to be elevating the temperature, it is desirable to obtain two measurements, one above any discharge into the stream and one below.

1. Place the thermometer a few centimetres into the waterway (see Figure 4.4) or immediately into the water sample as soon as it has been collected. If possible, take the temperature directly in the water. Measuring the temperature of a water sample in a bucket or jar is not quite as good.
2. Wait one minute, until the reading stabilises.

3. Read the temperature to the nearest 0.5°C while the thermometer bulb, or temperature probe, is still immersed in the water. Ensure that you take the reading as close as possible to eye level.
4. Repeat steps 1–3 at least once. If the results are variable, take up to 10 measurements.
5. Record all your results on a water quality results sheet (see pages 51–52).
6. Observe trends in temperature variation over the seasons and note any temperature that is unusually high or low.

Figure 4.4: Using a thermometer

Maintenance

After use, rinse the thermometer or meter probe with clean water, dry it and return it to its protective container. Keep the thermometer free from dirt and other contaminants. Make sure the glass does not get scratched or cracked.

Calibration

You should make sure your thermometer and digital meter read the same as at least two other thermometers — at room temperature, in an ice bath and in hot water — annually. This calibration is best done by a reputable laboratory.

Data confidence

Readings of temperatures should be accurate to ±0.5°C.

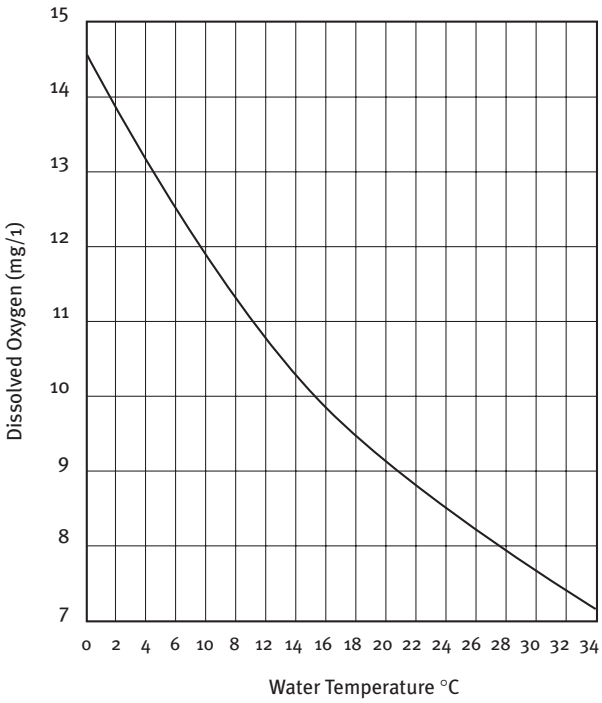
Interpreting your results

Aquatic organisms can experience stress where a temperature change of more than 2°C occurs in a 24-hour period.

Temperature is also an important consideration when interpreting dissolved oxygen and phosphate 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. But the amount of oxygen available in the water decreases! Figure 4.5 shows how dissolved oxygen varies with water temperature.

Interpreting temperature readings requires information about the natural range of temperatures at that site. Over a series of measurements through the year, build up a picture of the temperatures at your sampling site, noting time of day. If, on any particular sampling occasion, values differ markedly from those expected for that time of year or flow rate or time of day you should contact your Waterwatch coordinator and ask about the relevant trigger values discussed in the revised national water quality guidelines (ANZECC/ARMCANZ 2000).*

Figure 4.5: Dissolved oxygen at different temperatures at sea level (per litre of water)



* ANZECC & ARMCANZ (2000). *Australian and New Zealand Guidelines for Fresh and Marine Water Quality*. NWQMS Paper No. 4. Australian and New Zealand Environment and Conservation Council and Agriculture and Resource Management Council of Australia and New Zealand, Canberra.

Safety considerations when measuring temperature

Let someone know where you are going and when you will return.

Do not work alone.

Students must be fully supervised by their teacher in accordance with Education Department guidelines.

Ensure safe and easy access. Beware of slippery rocks and other ground.

If sampling near a road or from a bridge, be wary of passing traffic.

Be able to swim if you fall in.

Avoid contact with contaminated water. Use gloves while measuring, but take them off as soon as you've finished. Don't touch your skin with wet gloves.

Keep a first aid kit available.

Feet should be covered; remember sunblock, hat, t-shirt.

Turbidity

What is it and why does it matter?

Turbidity: opacity or muddiness caused by particles of extraneous matter; not clear or transparent

In general, the more material that is suspended in water, the greater is the water's turbidity and the lower its clarity. Suspended material can be particles of clay, silt, sand, algae, plankton, micro-organisms and other substances. Turbidity affects how far light can penetrate into the water. It is not related to water colour: tannin-rich waters that flow through peaty areas are highly coloured but are usually clear, with very low turbidity. Measures of turbidity are not measures of the concentration, type or size of particles present, though turbidity is often used as an indicator of the total amount of material suspended in the water (called total suspended solids). Turbidity can indicate the presence of sediment that has run off from construction, agricultural practices, logging or industrial discharges.

Suspended particles absorb heat, so water temperature rises faster in turbid water than it does in clear water. Then, since warm water holds less dissolved oxygen than cold water, the concentration of dissolved oxygen decreases.

If penetration of light into the water is restricted, photosynthesis of green plants in the water is also restricted. This means less food and oxygen is available for aquatic animals. Plants that can either photosynthesise in low light or control their position in the water, such as blue-green algae, have an advantage in highly turbid waters.

Suspended silt particles eventually settle into the spaces between the gravel and rocks on the bed of a waterbody and decrease the amount and type of habitat available for creatures that live in those crevices. Suspended particles can clog fish gills, inducing disease, slower growth and, in extreme cases, death.

Fine particles suspended in water carry harmful bacteria and attached contaminants, such as excess nutrients and toxic materials. This is a concern for drinking water, which often requires disinfection with chlorine to kill harmful bacteria.

What factors affect turbidity?

Turbidity is affected by:

- rainfall and catchment runoff
- catchment soil erosion
- bed and bank erosion
- bed disturbance, e.g. by introduced fish species such as carp
- waste discharge
- stormwater
- excessive algal growth
- riparian vegetation
- floodplain and wetland retention and deposition
- flow
- waterway type
- soil types
- salinity.

Regular turbidity monitoring may detect changes to erosion patterns in the catchment over time. Event monitoring (before, during and immediately after rain) above and below suspected sources of sediment can indicate the extent of particular runoff problems.

Suggested methods, equipment and reporting

Turbidity can be measured using a Secchi disk, a turbidity meter or a turbidity tube. The turbidity tube is adequate for most purposes, but if your waterways are generally very clear a turbidity meter may be more suitable. The Secchi disk is useful only in non-flowing, relatively deep water.

Turbidity is best measured on-site in the field, but if necessary it can be measured later, within 24 hours of sampling, provided the sample bottles are filled completely, leaving no air gap at the top.

Secchi disk

A Secchi disk allows you to measure the water's transparency. The clearer (less turbid) the water, the greater the depth to which the disk must be lowered before it disappears from view. This is why Secchi disks are not useful in shallow water.

The main advantage of Secchi disks is that they are cheap and easy to use.

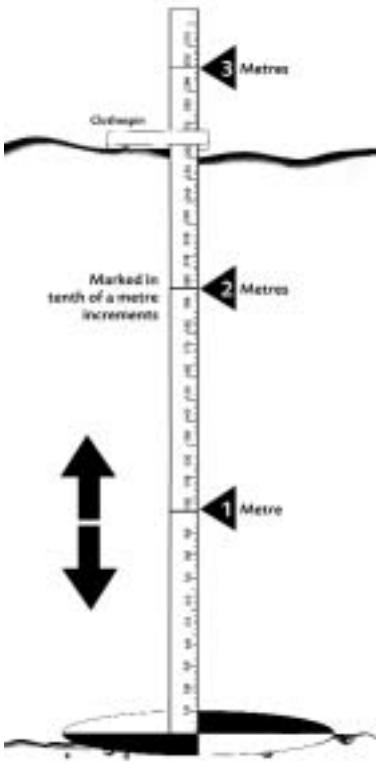
Equipment

The Secchi disk is a black and white 20 cm diameter disk which is attached to a long tape measure or cord marked in metres. Ask your Waterwatch coordinator how to obtain a Secchi disk.

Procedure

Lower the disk into the water until it disappears and then raise it until it reappears. The depth (as indicated on the tape) at which you can see the disk is the Secchi disk reading (see Figure 4.6).

Figure 4.6: Using a Secchi disk



Turbidity meter

Turbidity is a relative measure. It is usually expressed as nephelometric turbidity units (NTU) or as metres depth. Other units, such as formazin turbidity units (FTU) or Jackson turbidity units (JTU), are specific to particular types of turbidity meter and their methods of calibration. They are not absolute measures. (They can be converted to NTU by calculation, if you need to, and the method may be explained on the instrument.)

Turbidity meters measure the intensity of a light beam when it has been scattered by particles in the water. They are effective over a wide range — from 0 to 1000 NTU.

Turbidity tube

The turbidity tube reads turbidity by absorbing light rather than scattering light, so it overestimates turbidity in samples that are highly coloured and underestimates turbidity in samples containing very fine particulates, such as clay. However, it is very simple to use and gives good comparative measures.

Equipment

The turbidity tube is a long thin clear plastic tube, sealed at one end with a white plastic disc with three black squiggly lines on it (seen when looking down the tube). The tube has a scale marked on the side. Your Waterwatch coordinator can tell you how to obtain a turbidity tube.

Procedure

1. Collect water sample in a clean bucket or sample bottle.
2. Make sure sample is well mixed before testing.
3. Gradually pour the sample into the turbidity tube while looking vertically down the tube (see Figure 4.7). Hold the tube out of direct sunlight during this procedure. 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 squiggly lines on the bottom.
5. Note the reading from the scale on the side of the tube.
6. If the reading is above 200, dilute the sample 1:1 with distilled water. Repeat testing procedure and multiply the final result by 2.
7. 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, i.e. <10 NTU.*
8. Record the reading as NTU on a water quality results sheet (see pages 51–52).

*The 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 last number. If you can see the wavy lines when the water is at the top, record the result as 'less than 10 NTU'.

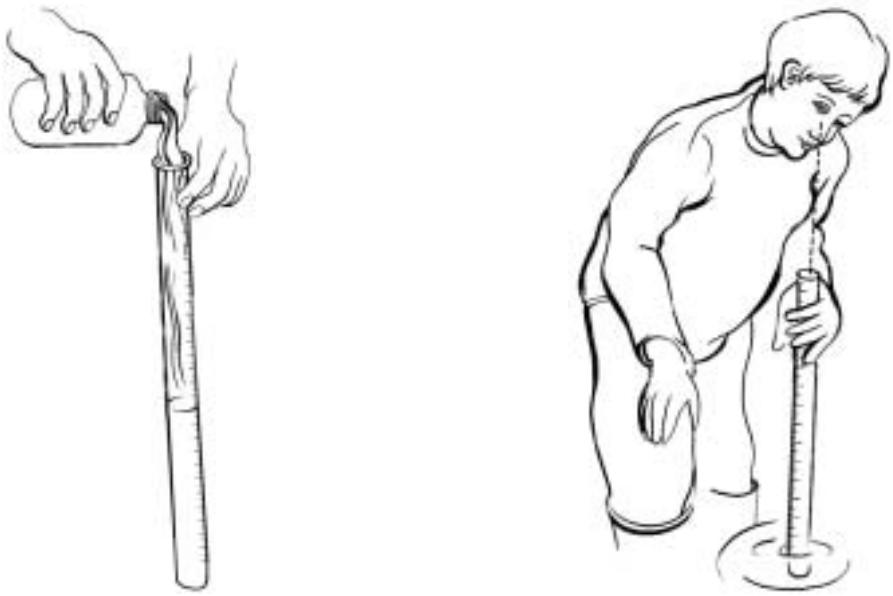
Maintenance

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

Calibration

No calibration is required and the tube reads from 10 to 400 NTU.

Figure 4.7: Using the turbidity tube



Data confidence

Secchi disk

Make sure the Secchi disk is clean. Have a second person check the result. Check the accuracy of markings on the Secchi disk cord. Perform the test in shade if possible.

Undertake a field replicate test every 10 samples.

For river monitoring, Secchi disks have limited use because the river bottom is often visible. Also, the disk is often swept downstream by the current, making accurate measurements impossible. You may consider using a Secchi disk if you wish to monitor the clarity of a lake or deep slow moving river or estuary, and the water is too clear — i.e. less than 10 nephelometric turbidity units (<10 NTU) — for accurate turbidity tube readings, and your group cannot afford to buy a turbidity meter.

Turbidity tube

To avoid error make sure the turbidity tube is clean and free of scratches. Perform the test in shade if possible. Have a second person check the result. Note if highly coloured water is present, because it may elevate the readings. Test a field replicate every 10 samples.

Interpreting your results

Natural (or background) turbidity levels in waterways vary from <1 NTU in mountain streams to hundreds of NTU during rainfall events or in naturally turbid waters. Turbidity is affected by river flow, so be sure to measure the river flow when you collect your sample.

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 Waterwatch coordinator, natural resource management agency or local council. Then, over a series of measurements, build up a picture of the turbidity and its variation in your own waterbody.

If, on any particular sampling occasion, values that differ markedly from those expected for that time of year or flow rate you should contact your Waterwatch coordinator and ask about the relevant trigger values discussed in the revised national water quality guidelines (ANZECC/ARMCANZ 2000).

Safety considerations when measuring turbidity

Let someone know where you are going and when you will return. Do not work alone.

Students must be fully supervised by their teacher in accordance with Education Department guidelines.

Ensure safe and easy access. Beware of slippery rocks and ground.

If sampling near a road or from a bridge, be wary of passing traffic.

Be able to swim if you fall in.

Avoid contact with contaminated water. Use gloves while measuring, but take them off as soon as you've finished. Don't touch your skin with wet gloves.

Keep a first aid kit available.

Feet should be covered; remember sunblock, hat, t-shirt.

Electrical conductivity

What is it and why does it matter?

Electrical conductivity: the property of a substance which enables it to serve as a channel or medium for electricity

Salty water conducts electricity more readily than purer water. Therefore, electrical conductivity is routinely used to measure salinity. The types of salts (ions) causing the salinity usually are chlorides, sulphates, carbonates, sodium, magnesium, calcium and potassium.

While an appropriate concentration of salts is vital for aquatic plants and animals, salinity that is beyond the normal range for any species of organism will cause stress or even death to that organism. Salinity also affects the availability of nutrients to plant roots.

Depending on the type of salts present, salinity can increase water clarity. At very high concentrations, salts make water denser, causing salinity gradations within an unmixed water column and slightly increasing the depth necessary to reach the water table in groundwater bores.

What factors affect electrical conductivity?

Electrical conductivity in waterways is affected by:

- geology and soils
- land use, such as agriculture (irrigation), urban development (removal of vegetation, sewage and effluent discharges), industrial development (industrial discharges)
- flow (electrical conductivity is generally lowest during high flows and increases as flows decrease, with extreme levels occurring during droughts)
- run-off
- groundwater inflows
- temperature
- evaporation and dilution.

Contamination discharges can change the water's electrical conductivity in various ways. For example, a failing sewage system raises the conductivity because of its chloride, phosphate, and nitrate content, but an oil spill would lower the conductivity. The discharge of heavy metals into a waterbody can raise the conductivity as metallic ions are introduced into the waterway.

Suggested methods, equipment and reporting

The basic unit of measurement of electrical conductivity is microSiemens per centimetre (µS/cm) or deciSiemens per meter (dS/m). MicroSiemens per centimetre are sometimes called EC units. The total dissolved solids (or TDS) content of a water sample, in milligrams per litre (mg/L), is also a measure of salinity. The sample's electrical conductivity can be converted to TDS.

The electrical conductivity of water samples should be measured on the spot at the waterbody. Measurement can be delayed by up to 1 month if the sample is refrigerated (but NOT frozen) immediately on being taken, and if the sample bottle is filled completely, with no air gap at the top.

Equipment

The equipment you will need for this method includes:

- electrical conductivity meter
- calibration solution
- deionised water

An electrical conductivity meter uses two electrodes, one of which detects an electrical current sent by the other. The meter should also measure temperature and automatically compensate for temperature in the conductivity reading, but non-compensating meters do exist.

If you have a non-compensating meter, you must measure the water temperature at the same time as the electrical conductivity.

When comparing salinities of different samples, it is important to standardise the reading to 25°C. Do this by increasing the electrical conductivity reading by 2% per degree for samples with temperatures below 25°C, and decreasing it by 2% per degree for samples above 25°C.

Different meters are available for fresh water (0–1990 µS/cm), and brackish (slightly salty) water, (0–19 900 µS/cm), and sea

water (~50 000 µS/cm). Use a meter that matches the expected conductivity range of your waterway.

Procedure

1. Before going to the site, calibrate your meter.
2. On site, rinse the electrode in deionised water.
3. Collect a water sample using the normal sampling technique.
4. Dip the electrode into the sample and, if appropriate, select the appropriate conductivity range.
5. Do not immerse the probe too far (some probes/meters are not waterproof above a certain point).
6. Move the electrode slowly in a circle for one minute until the digital read-out stabilises or continually jumps between two numbers.
7. Repeat the test on a replicate sample.
8. Record both results on a water quality results sheet (see pages 51–52).
9. Dispose of the sample downstream of your test site.
10. Rinse the electrode with deionised water before testing the next sample.

If the conductivity of the sample exceeds the range of the meter, you may dilute the sample. Be sure to perform the dilution according to the manufacturer's instructions because the dilution may not have a simple linear relationship to the conductivity.

Maintenance

Rinse the electrodes with deionised water from a squeeze bottle. Dry the electrodes with a paper towel, otherwise the electrodes will corrode. Replace the cap and place the meter back in your kit. The stainless steel electrodes need to be kept clean and dry.

To ensure accurate readings, you should periodically clean the meter with methylated spirits. Put the electrodes into a beaker with enough methylated spirits to just cover them, and leave them to stand for 15–20 minutes. Remove the electrodes and wipe them with a soft tissue soaked in methylated spirits. Finally rinse them thoroughly with distilled water.

Calibration

Use a conductivity calibration solution — usually potassium chloride (KCl) — to calibrate the meter to the range you will be measuring. For example, a 0.01 molar KCl solution will have a conductivity of 1413 µS/cm, and a 0.001 molar KCl solution will have a conductivity of 147 µS/cm.

To prepare a 0.01 molar conductivity solution, dissolve 0.7456 g of KCl (that has been dried overnight at 105°C) in freshly boiled deionised water and dilute to 1 L (can be stored for 6 months). To prepare a 0.001 molar solution, use only 0.0746 g of KCl (can be stored for 3 months). Store solutions in a dry, dark and cool room.

Significant errors can result from not calibrating your meter at 25°C, e.g. if the meter is calibrated using a solution at 15°C, it will give erroneous water sample readings that are 20% too high.

Tip a small volume of calibration solution into a small clean container for use when calibrating the meter. Do not immerse the meter or probe in the stock solution because this will contaminate it, making it unusable. Rinse the electrodes with deionised water.

Data confidence

For quality control, calibrate the meter with a standard before each sampling run. The standards must be at 25°C and of similar concentrations to test samples. Also, check that the meter has held its calibration at the end of sampling run. Test a Waterwatch mystery sample (available from your coordinator) every six months.

Interpreting your results

Each waterway or waterbody tends to have a relatively consistent range of electrical conductivity values that, once known, can be used as a baseline against which to compare regular measurements of conductivity. Significant changes in conductivity may then indicate that a discharge or some other source of contamination has entered the waterway.

The electrical conductivity of Australian rivers varies widely across the country. Trigger values, given by the revised national water quality guidelines for the protection of freshwater ecosystems (ANZECC/ARMCANZ 2000), range from 20 µS/cm (in upland rivers in tropical Australia and lakes in south-east Australia) to 5000 µS/cm (in lowland rivers in south-central Australia). If samples have salinities equal to or greater than those trigger values, management action is needed to reduce the salinity in that water. Values measured by Waterwatch groups in waterbodies should ideally be smaller than the local trigger values. Check with your Waterwatch coordinator for the range of salinities to be expected in your area, and to discuss the relevant trigger values. Table 4.3 compares typical salinity readings in various types of water.

Estuaries have a higher conductivity than freshwater since, as salinity increases, conductivity also increases. The electrical conductivity of bore water varies and can be several times saltier than sea water.

Table 4.3: Some electrical conductivity ranges

Water type	Electrical conductivity (µS/cm)
Deionised water	0.5–3
Pure rainwater	<15
Freshwater rivers	0–800
Marginal river water	800–1600
Brackish water	1600–4800
Saline water	>4800
Seawater	51 500
Industrial waters	100–10 000

Source: Suttar S., *Ribbons of Blue Handbook*. Scitech, Victoria, 1990.

Safety considerations when measuring electrical conductivity

Let someone know where you are going and when you will return. Don't work alone.

Students must be fully supervised by their teacher in accordance with Education Department guidelines.

Ensure safe and easy access. Beware of slippery rocks and ground.

If sampling near a road or from a bridge, be wary of passing traffic.

Be able to swim if you fall in.

Avoid contact with contaminated water. Use gloves while measuring, but take them off as soon as you've finished. Don't touch your skin with wet gloves.

Keep a first aid kit available.

Feet should be covered; remember sunblock, hat, t-shirt.

After each piece of used equipment has been rinsed with distilled water, pour the rinse water into the liquid waste bottle.

Do not put solid waste into the liquid waste bottle.

Place all used gloves, used paper towels, empty reagent packaging and any other rubbish from testing into a plastic garbage bag with no tears in it, and take it with you when you leave. Try to leave the site cleaner and tidier than you found it—pick up and transport out any rubbish.

Consult your Waterwatch coordinator about disposing of liquid waste.

ph

What is it and why does it matter?

pH: a measure of acidity (or alkalinity). Pure water has a pH of 7, acidic solutions have lower pH values and alkaline solutions have higher values.

Values of pH range from 0 (highly acidic) to 14 (highly alkaline). Where water has no net alkalinity or acidity it is said to be neutral and has a pH of 7. pH can be a little misleading unless you remember that one pH unit represents a ten-fold change. So if the pH of a water sample falls from pH 7 to pH 6, that is equivalent to a 10-fold increase in acidity. Figure 4.8 shows the pH of some common liquids.

Many compounds are more soluble in acidic waters than in neutral or alkaline waters. The pH of the wet area around roots affects nutrient uptake by the plants; pH also affects the solubility of heavy metals in water and the concentrations of total dissolved solids in rivers.

All animals and plants are adapted to specific pH ranges, generally between 6.5 and 8.0. If the pH of a waterway or waterbody is outside the normal range for an organism it can cause stress or even death to that organism.

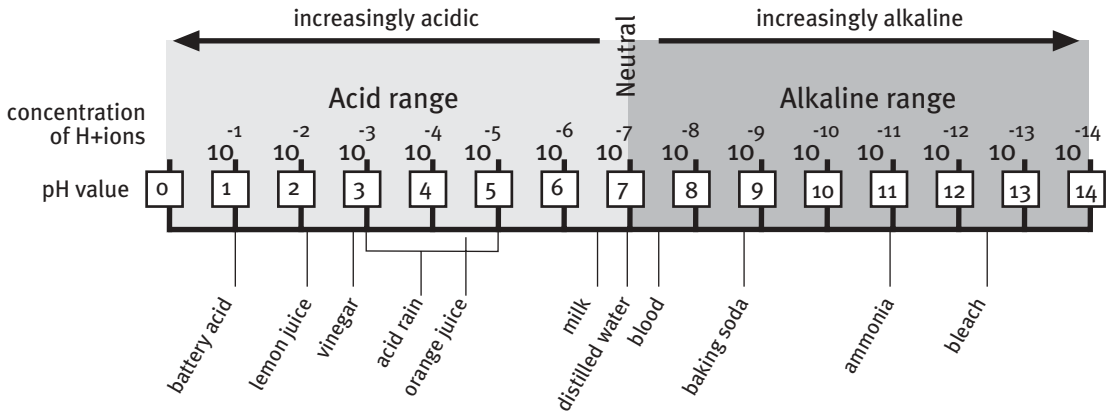
What factors affect pH?

A wide variety of factors may have an effect on the pH of water. These include:

- source of the water
- rainfall
- time of day
- water temperature
- amount of algal or plant growth in the water
- geology and soils, e.g. acid sulfate soils
- discharges of industrial wastes
- disturbance of acid sulfate soils due to agriculture, urban development or mining
- atmospheric deposition (acid rain, dry particle deposition)
- burning of fossil fuels by cars, factories and smelters
- photosynthesis and respiration
- salinity

The pH of a waterbody varies during the course of the day as the balance between photosynthesis and respiration changes with the light intensity and temperature. Inflowing water may affect the pH of the waterbody as well: rainfall is naturally slightly acidic because of carbon dioxide dissolved in it; water running off limestone areas has relatively high pH. On the other hand, streams and lakes in coastal dune areas may have very low pH (sometimes less than 5) due to the presence of naturally-occurring humic acids.

Figure 4.8: pH scale and pH of selected liquids



Suggested methods, equipment and reporting

The pH of a waterbody is best measured in the field, as the samples are being taken. A pH measurement can be delayed by up to 24 hours, but only if the sample is refrigerated immediately and the sample bottle is filled completely, with no air at the top.

To measure pH, you can use either pH strips (often called indicator paper) or a pH meter.

pH strips method

pH strips are coated paper strips that change colour according to the pH of the sample. The colour can be compared to a colour scale to estimate the pH value. pH strips have a long shelf life (3 years) if stored in cool dry conditions; and give reliable results for monitoring groups. Choose pH strips that can detect changes of 0.5 units in water samples and are suitable for weakly buffered waters.

Equipment

The equipment you will need for this method includes:

- La Motte pHydrion pH test kit
- sample bottle
- deionised water

Procedure

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 sticking out the top when the tube is recapped. This enables you to easily remove the indicator strip 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 full colour to develop.
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.
7. Repeat test on a field replicate water sample.
8. Record both readings on the water quality result sheet (see pages 51–52).

Maintenance

Pour the water into the liquid waste bottle and place the pH paper in the solid waste container.

Rinse the tube with deionised water and dry it before returning it to the kit.

Calibration

You cannot calibrate pH paper, but you can check it against known reference solutions. Prolonged storage may make the paper less accurate.

pH meter method

A pH meter measures pH and temperature, and it adjusts the readings according to the temperature of the sample (pH varies with temperature). pH meters usually display results in pH units. Meters vary a great deal, but the most important part is the electrode. Buy a good, reliable electrode and follow the manufacturer's instructions for proper maintenance. Infrequently used or improperly maintained electrodes are subject to corrosion, which renders them highly inaccurate. The electrode tends to last only 1 or 2 years, so you may consider purchasing a meter with a replaceable electrode.

Equipment

The equipment you will need for this method includes:

- pH meter
- Sample bottle
- Deionised water
- Calibration solutions and containers

Procedure

1. Rinse the electrode well with deionised water.
2. Place the electrode in the sample. Wait 2–3 minutes for the reading to stabilise but be aware that some change will occur as pH reacts with carbon dioxide dissolving from the air. Record the result on the water quality results sheet (see pages 51–52).
3. Repeat test on a field replicate sample and record the result on the water quality results sheet (see pages 51–52).
4. Periodically measure the pH of the calibration solution to test accuracy. If it has drifted off, recalibrate. Do not reuse buffer solutions.

Maintenance

Rinse the electrode well with deionised water, replace cap when finished.

Calibration

A good quality pH meter can detect minimum variations (sensitivity) of 0.1 pH units in river water and can be calibrated at two points giving more accurate readings over a wider range than one-point calibration meters.

Table 4.4: Quality control measures for pH

Relative data quality	Equipment method	Sensitivity (minimum change that can be detected)	Calibration	Type of quality control
Low or intermediate	pH strips	0.5 pH units.	None	Store pH paper in dark dry conditions
High	pH meter (one and two point calibration)	0.1 pH units	Calibrate meter prior to each use and check against calibration standards every 2–3 hours of use.	10% of tests to be internal field replicates and split samples or external field replicates.

Meters must be calibrated with buffer solutions before each sampling and periodically during sampling, e.g. every fifth sample, to check if the meter has drifted off calibration. Your check on the calibration standard should be within the sensitivity range, e.g. ± 0.1 pH units, of the equipment used.

If you are using a two-point calibration meter, use two buffer solutions at 4.0 and 7.0. Buffer tablets can be purchased from test kit supply companies and must be used within their expiry date. A buffer solution of pH 4.0 will last 3 months, but a solution of pH 7.0 will last 6 months if stored in a cool dark place.

Data confidence

pH strips

Minimise damage or staining of the colour chart by storing it in dark dry conditions (see Table 4.4) — water reacts with dyes in the paper.

Measure a field replicate after every tenth test.

Test a Waterwatch mystery sample every six months.

pH meter

Test a Waterwatch mystery solution every 10 tests; or set aside 10% of samples to be split and tested by a laboratory elsewhere, or an external field replicate sample to be tested by a water quality professional officer (see Table 4.4).

Interpreting your results

When measuring pH, you should sample at the same time of day on each occasion, being aware of the potential effect on pH of daily changes in photosynthetic activity of aquatic plants. When monitoring estuaries, note the state of the tide and also record conductivity readings before attempting to interpret variations in pH. Note the geology and soils and land use of the catchment you are monitoring, to help interpret pH changes from one site to another.

You should monitor pH from a suspected point source of contamination both at the reference site and at your test sites. For baseline monitoring, interpretation of pH values requires some knowledge of the natural ranges likely to be found in the catchment. For example, a pH of 6.5 might be normal in some streams, but if found in a limestone catchment, would indicate a possible problem.

Changes of more than 0.5 pH units from the natural seasonal maximum or minimum in fresh water should be investigated. Many freshwater systems have a pH close to 7.0 (for example, see Table 4.5). However, the range in limestone areas is 7.0–8.5 and in non-limestone areas 5.0–7.0. In marine waters the pH should not vary more than 0.2 units from the normal values. Marine waters normally have a pH close to 8.2.

Contact your Waterwatch coordinator and ask about the relevant trigger values discussed in the revised national water quality guidelines (ANZECC/ARMCANZ 2000).

Table 4.5: Guidelines for water quality as it affects rivers in Victoria

	Excellent	Good	Fair	Poor	Degraded
pH range	6.0–7.5	5.5–6 or <8.0	8.0–8.5	5.0–5.5 or 8.5–9.0	<5.0 or >9.0

Source: State of the Environment Report — Victoria's Inland Waters in Waterwatch Victoria, A Community Water Quality Monitoring Manual for Victoria 1994.

Safety and waste considerations when measuring ph

Let someone know where you are going and when you will return.

Don't work alone.

Students must be fully supervised by their teacher in accordance with Education Department guidelines.

Ensure safe and easy access. Beware of slippery rocks and ground.

If sampling near a road or from a bridge, be wary of passing traffic.

Be able to swim if you fall in.

Avoid contact with contaminated water. Use gloves while sampling, but take them off as soon as you've finished. Don't touch your skin with wet gloves.

Keep a first aid kit available.

Feet should be covered; remember sunblock, hat, t-shirt.

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.

Hold all test bottles over a wide-mouthed liquid waste bottle while adding the reagents or calibration solutions.

After each piece of used equipment has been rinsed with distilled water, pour the rinse water into the liquid waste bottle.

Do not put solid waste into the liquid waste bottle.

Place all used gloves, used paper towels, empty reagent packaging and any other rubbish from testing into a plastic garbage bag with no tears in it, and take it with you when you leave. Try to leave the site cleaner and tidier than you found it — pick up and transport out any rubbish.

Consult your Waterwatch coordinator about disposal of liquid wastes.

Dissolved oxygen

What is it and why does it matter?

Dissolved oxygen: a measure of the quantity of oxygen present in water (it has nothing to do with the oxygen atoms within the water molecules)

Oxygen is essential for almost all forms of life. Aquatic animals, plants and most bacteria need it for respiration (getting energy from food), as well as for some chemical reactions.

The concentration of dissolved oxygen is an important indicator of the health of the aquatic ecosystem. Persistently low dissolved oxygen will harm most aquatic life because there will not be enough for them to use.

In some circumstances, water can contain too much oxygen and is said to be supersaturated with oxygen. This can be dangerous for fish. Supersaturated conditions occur in highly turbulent waters in turbines and at spillways, because of aeration, and also on sunny days in waters experiencing algal blooms or with many aquatic plants, because of photosynthesis. In this supersaturated environment, the oxygen concentration in fishes' blood rises. When the fish swim out into water that has less dissolved oxygen, bubbles of oxygen quickly form in their blood, harming the circulation.

What factors affect dissolved oxygen?

The air is one source of dissolved oxygen, and aquatic plants, including algae, are another. The speed at which oxygen from the air enters and mixes through a waterbody depends on the amount of agitation at the water surface, the depth of the waterbody and the rate at which it mixes itself. As water temperature rises, oxygen diffuses out of the water into the atmosphere.

Shallow flowing waterways usually have high dissolved oxygen concentrations. In still waters, such as lakes, dissolved oxygen concentrations often vary from the surface to the bottom, with little dissolved oxygen in the deep, poorly mixed, layers.

Warm or saline water holds less dissolved oxygen than cold water or freshwater (see Table 4.6).

Dissolved oxygen concentrations change with the seasons, as well as daily, as the temperature of the water changes.

At very high altitudes, the low atmospheric pressure means dissolved oxygen concentrations are lower. For example, at 1850 metres above sea level, the amount of dissolved oxygen in the water, in absolute terms (mg/L), will be only 80% of the amount at sea level in otherwise identical conditions.

Deep muddy lowland rivers, which contain more organic matter than upland streams, are likely to have lower dissolved

Table 4.6: Effect of conductivity and temperature on potential dissolved oxygen concentrations (mg/L) in waters at sea level

Temperature (°C)	Conductivity µS/cm (salinity mg/L)				
	0 (0)	14400 (9000)	28800 (18000)	43200 (27000)	57800 (36000)
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

Source: Waterwatch Queensland Technical Manual 1994

oxygen concentrations than upland streams because bacteria are using the oxygen to break down the organic matter. Likewise, dissolved oxygen is usually lower than normal after storms have washed organic materials into any waterbody.

Aquatic plants photosynthesise during daylight and increase dissolved oxygen concentrations around them.

Figure 4.9 shows a hypothetical daily cycle for dissolved oxygen concentrations for both a river with much plant growth in it (eutrophic) and a normal river.

In summary, dissolved oxygen concentrations are affected by:

- water temperature
- photosynthesis by aquatic plants
- respiration by aquatic plants and animals
- breakdown of organic materials in the water
- water movement and mixing
- flow (discharge)
- salinity
- altitude
- depth
- daily and seasonal cycles
- presence of nutrients
- chemicals in the water
- thermal contamination
- removal of vegetation

Suggested methods, equipment and reporting

Oxygen concentrations are expressed as milligrams per litre (mg/L), but percentage saturation (% sat) allows direct comparison between results from sites with different salinity and temperature values. However, remember that warmer water, even when it is 100% saturated, will have less absolute oxygen dissolved in it than cooler water at the same percentage of saturation.

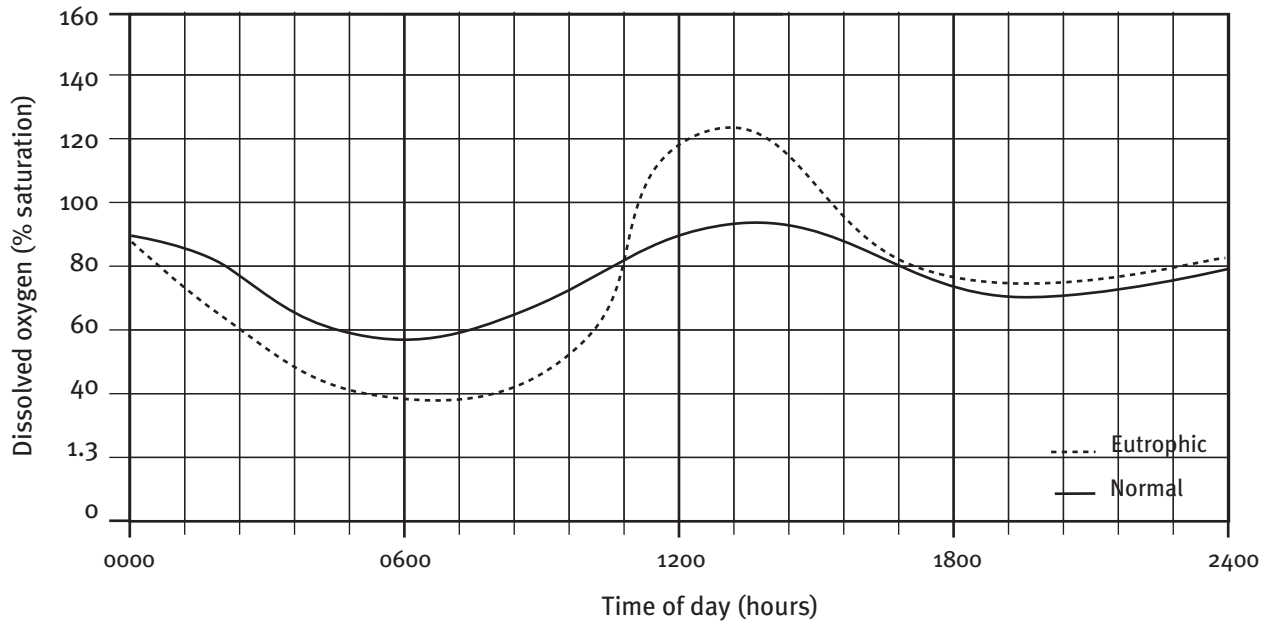
Dissolved oxygen is best measured on-the-spot in the field, with a meter and probe. Meter readings are not affected by contamination or colouring in the water.

Alternatively, dissolved oxygen can be measured by Winkler titration of water samples fixed in the field. Titration can be completed using an eye-dropper (sensitivity = 1 mg/L), a syringe (sensitivity = 0.2 mg/L) or a digital titrator (sensitivity = 0.1 mg/L). The method you choose depends on the data quality you need.

It is important to record the time of day on your results sheet when you sample or make a field test for dissolved oxygen because of the increase and decrease in concentrations over 24 hours. It is best to try and make measurements at the same time each day.

If testing in estuaries, be aware of the tidal flow that may carry contaminants upstream from discharge points. When measuring dissolved oxygen in saline water, adjust the percentage saturation concentration according to your conductivity measurement.

Figure 4.9: Variation of dissolved oxygen in a river with much plant growth compared with a clear river*



* Few Australian rivers are 'clear' because of heavy turbidity

Dissolved oxygen meter and probe

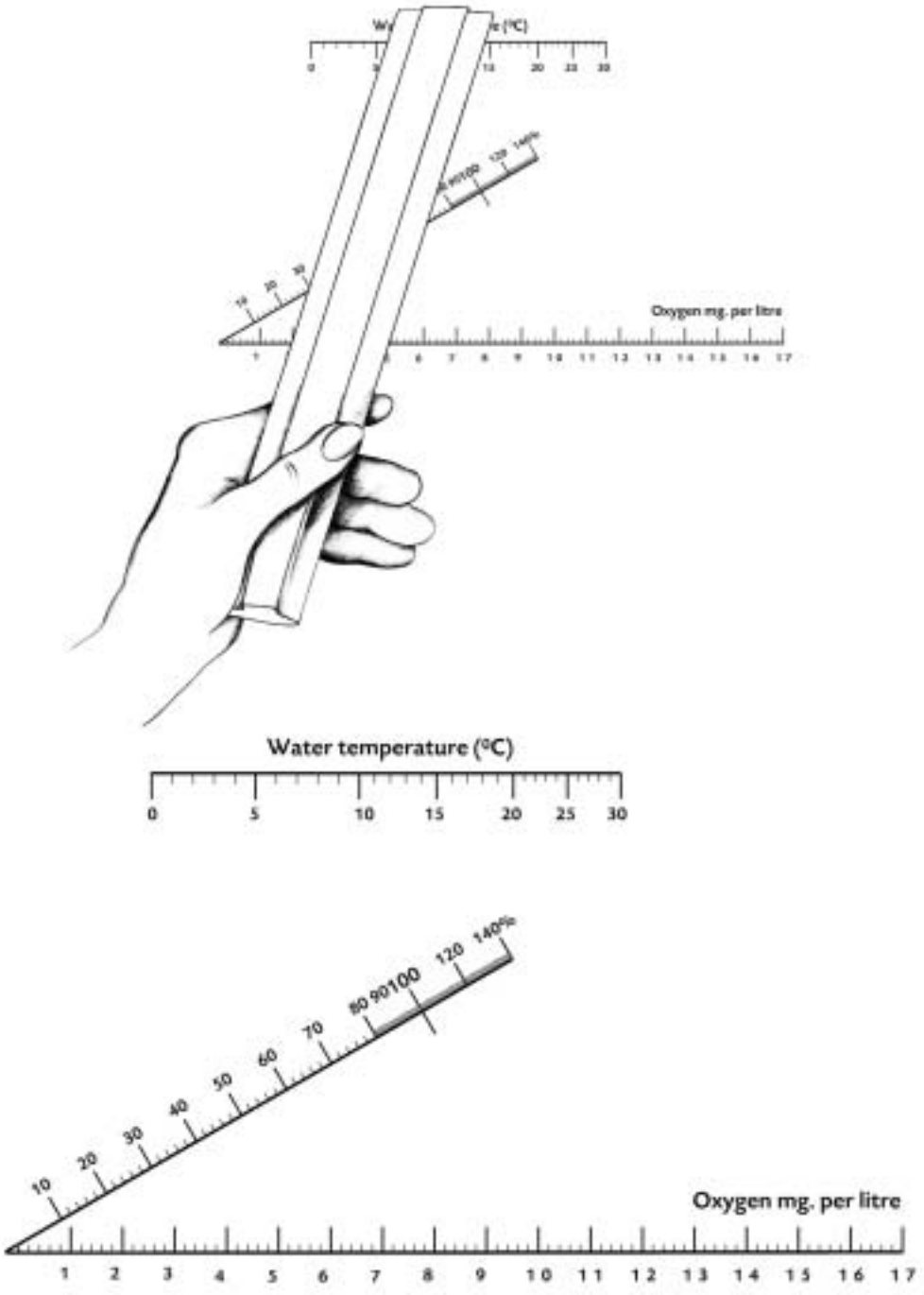
A dissolved oxygen meter is an electronic device in which oxygen diffuses across a membrane in a submerged probe, to complete an electrical circuit. It records the dissolved oxygen concentration in milligrams per litre or percentage saturation. Most meters also measure temperature. The advantage of this type of meter is that you can measure directly in the waterway.

Equipment

The equipment you will need for this method includes:

- dissolved oxygen meter and probe (electrode)
- operating manual for the meter and probe
- extra membranes and electrolyte solution for the probe
- extra batteries for the meter
- extension pole

Figure 4.10: Percentage saturation dissolved oxygen graph (see page 33 for instructions on how to use this graph)



Procedure

1. Turn the meter on and allow 15 minutes for the meter to reach equilibrium before calibrating.
2. Calibrate the meter before each use, according to the manufacturer's instructions. It can also be checked against readings from the Winkler method.
3. Place the probe in the stream below the surface (about wrist depth).
4. Set the meter to measure temperature and allow the temperature reading to stabilise. Record temperature reading on a water quality results sheet (see pages 51–52).
5. Switch the meter to read 'dissolved oxygen'. Record dissolved oxygen on the water quality results sheet.
6. If testing saline waters, measure the electrical conductivity level and record on the water quality results sheet as well.
7. Re-test water to obtain a field replicate result.

Calibration

Be sure to calibrate the meter according to the manufacturer's instructions, before each use. The calibration values for temperature and altitude should be printed in the manufacturer's instructions.

Calculating percentage saturation of dissolved oxygen

Refer to Figure 4.10 on page 32.

1. Mark your water temperature (°C) on the upper scale.
2. Mark the water's concentration of oxygen (mg/L) on the lower scale.
3. Hold a ruler between the two points.
4. The point where the ruler crosses the middle scale is the % saturation.
5. Record this result on the water quality results sheet (see pages 51–52).

For saline water samples (>1500 µS/cm) you need to know:

- the measured conductivity __ µS (salinity __ mg/L);
- the water temperature __ °C;
- the measured dissolved oxygen __ mg/L.

Use Table 4.6 to establish the potential dissolved oxygen:

- locate the nearest conductivity level across the top
- locate the nearest temperature on the left hand side
- where they cross, registers the potential dissolved oxygen for the water: __ mg/L.

Finally:

- divide the measured dissolved oxygen by the potential dissolved oxygen
- multiply this by 100 to get the per cent saturation: __ % saturation.

Winkler method

The Winkler method involves titrating a carefully taken and fixed sample. Titration involves the drop-by-drop addition of a reagent that neutralises the acid compound and causes a change in the colour of the solution. The point at which the colour changes is called the 'endpoint' and it indicates the amount of oxygen dissolved in the sample.

The sample can be fixed and titrated in the field at the sample site. It is also possible to fix the sample in the field and do the titration in the laboratory within 24 hours of sampling.

The low cost of this type of dissolved oxygen field kit is attractive if you are relying on several teams of samplers to sample a number of sites at the same time.

Equipment

The equipment you will need for this method includes:

- labels for sample bottles
- dissolved oxygen field kit and instructions (ask your Waterwatch coordinator)
- enough reagents for the number of sites to be tested
- commercial or home-made water sampler for collecting deep-water samples or bridge samples
- two numbered glass BOD bottles with glass stoppers (sample and replicate) for each site, if fixing dissolved oxygen on-site for transfer to laboratory for completion of test.

Biological oxygen demand (BOD)

BOD is a measure of the amount of oxygen used by biological and chemical processes in a sample of stream water over a 5-day period. BOD bottles have tapered necks and a ground glass stopper or a special plastic lid.

Procedure

1. Use glass BOD bottles which are free of contaminants. Rinse your sampling bottle in the water you are testing.
2. Fill the bottle directly from the stream if it is wadable or accessible by boat, or use a deep-water sampler that is dropped on a line or extension pole from a bridge or boat (ask your Waterwatch coordinator about deep-water samplers).
3. To stop surface scum entering the bottle, leave the lid on the sample bottle until the bottle is below the surface.
4. Turn the bottle on its side and lower it into the water until the surface of the water is up to your wrists.

5. When the bottle is below the surface, slowly remove the lid allowing the water to enter.
6. Carefully turn the bottle vertically the right way up while it is below the surface to allow it to completely fill and release all trapped air.
7. Recap the bottle while it is underwater, keeping it still — do not agitate the sample.
8. Remove the bottle from the water and invert the bottle slowly to check that no bubbles have been trapped inside.
9. When filling the dissolved oxygen bottle, take a water temperature reading at the same time and place.
10. Repeat steps 1 to 9 to collect a replicate sample.
11. Number and label both bottles and record the bottle numbers on the water quality results sheet (see pages 51–52).
12. Follow the manufacturer's instructions for testing both samples for dissolved oxygen (see also, Testing in the laboratory below).
13. If you are taking the sample to the lab for titration, you can store the fixed sample in the dark for up to 24 hours before completing the test.
14. Record dissolved oxygen (mg/L), temperature (°C) and electrical conductivity (mS mg/L). Determine % saturation by using Figure 4.10.
15. Record your readings on the water quality results sheet (see pages 51–52).

Testing in the laboratory

1. To the sample collected in a 250 or 300 mL bottle, add 1mL of manganous sulfate (reagent no. 1) and 1 mL alkaline iodide azide (reagent no. 2). Mix by inverting the bottle until a precipitate forms and settles.
2. When about half the bottle volume is occupied by clear liquid above the precipitate, add 1 mL of strong acid, usually concentrated sulfuric acid (reagent no. 3). Re-stopper the bottle and invert it several times until the precipitate has all dissolved. This step completes the 'fixing' of oxygen in the sample. The sample turns a yellow-brown colour, because free iodine has been released in it.
3. Finally, titrate the sample (corrected for the volume lost by adding reagents) by adding sodium thiosulphate until the colour is that of pale straw. Then add a starch indicator and continue to titrate until the blue colour first disappears.

Maintenance

- Rinse all bottles with deionised water, and dry them before replacing them in the dissolved oxygen field kit box.
- Put all liquid wastes into a waste bottle and solid wastes into a bag for removal from the site.

Safety with chemicals

The Winkler titration test uses a number of potentially hazardous chemicals so take care that chemicals are not flicked into eyes or spilt onto skin or clothes — wear safety glasses and rubber gloves. When testing, place the liquid waste bottle, paper towels and a squirt bottle of deionised water nearby, ready to wash or wipe off any chemicals that get onto skin or clothing or into the eyes or mouth.

Manganous sulfate (reagent no. 1) can irritate eyes and skin.

Alkaline potassium iodide azide (reagent no. 2) can cause severe burns, and is poisonous if swallowed.

Sulfuric acid (reagent no. 3) will cause severe burns, ingestion may be fatal, and inhalation can cause coughing and chest problems.

Data confidence

- Make a field replicate measurement for 10% of samples.
- Renew sodium thiosulphate every 12 months.
- Make twice-yearly tests on a saturated dissolved oxygen sample.
- Test a mystery sample (bi-iodate).

Interpreting your results

Increases in conductivity (salinity) reduce the maximum dissolved oxygen concentrations in water. For example, at 20°C and 7.3 mg/L dissolved oxygen, fresh water is 80% saturated but seawater is 100% saturated.

Dissolved oxygen concentrations should not fall below the 20th percentile of values typical for a waterbody in your region (ANZECC/ARMCANZ 2000). You may like to discuss this trigger value with your Waterwatch coordinator. A dissolved oxygen concentration of 2 mg/L will not support fish, and dissolved oxygen concentrations below 3 mg/L are stressful to most aquatic animals. At least 5–6 mg/L are required for fish growth and activity. Daytime concentrations of 6 mg/L are cause for concern as dissolved oxygen will decrease overnight.

Safety and waste considerations when measuring dissolved oxygen

Let someone know where you are going and when you will return.

Do not work alone.

Students must be fully supervised by their teacher in accordance with Education Department guidelines.

Ensure safe and easy access. Beware of slippery rocks and ground.

If sampling near a road or from a bridge, be wary of passing traffic.

Be able to swim if you fall in.

Avoid contact with contaminated water. Use gloves while sampling, but take them off as soon as you've finished. Don't touch your skin with wet gloves.

Keep a first aid kit available.

Feet should be covered; remember sunblock, hat, t-shirt.

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.

Hold all test bottles over a wide-mouthed liquid waste bottle while adding the reagents or calibration solutions.

After each piece of used equipment has been rinsed with distilled water, pour the rinse water into the liquid waste bottle.

Do not put solid waste into the liquid waste bottle.

Place all used gloves, used paper towels, empty reagent packaging and any other rubbish from testing into a plastic garbage bag with no tears in it, and take it with you when you leave. Try to leave the site cleaner and tidier than you found it — pick up and transport out any rubbish.

Consult your Waterwatch coordinator about disposal of liquid wastes.

Phosphorus

What is it and why does it matter?

Phosphorus (chemical symbol P): a mineral nutrient that is essential for all forms of life

The phosphorus found in both surface water and groundwater is in a form called phosphate (chemical formula, PO_4). It is naturally derived from the weathering of rocks and the decomposition of organic material, but it can also enter waterbodies in runoff or discharges — soil and fertiliser particles can carry phosphorus, and sewage is also rich in phosphorus.

Phosphates available to plants and animals are called orthophosphates, and exist in waterbodies as dissolved and particulate (suspended) and colloidal forms. Dissolved orthophosphate is immediately available to plants and animals. Particulate orthophosphate is potentially available to plants and animals. Colloidal polyphosphates are dissolved but not immediately available to plants.

Plant growth is limited by the availability of dissolved orthophosphate. A sudden increase in orthophosphate in inland waters can stimulate great increases in the growth of algae, particularly, as well as other aquatic plants. Algal blooms potentially produce toxins and also can cause large deficits of dissolved oxygen. Phosphates do not pose a human or animal health risk, so are not regulated in our drinking water.

What factors affect phosphate?

Phosphate concentrations in water are affected by:

- rock type and geology
- soil type
- seasonal conditions
- animal and human wastes
- phosphate-containing fertilisers
- disturbed land
- urban run-off, which usually contains it

Phosphate in domestic waste enters the waterway from leaking septic systems, sewage treatment facilities and stormwater drains. Many sewage treatment plants are allowed only a limited amount of phosphate in their discharges.

Suggested methods, equipment and reporting

Phosphate concentration is measured in milligrams per litre (mg/L). Since most results are reported in terms of phosphorus (rather than phosphate), Waterwatch has adopted the convention of reporting results as P. To convert phosphate (PO_4) to phosphorus (P), divide by 3 (i.e. 0.06 mg PO_4/L is equivalent to only 0.02 mg P/L).

Even small changes to low phosphorus concentrations (0.01–0.02 mg/L) can have a significant effect on the ecosystem, but existing field equipment cannot detect phosphate at concentrations below about 0.02 mg/L. There is little to be gained from monitoring if concentrations of phosphate are consistently lower than the detection limit of your equipment.

Phosphate concentration does not have to be measured on-site in the field, provided the samples can be refrigerated immediately, or frozen. The phosphate in refrigerated samples must be measured within 24 hours of sampling, and in frozen samples within 1 month of sampling. The sample bottle should be filled to three-quarters capacity.

The dissolved (or filterable) reactive test measures only dissolved orthophosphate and provides a measure of only the immediately available phosphate in the system at the time of sampling.

The total phosphorus test measures the immediately and potentially bioavailable forms of phosphorus in the sample. Total phosphorus concentrations are often many times higher than orthophosphate reported as phosphorus in the same sample. Therefore total phosphorus readings are more likely to come within the measuring range of your instrument.

Filterable reactive phosphate test

The ascorbic acid method is generally used for measuring phosphate in a sample. The ascorbic acid produces this test's characteristic blue colour.

It is best to filter the sample, but some Waterwatch groups do not have access to filters. If the sample can be filtered, the ascorbic acid method measures dissolved orthophosphate only

(also known as filterable reactive phosphate). This is a useful value.

In an unfiltered sample, the ascorbic acid method is likely to give inconsistent results, because the reagents are also reacting with other substances attached to the unfiltered particles.

For measurement of total phosphorus, all the forms of phosphorus in the sample are first converted to orthophosphate by 'cooking' the sample in suitable reagents. The sample is then neutralised and the orthophosphate is measured by the standard ascorbic acid method. Because the sample is not filtered, the procedure measures both dissolved and particulate (suspended) orthophosphate.

The need for a heat source means the total phosphorus test is better done in a laboratory. Even then, it is difficult for inexperienced operators to get accurate results.

Equipment

The equipment you will need for this method includes:

- dedicated sample bottles
- colour comparator or field colorimeter
- pre-packed reagents to turn the water blue
- deionised water to rinse the sample tubes between uses
- wash bottle to hold rinse water
- clean, lint-free cloth to clean and dry the sample tubes
- clean sample containers

Colour comparator

Colour 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. A colour comparator is a low-cost simple piece of equipment consisting of a blue colour spectrum. Intensity of the blue is in direct proportion to the amount of orthophosphate present. Reagents react with the water sample to result in a blue colour. The colour is matched against the spectrum to determine mg/L of phosphorus.

Colorimeter

The colorimeter is best used at sites where the expected concentrations of phosphates are relatively low (down to 0.02 mg/L). The colorimeter is a relatively expensive electronic device which measures the degree of 'blueness'. The colorimeter measures the amount of light transmitted or absorbed at a nominated wavelength.

- safety glasses
- latex gloves
- clearly marked 'chemical waste' bottle
- prepacked filters

Procedure

Field procedure for a colour comparator

1. Collect sample.
2. Filter it (if filters are available). If you are not filtering, you are measuring total reactive phosphate. It is important to note which method you are using so your data can be interpreted with the method your group is using.
3. Follow manufacturer's instructions for your colour comparator.
4. Make the closest possible colour match between the treated sample and the colour scale of the colour comparator.
5. Record the value in orthophosphate as P on your water quality results sheet (see pages 51–52).

Field procedure for a colorimeter

1. Follow the manufacturer's instructions for your model.
2. 'Zero' the meter using a blank (sample minus reagents) following the manufacturer's directions. Most manufacturers will instruct you to zero the meter using a reagent blank. The blank you use will depend on what you are testing. When testing your waterway samples your blank will be the sample without any reagents added to it. When testing glassware or reagents for data confidence, your blank will be deionised water plus the reagent powder.
3. Pour the recommended sample volume into a mixing container and add reagent powder. Swirl to mix. Wait the recommended time (usually a minimum of 10 minutes) before proceeding.
4. Pour the first water sample into the sample cell test tube. Wipe the tube with a lint-free cloth to be sure it is clean and free of smudges or water droplets. Insert the tube into the sample cell of the colorimeter.
5. Place the cover over the sample cell. Read the concentration of the sample, or percentage transmittance and convert to mg/L as P on the chart provided. Record your reading on the water quality result sheet. Note: if the sample concentration is below the minimum detection limit of your instrument, say 0.05 mg/L, report it as '<0.05 mg/L as P'.
6. Pour the used samples into a designated waste bottle.
7. Rinse the sample cell test tube and mixing container three times with deionised water. Avoid touching the lower portion of the sample cell test tube. Wipe with a clean,

lint-free cloth. Be sure the lower part of the sample cell test tube is clean and free of smudges or water droplets.

8. Be sure to use the same sample cell test tube for each sample. If the test tube breaks, use a new one and repeat step 1 to re-zero the meter.

Calibration

The procedure for calibrating a colorimeter in the laboratory is as follows.

1. Prepare six standard solutions that are in the range of the results expected. Generally 0.00 mg/L, 0.04 mg/L, 0.08 mg/L, 0.12 mg/L, 0.16 mg/L and 0.20 mg/L will be suitable concentrations.
2. Label six 25 mL volumetric flasks — one for each new standard solution.
3. Pour about 30 mL of a main standard solution containing 1 mg P/L into a 50 mL beaker.
4. Using Class A volumetric pipettes (pre-rinsed in standard solution) transfer 0–5 mL of the main standard solution from the beaker to the volumetric flasks, as shown in Figure 4.11.
5. Fill the volumetric flasks to the line. Swirl.
6. Analyse a portion of each of these new standard solutions in a colorimeter, as described above (see Field procedure for a colorimeter).
7. Construct a standard curve from your measured concentrations (mg P/L), with measured concentration on the y axis and desired concentration on the x axis. The points should fall on a straight line (see Figure 4.12).

Figure 4.11: Proportion of main standard solution to concentration of new standard solution

Concentration of new standard solution	Volume of main standard solution
0.00 mg/L	0 mL
0.04 mg/L	1 mL
0.08 mg/L	2 mL
0.12 mg/L	3 mL
0.16 mg/L	4 mL
0.20 mg/L	5 mL

where volume of main standard solution needed =

$$\frac{\text{Desired concentration of new standard} \times \text{Final volume (mL) of new standard}}{\text{Concentration of main standard solution}}$$

Total phosphorus method

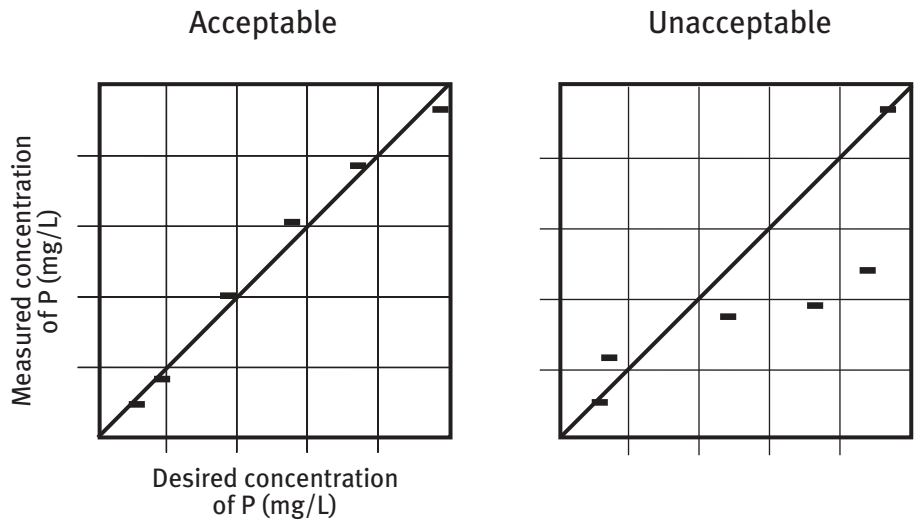
It is very difficult to obtain results that agree with those measured in external laboratories.

Equipment

The equipment you will need for this method is as listed above, plus:

- potassium persulphate
- a pressure cooker

Figure 4.12: Acceptable and unacceptable calibration curves for phosphate



Procedure

Follow the manufacturer's instructions for 'cooking' (digesting) and neutralising the sample before testing for orthophosphate with either a colour comparator or colorimeter, as described above.

Because of the digestion step, measurement of total P is very difficult to do under field conditions. Extreme caution must be taken when carrying out the total P test. Also take care with the disposal of waste from the reactions.

Because of the extra equipment needed, use of acid and the much longer time needed to complete a total phosphorus test you should consider only testing for orthophosphate using the ascorbic acid method on an untreated sample.

Extra safety tips for testing phosphate

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

Data confidence

- Contamination can significantly affect the results in this test. All sampling equipment must be phosphorus-free; phosphorus molecules from samples have a tendency to attach to the inside surface of sample containers and bottles.
- Check for contamination by calibrating sample bottles with a reagent blank (deionised water) field sample in the comparator before each sampling run.
- Before testing samples, containers must be acid-washed to remove adsorbed phosphorus before re-use.
- The bottles must be able to withstand repeated contact with hydrochloric acid. Plastic bottles (high density polyethylene or polypropylene) are preferable to glass because they will better withstand breakage. Many laboratories now use phosphate-free detergents, so contamination during washing is no longer a common problem. However, phosphate contamination can still occur from samples.
- The light source should be the same and in the same position relative to the colour comparator when matching colours for each sample.
- As a quality control check, ask someone else to read the comparator after you.
- Follow the manufacturer's directions for your colour comparator.
- Calibrate the colorimeter with prepared standards at least twice a year, or before each use, if so directed by the manufacturer.
- Always wear plastic disposable gloves when analysing samples. They protect you from the reagents and samples, and also protect the samples from contamination by the phosphorus and nitrogen that are typically present on the hands of smokers.
- Test field replicates for 10% of samples.
- Measure a Waterwatch mystery sample every six months.
- Arrange an external check on 10% of samples, by splitting them and sending half to another laboratory elsewhere.
- Make sure reagents are not out-of-date.
- Keep all glassware acid-washed and rinsed.

Acid-wash cleaning method

Reused sample containers and all glassware used in this procedure must be cleaned before the first run and after each sampling run by:

1. washing each bottle with a brush and phosphate-free detergent;
2. rinsing three times with tap water;
3. rinsing with 1M or 2M hydrochloric acid;
4. rinsing three times with deionised water;
5. when clean and dry, covering the bottle opening with aluminium foil or plastic film to avoid contamination.

If factory-sealed, disposable Whirl-pak® bags are used for sampling, no preparation is needed.

Interpreting your results

When you have enough measurements of phosphate through time in your waterbody, especially in comparison with a local or regional reference waterbody, you will know when a particular phosphate value does not fit the usual pattern. Alternatively, contact your Waterwatch coordinator about the water quality guidelines' (ANZECC/ARMCANZ 2000) suggestions of relevant trigger values for your type of waterbody, its environment and its designated uses.

Safety considerations and waste disposal tips when sampling and measuring phosphate

Let someone know where you are going and when you will return.

Don't work alone.

Students must be fully supervised by their teacher in accordance with Education Department guidelines.

Ensure safe and easy access. Beware of slippery rocks and ground.

If sampling near a road or from a bridge, be wary of passing traffic.

Be able to swim if you fall in.

Avoid contact with contaminated water. Use gloves while sampling, but take them off as soon as you've finished. Don't touch your skin with wet gloves.

Keep a first aid kit available.

Feet should be covered; remember sunblock, hat, t-shirt.

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 possibly 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.

Place all used gloves, used paper towels, empty reagent packaging and any other rubbish from testing into a plastic garbage bag with no tears in it, and take it with you when you leave the field site.

After each piece of used equipment has been rinsed with distilled water, pour the rinse water into the liquid waste bottle.

Do not put solid waste into the liquid waste bottle.

Consult your Waterwatch coordinator about the disposal of liquid wastes.

Nitrogen

What is it and why does it matter?

Nitrogen (chemical symbol N): an element that is essential for all forms of life

Nitrogen is derived from the atmosphere, where nitrogen gas (N_2) is the main constituent. Few living things can use gaseous nitrogen, but most depend on compounds of nitrogen.

The most common nitrogen compounds are ammonia (NH_3), nitrate (NO_3) and nitrite (NO_2). They occur in dissolved, particulate and gaseous forms.

- As nitrate (NO_3) is soluble and easily taken up by aquatic organisms, it is the most meaningful form for Waterwatchers to test.
- Ammonia (NH_3) is a product of the decomposition of organic waste and can be used as an indicator of the amount of organic matter in the waterway.
- Nitrite (NO_2) is toxic to humans and other animals.

Nitrogen compounds can be found in surface waters and in groundwater. The element nitrogen is recycled continually by plants and animals, and is present in freshwaters at higher concentrations than phosphate. Although both nutrients are required for plant growth, phosphate is considered to be the limiting factor in freshwater. In saltwater ecosystems, however, nitrogen is much less abundant, and it becomes the nutrient that limits algal growth.

What factors affect nitrogen?

As explained above, nitrogen is actually measured by the concentration of nitrate (NO_3). The main factors affecting nitrates are:

- rock type and geology
- soil types
- vegetation
- seasonal conditions
- animal and human wastes (sewage)
- decomposing plants and animals
- nitrogen-containing fertilisers
- industrial discharges
- run-off

Suggested methods, equipment and reporting

Nitrates readily dissolve in water and enter rivers more quickly than other nutrients. As a result, nitrates serve as a better indicator than other nutrients of sewage or manure pollution during dry weather.

Waterwatch groups that have chosen to test for nitrate usually use either the cadmium reduction (colour comparator) method or the zinc reduction (colorimeter/ spectrophotometer) method. Both produce a colour reaction that is then measured either by comparison to colours on a colour comparator or by use of a colorimeter.

The cadmium reduction method appears to be more accurate at lower concentrations of nitrate than the zinc reduction method but is far more hazardous because cadmium is very toxic.

Monitoring nitrate is challenging because it can involve measuring very low concentrations — down to 0.01 mg/L as N.

Your first consideration should be the purpose of monitoring for nitrate and the concentrations likely to be found. For example, if your group is monitoring for background changes in nitrate concentrations in a catchment, environmentally significant changes in nitrate may occur but be undetected if they are smaller than the detection limit of your equipment. There is little to be gained if the concentrations of nitrate are persistently less than the detection limit of your equipment, or concentrations are right on the detection limit, where accuracy is often less than for mid-range values.

Colour comparator method

A colour comparator is a low cost, simple piece of equipment with a colour wheel or colour bar. For nitrates the degree of redness of the solution is measured using the colour comparator. The redder the solution, the higher the concentration of nitrates.

Matching the colour of a treated sample to a comparator can be subjective, especially at low concentrations, and can lead to variable results. In addition, people who suffer from colour blindness can find it difficult to read the results.

Colour comparators are useful for identifying the high concentrations (greater than 1 mg/L) that can be expected

at heavily polluted sites in a waterbody, e.g. stormwater runoff in urban streams and wastewater treatment outfalls.

The cadmium reduction method requires that the water samples are not turbid. Turbid samples should be filtered (if filters are available to the group). If copper, iron, or other metals are present in concentrations above several mg/L, the reaction with the cadmium will be slowed down and the reaction time will have to be increased.

The reagents used for this method are often pre-packaged for various concentration ranges of nitrate in the water. It is not possible to know the appropriate range for your waterbody, unless other measurements have been made previously. Therefore, make some trial measurements with reagents for one range (perhaps chosen according to the trigger values for the designated uses for your waterbody), and then move to a more suitable range of reagents if necessary, once you get a feel for the values likely for that waterbody.

Your Waterwatch coordinator may have access to local values for nitrate in other waterbodies, and will be able to discuss the appropriate trigger values for nitrate suggested by the revised water quality guidelines (ANZECC/ARMCANZ 2000).

Equipment

The equipment you will need for this method includes:

- acid-washed sample bottles or disposable Whirl-pak® bags
- latex gloves, safety glasses
- colour comparator and its glassware
- prepacked reagents
- deionised water to rinse the sample tubes between uses
- wash bottle to hold rinse water
- clean, lint-free cloth to clean and dry the outside of sample tubes
- waste chemical bottle with secure lid for holding cadmium — clearly labelled

Procedure

1. Collect your sample using the standard technique and using dedicated sample bottles. If not testing nitrate in the field, keep the samples on ice and test them in the laboratory as soon as possible (within 24 hours).
2. Use safety glasses and gloves to minimise risk of harm from the reagents.
3. Follow the manufacturer's directions for your particular kit to analyse the sample.
4. Record your reading on the water quality results sheet (see pages 51–52).
5. Pour the treated samples into the 'waste chemical bottle' for disposal as a hazardous toxic waste.
6. Thoroughly rinse all containers with deionised water before testing the next sample.

Extra safety tips for testing nitrate

Always wear plastic disposable gloves and goggles when analysing samples. They protect you from the reagents and samples, and also protect the samples from contamination by the nitrates and phosphorus that are typically present on the hands of smokers.

Be very careful when you are testing nitrate with the cadmium reduction method. Cadmium is present in the reagent powder and precipitates to the bottom of the test tube at the end of the test. Waste from this test should not be poured down the drain but instead should be stored separately in a hazardous waste jar labelled 'Toxic Waste'. This jar must be disposed of as 'special waste'.

Maintenance

Follow normal acid wash procedures between sampling runs (see Acid-wash cleaning method on page 39).

Colorimeter/Spectrophotometer method

Colorimeters and spectrophotometers measure the degree of redness of the treated sample electronically. They measure the amount of light transmitted through the solution or absorbed by it. The light used is at a wavelength of 543 nanometres (nm).

The use of one of these instruments reduces the subjectivity of determining colour and is much more accurate than other instruments. However, colorimeters and spectrophotometers require maintenance and regular calibration.

At very high transmittance (above 90%) the presence of moisture, fingerprints or variable positioning of the sample cells can cause a significant change in readings. Some meters require that you prepare and analyse known standard concentrations before testing in order to convert the transmittance readings of your river sample to milligrams per litre. Other meters read percentage transmittance of light through the sample which can then be converted to milligrams per litre as N, using a chart. The most convenient meters directly display the sample concentration as mg/L of N.

For many rivers, lakes and estuaries in near-natural catchments, environmentally significant changes in nitrate concentrations are very low. As a guide, a field colorimeter or spectrophotometer should have a minimum detection concentration of 0.02 mg/L and accuracy of within 20% of the true value. Measuring lower concentrations can be achieved by sending a sample to a commercial laboratory for testing (see Table 4.7 on page 45).

Equipment

The equipment you will need for this method includes:

- dedicated sample bottles
- field colorimeter with sample tubes
- prepacked reagents to turn the water red
- deionised water to rinse the sample tubes between uses
- wash bottle to hold rinse water
- clean, lint-free cloth to clean and dry the sample tubes
- clean sample containers
- safety glasses
- latex gloves
- chemical waste bottle clearly marked

Procedure

These instructions are generalised for a variety of colorimeters. Follow the manufacturer's instructions for your model.

1. Collect your sample as per standard technique using dedicated sample bottles. If not testing nitrate in the field, keep the samples on ice and test them in the laboratory as soon as possible (within 24 hours).
2. 'Zero' the meter using a blank (the sample without reagents added to it following the manufacturer's directions).
3. Pour the recommended sample volume into a mixing container and add reagent powder. Swirl to mix. Wait the recommended time (usually a minimum of 10 minutes) before proceeding.
4. Pour the first water sample into the sample cell test tube. Wipe the tube with a lint-free cloth to be sure it is clean and free of smudges or water droplets. Insert the tube into the sample cell of the colorimeter.
5. Place the cover over the sample cell. Read the concentration of the sample or percentage transmittance, and convert to mg/L as N on the chart provided. Record your reading on the water quality result sheet. Note: if the sample concentration is below the minimum detection limit of your instrument, e.g. 0.05mg/L, report the result as <0.05mg/L as N.
6. Pour the treated samples into the liquid waste bottle.
7. Rinse the sample cell test tube and mixing container three times with deionised water. Avoid touching the lower portion of the sample cell test tube. Wipe with a clean, lint-free cloth. Be sure that the lower part of the sample cell test tube is clean and free of smudges or water droplets. Be sure to use the same sample cell test tube for each sample. If the test tube breaks, use a new one and repeat step 1 to zero the meter.

Maintenance

Follow normal acid-wash procedures between sampling runs.

Calibration

The laboratory procedure for calibrating a colorimeter is:

1. Prepare six standard solutions that are in the range of the results expected. Generally 0.00 mg/L, 0.04 mg/L, 0.08 mg/L, 0.12 mg/L, 0.16 mg/L and 0.20 mg/L will be suitable concentrations.
2. Label six 25 mL volumetric flasks, one for each new standard solution.
3. Pour about 30 mL of a nitrate standard solution containing 1 mg N/L into a 50 mL beaker.
4. Using Class A volumetric pipettes (pre-rinsed in standard solution) transfer 0–5 mL of the main standard solution from the beaker to the volumetric flasks, see Figure 4.13).
5. Fill the volumetric flasks to the line. Swirl.
6. Analyse a portion of each of these new standard solutions in a colorimeter, as described above, and record the results.
7. Construct a standard curve from your measured concentrations (mg N/L), with measured concentration on the y axis and desired concentration on the x axis. The points should fall on a straight line (see Figure 4.14).

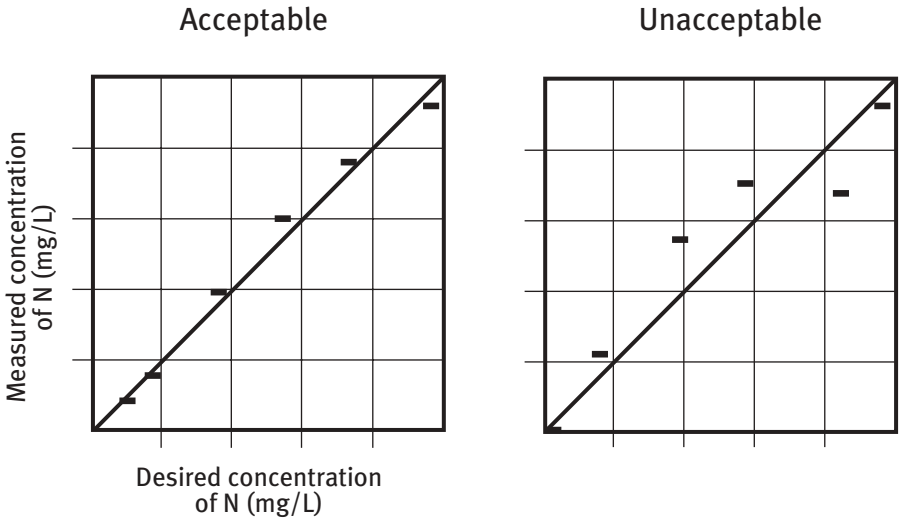
Figure 4.13: Proportion of main standard solution to concentration of new standard solution

Concentration of new standard solution	Volume of main standard solution
0.00 mg/L	0 mL
0.04 mg/L	1 mL
0.08 mg/L	2 mL
0.12 mg/L	3 mL
0.16 mg/L	4 mL
0.20 mg/L	5 mL

where volume of main standard solution needed =

$$\frac{\text{Desired concentration of new standard} \times \text{Final volume (mL) of new standard}}{\text{Concentration of main standard solution}}$$

Figure 4.14: Acceptable and unacceptable calibration curves for nitrate



Data confidence

Colour comparator

- Check for contamination by testing a calibration blank (deionised water) before testing a sample. Always use the same type of light and from the same direction when comparing colours.
- The light source should be in the same position relative to the colour comparator when matching colours for each sample.
- As a quality control check, ask someone else to read the comparator after you.
- Test a field replicate every 10 samples.
- Test a Waterwatch mystery sample every six months.

Colorimeter

Calibrate the colorimeter with a reagent blank before each use. To check if sample bottles are contaminating a sample, test a field blank. Test a field replicate after every tenth sample. Every six months, measure a mystery solution supplied by your Waterwatch coordinator.

Check the calibration of the colorimeter at least twice yearly with prepared standards as described below. Some colorimeters require calibrating with prepared standards before each use. For an external quality control check on 10% of samples, split every tenth sample, measure one part and send the other part to another laboratory. Alternatively, during field sampling, make every eleventh sample a replicate of every tenth sample. On measurement, the two samples should give the same results.

Colours of the comparator must be free of scratches and contaminants.

Interpreting your results

Nitrate readily dissolves in water and the concentration in streams can increase during wet weather because of input from run-off and rainfall. So it is important for you to consider stream flow rates and recent weather conditions when interpreting nitrogen data. It is a good idea to measure concentrations at one or more near-natural locations near your study site, to determine typical background concentrations for streams in your catchment.

The natural concentration of ammonia or nitrate in surface water is typically low (less than 1 mg/L). Nitrite is commonly less than 10% of the nitrite/nitrate total. In excessive amounts, nitrates can cause significant water quality problems.

It is not possible to define an upper limit for nitrogen concentrations in surface water that will ensure protection of all ecosystems. Many other factors are important: a combination of flow rate, turbidity, temperature, turbulence, phosphorus concentration and other factors determine the effect of a particular nitrogen concentration in a specific ecosystem. In freshwater ecosystems, increases in concentrations of phosphorus, rather than nitrogen, are believed to trigger eutrophication problems.

Your Waterwatch coordinator will be able to discuss the relevant trigger values for your type of waterbody, its location and designated uses, as suggested by the revised water quality guidelines (ANZECC/ARMCANZ 2000).

Table 4.7: Quality control measures for nitrate

Relative data quality	Equipment method	Sensitivity (minimum detection level)	Calibration	Type of quality control
Low	Colour comparator.	1 mg/L	None.	Colours must be free of scratches and contaminants
Intermediate	Colour comparator or colorimeter	0.02 mg/L	For comparator test a calibration blank before each sampling run. For colorimeter, use calibration blank prior to each sample test. Calibrate colorimeter with prepared standards at least twice yearly.	Colours of comparator must be free of scratches and contaminants. Test field replicate every 10 samples. Test Waterwatch mystery sample every six months.
High	Collection and dispatch of sample under ice to professional laboratory	Not applicable	As per professional lab practice	For 10% of samples, use external field replicates or split sample and send to different laboratories.

Safety considerations and waste disposal tips when sampling and measuring nitrate

Let someone know where you are going and when you will return.

Don't work alone.

Students must be fully supervised by their teacher in accordance with Education Department guidelines.

Ensure safe and easy access. Beware of slippery rocks and ground.

If sampling near a road or from a bridge, be wary of passing traffic.

Be able to swim if you fall in.

Avoid contact with contaminated water. Use plastic disposable gloves while sampling, or analysing, but take them off as soon as you've finished. Don't touch your skin with wet gloves.

Keep a first aid kit available.

Feet should be covered; remember sunblock, hat, t-shirt

Take some clean water with you for washing down chemical spills on your skin and clothes.

Have a squirt bottle ready to wash out eyes in case of chemical exposure.

Use methods that minimise your possible contact with chemicals.

To avoid contamination and contact with possibly 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.

Be very careful if you are testing nitrate with the cadmium reduction method. Cadmium is present in the reagent powder and precipitates to the bottom of the test tube at the end of the test. Waste from this test should not be poured down the drain but stored separately in a hazardous waste jar labelled 'Toxic Waste'. This jar must be disposed of as 'special waste'.

Hold all test bottles over a wide-mouthed liquid waste bottle while adding the liquid and powder reagents.

Place all used gloves, used paper towels, empty reagent packaging and any other rubbish from testing into a plastic garbage bag with no tears in it, and take it with you when you leave the field site.

After each piece of used equipment has been rinsed with distilled water, pour the rinse water into the liquid waste bottle.

Don't put solid waste into the liquid waste bottle.

Consult your Waterwatch coordinator before disposing of liquid wastes.

Record sheets

This section includes the record sheets you will need to record your data. Make sufficient copies of each. The forms are:

- Equipment maintenance and calibration record
- Preparing your equipment for sampling
- Water quality results

Waterwatch equipment maintenance and calibration record

Make sufficient copies of this page for all equipment items used by your group. You can record data for equipment requiring one-point or two-point calibration in the table.

Test equipment name: _____

Identification number: _____

Inspection frequency: _____

Type of inspection: _____

_____

Calibration standards used and expiry date: _____

Calibration frequency: _____

Expiry date of reagents (if applicable): _____

_____

Use the table below to record the results of calibration checks.

Date	Expected value	Measured value	Expected value	Measured value	Comments

Preparing your equipment for sampling

Use this checklist to ensure that all equipment and reagents used for sample collection and analysis are working correctly before going into the field. Tick (i.e.✔) the equipment you need to take on your visit to the test site. Put another line through it (making a cross) when you are packing up to return (i.e. ✘).

Date			
Collate documents and equipment for recording data			
Waterwatch Technical Reference Manual			
Waterwatch Field Handbook			
Data Result Sheets			
Sticky labels			
Pens, pencils, note paper, eraser			
Marker pen (waterproof)			
Camera and film			
Prepare water testing equipment for use			
Clean sample bottles (sterilise bacteria sample bottles)			
Check batteries in meters, replace if necessary			
Check condition of meters and probes — no dirt, salt or algae, etc			
Dissolved oxygen meter — fill probe			
Calibration standards and reagents still useable — within expiry date, no unexpected colour change, unusual smells or precipitation on the bottom			
Last calibration performed is acceptable			
Calibrate meters — details recorded and acceptable			
Correct reagents and quantities present in kits			
Pack test equipment for parameters to be measured			
Macro-invertebrates			
Algae			
Velocity			
Flow			
Temperature			
Turbidity			
Conductivity			
pH			
Dissolved oxygen			
Phosphate			
Nitrate			

Collate sampling equipment			
Sample bottles			
Sampling pole and bottle holder			
Buckets			
Liquid chemical waste bottle			
Toxic chemical waste bottle (nitrate test)			
Rubbish bag			
Clean tap water for washing hands			
Tissue for colorimeter tubes			
Paper towel			
Deionised water for rinsing test tubes and equipment			
Safety equipment			
First aid kit			
Sun cream and hat			
Gum boots			
Latex gloves and safety goggles			
Other			
Drinking water and food			
Emergency phone numbers:			

Before you leave the site, check the following:

- Is all the equipment cleaned?
- Is there any rubbish left behind?
- Has equipment in the kit been checked?
- Is any equipment broken or lost and so needs to be replaced?
- Have all the results been recorded?

Water quality results

This sheet is for recording your results. Photocopy the sheet each time you intend collecting data.

Background Information

Date: _____ Time: _____ Name of Group: _____

Name of investigators: _____

Name of waterbody: _____

Site code: ☐☐☐☐☐☐ Map Name: _____

Easting (6 figs): ☐☐☐☐☐☐ Northing (7 figs): ☐☐☐☐☐☐☐

Type of Waterbody (tick a box):

Pond/wetland	☐	Lake/dam	☐	Bore/piezometer	☐
Drain	☐	Estuary	☐	Ocean	☐
Creek/stream	☐	River	☐	Irrigation channel	☐
Spring	☐	Inlet/bay	☐		

Position in the catchment:

upper	☐	middle	☐	lower	☐

Estimated elevation: _____

Name of suburb, nearest town or settlement: _____

Brief description of site: _____

Comments: _____

_____

_____

Describe the weather both now and in the past 24 hours (tick a box):

Weather now	Clear/sunny	☐	Overcast	☐	Showers	☐	Rain (steady)	☐	Rain (heavy) ☐
Past 24 hours	Clear/sunny	☐	Overcast	☐	Showers	☐	Rain (steady)	☐	Rain (heavy) ☐

Water quality results

Record your results and the type of equipment and method and any preservation method you used, and mystery or replicate sample results

Parameter	Equipment item and number	Sample result (delete units that do not apply)	Replicate sample results	Mystery sample result	Mystery code no
Flow velocity		m/s	m/s		
Flow volume		L/s	L/s		
Temperature		°C	°C		
Turbidity		NTU metres	NTU metres	NTU	
Conductivity		µS mg/L	µS mg/L	µS mg/L	
pH		pH units	pH units	pH units	
Dissolved oxygen		mg/L % sat	mg/L % sat		
(Filterable) Dissolved reactive phosphate		mg/L P	mg/L P	mg/L P	
Total phosphate		mg/L P	mg/L P		
Nitrate		mg/L N	mg/L N		