Methodology for the Sampling of Groundwater

This Advisory Note has been prepared to assist operators in the development and refinement of procedures for the collection and treatment of ground water samples.

The information contained in this document has been developed from Australian/New Zealand Standards for Water Quality – Sampling parts 1, and 11 (numbers 5667.1:1998; and 5667.11:1998) and other referenced sources

The improvement in precision and accuracy of laboratory analytical procedures and equipment and the corresponding increase in the types and complexity of sample collection equipment and field analysis has resulted in an increased potential for inadvertent contamination of samples.

A consistent methodology employing best practice techniques and equipment, and appropriate quality assurance and quality control (QA/QC) ensures that the risk of contamination is minimised in the collection of samples informing the development of appropriate environmental management systems for Northern Territory (NT) mine sites.

The diverse conditions experienced by and remote locations of mining operations in the NT means that one standard system for the collection and treatment of samples is not possible. For this reason, this advisory note is not intended to prescribe a methodology but to provide general principles for mine operators, who are encouraged to expand on the information provided in this document in the implementation of site specific methods.

NORTHERN TERRITORY GOVERNMENT

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1.0 Purpose

In general terms, the purpose of a ground water monitoring program and the collection of samples within that program is to obtain representative portions of the aquifer and to obtain in situ measurements at a selected time and place. Those samples and the results of subsequent analyses are used in the:

- identification of contaminant sources
- regulation of activities to ensure compliance with Mining Management Plan, Waste Discharge Licence, and water extraction commitments
- assessment of ground water quality against defined guidelines and standards and background or pre-operational levels
- development of water management plans, water balances, and rehabilitation strategies
- demonstration of environmental due diligence.

1.1 Scope

This advisory note is intended to aid the operator in the development of ground water sampling methods, and provides information on the general principles involved in the collection of physical and chemical parameters of ground water samples. An overview of the different types of samples and field parameters is included in addition to the methodology employed in their collection, preservation, and transport.

1.2 Legal framework

The principal legislation dealing with surface and groundwater monitoring in relation to mining activities in the NT are the *Mining Management Act* (MMA). Depending on the specific circumstances of the mining operation and location, other legislation such as the *Water Act* may apply. It is the responsibility of the operator to ensure compliance with all applicable legislation for their operation.

Under Part 3, Division 1 (s16 (c-e)) of the MMA, the operator of a mining site:

> *"…must ensure that the environmental impact of mining activities is limited to what is necessary for the establishment, operation and closure of the site. For that purpose, the operator must:*
>
> *(c) establish, implement and maintain an appropriate environment protection management system for the site; and*
>
> *(d) provide adequate resources for the implementation and maintenance of the management system; and*
>
> *(e) ensure, by regular assessment, that the management system operates effectively."*

It is within this legal framework that Environmental Management Systems and monitoring programs are developed and implemented in mining operations.

1.3 Further guidance

The following documents were used in the development of this guidance note and should be consulted in the development of monitoring programs and activities tailored to site specific and operational conditions:

Australian/New Zealand Standards:

- 5667.1:1998 Part 1: Guidance on the design of sampling programs, sampling techniques and the preservation and handling of samples.
- 5667.11:1998 Part 11 Guidance on sampling of ground waters.

The Mine Site Water Management Handbook (Minerals Council of Australia 1997) was also used in the development of this advisory note. The Handbook is a comprehensive reference for the design and implementation of water quality monitoring programs, surface and ground water collection methodology, and review and interpretation of collected data.

2.0 Groundwater sampling methodology

Preparation for a sampling event must include knowledge of and compliance with site Occupational Health and Safety (OH&S) protocols for the intended activities, including familiarisation with relevant Material Safety Data Sheets (MSDS) and precautions necessary for handling chemicals.

The principle purposes for the implementation of a ground water sampling program within a mining operation may include the surveying of the quality of groundwater supplies, to detect and assess groundwater pollution, and to provide information for groundwater resource management programs. To collect a representative sample within an aquifer, the methodology employed needs to accurately withdraw samples whose composition reflects the spatial and temporal variation present in the aquifer. Where known variation in vertical or areal composition of the groundwater occurs, specific methodology should be employed that is capable of detecting such variation.

Standing water within a bore is exposed to atmospheric conditions and can undergo changes to its physical and chemical characteristics and is not representative of the water in the aquifer. For this reason, boreholes should be purged before sampling by pumping 'to waste' a volume of water equivalent to at least 4 to 6 times the internal volume of the borehole. Where purging of a borehole is required prior to sampling, it is not recommended to use an air lift pump as the introduction of dissolved oxygen to the ground water may alter the sample. There are two sampling methods that are commonly employed; 1) pumped and 2) depth sampling. Samples can be collected using a bailer but due to the volume of water that needs to be removed, this method is not commonly selected over other methods. Where these methods are thought to be inadequate or cannot be used, a variety of in-situ sampling methods may be employed. Refer to AS/NZS 5667.11:1998 for more information on these methods.

It is important that as many parameters as practicable are determined in the field, or as soon as possible after the sample has been collected. This is particularly important for physical parameters such as pH, electrical conductivity, or dissolved oxygen. To accurately determine these parameters a continuous measurement technique, such as a flow through cell system, which minimises contact between the sample and the atmosphere, should be employed. The use of such a flow through cell system will also assist in the determination of stable chemistry prior to sample collection.

2.1 Integrity of samples

To ensure the reliability and interpretability of the collected data, appropriate documentation should be incorporated into the monitoring program that records sample movement from collection to data reporting and ensures that analytical data is ascribed to the correct location. Appropriate chain of custody information for collected samples commences with the completion of a sampling report. Sampling reports should contain at least the following information:

- location (and name) of monitoring bore or piezometer, with coordinates and any other relevant information
- details of bore, eg depth, screened interval, casing condition
- standing water levels
- date of sampling
- volume of water purged from bore or duration and rate of pumping prior to sampling
- time of sampling
- name of sampler
- nature of pre-treatment
- preservation procedure
- water quality parameters collected in the field
- any information which may affect the results of analysis, eg generation of bubbles, smell, colour, sediment etc.

Once collected, samples should be stored, handled, and transported in such a manner as to prevent damage to containers or labels, minimise or eliminate degradation of the sample, and prevent contamination of the sample. Upon delivery to the analytical laboratory information relating to the time between sample receipt and analysis, storage and preservation methodology employed at the laboratory, and analytical technique used should be documented.

2.2 Pump sampling

Pump sampling is undertaken by lowering a pump into a borehole to extract a volume of water sufficient to determine representative groundwater chemistry. A variable pump rate can be employed to match extraction rates with borehole recharge rates and expedite the collection process. Once stable water chemistry (as inferred from stability in physical parameters measured) is reached, the sample can be collected and transferred to an appropriate container.

Notes:

- Samples collected in this manner may comprise a mixture of groundwater entering the borehole via the open or screened casing from different depths.
- For this reason, this methodology can be considered to produce a composite sample or one of approximately average composition, unless the aquifer quality is known to be vertically uniform.
- Samples should not be collected until the pump has been running for sufficient time to remove all of the standing water in the borehole.
- The quantity of water that should be pumped prior to sampling can be calculated using the average pumping rate and the dimensions of the borehole.
- Where physical parameters are being used no samples should be collected before there is no significant variation in the physical parameters. That is changes of less than ± 10% for pH, conductivity or dissolved oxygen or less than ± 0.2 ˚C.

2.3 Depth sampling

Depth sampling is undertaken by lowering a specific sampling device into the borehole and activating it once the required depth has been reached. Upon retrieval the sample is then transferred to the appropriate container.

Notes:

- This method is only suitable where the depths of water inflow to the borehole (and therefore the origin of the samples) are known.
- Depth samples should not be collected from within the solid casing of a borehole as the water cannot have originated at that depth. Even samples collected at the open or screened portion of a borehole may not be representative of chemistry at that depth due to natural or induced flows in the aquifer.

2.4 Equipment

Equipment to be used to collect samples must be appropriately cleaned and decontaminated. Field meters should be calibrated according to the manufacturer's instructions and a sufficient number of sample bottles prepared. The chemical elements of interest in subsequent laboratory analysis dictate the type of container to be used for sampling and for sample storage, eg plastic or borosilicate glass. An example of the equipment necessary for the collection of groundwater samples includes:

- field sheets, sample labels, and chain of custody forms
- pump or bailer appropriate for the dimensions (diameter and depth) of the borehole(s) to be sampled
- container for field measurements, ideally a flow-through cell system or other container that minimises contact between the atmosphere and the groundwater
- container for collecting sample
- powder-less nitrile gloves
- sample bottles
- filtration equipment
- field parameter meters and test kits (eg alkalinity/acidity test kit)
- esky or portable refrigerator
- if required, appropriate preservative – eg nitric acid
- Personal Protective Equipment, first aid and communication equipment.

2.5 Field sheet details

At each sample location, details relevant to the subsequent analysis and interpretation should be recorded on the field sheets. The details included on field sheets will vary according to the objectives of the sampling program but should include all the information necessary to assist in data interpretation and repeatability of sampling efforts. Information which could be considered for inclusion on field sheets includes:

- name and location of sampling point
- date and time of sample collection
- nature of aquifer and water bearing strata
- any relevant descriptive information, eg bore dimensions, condition of bore casing, standing water level, depth of pump, height of bore collar
- sample appearance at the time of collection, eg colour, clarity and odour
- purged volume or physical parameters over sufficient time to attain stable readings
- field parameters measured or results of any on site analysis, eg alkalinity
- sample treatment post collection, eg filtration, acidification, etc.

2.6 Field parameters

pH: The pH meter should be calibrated according to the manufacturers requirements, using a two or three point calibration with buffers of known concentration. The selection of the calibration standards to be used is dependent on the anticipated nature of the water to be sampled, with strongly acidic or basic waters requiring calibration with standards appropriate to the anticipated range. Calibration standards should be stored appropriately (eg do not exceed 'use by' dates, refrigeration) to ensure their accuracy.

Temperature: The temperature of the water to be sampled will generally be the mean temperature of the region that the monitoring bore is located. Temperature will move toward ambient upon sampling so should be recorded as soon as a stable reading is obtained after collection.

Conductivity: The electrical conductivity (EC) of the water is a measure of the concentration of chemical ions in the water. The total dissolved solids in the sample water can be calculated from this reading using the following formula:

$$TDS = (0.548 \times EC) + (2.2 \times 10^{-6} \times EC^2)$$

As with pH measurement, calibration of conductivity meters should be performed using standards of a known concentration that are appropriate to the anticipated range of conductivity of the water to be sampled. Calibration standards should be stored appropriately (eg do not exceed 'use by' dates, refrigeration) to ensure their accuracy.

Dissolved Oxygen: The amount of dissolved oxygen in a sample can vary with depth, temperature, and biological demand. Measurements of dissolved oxygen can be most accurately obtained by placing the probe within a closed flow cell, which excludes atmospheric contact with the water.

Reduction/Oxidation potential (Redox): Measures the reducing or oxidising potential of a water body. Field meters will return a value in Volts or millivolts with a negative value indicating a reducing environment and a positive value indicating an oxidising one.

Turbidity: A measure of the quantity of suspended material in a water body. Turbidity can be measured using field meters or estimated by the operator.

Alkalinity/Acidity: Tests the relative acidity or alkalinity of a water body. Alkalinity/Acidity can result from natural sources such as the dissolution of carbonates or the presence of mineral or humic acids. Field testing of Alkalinity or acidity can be performed using commercially available test strips or indicator solutions to provide approximate values. Laboratory analysis of appropriately preserved samples provides more accurate values.

2.7 Collection for subsequent analysis

Physical and chemical changes to groundwater can occur following removal from the aquifer through exposure to the atmosphere, changes in temperature, and changes in pressure. For these reasons it is ideal to minimise the handling of samples following collection and that following filtration and/or preservation, the samples are delivered to the laboratory in tightly sealed containers that have not been exposed to excessive heat or light. If using a flow-through cell system to determine field parameters, it is imperative that samples are diverted to filtration or dispensing outlets prior to entering the cell to avoid potential contamination from field meters.

2.8 Low-flow / flow-through cells.

There are a variety of flow-through cell designs available commercially. The principles behind the use of flow-through cells employ several common features:

- Small volume, transparent cell. Ensures that the sampler can visually inspect the water as it passes through the cell for physical characteristics such as turbidity or air bubbles. A small volume cell ensures adequate turnover of the water.
- Tubing and valves that: direct sample water into the bottom of the cell and away from the cell from the outlet at the top; bypass the cell and direct the sample toward filtration of dispensing outlets.
- Locations for probes that enable the probes to be removed and cleaned between sample locations and calibrated as per the manufacturer's instructions.

2.9 Field Filtration

Sample filtration in the field can extend the period of time in which accurate results can be obtained from analysis. For example:

- Concentrations of ammonia or nitrate can decrease over time in water samples. Filtration extends the period of time that a representative result can be returned from a sample following collection.
- For samples requiring analysis for the soluble metals content, filtration soon after collection can remove colloidal or particulate material which provides additional facies for adsorption.

There are two main methods employed in the filtration of water samples; 1) pressure systems employing syringe or gravitational pressure and 2) vacuum filtration systems.

Syringe filtration:

- Agitate sample bottle to ensure thorough mixing.
- Draw an aliquot of the sample into the syringe from the sample collection container taking care to maintain an air gap between the base of the plunger and the sample to minimise contact and potential contamination.
- Dispense aliquot to waste to rinse syringe. Repeat.
- Draw an aliquot of the sample into the syringe taking care to maintain an air gap between the base of the plunger and the sample to minimise contact and potential contamination.

- Affix appropriate filter unit to syringe (between 0.4 and 0.5 μm) and dispense to laboratory sample container.
- Add any preservative to be used (eg acid), reseal laboratory sample container and invert to mix thoroughly.

Note: A similar principle is employed in gravity filtration with the exception that the pressure employed to force the sample through the filter is provided by gravitational forces.

Vacuum filtration

When using vacuum filtration, the pressure difference across the filter material is supplied via the application of a vacuum between the collected sample and the laboratory sample container.

- Thoroughly clean filtration unit employing a method appropriate for the analyte of interest. For example, a filtration unit that is to be used for the collection of samples for metals analysis should be rinsed using a solution of 10% Hydrochloric acid followed by water of appropriate quality.
- Rinse the filter unit with the water to be sampled.
- Assemble filter unit taking care to not touch areas of the filter unit components that are in contact with the sample or introduce small tears to the filter membrane.
- Apply vacuum, collect sample and distribute to laboratory sample containers.
- Add any preservative agent to be used, re-seal sample container and invert to mix thoroughly.

2.10 Preservation, transport and storage

2.10.1 Preservation

Australian and New Zealand Standard 5667.1:1998 includes a comprehensive table of analytes of interest and the appropriate sample container, preservation technique, and holding time. The following table is a summation of the information contained in the table and the reader is directed to the standard or ISO 5667-3 for specific or more comprehensive information.

2.10.2 Transport

While sample preservation will limit degradation, it is recommended that dispatch to the laboratory for analysis occurs as soon as practicable.

2.10.3 Storage

Samples should be stored according to the preservation procedure summarised from AS/NZS 5667.1:1998 above. The appropriate method and period of storage is dependent on the analyte of interest and should be followed to ensure that representative results from analysis are obtained.

Table 2: A Summary of water sample storage and preservation procedures for common analytes of interest.

Determinant	Type of container	Preservation procedure
Acidity and alkalinity	Plastic or glass	Fill container completely to exclude air and refrigerate.
Ammonia	Plastic or glass	Refrigerate.
Metals	Acid washed plastic or glass	Acidify with nitric acid to pH 1 - 2 and refrigerate. Filtration of the sample must be performed prior to acidification.*
Major cations, eg Calcium	Plastic	Acidification is not required, though the addition of nitric acid sufficient to lower pH to 1 - 2 will enable determination of concentration with metals analysis.
Chloride	Plastic or Glass	None required.
Cyanide	Plastic or Glass	If no interfering compounds are present, then add sodium hydroxide to a pH greater than 12. **
Nitrate	Plastic or Glass	Filter on site and freeze.
Nitrite	Plastic or Glass	Freeze
Total Nitrogen	Plastic or Glass	Freeze
Phosphorus	Plastic or Glass	For dissolved concentration determination filter on site and freeze. For total concentration determination, freeze.
Sulfate	Plastic or Glass	Refrigerate
Hydrocarbons	Glass, solvent washed.	Do not pre-rinse sample container. Do not completely fill sample container. Acidify with sulfuric acid or hydrochloric acid to pH 1 to 2 and refrigerate.
Filter through 0.45 µm cellulose acetate membrane filter. Total metals analysis does not require filtration.		
*** The preservation technique employed will depend on the interfering compounds present. Operators are advised to liaise with the laboratory performing the analysis to determine appropriate sample treatment.*		

3.0 Quality Assurance / Quality Control procedures

Quality assurance (QA) and quality control (QC) procedures must form an integral part of monitoring activities to ensure the representativeness and integrity of water samples and that the resulting data used in review and reporting is accurate and reliable. Use of a laboratory certified by the National Association of Testing Authorities (NATA) provides assurance that suitable QA/QC procedures including equipment, reagents and analytical methods are employed in the analysis of collected samples. Some examples of field QA/QC measures that are useful in the assessment of monitoring accuracy and methodology effectiveness are as follows:

- **Selection of appropriate sampling and preservation methodology:** Sample collection methodology should be easily reproducible and designed to minimise potential contamination of samples occurring. Appropriate preservation of the collected sample depending on the analyte of interest should be undertaken to ensure representative results.

- **Use of control sites:** These are generally located upstream of, or at a sufficient distance from, operations to provide data relating to the background conditions at the time of sampling. Monitoring bores to be used as control sites should be located within the same geological formation as comparison sites.

- **Duplication of samples:** Separate samples collected from the same site at the same time are used to determine the extent of impact (if any) of heterogeneity of the water being sampled and can be used to give a measure of the sampling precision.

- **Collection of field and sample blanks:** Water of a known low analyte concentration is used as a 'blank' sample to detect whether sample contamination is occurring during the sampling process. Field blanks are samples of water of a known low analyte concentration that are exposed to field conditions during the sampling activity.

4.0 Data interpretation, system analysis and reporting

The obligation of an operator of a mining site in the NT is stipulated in the MMA Part 3, Division 1 s 16 (1) as ensuring that the environmental impact of mining activities is limited to what is necessary for the establishment, operation and closure of the site. Further, the operator must establish, implement and maintain an appropriate environment protection management system and ensure by regular assessment of that system that it operates effectively. This can be adequately demonstrated by the regular submission of a report detailing the analysis and interpretation of monitoring data, and comparison with background or pre operation data. These obligations are in addition to any stipulated by the Controller of Water Resources the *Water Act* following the issue of a Waste Discharge Licence (WDL).

4.1 Data interpretation

Water quality data should be analysed and interpreted on a regular basis to identify potential impacts and/or assess the status of existing known impacts. For example, when water quality data are obtained from either the field or laboratory, these should be compared with previous data and/or trigger values (eg ANZECC or site-specific) to assess trends. Trigger values should be linked to management actions to mitigate potential downstream impacts.

4.2 System performance analysis

An integral part of a sound environmental management system is the review of that systems performance. The collection of monitoring data provides valuable information for that review and helps provide direction for improvement initiatives.

4.2.1 Field and sample blanks

The collection of field and sample blanks (refer to Quality Assurance/Quality Control section) enables the identification of any deficiencies in the methodology employed in sample collection or any further training required by the environmental officers collecting the sample. Sample blanks that return greater than anticipated values for analytes may indicate exposure to atmospheric contaminants or introduction of contaminants to the sample by the operator during collection and treatment of the sample.

4.2.2 Duplicate samples

Duplicate samples should return results within a determined acceptable relative percentage difference. This acceptable difference between results can be determined using the detection limits of the analytical procedure employed by the testing laboratory. For example, duplicate samples that return a large relative percentage difference (≥20%) for high concentrations of analytes when compared with the detection limits are potentially indicative of a problem with sampling methodology and warrant further investigation and/or training. The converse is true when samples return a large relative percentage difference for low concentrations of analytes that are close to the detection limits of the analytical procedures employed. In these situations the large relative percentage difference is less indicative of potential methodological problems but does warrant further scrutiny with future sampling efforts. To calculate relative percentage difference:

$$\text{RPD} = \left[(C_1 - C_2) \div \frac{(C_1 + C_2)}{2} \right] \times 100$$

where C1 = Concentration of analyte in sample 1 and C2 = Concentration of analyte in sample 2.

4.2.3 Control sites

Control sites are sampling locations that are located upstream of or at sufficient distance from mining operations so as to provide indicative background concentration information. These are important to determine typical aquifer or surface water chemistry for the region and aid in the determination and quantification of mine related impacts. Comparisons with pre-operational water chemistry can be made to ascertain if any cumulative impacts are occurring and can be useful in determining the relevance of the control sites selected.

4.2.4 Reporting

Reporting to regulatory authorities and stakeholders at the appropriate level of detail is important to demonstrate the effective implementation of an environmental management system on site. In addition, reporting of the analysis and interpretation of surface and ground water chemistry will demonstrate compliance with agreed standards and criteria such as the Australian and New Zealand Environment and Conservation Council guidelines for the protection of fresh and marine aquatic ecosystems.

Examples of information that should be included in water quality reporting include:

- water quality data and interpretation of this data (ie comparison to triggers)
- identification of any issues (eg degrading water quality in a specific site/area)
- potential causes of issues
- details of any incidents potentially affecting water quality
- details of actions taken to address any water quality issues
- commitments to specific areas for improvement in the next reporting period.

5.0 References and further reading

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