Chapter Four
Field Sampling Program

4.1. Introduction

The study design phase, described in Chapter 3, broadly specified the measurement parameters that were needed for satisfying the monitoring program objectives. Now that the basic outline of a sampling program has been settled, the next stage is the implementation of this design in the field.

First, the monitoring team defines or specifies the population that is to be sampled. Then it considers the specific data requirements — measurement parameters, scale and frequency of sampling, accuracy and precision required — and decides whether to measure the parameters in the field or the laboratory. Costs must be planned so that they fall within the agreed budget, remembering the trade-off between maximum statistical power and cost of sampling and analysis.

In all instances, there are appropriate protocols for field measurements, and for sample collection, preservation, preparation and storage, that need to be followed prior to any laboratory analyses. A framework for applying these protocols is shown in Figure 4.1. A checklist is presented in Table 4.1.

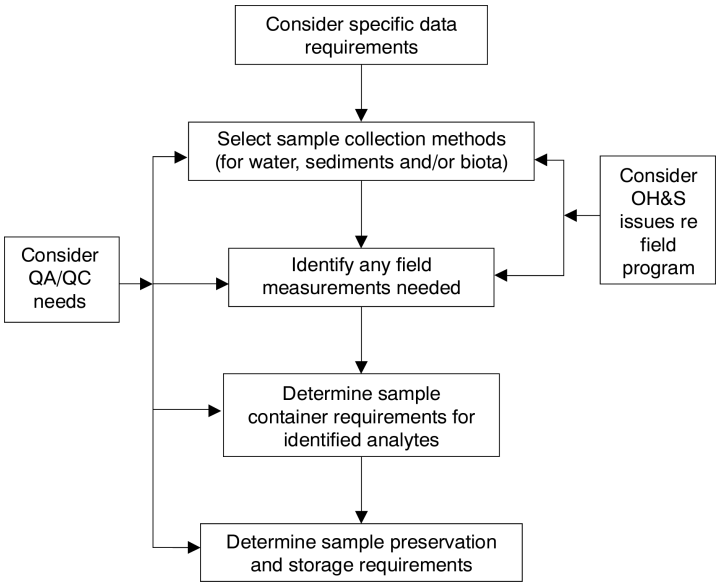

Figure 4.1. A framework for designing sampling programs

4.2. Field Measurements and Observations

Some parameters (e.g. flow, temperature) can only be measured in the field. For other parameters (e.g. dissolved oxygen, redox potential and possibly pH), field measurements are highly desirable because the value of the parameter might change in the sample after collection. The reliable sensors

that are available nowadays make it often convenient to measure many parameters in the field. Not only does field monitoring give on-the-spot values, but also the results can be checked immediately and then the choice of sampling sites can be refined rapidly if necessary. Whether measuring or sampling, quality control and quality assurance are important; they require planning because they are not easy to achieve in the field.

Table 4.1. Checklist for designing sampling programs

1. Have the specific measurement parameters been identified and the data requirements stated?
2. Can the data required be obtained by field measurements?
3. Have appropriate field measurement techniques, including calibration procedures, been selected?
4. How are the positions of sampling sites to be recorded?
5. What ancillary field observations are to be taken?
6. Will the sampling device collect a representative sample?
   (a) Do disturbances occur in the environment being sampled?
   (b) Will the sample be altered by contact with the sampling device?
   (c) Will the sample device contaminate the sample? If yes, how is the sample device to be cleaned?
   (d) What are the effects of the sampling device being in contact with media other than the sample of interest?
7. How are samples to be collected to prevent contamination?
8. Will the sample container contaminate or affect the stability of the sample? If so, how are these problems to be overcome?
9. What size sample containers are required?
10. How are samples to be preserved before analysis?
11. Are procedures in place to track samples and field data?
12. What program is in place to identify, measure and control errors?
    (a) Have sampling protocols been written?
    (b) How are sampling staff to be trained?
    (c) How is the sampling staff's competence to be tested?
    (d) Can the integrity of the sample be guaranteed?
    (e) Have blanks, duplicates and replicates been incorporated into protocols?
    (f) How are problems to be rectified?
13. Are there enough resources to prevent any bottlenecks occurring in field or laboratory that would hinder analyses and compromise data quality?
14. How are data to be stored and accessed?
15. Have all reasonable steps been taken to protect health and safety of employees?
    (a) Have possible hazards been identified and documented?
    (b) Have sampling staff been made aware of possible hazards, and have risk minimisation plans been developed?
    (c) Have sampling staff been trained to ensure that sampling is done safely?
    (d) Will sampling staff be appropriately supervised during sampling activities?

Field data can also be obtained automatically and by remote sensing, and the data can be logged and/or transferred to laboratories by telemetry. This has the advantage of providing measurements that are either continuous or at fixed intervals, allowing very cost-effective studies of temporal trends.

For parameters that do not change during transport and storage, field sampling is adequate. Macro-invertebrates, for instance, collected by sampling a waterbody, can immediately be stored in alcohol in vials and kept there until they are identified and counted. However, for samples that must be field-

sampled and then analysed in a laboratory, fixative, preservatives and cold storage during transport can minimise changes.

Guidance on the various physical, chemical and biological measurement parameters that can be field sampled is provided in *Standard Methods for the Examination of Water and Wastewater* (APHA 1998) and USEPA (1996b), or the most current editions. An example of a field sampling program record sheet is provided in Appendix 6.

It is important to record the position of each sampling site so that it can be re-used in subsequent studies. It is also essential to make careful and thorough descriptions of the means of access and of the sites themselves and of the exact spots from which samples were taken. Key on-shore reference points should be identified, or the site should be located by the global positioning system (GPS), a satellite navigation system that enables points on the Earth's surface to be identified relatively accurately. Measurements by GPS are now becoming reasonably precise (to within 20 m). If exact positioning of sample sites is necessary, then basic GPS will be inadequate and a more accurate method (differential GPS) will be required. With high quality receivers and differential GPS the accuracy can be to within 1 m of the position or location. However, it is important to use a single coordinate system and to record which coordinate system is used, especially the datum and projection. A site identified by a latitude and longitude based on one datum can be up to 200 m away from a site identified by the same latitude and longitude numbers based on a different datum.

At each visit, the condition of the water body and the weather conditions must also be noted because these factors may influence the variables being measured. For example, changes in the wind speed and cloud cover may affect the temperature and subsequently the dissolved oxygen within the water column. Other field observations might include descriptions of odour, colour and floating material, and riverine vegetation or other conditions relevant to water quality. Video or photographic records are highly desirable for future reference.

4.3. Sampling of Waters and Sediments

4.3.1. Equipment and Methods

What are the most appropriate ways in which to actually collect samples or data from each sampling station and water body? Methods include:

- collection of a sample by hand,
- collection by automatic sampler,
- samplers that collect and integrate samples over a given time,
- real-time measurement by automatic means,
- measurements in the field by hand,
- remote sensing,
- field observation.

The choice of sampling method depends on the parameter to be measured and the nature of the information required. Differing sampling methods can provide differing information and have differing advantages and drawbacks. For example, grab samples could be easier to preserve, or less liable to contamination, or of a better size than samples integrated over time (or flow) by automatic devices. All the methods or equipment used must meet the relevant Australian and/or ISO Standard (e.g. AS/NZS 1998 a–e). This recommendation applies to all methods described in this document.

Selection of a sampling method should be guided by:

- the objectives of the monitoring program,
- the local conditions (i.e. the need to obtain representative samples),
- the safety of operation (the overriding principle should be the safety of the sampling staff),

- the acceptability of the method,
- commonsense.

Continuous sampling methods and equipment are being developed for waters and are able to operate reliably in some areas (Hart et al. 1993). They provide information on significant short-term variations in water quality parameters that are usually missed by discrete samples. Continuous sampling should be more widely used in the future as methods, equipment and data handling become more reliable. The procedures in this Monitoring Guidelines document nearly all involve individual sample collection, so they will need to be regularly assessed and updated or changed as technology improves.

Time-integrated sampling reduces analysis costs and enables mean values to be calculated simply. However, integrated sampling is not recommended where the objective is to assess variations in water quality.

Samples can be taken at the water surface, or at specific depths in the water column, or integrated over depths. For particular analytes (e.g. trace metals), the equipment must have a specific composition and be cleaned in certain ways to avoid sample contamination. A standard text for the general procedures and principles of collecting water samples is the *Standard Methods for the Examination of Water and Wastewater* (Methods 1060A and 1060B) (APHA 1998 or most current edition), mentioned above. Additional guidance on sampling lakes, rivers, streams, marine waters, groundwaters and sediments is found in the range of Australian and New Zealand Standards (AS/NZS 1998a–e, 1999).

The sampling operation includes the preparation and labelling of containers, appropriate selection of sampling sites, collection of samples, good housekeeping and field record books, photographic and video records, the use of boats and cars, and the recording of parameters such as depth and light intensity.

Green (1979), in his ten principles of sampling, says:

> verify that the sampling device is sampling the population you think it is sampling with equal or adequate efficiency over the entire range.

For this, the monitoring team must specify the population that is to be sampled and its likely spatial and temporal variability. In Australian rivers, discharge can change by two orders of magnitude, and the effectiveness of sampling devices may vary over this velocity range. Device-related sampling errors cannot be removed or accounted for by statistical methods or by replication, and in many cases they will be undetectable unless specific tests have been made.

The sampling device should not significantly disturb the environment being sampled or alter the samples taken, because if it does the samples will not reflect what ‘was’ or ‘is’. The problems in sediment sampling illustrate these difficulties. Blomqvist (1991) reviewed the problems of using several types of grab samplers and coring devices to obtain sediment samples. Grab samplers often do not enter sediments perpendicularly, and the sediment layers mix when they close. Most grab samplers have jaws that close semi-circularly, and sediment layers below the initial penetration are only semi-quantitatively sampled. For quantitative sampling it is necessary to know the area and depth sampled. Coring devices must be designed to ensure that easily resuspended surface materials are not washed away. If rotation of cores occurs, shear stress may mix the sediment and cause core shortening.

Some consideration must also be given to the environment traversed by the sampling device, so that no sampling errors are caused by the device being in contact with media other than the sample of interest. For example, when collecting sub-surface water samples for hydrocarbon analysis, the sample collection device must enter the water closed or it will pick up hydrocarbons from the water surface microlayer. On the other hand, when shallow water is being sampled, care should be taken not to stir up bottom sediment.

Sampling devices should be tested under controlled conditions to check that they quantitatively collect the sample of interest. In lieu of this, some studies reported in the literature compare the efficiency of sampling devices and document the limitations of various alternatives, e.g. water samplers (Harris and Keffer 1974), sediment samplers (Blomqvist 1991; Schneider and Wyllie 1991), biota samplers (Devries and Stein 1991). Using this information a choice of sampling device can be made based on the matrix to be sampled and the unique conditions at the chosen sample site.

The sampling of waters for trace and ultratrace contaminants is increasingly a requirement for monitoring studies, especially for conformity with a guideline. To avoid sample contamination, much greater care is needed than for general water quality parameters. Non-contaminating equipment is essential, and it should be cleaned with acids for sampling metals, or cleaned with detergents and solvents for sampling organic compounds. Ahlers et al. (1990) elegantly describe the type of rigour required for preparing containers and for sampling methods. For trace metal surveys, avoid samplers with components that may contribute trace metals (Batley 1989). Use Perspex poles with all-plastic fittings to hold Teflon or polyethylene bottles for sampling shallow surface waters. Avoid depth samplers with rubber closures. For nutrient sampling, take care that samplers are free from residual nitric acid or phosphate-containing detergents that may have been used in their pre-cleaning. With samples for trace contaminants, the possibility of sample contamination is high; experienced staff may be required for such sampling. This is also true for samples of filtered nutrients where filtering is to be done in the field.

Many of the contaminants to be measured, particularly in relatively pristine marine or alpine waters, will be present at extremely low concentrations, which may influence:

- the volume of sample required (and hence the type of sampling device that may be suitable);
- the precautions required to avoid contamination (this could include the use of a suitable vessel such as a dinghy which can work away from the mother vessel, and the selection of sampling devices constructed out of non-contaminating materials); and
- the suitability of analytical methods.

Local conditions will further dictate the method and equipment used. To sample from a bridge a bucket can be used, while to sample from a river bank a telescopic pole would be more useful. For sampling in estuarine waters, the experimental design needs to take into account the complex and highly variable nature of the water body. In estuaries, waters intermix that have very different chemical composition and physical and chemical properties, producing great variation, vertically, horizontally and temporally (with tidal stage). As a result, large numbers of samples or stratified sampling may be required, which in turn is likely to have a bearing on the selection of the sampling method.

Details of specific sampling techniques for estuarine and marine waters are described by Grasshoff et al. (1999) and Crompton (1989), and can be found in the Australian and New Zealand Standard (AS/NZS 1998b).

4.3.2. Sampling of Surface Waters

Equipment for sampling surface waters (as opposed to groundwater) falls into five basic categories:

- bottle samplers for shallow waters,
- pumping systems for surface to medium (10 m) depths,
- depth samplers (50 m to >100 m depending on design),
- automatic samplers,
- integrating samplers.

4.3.2.1. Bottle Sampling of Shallow Waters

Many water bodies are shallow and well mixed, and surface (0–1 m) water sampling is all that is required. For this purpose, immersion of a sample bottle by hand to just below the surface (typically

0.25–0.5 m depth), is satisfactory, provided the hand wears a plastic disposable glove, and any contribution from surface films is avoided, and the sampler is downstream of where the sample is to be collected. This may be done from the shore, or by standing in shallow water, or from a boat. Whatever the vessel used it is important to face it into the ongoing current and to take water samples from the front of the vessel (Apte et al. 1998). This procedure minimises contamination from the boat itself. To maintain an adequate distance between the sampling point and the sampling vessel, the sample bottle can be held in acrylic jaws at the end of a 1–2 m long polycarbonate pole, 2 cm in diameter. This technique is also applicable for sampling from fixed structures. The alternative is a bottle or bucket fixed to a plastic rope. Both require cleaning before use and must be kept clean between uses by being housed in a plastic bag that is then placed in a clean plastic sealable container.

4.3.2.2. Pumping Systems

Pumping systems are effective for sampling, although they are not desirable for work on ultra-trace contaminants because the tubing gives the apparatus a large surface-area-to-volume ratio that increases the chance of adsorption of analyte. They are suitable for µg/L metal concentrations, and for all general water quality parameters. They typically involve a vacuum pump or, for shallower depths, a peristaltic pump. Water is sucked to the surface via appropriate lengths of pre-cleaned tubing of polyethylene or silicone or PTFE or PVC (approximately 1 cm diameter), and into a large acid-washed Pyrex glass Ehrlenmeyer flask (for a vacuum pump) or directly into a plastic sample bottle (for a peristaltic pump). The tubing is conditioned by pumping a large volume of water to waste prior to sampling. This procedure has been widely used for mercury sampling (USEPA 1996c) during which on-line filtration is also applied.

4.3.2.3. Depth Samplers

For depth sampling a range of purpose-built samplers are available (Batley 1989). Their basic operation involves a bottle, which can be opened at both ends via a wire or plastic line, which is deployed to the required depth. A weight is then sent down the line to trigger closure of the bottle and collection of the water. The bottle closures should be considered when determining the suitability of depth samplers; e.g. rubber closures are not recommended for low metal concentrations. In samplers for trace analysis, it is important to blank test the samplers by filling with them with clean water for the same length of time as the sampling event and then analysing the water for the analytes of interest. Contamination often increases with the age of the sampling device. The blank tests should therefore be carried out at regular intervals. The Mercos sampler, which uses a group of Teflon bottles, is ideal for obtaining water column depth profiles of trace metals including mercury at depths below 100 m.

4.3.2.4. Automatic Samplers

For unattended water sampling, an automatic sampler can be pre-programmed to collect samples continuously or on a flow-related or time-related basis. Such an arrangement is ideal for collecting stormwater runoff for example, and collection can be triggered by the commencement of water flow. A number of commercially available devices perform this function. They basically consist of a pump system, a controller and an array of sample bottles within a housing. Most instruments have purpose-made glass or polyethylene sample bottles that are designed so that a fixed number fit around the circumference of the housing. Glass is preferable for organic compounds and general water quality parameters, and polyethylene is better for metals. The bottles and all surfaces are acid washed before use. To check that the bottles are suitable for trace metal applications, clean water blanks are analysed after they have been in the bottles for a suitable test period.

Very large numbers of samples can be acquired using continuous samplers (AS/NZS 1998 b–d). The samples thus acquired can be bracketed, so that only a subset reflecting the conditions of particular interest need be analysed. It should always be borne in mind that the integrity of samples collected by automatic devices may be compromised by delayed preservation. This would normally require that samples be collected and processed as soon as possible after the relevant event. Refrigerated samplers

are also available, however, to assist in sample preservation. Automatic samplers may not be appropriate for sampling bacteria, pH or other variables that are likely to change significantly between the time of collection by the automatic sampler and retrieval from the field for analysis.

4.3.2.5. Integrating Samplers

For some sampling programs, single samplings are poorly representative of a site because water quality can vary considerably with time. In these cases samplers that integrate water samples over a fixed time period or volume are preferred. The samplers usually contain collector adsorbants that can quantitatively remove organic contaminants or metals, and are usually restricted to these parameters (Hart and Davies 1977; McLaren et al. 1985; Zhang and Davison 1995). The automatic samplers described above can perform as integrating samplers, although they are designed to collect a number of discrete samples.

Membrane-based passive samplers are a promising tool for the time-integrated monitoring of hydrophobic contaminants in aquatic ecosystems. In these devices, the uptake of chemicals is based on the partitioning of a compound between water and a lipophilic solvent enclosed in a semi-permeable polymeric membrane. Thus the passive samplers can be used as indicators of bioavailability of these contaminants. Laboratory analysis of the solvent is generally both faster and less expensive than water analyses for these compounds.

Several designs of membrane samplers have been proposed, including polyethylene bags filled with isooctane (Peterson et al. 1995). The main advantage is that they give a time-integrated measure of toxicant exposure at sites that can be related to any observed ecological changes. For example, endosulfan runoff from cotton fields measured by in situ passive samplers was found to be a good predictor of changes in density of benthic organisms (Leonard et al. 1999). Passive samplers have been adopted as a quantitative sampling method for pesticides in New South Wales to detect chemicals that standard sampling methods may have missed (Muschal 1998).

4.3.3. Sampling Groundwaters

Groundwater occurs in aquifers at various depths below the ground. Recharge may be by direct infiltration of rainfall, by seepage from rivers or other bodies of surface water, or by transfer from one aquifer to another. The area of recharge may be at the sampling site or many hundreds of kilometres away. The water may have been resident in the aquifer for a few days or millions of years.

The quality of groundwater can vary from almost pure water to extremely concentrated brines. Its quality depends on the geology of the aquifer and can be subject to contamination from substances that come into contact with the ground. Fertilisers, pesticides, petroleum products, landfills, mining, household and farm and industrial wastes all contaminate groundwaters to varying degrees, often much more than surface waters.

Monitoring of the quality of groundwaters involves techniques different from those used for surface water quality investigations because groundwater, by its very nature, cannot be sampled without some disturbance from the construction of a bore or other access hole and the effects of sampling devices and procedures. These may also cause chemical and biological contamination unless stringent precautions are taken. Hence sampling staff must make extreme effort to ensure that the samples are representative of the water in the aquifer. Groundwater sampling should generally be carried out by experienced field staff or in close consultation with experts, to ensure sample integrity.

To retrieve a representative sample, these principles should be considered (see also Table 4.2 and QDME 1995):

- the sampling equipment should not change the water quality in any way; particular effort should be made to avoid cross-contamination between bores and sampling equipment;
- sufficient water should be removed to ensure the sample is newly derived from the aquifer itself rather than from water that has sat in the bore; and

- the methods of collection and storage in bottles and transportation to the laboratory should be suitable for the type of analysis required.

Guidance is provided in the Australian/New Zealand Standard for groundwater sampling (AS/NZS 1998e).

Groundwater sampling may produce a large volume of purged water. If necessary, this should be stored on site in drums for proper disposal.

Table 4.2. Groundwater samplers (from QDME 1995)

Type of sampler	Remarks
Displacement pumps	These types of pumps provide a gentle pumping action which is suitable for purging and producing a high quality sample for all reasonable purposes.
(i) Positive or gas bladder displacement	If the pump is made from sufficiently high quality materials, the types of media used to work the pump are not important.
(ii) Mechanical displacement	These pumps are very suitable for well purging, though they are often slow. Specific design is very important in performance.
Submersible pumps	Several varieties of this type of pump are available, from very cheap to quite expensive. They rely on a motor below water level powering a pump to push water to the surface via a delivery line.
	These pumps are efficient in purging bores and can produce an acceptable sample for most purposes, though minor gases may be lost.
Suction pumps (centrifugal)	An excellent method for purging wells, but limited to about 6 m depth. The 'suction' type action has little effect on the water remaining in the well, though the samples pumped may lose some gases or organic compounds. Following purging with this type of pump, high quality samples can be taken with balers, with care.
Down-hole grab samplers	Of little use in sub-artesian bores. Can obtain high quality samples from different depths in flowing bores. Quality control must be exercised in the transfer of samples.
Balers	Difficult or impossible to use for purging bores. Require extreme care to prevent contamination, because samples have to be pulled to surface. Rope needs to be sterilised, cleaned or replaced frequently.
	Good quality samples can sometimes be obtained if bores are purged by other approved means. Quality control must be exercised in transfer of samples.
Air-lifting	This is generally considered to be a poor method of obtaining high quality samples. The air-lifting method strips gases and organic compounds from the water, changes pH, and may cause minor chemical changes. However, it is efficient in purging bores, and has little if any effect on major ion chemistry. Generally, results of analyses of air-lifted samples are considered acceptable for monitoring major ions.
	Samples should not be submitted for higher quality types of analyses.
	This method is not considered suitable for well purging for high quality samples even if sampled with a baler. Air-lifting has an effect on the whole water column and the whole volume would have to be removed before a high quality sample could be obtained.

4.3.4. Sampling of Precipitation

This Monitoring Guidelines document does not cover collection of deposited rain, snow and airborne particulates in detail, although the analytical methods described in Chapter 5 are applicable to these types of samples. The user is directed to the WMO *Manual on Water Quality Monitoring — Planning and Implementation of Sampling and Field Testing* (1988). The Commonwealth Bureau of Meteorology and the relevant state and territory agencies that undertake sampling for these measurement parameters should be consulted for guidance and additional information.

4.3.5. Sediment Sampling

Sediments often are surveyed to determine the composition and concentration of contaminants in them, as well as the numbers of organisms located at various depths. There are two broad-based sediment classifications: *suspended sediments* and *bottom sediments*. In water quality terms, suspended sediments are generally dealt with as part of the water column, although specialised sampling techniques are required for obtaining representative samples (USEPA 1991b; AS/NZS 1999). The benthic organisms in bottom sediments are investigated as measures of aquatic health, pollution or contamination, and as part of the ecology of aquatic systems. In this section we are only concerned with sampling the sediment, not the benthic organisms within the sediment. The monitoring team must decide what to include in the sample before beginning sampling. For example, when the objective is to sample sediments from within a seagrass bed, it is normal practice to remove the rhizomes of the seagrasses and to sieve sediments to remove small molluscs.

It is recommended that sampling for sediments should follow internationally accepted protocols and procedures. The choice of sampling method will be dictated largely by the nature of the investigations being undertaken. However, it may be necessary to consult with the relevant state and territory agencies about any internal guidelines that they may have for sampling sediments. Table 4.3 lists a number of sediment sampling methods that can be used both for biological and for non-biological parameters. Sampling for determination of sediment transport is not covered in the Monitoring Guidelines.

Table 4.3. Methods for sampling sediments

Method	Reference
Method 9060A Sample collection	APHA (1998)
Method 10500B Soft-bottom dredge	APHA (1998)
Method 10500B Hard-bottom dredge	APHA (1998)
Method 10500B Rocky-bottom samplers	APHA (1998)
Dredging method	APHA (1998)
Grab method	EPAV (1992)
Corer method	EPAV (1992)
Integrating samplers	EPAV (1992)
Grab samplers	WMO (1988)
Core samplers	WMO (1988)
Protocols for sampling	Environment Canada (1994)

For most applications, sediment coring is recommended (Mudroch and Azcue 1995). With this technique, samples can be taken to a measurable depth and then subsampled to provide depth profile information. Corers generally vary in diameter from 2.5 cm to 5 cm, and range from long PVC pipe (2–3 m), that can be immersed in shallow waters from a boat, to shorter Perspex, polycarbonate or other tubes that can be immersed by hand by divers. The tubes have a bevelled leading edge to ease their movement through the sediment. In shallow waters, cores can be extruded by gas pressure and subdivided, but this is not recommended where sediment oxidation is an issue. If divers are not available, vibrocorers are essential for use from vessels in waters deeper than about 3 m. Vibrocorers usually contain plastic liners that protect the sample from contamination. Some corers enable in situ freezing of the sample.

A grab sampler or dredge is a useful alternative for obtaining large volumes of surface sediments. A range of types of dredge sampler is available and most of them are suitable for sampling in shallow water depths (<20 m). However, care should be taken in deeper waters to ensure that fines are not lost during the passage of the sampler to the surface (APHA 1998), because it is these particles that are most enriched in trace contaminants (Mudroch and Azcue 1995).

When the chemical forms of contaminants and their associations with sediment phases are to be determined, it is necessary to ensure that the redox state of the sediments (oxic or anoxic) is not altered, because oxygenation (or reduction) will cause irreversible changes. Sediments become oxygenated on contact with air, so the sediment samples need to be capped immediately at sampling and stored in a nitrogen glove box. Oxidation can be minimised if samples are frozen at –20°C.

4.3.6. Sample Containers

The monitoring team must decide on appropriate sample containers (type and volume) and how to clean them before use. The sample container can affect the composition of the sample by adsorbing some of its constituents (Batley 1989); for example, glass containers tend to adsorb phosphate. On the other hand, as mentioned above, containers can also be a source of contamination unless they are carefully prepared.

Metals can be present at trace concentrations both on glass and on plastic surfaces, while organic compounds are more likely to be found on plastic containers. Bacteria on container walls may use nutrients from solution (Maher and Woo 1998). The caps of containers often contain inserts of cardboard, cork or rubber that should be removed because they can cause contamination. A range of plastic materials have been used and their propensity for sample contamination has been thoroughly reported (Hunt and Wilson 1986; Hall 1998; Reimann et al. 1999). For metals, the preferred sample containers are fluorocarbon polymers, PTFE (Teflon) or FEP, as well as high-density polyethylene. Bottles made of FEP are usually only used for mercury analysis because they are so costly. High quality bottles are recommended, e.g. Nalgene, because these have good closures that prevent sample leakage. For samples to be analysed for selenium, bottles made of polycarbonate and some types of polyethylene are not suitable. For nutrients, polyethylene (low density or high density) sample bottles are the most favoured type. Glass is not favoured because there can be high concentrations of trace metals in the glass and there is potential for adsorption losses.

Some degree of cleaning is usually applied to bottles before they are used. This often involves soaking in acid, but the rigour of the procedure varies from laboratory to laboratory. Some authors have advocated direct use of certain bottle types without any cleaning (Reimann et al. 1999). Such sweeping statements are ill-advised because the quality of sample bottles often changes between batches. In the authors' laboratories, the bare minimum cleaning procedure involves soaking sample bottles in 10% nitric acid for at least 24 hours and then rinsing them with copious quantities of deionised water. Such precautions are worthwhile on most occasions, given the cost of sampling (especially if helicopters or boats are involved in the sampling programs). In our laboratories, acid washing is carried out in a dedicated dust-free room, and the acid baths are stored in a bunded and vented area similar to a very large domestic shower recess. The emptied bottles are double-bagged using two zip-lock polyethylene bags. For waters for zinc analysis, Ahlers et al. (1990) advocated that Nalgene bottles be soaked in hot 50% nitric acid for two days, rinsed with high purity water, then leached in 1% nitric acid for two weeks. The value of such extreme care was clearly demonstrated in the reliability of the resultant analytical data. In any case, sampling staff should check with their analytical laboratory to ensure bottles have been appropriately prepared before use.

4.3.7. Sampling Protocols

When sampling waters containing trace metals, nutrients or organic compounds, a single person wearing plastic disposable gloves and taking appropriate care can carry out the operation without sample contamination if he or she is alert to potential sources of contamination. Lavish use of polyethylene sheeting to wrap equipment and to cover work areas on boats, river banks, etc., is part of the good practice that follows automatically from this alertness. Dust, powder, skin and hair are obvious external sources of metals, and rigorous care is required to minimise their effects. Detailed protocols for ultra-trace sampling have been described in the literature (Ahlers et al. 1990; Nriagu et al. 1993; Nolting and de Jong 1994; Apte et al. 1998); see also section 4.6.2 below.

The recommended sampling protocol for ultra-trace analysis uses the 'dirty hands–clean hands' approach. This involves two people both wearing (powder-free) polyethylene gloves. The double-bagged bottles are sequentially unwrapped. The first 'dirty' assistant removes the outer bag and hands the bottle to the 'clean' assistant, who removes the inner bag. The 'clean' assistant then immerses the bottles by hand or from the end of a pole (as discussed above), or fills them with the sample collected using the depth sampler. Bottles are usually rinsed with sample material first — filled, capped, shaken and emptied —before being refilled with the sample to be analysed.

Other precautions also help avoid contamination: reagents for use in the field are stored in decontaminated containers; sample and reagent containers are transported in separate sealed plastic bags; all field equipment is pre-cleaned to the same standard as the containers; containers are uncapped or removed from their transport bags for minimum amounts of time; containers that were filled with water as part of the preparation protocol are emptied well away from and downstream of the sampling location before being rinsed with sample and refilled.

4.4. Sampling of Aquatic Organisms

For aquatic organisms, selection of a sampling method should be again be guided by:

- the objectives of the monitoring program;
- the local conditions (i.e. the need to obtain representative samples);
- safety of operation (the overriding principle should be the safety of the sampling staff);
- acceptability of the method; and
- commonsense.

The organisms typically sampled comprise plankton, bacteria, periphyton, protozoa, algae, fungi, macrophytes, macroinvertebrates, benthic macroinvertebrates and algae, bivalves and fish. Methods for their sampling are described in APHA (1998 or most current edition) and Hellawell (1986) and summarised in Table 4.4.

The monitoring team will have decided which organisms to collect at the study design stage (section 3.5.2 in Chapter 3) and now must choose the appropriate equipment and procedures to use. Several devices may be needed to ensure quantitative sampling of all the required organisms. There may need to be a compromise between these and more rapid methods. Devries and Stein (1991), in their comparison of the efficiency of three sampling devices (tube sampler, vertical tow net and Schindler–Patalas trap) for collecting zooplankton, found there was no best method. Zooplankton consist of a mixture of copepods, cladocerans and rotifers. Generally copepods and cladocerans were best collected using the tube sampler, while rotifers were best collected using the Schindler–Patalas trap. Some species were best collected using the vertical tow net. It is important to decide which biota is to be collected before sampling begins. Aquatic biologists should be asked for specific guidance about the best way of sampling this biota. As indicated above, there is no universal method for collecting biota and if a range of biota is collected, several sampling procedures can be needed.

Table 4.4. Methods for sampling aquatic organisms

Organism sampled	Method	Reference*
Plankton	Grab sample/plankton (cone) nets, hose-pipe sampler, Patalas–Schindler plankton trap	APHA (1998), Hellawell (1986)
Bacteria	Grab sample	APHA (1998), Ward and Johnson (1996)
Periphyton	Artificial and natural substrates (Paddlepop sticks, modified brushes)	APHA (1998)
Protozoa	Grab samples	APHA (1998)
Algae	Grab samples/nets, hose-pipe samplers	APHA (1998), Falconer (1994), Hotzel and Croome (1998)
Fungi	Grab samples	APHA (1998)
Macrophytes	Various	APHA (1998)
Benthic macroinvertebrates and algae	Bottom grabs/samplers/diver-held cores/nets	APHA (1998), Growns et al. (1999)
Macroinvertebrates	Sweep nets, hand search, quadrats, long-handled pole with net (deep waters)	APHA (1998)
	For shrimps, crayfish: gee-traps, net traps	
Bivalves	Cage, basket sampler, by hand	APHA (1998)
Fish	Nets, traps, electro-fishing	APHA (1998), Harris and Gehrke (1997)

*for APHA (1998) use this or the most current edition of this text

4.5. Sample Preservation and Storage

In most cases, samples are collected for later chemical or biological analysis. In all cases, clear and distinctive sample labelling is important. After collection, it is important to maintain the integrity of each sample and to ensure that it does not become contaminated or change between collection and analysis. It is usually necessary to preserve the samples to retard biological, chemical and physical changes. Protocols must specify both the appropriate sample container and the preservation technique. Preservation choices will vary depending on the parameter to be measured. Some possible changes, and suitable preservation strategies or storage procedures are given in Table 4.5.

Matters for consideration to ensure successful preservation and storage include selection and decontamination of sample containers, selection of a preservation technique and the time lapse acceptable between sample collection and analysis. Choices available will depend on the variable to be measured. Comprehensive information on the selection of containers and preservation of water samples for chemical and microbiological analysis can be obtained by consulting the Australian Standards (AS 1987a,b). Complete and unequivocal preservation of samples is a practical impossibility. At best, preservation techniques only retard the chemical and biological changes that inevitably take place after sample collection.

Normally, to prevent chemical and biological changes, water samples are cooled to 4°C, or frozen, or filtered, or given a chemical additive. Freezing (–10°C) reduces, but does not eliminate, biological activity in samples. All biological activity is only effectively eliminated at –40°C. Chemicals such as chloroform and mercury (II) acetate have also been used to prevent biological activity. Acid is often added to prevent adsorption of metals from water samples to containers and precipitation of insoluble salts.

Table 4.5. Preservation and storage strategies for physical, chemical and biological samples

Change	Preservation techniques
Physical	
Adsorption/absorption	Inorganic: reduce pH on storage
Volatilisation	No head space
Diffusion	Choose correct container type and cap liners
Chemical	
Photochemical action	Use dark containers
Precipitation	Lower pH, avoid use of chemicals which cause precipitation (e.g. sulfates)
Speciation	Refrigerate at 4°C. Add fixing agent
Biological	
Microbiological action	Reduce pH, filter, add bactericide, e.g. for sulfide add zinc acetate; if chlorine present add thiosulfate, leave small airspace to preserve viability, avoid light, refrigerate (4°C)
Cell degradation	Freeze, add fixing agent, e.g. formaldehyde, ethanol

Chemical preservatives should be avoided, if possible, because they may contaminate samples or interfere in chemical or biological analysis. For example, mercury can interfere in the colorimetric determination of phosphate. If preservatives are used they should also be taken into account in the analysis of blanks.

Even if a sample is frozen or a preservative is added, samples can be stored only for a finite time. In some cases this period may be years, e.g. phosphorus in seawater, but in other cases it may be much shorter, e.g. six hours for *Escherichia coli* samples. The preservation time needs to be determined before samples are collected, and protocols must be designed to ensure that samples are analysed before a significant change in composition occurs.

4.6. Quality Assurance and Quality Control in Sampling

A quality assurance and quality control (QA/QC) program for field sampling is intended to control sampling errors at levels acceptable to the data user. Thus it includes procedures designed to prevent, detect and correct problems in the sampling process and to characterise errors statistically, through quality control samples. Major errors to be avoided are faulty operation of the sampling device, changes in the sample before measurement (contamination, chemical or biological changes), and incorrect sample labelling.

Field staff should be competent in sampling and making field measurements even though they may also have qualities, such as vehicle handling or bush skills, unrelated to the assurance of sample integrity. Before sampling staff are permitted to do reportable work, they should demonstrate competence in field procedures. As a minimum this would include being able to adhere to protocols, being able to avoid contaminating samples, and being able to calibrate field instruments and make field observations.

All equipment and field instruments should be kept clean and in good working order, and calibrations and preventative maintenance should be recorded carefully. All repairs to equipment and instruments should be noted, as well as any incidents that could affect the reliability of the equipment. When automatic sampling devices are used, their timing mechanisms must be calibrated to ensure that the samples are acquired at the specified intervals. This is especially important where hydrological or other conditions result in significant short-term concentration variations.

4.6.1. Tracking Samples and Field Data

During sampling or field measurements, it is important to fill in a field data sheet or similar record that describes the samples taken, their labels and other details about them (e.g. see Appendix A6.1). All field data and instrument calibration data are recorded on this sheet. All field records must be completed before leaving a sampling station. Any observations or information on the conditions at the time of sampling that may assist in interpretation of the data should be noted on a field-record sheet or in a field notebook. This information may explain unusual data which otherwise might be attributed to problems in sampling or analysis.

Table 4.6. Chain of custody documentation

Process step	Quality Assurance Procedure
Field sampling	Field register of sample number, site, type/technique, time, date, technician, field data sheet
Sample storage and transport	Field register of transport container number and sample numbers, time, date
Laboratory receipt of samples	Laboratory register of transport container number and sample numbers, time, date
Laboratory storage of samples	Laboratory register of storage location, type, temperature, time, date
Sample preparation	Analysis register of sample (laboratory) number, pre-treatment, date, technician
Sample analysis	Analysis register of instrument, calibration, technician, standard method, date, result

If samples are to be the basis for legal proceedings at some time in the future, the following questions are likely to be asked:

- exactly where was the sample taken?
- was the person who took the sample competent to do so?
- how was the sample labelled to ensure no possibility of mix up or substitution?
- was there any possibility of contamination, e.g. of the container, of the sample during filling, or later?
- did the sample deteriorate after collection?

Chain of custody documentation (Table 4.6) ensures that these questions can be answered.

4.6.2. Documented Sampling Protocols

Sampling errors can be minimised by ensuring that correct procedures have been followed during the field sampling, transport and storage. Sampling protocols need to be written and adhered to: they must include detailed descriptions of the procedures for collecting, labelling, transporting and storing the samples and necessary ancillary field data. Protocols must be specific to each matrix and constituent, and specify the sample collection device, type of storage container and preservation procedures.

The protocol must also specify the types and numbers of quality control samples to be taken. Before this protocol can be written, the nature of errors, both systematic and random, and the level of accuracy desired must be assessed. Sources of error include reaction with sample or sample container, contamination (field, sampling device, containers), chemical and physical instability, and biological changes.

The exact locations of sampling sites and any sub-sites must be recorded in the sampling protocol. Field notes must accurately describe where samples were collected, to allow cross-checking with the

sampling locations specified in the sampling protocol. If transects are to be sampled the location range must be specified if this is within the precision of the positioning instrument. Taking note of the time when samples are taken (standard or daylight-saving time) is an obvious but frequently overlooked requirement of rigorous sample definition (Appendix 6).

Protocols should specify how sampling staff are to be trained to use sampling equipment. Problems that may occur in the field should be anticipated: sample containers may be lost; sample volumes may be low; should foreign objects be included? on the basis of what criteria is foreign matter rejected? what if sites cannot be sampled?

One of the major challenges of sampling is to prevent contamination. Protocols must include the following basic precautions for avoiding contamination:

- field measurements should be made on separate sub-samples of water;
- new or reused sample containers must be appropriately cleaned (use of containers supplied by the analytical laboratory is recommended);
- only the sample bottles recommended for each parameter should be used;
- container lids should be checked for liners that may cause contamination or adsorb particular analytes;
- containers that have already been used for other purposes should be discarded;
- the insides of containers and lids should not come in contact with hands or objects;
- sample containers and filter units should be kept in a clean environment away from dust, dirt, fumes, etc.;
- preservatives should be tested for contamination;
- care should be taken to avoid cross-contaminating samples when adding preservatives;
- sample containers used for collecting samples for microbiological analyses must be sterilised;
- sampling staff should use plastic disposable gloves when handling sample containers at every stage during sampling (to avoid touching the sample, and the insides of caps or containers).

4.6.3. Sample Blanks and other QA/QC Practices

4.6.3.1. Blanks to Check on Field Procedures, Containers, Equipment and Transport

If it is possible that there could be contamination during the sampling process, blank samples should be devised to detect and measure the contaminant.

For field blanks, extra containers with suitable contents are taken to the site. There, the containers are opened and closed and the contents are handled just as if these were real samples during transfer and storage. For freshwaters, sample bottles filled with deionised water are used as field blanks. For marine work, water of the appropriate salinity is used. One blank per 10 samples is prepared, adding any preservative in the field. Field blanks mainly detect contamination from dust and other atmospheric fallout.

Filter blanks allow estimation of contamination by filtration in the field. They are prepared in the field by passing a sample of distilled water through a pre-cleaned filter and adding preservative to the water sample.

Container blanks determine the contamination from the container. Containers of each type to be used for sampling (about 1 in 10) are selected at random and filled with deionised water and preserved in the same manner as field samples. Analysis of these blanks detects contamination by the container washing process. This is sometimes measured as a rinse blank, and for this the last of several distilled water rinses of sampling equipment in the field is analysed.

Equipment blanks measure contamination introduced through contact with sampling equipment or sampler. They consist of the water or solvent that is used to rinse the sampling equipment between samples.

Trip blanks can be used to assess gross cross-contamination of samples during transport and storage. The simulated samples are similar to the samples to be collected, but in them the substance to be analysed (analyte) is at background or low concentrations.

Often it is not possible to achieve no contamination, but stable contamination levels are aimed for instead. When levels of contamination are outside the agreed acceptable limits, the contamination is likely to be coming from new sources.

Checks for QA/QC are partly reactive. If changes in samples are detected by using standard additions or blanks, a specified procedure is devised to determine and rectify the problem. The water is re-sampled if possible.

4.6.3.2. Duplicate Samples

Besides blanks, other sample QA measures include the use of multiple samples. Duplicate samples reveal the magnitudes of errors (contamination, random and systematic) occurring between sampling and sample analysis. They are obtained by dividing a sample into two or more sub-samples. On the other hand, replicate samples are two or more samples collected simultaneously to establish the reproducibility of sampling. Ideally three samples are required to enable testing of inter- and intra-laboratory accuracy and precision.

4.6.3.3. Sample Spiking

Another alternative is to 'spike' sub-samples in the field to detect change: a known amount of the analyte of interest is added to the sub-sample and subsequently measured. Samples for QA/QC should be labelled in such a way that they are not distinguishable from other samples in the batch.

4.6.4. QA/QC in Biological Sampling

The main question to be addressed for biological sampling is whether it is quantitative and representative. Alternative sampling strategies need to be devised and tested to establish the suitability of any preferred sampling technique.

4.6.5. QA/QC in Data Storage and Access

Transfer of results from the field to a database should be automated where possible, and the printout of the entry should be checked against the field record sheet and the laboratory register. Entries can be validated by electronic screening against the expected range and against other analytes for the same site and sampling date, and against field measurements. There should be agreed procedures for handling and tracking updates and corrections to data. There should be provision for handling censored data (see section 6.2.1 in Chapter 6). There should be fields for all necessary identifiers, for traceability purposes, e.g. sample and laboratory numbers.

Quality assurance also relates to data security and backup. With respect to security, those personnel who have read- or write-access to the data must be specified. Data backup is always essential in case of system or file failures.

4.7. Occupational Health and Safety

4.7.1. Identification of Hazards

Hazards or risks involved with field sampling need to be identified and documented on a preliminary site visit. The major questions to be resolved are these:

- can staff reach the site in safety?

- can a sample be safely taken? Is the water fast flowing? Is a boat to be used? Is there safe boat access? Is the site prone to flash floods? Is the bank stable? Are tidal changes likely?
- will sampling staff be exposed to toxic or other hazardous substances?
- will sampling staff be exposed to any pathogens, e.g. Ross River virus, malaria, etc.?
- will any potentially dangerous fauna be encountered, e.g. spiders, ticks, snakes, leeches, crocodiles, sharks, pigs, etc.?
- are weather conditions likely to endanger personal safety? In alpine areas especially, weather patterns are extremely variable.

Personnel who are to conduct sampling should be physically and mentally able to carry out field work. For example, if sampling staff fall into a water body, they must be physically fit enough to get out without assistance (although staff should never work alone in the field). Sampling staff working near water must be able to swim. They must also be able to climb up river banks. In proper professional practice, risks must be reduced as much as possible, and staff must not be required to operate in conditions that are unsafe.

4.7.2. Education About Hazards

All staff must be appropriately trained as part of the formal risk minimisation strategy. Training will include:

- familiarisation with environmental hazards that may be encountered;
- familiarisation with sampling protocols (sampling procedures, chain of custody considerations, etc.);
- use of sampling equipment;
- qualifications to drive appropriate vehicles, e.g. off-road 4-wheel-drive vehicles, bikes, tractors or boats;
- familiarisation with safety procedures;
- qualifications in advanced first aid.

4.7.3. Risk Minimisation Plans

The following directives should reduce risks during sampling operations.

- Limit continuous driving. If sampling sites are at a considerable distance, do not drive there without a stop. Take breaks of at least 15 minutes every 3 hours, and sample for no more than 10 hours in one 24 hour period.
- Choose safe sites with safe access. Visit potential sites and check them after they have been tentatively selected from map surveys. They should have reasonable access, be free of dangerous animals or prickly or poisonous plants, have no steep, slippery or unstable banks, and not be prone to rapid flooding or tidewater rise without warning.
- Wear appropriate clothing. Obtain weather forecasts for an area to be sampled. Be prepared, for example, to wear raincoats if there is likelihood of rain, warm clothing if it is cold, hat and sunscreen at all times, and footwear with a good grip for wet rocks (do not go barefoot, risking injury from sticks or broken glass). Note that sunscreen can be a source of contamination and should be used with due care for this reason. Take extra clothes and a towel in case of someone falling in the water.
- Take appropriate safety gear and a first aid kit. Wear lifejackets when sampling near deep water with poor footing or from a boat. Plastic gloves are essential to anyone who has an open or bandaged wound when handling chemicals or contaminated water or even if the water quality at the site is unknown. Take a fully stocked first aid kit to the monitoring site; ideally, someone in the monitoring party should have first aid training.

- Maintain contact with help and never sample alone. Work with at least two others and stay in contact with someone who can raise the alarm; carry a mobile telephone if available or at least keep coins or phonecard to be able to make a telephone call. In remote areas, carry maps, compass, mirror and matches and inform a responsible person of intended movements. There must be written procedures describing how emergency services are to be accessed.
- Never go into deep water. Sampling in deep water requires the use of an appropriate boat with the necessary safety equipment (life jackets, flares, etc.); preferably, sample from a bridge or use a cableway if installed at the site.
- Avoid contact with contaminated water. Carry drinking water. Do not drink from the source being monitored. Always wear plastic gloves when water quality at the site is unknown and in particular when collecting samples in which the presence of algae, pathogenic organisms or toxins can be expected (blue–green algae can cause skin and eye irritations). Wash hands after monitoring and before eating; treat all bacterial cultures as pathogenic.

Professional practice also requires sampling staff to:

- obtain approval as required, such as permits to collect fauna and flora or take water samples;
- have access to sites; land-holders' permission may be required to enter private land;
- use appropriate etiquette. It is good practice to inform local authorities, park rangers, etc., even if formal permission is not required. Local people can give useful information that helps in the choice of safe sampling locations and warns of local hazards.

Individual sampling staff have a duty of care to other personnel. Considerations include these:

- if one person cannot carry out all aspects of field work then he or she must have colleagues to assist;
- there should be no discrimination;
- privacy of individuals should be respected.

There is a duty of care to avoid damaging the environment during sampling:

- do not litter;
- observe fire restriction requirements;
- do not wash in streams, lakes, estuaries, etc.;
- remove human wastes;
- do not feed native animals;
- minimise environmental damage by keeping to paths, tracks, etc.