Chapter 10 — Waters

Field tests for waters

Field tests are useful as a preliminary survey of the extent and distribution of salinity in a catchment or area. Water samples can be obtained from existing water access points (streams, wells, bores, irrigation channels, dams), but the accuracy of the survey will be limited by the spatial distribution of these points. Ideally, sampling points should be selected to represent a range of local geomorphological features (including soils and aquifers) and land uses.

Table 29 (page 67) discusses a number of common field tests. For more detailed investigations or monitoring, specific advice is available from the Department of Environment and Resource Management.

Sources of information

- As well as directly sampling surface waters and groundwaters, further information on waters in a number of areas is available from the Department of Environment and Resource Management, where an extensive database of this information is maintained.
- The Saltwatch program has resulted in the collation of a substantial database on the salinity of surface waters and groundwaters. Further information is available from the Department of Environment and Resource Management.
- Existing databases or reports of water or groundwater quality in an area may be listed with Queensland Spatial Information Council.

Salinity and chemical composition

Salinity in water samples can be determined on-site using an EC meter, or samples can be forwarded to a laboratory for testing of salinity and chemical composition.

Samples for laboratory analysis should be forwarded as quickly as possible. Delays and high temperatures will result in salts precipitating out of solution, changing the chemical composition of the water.

A wide range of EC meters is available, ranging from small pocket meters costing around \$80, to small field meters with temperature compensation costing about \$250, to multi-function extended range EC meters costing upwards of \$300. Mid-range meters with builtin temperature compensation are appropriate for most salinity investigations. The accuracy of the cheaper models is limited and these models are not calibrated readily. Cheaper meters are often unable to read salinity levels less than 0.1 dS/m or greater than 20 dS/m. If dealing with an EC greater than 20 dS/m using a cheaper EC meter, a measure can be obtained by diluting the sample, measuring the diluted sample, and multiplying the result by the dilution factor.

Temperature has a significant effect on EC. If the EC meter in use does not have a temperature compensated probe, readings should be adjusted to the standard temperature of 250C using the following formula (Wells 1978):

$$\ln K_{t_2} = \ln K_{t_1} + \beta_1(t_2 - t_1) - \beta_2(t_2^2 - t_1^2) \dots \dots 22$$

where

K _{t1}	is	conductivity (EC reading) at field temperature of sample
<i>K</i> _{t2}	is	conductivity (corrected EC reading) at standard temperature of 25°C
<i>t</i> ₁	is	field temperature of sample being tested for conductivity
t ₂	is	25 (standard temperature)
β_1	is	o.o29 (coefficient for local natural waters)
β_2	is	o.ooo19 (coefficient for local natural waters).

Depth to the watertable

The depth to the watertable can be measured using a **plopper** or other indicating device attached to a tape measure that can be lowered down a bore. A plopper is simply a device that makes a plopping sound when it strikes the water surface. Old valves from internal combustion engines (preferably with concave faces) and brass plugs with concave faces make serviceable ploppers.

A plopper can also be constructed from a 20–25 mm pipe with a cork or stopper blocking the inside of the pipe about 5 mm from the bottom end. Whistles and electrical devices can also be used.

It is important to record the reference point usedfor measurement; this is usually either ground level or the top of the bore. For salinity investigations, it is preferable to measure from the watertable to ground level. The following steps should ensure an accurate measure:

- Measure the distance from the bottom of the plopper to the end of the tape where it is attached to the plopper. Add on this amount each time a measurement is taken.
- Lower the plopper into the bore until the plopper enters the groundwater. Pull up the tape slowly, jiggling the plopper up and down over a depth of about 50 mm until a plopping sound is heard every time the plopper is lowered. Obtain an accurate reading from the watertable to the top of the bore casing or piezometer by jiggling the tape less and less. Using this method, it is possible to accurately measure the depth to the watertable to within 5 mm.
- To correct for the height of the bore or piezometer casing, hold the tape at the top of the inner edge of the casing, and then pull the tape down to ground level (Figure 42). Now read the measurement on the tape at the top inner edge of the bore casing or top of piezometer.
- Add the distance between the end of the plopper and the beginning of the tape to the measure at the top of the bore casing. This will be an accurate measure of the depth to the watertable corrected for the height of the bore casing.

Figure 42. Using a plopper to measure depth to the watertable (Saltwatch Instruction Book, DPI 1994).



Use of piezometers

Piezometers are very useful for assessing depth to the watertable, changes in water level with time and rainfall events, elevation of the watertable above a datum and hence the gradient of flow, estimated flow capacity of the aquifer material, chemistry of the water, and long-term monitoring of changes associated with land use.

To assess flow regimes and the interrelationships of aquifers, hydraulic head (the pressure of the groundwater) needs to be assessed. This is usually done using piezometers. By definition, a watertable level will not exceed ground level, whereas the hydraulic head associated with water in a confined aquifer (such as the Great Artesian Basin) may be many metres above ground level.

Piezometers measure pressure. The open well is a specialised type of piezometer which indicates the free water height of the watertable. Because water tends to flow from areas of high potentiometric potential to areas of low potential, water levels in piezometers are useful for indicating the direction of water flow.

The chemistry of dissolved salts in waters drawn from piezometers is useful for indicating the origins of the water and the chemical processes involved in determining the composition of the water. Trilinear diagrams (described in *Interpretation using trilinear diagrams* page 76) can be used to graph chemical information for interpreting water sources and processes. Information on the installation of the piezometers can be used in conjunction with water level information to determine aquifer hydraulic conductivity, using, for example, the bail test of Bouwer and Rice (1976).

Other information is needed to obtain a comprehensive interpretation of the water level and chemistry information obtained from piezometers. This information includes:

- the bore log
- installation information, including depth, position and length of the slotted section of the tube and the sealing material
- rainfall records for the area (essential)
- elevation of each piezometer, preferably above Australian Height Datum or otherwise some arbitrary height reference
- any information from deep bores in the surrounding catchment
- observations of stream or spring flow, including water composition
- observations on land clearing or other human activities, such as dams, roads etc.

Table 29. Common field tests for surface and groundwaters.

Field test	Information provided	Useful for	Points to note
Surface water sampling	 salinity of surface water samples for chemical composition analysis 	 can be used to construct a preliminary map of salinity in the catchment can indicate salinity processess and water sources 	 calibrate EC meter in a standard solution measure EC as soon as possible after obtaining the water sample if the sample is to be stored or transported before EC or laboratory testing, fill the container completely with the water sample to exclude air
Surface water flow rate	• data for calculating volume of surface water flow	 useful in calculating catchment salt and water balances 	
Groundwater sampling	 salinity of groundwater from existing bores or wells 	 identification of recharge and discharge areas and groundwater 	 see notes for 'Surface water sampling' above if a windmill is in operation, water can be collected from an outlet valve salinity maps
	• samples for chemical composition analysis	 can indicate water sources 	 if using a pump to collect water, run the pump for some time (preferably 10 minutes) to clear stagnant water from the bore hole before taking a sample
			 if a pump is not available, a bailer (a plastic tube with a valve at the bottom that opens as the bailer falls and closes as the bailer is lifted) can be used to collect a sample. For accurate results, water should be bailed from the groundwater access point until new water flows in; as this is often impractical with a bailer, a compromise (less accurate than pumping) is to bail a few times and then let the bailer fall almost to the bottom of the bore or piezometer
Depth to watertable	 current depth of watertable 	 possible groundwater restrictions and likely 	 it is important to use a consistent reference point for measurements
		implications for surface salting and plant growth; gradient of water flow; possible response of groundwater to rainfall	 flow gradients and directions can be determined if piezometers are surveyed for elevation

Installation

To obtain reliable information, piezometers must be installed correctly (Figure 43). In defective installations, water response may be slow, surface water could leak around the tube, or the sealing around the tube may be inadequate, so that the pressure head will be under-estimated. Geritz (1985) provided specific details of piezometer installation and use.

To determine the vertical direction of water movement at a particular site, a series of two or more piezometers (a 'nest') is sometimes installed. The nest of piezometers may be installed in separate holes or in the same hole with each individual piezometer terminating at a different depth, thus indicating the groundwater situation at each depth. Separate holes are preferred because the space around the piezometers can be sealed more effectively.

Siting

The design of piezometer installation will depend on the scale of the investigation. There are three broad types of installations:

- Exploratory—a few piezometers are installed in selected areas to obtain a general picture of the area.
- 2. Overall trends—a broad network of piezometers is installed across and up the catchment and monitored in conjunction with existing bores and windmills (with the information from the existing installations being interpreted with caution).
- 3. Hydrologic modelling or detailed site analysis a detailed network of piezometers is installed with piezometers set at several different depths and in all landform features in the catchment.

Figure 43. Method for installing a piezometer (after Geritz 1985).



Drilling the hole

Holes can be drilled using mechanical drilling rigs or alternative methods such as a hand auger or water jetting. A cutting head fitted with a replaceable tungsten carbide cutting tip is invaluable for drilling through occasional rocks as well as soil. Compressed air rock hammers may be required in hard rock.

Isolated rocks (floaters) can give the impression that hard basement rock has been reached. With experience, drill operators develop a feel for rock hardness and this, together with local knowledge and observation of material emerging from the drill hole, is an acceptable guide for hole depth.

The material brought up when holes are drilled provides valuable information about possible water pathways. It is important to keep a written log of observations while the holes are being drilled. **Record** any changes in the material (colour, texture, particle shape and size, concretions, wetness etc.), as well as the depth at which these changes occur.

When drilling in an unknown area, there may be aquifers at various depths. An exploratory hole is necessary to identify the relevant aquifers, not only the first encountered. Each aquifer may be tapped by a separate piezometer and it will usually be simpler to put these down separate drill holes. Separate holes make it easier to seal the hole between the aquifers. It is important to seal immediately above the tapped aquifer, especially if it is below other aquifers.

Differences in water heights in piezometer tubes can indicate the presence of perched watertables or changes in the permeability of an unconfined aquifer.

Installing the piezometer

PVC pipe is recommended for the piezometer tube 40–50 mm in diameter, class 9 or 12. This tubing is robust and should withstand rough treatment during installation and operation. A section of the tube needs to be slotted to match the depth interval of the aquifer of interest. This is best done by hand, using a hacksaw frame fitted with two hacksaw blades spot-welded together to increase the thickness of the cut, or a power hacksaw can be used. Wider slots are recommended because thin ones can clog with fine material and restrict flow. As an alternative to slots, holes can be drilled in the tube. **Record** the length of the slotted section before installing the tube in the ground.

If the drill hole remains dry or has little water in it after the drill is removed, installation should be straightforward.

Figure 44. Installation of piezometers using a small geotechnical drill rig in central Queensland.



Figure 45. Measuring the groundwater depth and groundwater electrical conductivity simultaneously in a piezometer.



In coarse sandy material, the piezometer tube can be jetted down with high pressure water. In rigid materials, water can be poured into the hole and the resulting slurry pumped out with a sludge pump. Jetting is another technique for clearing the hole injecting compressed air down the piezometer tube as it is inserted so that material in the hole is lifted to the surface around the outside of the tube. This method is generally only effective if the slotted length of tube is relatively short.

In unstable materials, the walls of the hole may collapse, making installation more difficult. Compressed air can sometimes be used to blow out slurried material but this can enhance the collapse of the walls. Jetting water down an open-ended piezometer tube can also be used to clear the hole but, depending on the material, this could reduce the permeability of the material around the slots.

A mirror or a flat watch face is useful for inspecting holes by reflecting sunlight (when it is not overcast).

After setting the tube in the ground, pack gravel around the slotted section of the tube to prevent the hole from collapsing at this point and to maintain good hydraulic conductivity. Recommended gravel size is 5–7 mm river gravel (passing a 5 mm sieve, retained on a 7 mm sieve). With 5–7 mm gravel, there is still sufficient pore space to permit water flow. Crushed metal (sometimes sold as gravel) has flat surfaces and may pack in the annulus of the tube. Coarser gravel can sometimes bridge around the annulus and block gravel falling to the bottom of the hole. The larger the gravel, the larger the pore space that will result. Coarse sand is more appropriate for sandy aquifer materials. **Record** the length of the gravel pack around the tube.

Above this gravel pack, a watertight seal is essential to prevent leakage into the tube from other aquifers (usually higher) or from the surface. The recommended material for sealing above the gravel pack is granulated bentonite. Carefully pour the bentonite around the tube to a depth of about 100 mm, and preferably top this with a shallow layer of gravel. In theory, where the water level is above the slotted section, the bentonite will settle through any water in the hole and swell to form a seal. However, sometimes the bentonite swells before reaching the desired position and air gaps are formed. A more reliable seal can be obtained by pumping the piezometer to lower the water level below the top of the gravel layer before pouring in the bentonite.

After the sealing layer is in place, backfill the rest of the hole to the surface and tamp the backfill into place. Build up a mound of soil around the tube at the surface. **Record** details of sealing methods and depths.

The piezometer above ground

If the water level in the aquifer is not likely to rise above ground level, leave about 30–40 cm of the tube above ground level. This height is a compromise between being high enough for the site to be easily identified and low enough to limit damage from cattle, who often scratch themselves against the tube. The tube can be further protected from cattle by driving three steel pickets (painted for visibility) into the ground around the piezometer and wiring the stakes together. For more permanent installations, a steel protective casing can be concreted around the tube.

If the water in the aquifer is under considerable pressure with a hydraulic head above ground level, the water pressure may break through the bentonite seal. In this case, a longer tube will be needed, with appropriate support, and a cement grout should be used instead of bentonite. Place a slip-on PVC cap onto the top of the tube. Ensure that there is a small hole in the cap or in the side of the tube near the top to relieve air pressure in the tube. Mark a unique identifying label inside the cap or the tube. Record this identification information with the other information on the installation of the tube.

Operation

By reading the water level in piezometers frequently during the first few months after installation, the response of the piezometer and an indication of likely future response can be determined. Information on the response of the water level to rainfall events is particularly useful. From this information, patterns of recharge and delayed response can be detected, used to interpret readings on a catchment scale, and related to soils, landforms and other features. (Refer to **Depth to the watertable** page 65). Piezometer loggers, which can be obtained fairly cheaply, can be installed to obtain regular readings on changes in water level response.

To be able to assess flow directions, piezometer heights need to be surveyed to a common height datum. Because the elevation of the water surface (pressure head) is being surveyed, standard survey methodology can be used. If the head is higher in one piezometer than others, this does not necessarily indicate that water is flowing. Head differences usually indicate some restriction to flow (see *Landform feature identification* page 39).

Pump tests on piezometers can indicate flow rates in surrounding areas. There are a number of standard pump test procedures available, ranging from the simple bail tests of Bouwer and Rice (1976) and later modifications, to more detailed pumping schedules combined with taking measurements in surrounding piezometers. Interpreting pump tests, particularly in regions with strong geologic flow controls, can be difficult. Technical advice should be sought before carrying out these tests.

Catchment groundwater balance estimation

An estimate of catchment water balance can be useful for initially assessing the magnitude of a salting problem, determining the most appropriate management options, and evaluating the amount of water to be managed in a salted catchment.

Such an estimate will be rough because detailed hydrologic measurements are generally not available.

A complete catchment water balance would require measurements of runoff, evapotranspiration from existing vegetation, and deep drainage (groundwater recharge) as well as groundwater and surface water flow out of the catchment. Some of these measurements, particularly estimation of evapotranspiration using water balance models, require a considerable amount of land use data and are not sufficiently precise to accurately estimate deep drainage if this is less than 50 mm/yr. Estimating groundwater flow out of a catchment is also very difficult. Hence, the results of catchment water balance calculations need to be evaluated in the context of possible large errors.

Groundwater balance model

As discussed previously (in *Rate of water movement in the landscape* page 19), groundwater recharge is balanced by discharge in the form of subsurface outflow, surface seepage, evaporation and evapotranspiration. Expressing this relationship in the symbols used to express quantities of water (*Salt mass balance* page 17):

$$Q_d = Q_q + Q_s + Q_e + Q_t$$
23

This relationship can be expanded to incorporate measurable parameters for investigating groundwater balance:

$$D_{d}A_{r} = K_{s}\Delta HA_{a} + S + EA_{b} + ETA_{v} \dots 24$$

where, using a time period such as a day,

Deep drainage rate $(D_d A_r)$ (m³/d) (volumetric rate at which water drains below the root zone, approximating recharge to groundwater) is

the deep drainage rate (D_d) (m/d) by the area over which deep drainage (recharge) is occurring (A_r) (m²)

Subsurface outflow from the discharge area $(K_s \triangle HA_g)$ (m³/d) is

the potential of the aquifer medium to conduct water (K_s) (m/d), by the hydraulic gradient (ΔH) (m/m), by the cross-sectional area of the vertical discharge face of the aquifer at the lower catchment boundary (Ag) (m²)

Surface seepage from the groundwater in the discharge area (S) (m^3/d) is

the volumetric rate of water seeping from the groundwater in the discharge area, including base flow in drainage lines intersecting the discharge area (S) (m³/d)

Evaporation from bare areas in the discharge area (EA_{h}) (m³/d) is

the evaporation rate from bare areas per day (*E*) (m/d), by the amount of bare area in the discharge area (*Ab*) (m^2)

Evapotranspiration from vegetation in the discharge area (ETA_v) (m³/d) is

the evapotranspiration rate from vegetation in the discharge area per day (*ET*) (m/d), by the amount of vegetated discharge area (Av) (m²).

In some situations, aquifer parameters can be determined by conducting pump tests to determine transmissivity, which is the potential of a particular aquifer to transmit water per unit width. Hydraulic conductivity can be determined from transmissivity as follows:

where

V	ic	caturated bydr	raulic condu	ctivity (m	(d)
n _s	15	Saturateu nyui	autic condu	cuvity (iii	/u)

- T is transmissivity per unit width of aquifer (m³/m/d)
- *h* is thickness (vertical) of aquifer (m).

Using transmissivity information to calculate groundwater balance, the expression for the subsurface outflow component is modified as follows:

 $D_d A_r = Tw\Delta H + S + EA_b + ETA_v \dots 26$

where

Т	is	the transmissivity of the aquifer per unit width (m²/d)
W	is	the width of the aquifer at the point of subsurface outflow from the discharge area (m)
ΔH	is	the hydraulic gradient in the system (m/m).

Sources of information and default values

Table 30 lists methods for estimating catchment groundwater balance parameters and some default values. Some parameters can be estimated from aerial photos. A number of software packages provide other information (see the appendix **Useful software packages** page 141).

Practical example

Data collected in the Darbalara catchment in the Lockyer Valley were used to estimate the amount of excess water contributing to a salinity problem. (The extent and progression of salting in this catchment is illustrated in Practical example following Human land use and records page 88). Because the area of salting appeared to be in equilibrium with rainfall inputs, it was assumed to have reached equilibrium.

Results from catchment water balance calculations (provided in this section) were used to evaluate possible management strategies for the site.

Groundwater inputs

Table 31 illustrates calculations of deep drainage based on generalised information on soil properties available from a soil survey in the Lockyer Valley. Deep drainage below the root zone can be estimated from soil salinity EC or from soil properties using SALFCALC (in this case, SALFCALC was used). The catchment is 800 ha in area, and receives an average annual rainfall of 800 mm/yr. Three major soil types identified in the catchment are heavy clay in the lower catchment (approximately 50% of catchment), alluvial (approximately 25%), and upslope soils (approximately 25%).

Reading from the calculations in Table 31, estimated deep drainage across the catchment is approximately $306 \text{ m}^3/\text{d}.$

Groundwater outputs

Values for groundwater output parameters and methods of measurement or approximation are shown in Table 32.

From the data in Table 32, outputs (discharge):

- subsurface outflow + surface seepage + evaporation from bare area + evapotranspiration from vegetated area
- $= K_{s} \Delta HA_{a} + S + EA_{b} + ETA_{v}$
- = 50 + 0.2 + 200 + 60
- $= 310.2 \text{ m}^3/\text{d}.$

Inputs versus outputs

Because of conservation of mass, groundwater inputs and groundwater outputs should equate once equilibrium has been achieved. This calculation using approximate figures provides working values for groundwater input and output. The sensitivity of some of the parameters can be evaluated by substituting different values and evaluating the results. Area terms are particularly sensitive variables. This serves to emphasise that this is only a rough estimate of catchment groundwater balance.

Table 30. Guides for estimating or measuring catchment groundwater balance parameters, with some default values.

Symbol	Parameter	How to estimate or measure	Units
D _d	deep drainage rate	Estimate an 'average' figure for deep drainage across the whole catchment, giving proportional weight to each soil type depending on the percentage of the catchment that it covers. Can also be estimated from soil properties (using SALFPREDICT) or soil EC (using SALFCALC). Estimates range from approximately 50–100 mm/yr for shallow, well-structured soils or shallow soils in the rainfall range of 800–1 000 mm/yr, to approximately 1 mm/yr for sodic heavy clay soils. While deep drainage rates are often expressed on a yearly basis and deep drainage only occurs intermittently, for these water balance calculations mm/yr can be divided by 365 to give mm/day.	m/d
A _r	area over which deep drainage (recharge) is occurring	Measure on an aerial photo (use vegetation, soils etc. to identify zones) in conjunction with soil mapping	m²
K _s	hydraulic conductivity (of the aquifer)	Can be determined from piezometers set at appropriate sites; typical values can be used for types of underlying rock, obtainable from hydrology or groundwater reference texts. Values will be in the range 20–1 000 m/d. Alternatively, can be calculated from transmissivity values if these are available.	
ΔΗ	hydraulic gradient (in the vicinity of the discharge area)	In the absence of detailed information on upslope water gradient, use soil surface gradient, estimating this from a contour map.	m/m
A _g	cross-sectional area of subsurface outflow (area of the vertical discharge face of the aquifer at the lower catchment boundary)	Estimate from geology cross-sections, drill records, experimental drilling.	m²
S	volumetric rate of surface seepage from the groundwater in the discharge area and base flow in drainage lines	Estimate from seepage flows and base flow in drainage lines intersecting the discharge area. Surface seepage will vary over time, so observed flow will provide an approximate value. Estimated as volume of seepage or flow rate by cross-sectional area of the seepage and/or intersecting the discharge area base flow.	m/d
E	evaporation rate from bare area in the discharge area	Value will vary with salinity of surface water and depth to watertable. A range of values may need to be tried. One option is 0.5 x Class A pan evaporation. The value 2 mm/d would be generally appropriate unless the watertable is at the soil surface. If the watertable is at the soil surface, evaporation rates will approximate class A pan evaporation rates and can be determined from Bureau of Meteorology climate maps and shire handbooks.	m/d
A _b	amount of bare area in the discharge area	Measure on the ground or from an aerial photo taken in a year with near to average rainfall.	m²
ET	evapotranspiration rate from vegetation in the discharge area	A value of around 1 200 mm/yr is probably reasonable.	m/d
A _v	amount of vegetated discharge area	Measure on the ground or from an aerial photo taken in a year with near to average rainfall.	m²

These results indicate that evaporation from the bare area is the major mechanism balancing inputs and outputs. This is why evaporative areas develop following hydrologic imbalance in catchments.

Converting the above information to ML/yr (m³/d x 365/1000), the above calculation indicates that recharge of approximately 112 ML/yr is balanced by discharge of approximately 73 ML/yr by evaporation,

22 ML/yr by evapotranspiration, 18 ML/yr by subsurface outflow, and a comparatively negligible amount by surface outflow from the groundwater.

To bring the catchment into equilibrium and reclaim the salt-affected area, more than 73 ML/yr of water will need to be disposed of by means other than evaporation. Table 31. Estimated deep drainage below the root zone for soils of the example—Lockyer Valley catchment. (Predicted leaching fraction is based on the assumption that present soil salt profiles reflect the new equilibrium under clearing, determined using SALFCALC.)

Soil type	Predicted leaching fraction	Deep drainage (Predicted leaching fraction x rainfall of 800 mm/yr)		Area-weighted contribution to deep drainage (area x deep drainage as m/d)	
Son type	(determined using SALFCALC)	(mm/yr)	(m/d)	Area (m²)	(m³/d)
Heavy clay	0.006	4.8	1.3 X 10 ⁻⁵	400 X 10 ⁴	52
Alluvial	0.020	16	4.4 X 10 ⁻⁵	200 X 10 ⁴	88
Upslope	0.038	30.4	8.3 x 10 ⁻⁵	200 X 10 ⁴	166
Totals				800 x 10 ⁴	306

Table 32. Estimated values for groundwater output parameters for the example—Lockyer Valley catchment.

Symbol	Method of approximating value	Calculation	Value	Units
K _s	Estimated value from local knowledge		5.0	m/d
ΔH	Soil surface gradient from contour map used in the absence of detailed hydraulic gradient measurements	1 m/100 m =	0.01	m/m
A_{g}	Apparent width at point of subsurface outflow from the catchment and depth determined by drilling	200 m x 5 m =	1 000	m²
S	Approximate value based on observed flow	200 L/d ÷ 1 000 =	0.2	m³/d
Е	Approximate value of 2 mm/day assumed	2 mm/d ÷ 1 000 =	0.002	m/d
A _b	Bare area measured on an aerial photograph taken in a year having close to average rainfall (1982)	10 ha x 104m²/ha =	10 ⁵	m²
ET	Value of 1 200 mm/yr assumed	1 200 mm/yr ÷ 365 =	0.003	m/d
A _v	Vegetated area measured on an aerial photograph	2 ha x 104m²/ha =	2 X 10 ⁴	m²

Note: * Full conversions of units are shown. For example, $1 L/d = 0.001 m^3/d$; 1 mm/d = 0.001 m/d; $1 ha = 10^4 m^{2^2}$.

Water chemistry and salt sources identification

Laboratory analyses of water composition provide useful information for interpreting:

- likely sources of the water
- processes determining the composition (this is particularly so on a catchment scale if more than a few samples are available)
- possible uses of the water.

This information is also useful when deciding on appropriate management strategies.

Laboratory analyses

Routine laboratory analyses are:

- soluble cations (Ca²⁺, Mg²⁺, Na⁺ and occasionally K⁺) in meq/L, mg/L or mmole/L
- soluble anions (Cl⁻, HCO₃⁻, CO₃⁻²⁻, SO₄⁻²⁻ and NO₃⁻) in meq/L, mg/L or mmole/L.

Electrical conductivity (EC at 25°C in dS/m) and pH are also measured in the laboratory. These tests, which can also be carried out in the field, have been described elsewhere.

Calculations from the water analysis are made to estimate total dissolved ions (TDI) and sodium adsorption ratio (SAR). (This information can be used to assess water quality for various purposes, as discussed in *Water quality* page 79.)

Theoretically, a balance between the total number of positively charged ions (cations) and the total number of negatively charged ions (anions) is expected in the analysis of any water sample. In practice, due to analytical errors and/or the existence of species which, although present, are not measured, some degree of charge imbalance is likely. Usually, the results should be within $\pm 5\%$. Large discrepancies indicate an unusual water or an error in the analysis.

Processes controlling ionic composition

A natural water is an aqueous mixture of many components, the concentrations of which are controlled by complex and interrelated chemical processes as well as by the nature of the material the water has been moving over or through.

Basic chemical processes and solubility of salts

When water comes into contact with a mineral, dissolution begins and continues until equilibrium concentrations are attained or until all the mineral is consumed. This may take thousands of years if weathering is occurring, or days in the case of sparingly soluble salts. Thus, depending on the minerals encountered by natural waters, the salinity of natural waters can vary from only slightly more salty than rainfall to even more salty than seawater.

Table 33 lists the solubility of common salts. In solution, these salts dissociate into ions—positively and negatively charged—and do not specifically exist as the theoretical compounds in the table. However, once the concentration of an ion in solution exceeds the solubility of that ion, the compound precipitates out of solution. For example, if a water containing calcium, carbonate and bicarbonate is concentrated by the plant or surface evaporation, calcium carbonate (CaCO₃) would precipitate out of solution before calcium bicarbonate (Ca(HCO₃)₂) (see relative positions of these salts in Table 33).

Table 33. Solubility of common salts in millimoles_{charge} per litre of water (Doneen 1975).

Salt	Formula	Solubility (mmolec/L)
Calcium carbonate	CaCO ₃	0.5
Magnesium carbonate	MgCO ₃	2.5
Calcium bicarbonate	Ca(HCO ₃) ₂	3-12*
Magnesium bicarbonate	Mg(HCO ₃) ₂	15-20*
Calcium sulfate	CaSO ₄ .2H ₂ O	30
Sodium sulfate	Na2SO ₄ .10H ₂ O	683
Sodium bicarbonate	NaHCO3	1 642
Magnesium sulfate	MgSO ₄ .7H ₂ O	5 760
Sodium chloride	NaCl	6 108
Magnesium chloride	MgCl ₂ .6H ₂ O	14 955
Calcium chloride	CaCl ₂ .6H ₂ O	25 470

Note: * Solubility of carbonate minerals will be influenced by the concentration of carbon dioxide (CO2) in the solution and soil air.

This dissociation into charged ions is the reason electrical conductivity measurements can be used to assess salt content.

As the concentration of the solution increases, the EC does not linearly increase with salt concentration. This is because neutral ion pairs can form without any charge, such as $CaCO_3^{\circ}$ or $CaSO_4^{\circ}$, or with reduced charge, such as $CaHCO_3^{+}$. Gypsum is a classic example of this effect. For most salts in Table 33, the EC in dS/m is close to one-tenth of the concentration in meq/L (for example, 10 meq/L NaCl \approx 1 dS/m NaCl). For a saturated gypsum solution, however, 30 mmolec/L at saturation has an EC of 2.2 dS/m, due to ion pairing. Chemical analysis of a water assesses the total concentration of an element such as calcium and thus will give a higher salt reading.

The low solubility of calcium compounds is the reason for the prevalence of lime $(CaCO_3)$ and gypsum in soils. Lime and gypsum are associated with salting in alkaline soil areas. In some regions, thick layers of lime are a good indicator of the presence of historic salting or wetness. Large gypsum crystals can be present in seawater-affected tidal areas.

Effect of CO2 on solubility of carbonate compounds

The partial pressure of CO₂ affects the solubility of carbonate compounds. Rainfall dissolving CO₂ from the atmosphere forms a weak acid (carbonic acid HCO,⁻) which is responsible for a considerable amount of rock weathering. This is particularly evident in limestone areas where flowing water can dissolve CaCO₃. In soils and groundwater, the partial pressure of CO₂ is greater than the atmospheric CO₂ partial pressure. In soils, this is due also to the effect of roots which increase the amount of CO₂. When waters with higher partial pressures of CO₂ are exposed to the atmosphere, there is a release of CO_2 (as in soft drinks) which can cause CaCO₃ to precipitate. Evaporation or evapotranspiration from a watertable fluctuating close to the soil surface can result in the precipitation of CaCO₃.

Total salinity and common ion effect

The data in Table 33 are based on pure salt solutions in water. For some salts, as the total salt concentration increases (also called ionic strength) the solubility of the sparingly soluble salts increases. This is particularly the case when salts are dissimilar. For example, NaCl will enhance the solubility of $CaSO_4$. On the other hand, if the ions are the same, for example $CaCl_2$ and $CaSO_4$, or MgSO₄ and $CaSO_4$, there is a common ion effect where the amount of the less soluble salt in solution decreases. This is readily illustrated by the data of Arslan and Dutt (1993) plotted in Figure 46 which shows the effects of different salt solutions on gypsum solubility.

Sources of common ions

Calcium

Calcium (Ca²⁺) occurs in waters which have been in contact with igneous and metamorphic rocks containing the chain silicates (pyroxenes and amphiboles) and feldspars. In sedimentary rocks, calcium commonly occurs as carbonates, for example limestone which consists mainly of calcite with admixtures of magnesium and other impurities. Also, calcium carbonate can be present as a cement between particles in sandstone and other detrital rock.

The solubility of calcium in most natural waters is limited by processes involving carbon dioxide. The behaviour of calcium is generally governed by the availability of the more soluble calcium-containing solids and by solution- and gas-phase equilibria processes, or by the availability of sulfate anions.

Magnesium

In igneous rocks, magnesium (Mg²⁺) is a constituent of the ferromagnesian minerals including olivines, pyroxenes, amphiboles and dark-coloured micas. Metamorphic rocks have magnesium-rich species such as chlorite, serpentine and montmorillonite. In sedimentary rocks, forms of magnesium include carbonates (magnesite), hydroxides (brucite) and calcium mixtures.

Magnesium carbonate solubility is more complex than that of calcium because of the many different forms of magnesium carbonates, hydroxycarbonates and hydroxides. Generally, these are more soluble than calcium carbonates.

Sodium

It has been estimated that feldspars make up about 60% of igneous rock minerals in the earth's outer crust. Calcium and sodium feldspars are relatively more susceptible to weathering than potassium feldspars. Acid igneous rocks (such as granite) contain higher proportions of sodium feldspars than basic igneous rocks (such as basalt), which contain higher proportions of calcium and magnesium feldspars.

In sedimentary rocks, sodium may be present in unaltered mineral grains, as impurities in the cementing material or as crystals of readily soluble sodium salts deposited with the sediments or retained following intrusions of sea water. Figure 46. Effects of different salt solutions on gypsum solubility (plotted from data of Arslan and Dutt 1993).



Sodium bicarbonate is the least soluble of the common sodium salts. At room temperature, a pure solution of this salt would contain around 1 642 meq/L of sodium. In natural waters, conditions favouring the precipitation of NaHCO₃ are unlikely to be attained. In general, the solubility of sodium is rarely exceeded in Australian waters. There is, however, some evidence of the presence of solid NaHCO₃ in some Burdekin soils. The presence of solid NaCl (halite) is unlikely in normal agricultural situations, as a saturated solution of NaCl can contain up to 6 108 mmolec/L of sodium and chloride (Table 33, page 74). Precipitation of NaCl can occur in agricultural situations only where soil water, usually associated with shallow watertables, is concentrated at the soil surface by evaporation.

Sulfur

Sulfur (S) is not a major constituent of the earth's outer crust. However, sulfur is widely distributed, both in igneous and sedimentary rocks, as metal sulfides. Sulfur can also occur in certain igneous rock minerals of the felspathoid group. In sedimentary rocks, sulfides or pyrites are commonly associated with biogenic deposits such as coal. Evaporite sediments (such as gypsum) are another source of sedimentary sulfur.

Sulfides can be oxidised by aerated waters to yield $SO_4^{2^{\circ}}$. Sulfate is chemically stable in aerated waters. $CaSO_4$ is the least soluble common sulfate, with sodium and magnesium sulfates being many times more soluble (Table 33).

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Chloride

The chloride (Cl) content of rock minerals is generally very low. Residual water in pores or included within crystals of igneous rocks may be a source of chloride. More important sources are rainfall and sedimentary rocks where soluble chlorides may be present as a result of inclusion of waters in the sedimentary process. Porous rocks formed in the sea or submerged after their formation may also become impregnated with chloride salts.

Chloride in natural waters is not altered by oxidation/ reduction reactions, does not form important solute complexes with other ions, does not form salts of low solubility (Table 33), and is not significantly adsorbed onto mineral surfaces.

Interpretation using trilinear diagrams

There are a number of graphical and statistical methods for assessing water analyses (some are reviewed by Freeze and Cherry, 1979).

One useful method developed by Piper (1944) graphically illustrates the composition of a water in a form that can be linked to common geological compositions and illustrates the processes of change in composition that will occur. Using this approach, the composition and concentration of salts can be represented together. The method is useful for examining the similarity of waters in a region and for evaluating concentration–precipitation reactions and the mixing of waters of different origins.

Method

The contribution of each of the major cations or anions is normalised by being expressed as a percentage of the total ions of the same type. The results are then plotted spatially. For example, for the cations Na⁺, K⁺, Ca²⁺ and Mg²⁺ and the anions Cl⁻, HCO₃⁻, CO₃⁻²⁻ and SO₄⁻²⁻, percentages are calculated as follows:

$$Na\% = \frac{Na}{(Na + K + Ca + Mg^{2^{+}})} *100 \dots 27$$

and

$$HCO_{3}\% = \frac{HCO_{3}}{(HCO_{3} + CO_{3} + Cl + SO_{4})} *100 \dots 28$$

Separate cation and anion plots and a combined cation/anion plot are shown in Figure 47. Traditionally, combined plots have been drawn on diamond-shaped quadrangular plots, but here the combined plot is presented on a standard rectangular plot for ease of plotting.

Interpretation

The direction in which points are plotted from the axes is shown in Figure 47. The example point in Figure 47 thus has an approximate analysis of 60% Ca²⁺, 20% Mg²⁺, 20% Na⁺, 10% SO₄²⁻, 25% HCO₃⁻ and 65% Cl⁻. Analyses dominated by Ca²⁺ will be plotted towards the bottom left corner of the cation triangle. Similarly, analyses dominated by Mg²⁺ are plotted towards the top of the triangle and Na⁺ the bottom right. For the anion triangle, analyses dominated by SO₄²⁻ are plotted towards the bottom right corner, Cl⁻ towards the top, and HCO₃⁻ towards the bottom left corner.

On the square plot, the X axis (left to right) corresponds with the proportion of $Ca^{2+} + Mg^{2+}$. High $Ca^{2+} + Mg^{2+}$ analyses are plotted towards the left side, and high Na⁺ + K⁺ analyses (which must have low $Ca^{2+} + Mg^{2+}$) towards the right side. Similarly, high $Cl^{-} + SO_4^{2-}$ analyses are plotted towards the top of the square, and high $HCO_3^{-} + CO_3^{2-}$ (low $Cl^{-} + SO_4^{2-}$) towards the bottom of the square.

As discussed in *Processes controlling ionic composition* (page 74), when the concentration of a mixed salt solution increases (for example by evaporation of water), salts of low solubility precipitate and the composition of the soluble salts changes. An example of this is the concentration of groundwaters by evaporation which commonly occurs at saline seepages. When concentrated, soluble salt solutions tend to move toward the composition of seawater.

Figure 47. Trilinear and quadrilinear diagrams, illustrating how points are plotted (after Shaw et al. 1987).





Practical example

Figure 48 overleaf illustrates the practical use of trilinear diagrams in the Lockyer Valley to determine the most probable source of waters in the alluvial aquifers. In this case, chemical analyses of the water and interpretation using trilinear diagrams revealed that the common belief that the groundwater was coming from the uplands was likely to be incorrect. Southern tributaries in the Lockver Valley have been known to have variable salinity in the alluvial groundwater. This alluvium is sourced mainly from basalt materials. The surrounding uplands are sandstones. The commonly accepted theory was that clearing on the sandstone ridges resulted in increased seepage of sandstones waters into the alluvia. The use of simple trilinear diagram plots indicated that historic processes of salting in the basalt alluvium were the source of the salts, and not the sandstones.

Waters from the two major hard rock geologies in the region, basalt and sandstone, are illustrated in the sandstone geology plot on the left side. Basalt waters (green crosses) show a greater Ca^{2+} and Mg^{2+} dominance than Na⁺ in contrast to the sandstone (black crosses). This is reflected in both the cation plot and the combined cation/anion plot. Some areas of overlap were expected because basalt overlies the sandstones and basalt recharge will enter the sandstone. Also, the composition of very low salinity waters (EC < 0.05 dS/m) will reflect that of rainfall, which is similar to the composition of seawater.

The composition of the waters in the alluvial aquifers of Tenthill Creek indicates a tight distribution of composition in a relatively narrow salinity range in the combined cation/anion plot. The cation plot indicates some relative enhancement of Mg²⁺ and Na²⁺ concentration and a loss of Ca⁺ with respect to basalt, as expected, due to the change in solubility with increasing concentration. The composition of the waters is dominantly of basalt origin.

The waters in Sandy Creek alluvial aquifers are generally of higher salinity than Tenthill Creek and show an increasing component of sodium as expected from Figure 48. The combined cation/anion plot suggests that, even with the increased relative concentration of sodium, the waters reflect the composition of a concentrated basalt-type water more than that of a water derived from a sandstone geology, since there is a strong absence of water composition in the top right corner of the combined cation/anion plot compared with the sandstone geology plot. If sandstones were making a significant contribution, there would be a higher sodium concentration.

This is confirmed by the analyses of Hardie and Eugster (1970) who evaluated the evaporative concentration curve for closed evaporative basins of various geological water compositions. Figure 49 shows their line for a basalt water and the respective composition of waters for given salt concentrations in Sandy Creek in the Lockyer Valley.

Waters derived from basalt sources have approximately equal proportions of Ca^{2+} , Mg^{2+} and Na⁺ at low concentration (< 1 dS/m). As these waters concentrate to 2 to 4 dS/m, Ca2+ salts precipitate. Further concentrations result in Mg^{2+} as well as Ca^{2+} precipitation. In basalt waters, this process leads to an increase in Na⁺ dominance.

Thus a simple analysis of waters using the trilinear diagram approach provides useful insights into chemical processes and geological sources of salts. In this case, the implications for catchment management were that revegetation of the uplands, advisable if the sandstones had been the groundwater source, would make essentially no impact on the alluvial salinity. Figure 48. Use of trilinear diagrams to distinguish geological sources of water in relation to aquifer chemical composition and the effect of solution concentration on chemical composition (after Shaw et al. 1987).



Figure 49. Changes in cation composition with concentration for water derived from basalt in the Lockyer Valley compared with the data of Hardie and Eugster (1970) for a basalt water derived from closed evaporative basins in the USA (after Shaw et al. 1987).

