Methodology for the Sampling of Surface Water

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

The information in this paper has been has been developed from Australian/New Zealand Standards for Water Quality – Sampling parts 1, 6, and 11 (numbers 5667.1:1998; 5667.6:1998; 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 mine sites.

The diverse conditions experienced by and remote locations of mining operations in the Northern Territory (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 collecting surface water samples within a monitoring program is to obtain chemical and physical system attributes. 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, and Waste Discharge Licence commitments
- assessment of water quality against defined guidelines and standards such as the Australian and New Zealand Environment and Conservation Council (ANZECC) water quality guidelines for ecosystem protection
- development and refinement of water management plans, site water balances, and rehabilitation strategies
- demonstration of environmental due diligence.

1.1 Scope

This advisory note is intended to aid operators in the development of surface water sampling methods and provides information on the general principles involved in the collection of physical and chemical parameters of surface water samples from streams, rivers, lakes and billabongs. An overview of the different types of samples and field parameters that are commonly monitored is included in addition to the methodology employed in their measurement, 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*. 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 (16 (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.
- 5667.4:1998 Part 4: Guidance on sampling from lakes, natural and man-made.
- 5667.6:1998 Part 6: Guidance on sampling of rivers and streams.
- 5667.9:1998 Part 9: Guidance on sampling from marine waters.
- 5667.10:1998 Part 10 Guidance on sampling of waste waters
- 5667.11:1998 Part 11 Guidance on sampling of groundwaters.
- 5667.12:1998 Part 12 Guidance on sampling of bottom sediments.

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 Surface water sampling methodology

Sampling should only be undertaken by appropriately trained and experienced personnel. Preparation for a sampling event must include knowledge of and compliance with site Occupational Health and Safety (OH&S) protocols for the sampling activities, including familiarisation with relevant Material Safety Data Sheets (MSDS) and precautions necessary for handling chemicals.

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 sampling site, with coordinates and any other relevant information.
- Details of sampling point.
- Date of sampling.
- Method of sampling.
- Time of sampling.
- Name of sampler.
- General environment and climatic conditions.
- Nature of pre-treatment.
- Preservation procedure.
- Water quality parameters collected in the field.
- Any information which may affect the results of analysis.

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 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 sufficient sample bottles prepared. The chemical elements of interest in subsequent laboratory analysis dictate the type of container to be used for sampling, sample treatment, eg filtration and/or refrigeration, and for sample storage, eg plastic or borosilicate glass. An example of the equipment necessary for the collection of surface water samples follows:

- Field sheets, sample labels, and chain of custody forms
- Sample collection equipment:
    - If necessary, equipment for collection of samples from a safe distance – eg sample pole.
    - Container for field measurements
    - Container for collecting sample
    - Sample bottles for dispatch to laboratory
    - Filtration equipment
- Field parameter meters or test kits (eg alkalinity/acidity test kit)
- Powder-less nitrile gloves
- Esky or portable refrigerator
- If required, appropriate preservative – eg nitric acid
- Personal Protective Equipment, first aid and communication equipment.

2.3 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
- Any relevant descriptive information, eg water level/flow:
    - Sample appearance at the time of collection, eg colour, clarity and odour
    - Field parameters measured or results of any on site analysis, eg alkalinity
- Sample treatment post collection, eg filtration, acidification, etc.

2.4 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 expected 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 change throughout the day and influence parameters such as pH and Dissolved Oxygen. 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 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 directly into the water body to be sampled in an area with flow or moved, not too vigorously, to simulate flow.

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 approximated using equipment such as a Secchi disk.

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.

2.5 Collection for subsequent analysis

The choice of sample collection device is influenced by the nature of the sample site and the type of sample required. For example, a sample pole and container may be necessary where steep banks make accessing the water a safety risk. A clean pair of gloves should be worn at each sample site to minimise potential contamination problems. To collect a grab sample from shallow water body or a channel of flowing water:

- Select a point in the stream that is downstream of any channel braiding or inputs from tributaries to allow thorough mixing.
- Remove sample container lid (for locations with known very low concentrations of analytes this may need to be performed beneath the surface of the water to reduce contamination risk).
- Immerse sample container with the opening pointing directly down to maintain a volume of air in the container, thereby avoiding the collection of any surface films.
- Once under the surface of the water point the mouth of the sample container up stream so that gloved hands, sample container and/or sample collection device is downstream of the sample being collected.
- When sampling from a shallow water body, where possible select a point that is a reasonable distance from the edge. If the water is still (or flowing very slowly) move the sample container forward away from the sampler and any equipment to collect a continuous uncontaminated sample.
- Fill container, rinse and empty rinse water downstream or at a sufficient distance from sample site to prevent mixing of rinse water with the water to be sampled. Repeat.
- Fill container completely to exclude air and replace cap.

- Perform necessary filtration and/or preservation procedures, ensuring that sufficient sample is collected to perform the required analyses and any repeat analyses necessary.
- Complete sample labels and field data sheets.

To collect a grab sample at depth:

- Specific depth sampling equipment is required, either pump and tubing, or sample collection device.
- If the sample is to be pumped, ensure that sufficient volume has passed through the collection tubing to rinse the tube thoroughly.
- Sample collection for field measurements and for laboratory analysis can then be performed as above.

2.6 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, pressure systems employing syringe or gravitational pressure and 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, 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.
- Agitate sample bottle to thoroughly mix sample.
- Rinse the filter unit with the water to be sampled.

- Assemble filter unit taking care to not touch filter unit components that will be in contact with the sample or introduce small tears to the filter membrane.
- Apply vacuum, collect sample and distribute to laboratory sample containers.

2.7 Preservation, transport and storage

2.7.1 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 for specific or more comprehensive information (www.saiglobal.com).

2.7.2 Transport

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

2.7.3 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 1: 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. If possible, control sites should be located within the same catchment or in one with a similar geology/mineralogy to the potentially impacted 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 under 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.

4.3 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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