Groundwater monitoring and Management Plan

Zeehan Zinc Limited
Comstock Mine

FINAL REPORT

Prepared for

Zeehan Zinc Limited

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1 INTRODUCTION

1.1 Background

Resource & Environmental Management Pty Ltd (REM), in association with Sloane Geoscience Pty Ltd (SGeo), has been engaged by Zeehan Zinc Limited (ZZL) to develop a Groundwater Monitoring and Management Plan (the Plan) for the proposed Comstock Mine Site. The Plan has been prepared to assist ZZL in evaluating environmental performance of the proposed future mining operation and to meet potential regulatory approval requirements for commissioning of the Comstock open cut mine.

The Comstock Mine Site is located on the Trial Harbour road 4 km west of Zeehan Township, on the west coast of Tasmania (Figure 1). Three mining leases, ML 43M/85, ML 123M/47, and ML19M/95, over the area of interest were originally held by Oceania Tasmania Pty Limited. Zinc is the principal commodity of interest.

Groundwater at the Comstock Mine Site is known to be acidic and contain high concentrations of heavy metals as a result of historical activities. It is also believed that some groundwater is being discharged into the environment, mainly through an old mine adit, which provides a conduit for the discharge of acidic waters into Comstock Creek.

Acid drainage (AMD) from mining rock tailings has been identified as a widespread problem during a recent review of historic Tasmanian mining operations by Mineral Resources Tasmania (MRT). From the more than 4000 recorded mineral activity sites in Tasmania, the MRT survey identified 251 abandoned metal mining sites, containing sulphide minerals, as having potential for producing AMD. Geochemical analyses undertaken by MRT indicate anomalously high concentrations of trace metals (Al, As, Cd, Cu, Pb, and Zn) in both rock tailings and surface water/stream sediments proximal to abandoned mine sites, suggesting that there is a significant release of these metals into the receiving environment.

1.2 Objectives

The objectives of this Plan include:

- providing recommendations for the siting and installation of infrastructure to assist in monitoring potential changes in groundwater conditions that may occur in response to activities on site; and
- identifying potential management response measures in the event that monitoring indicates containment of potential contaminants (eg. heavy metals) associated with the mine operation and process is impaired for whatever reason.

1.3 Scope of work

This Plan outlines preliminary groundwater monitoring and management requirements for the site and should be modified as necessary during future commissioning of various stages of the mine project. ZZL has requested the Plan specifically address the following:

- Siting of an appropriate number of groundwater monitoring wells, and construction specifications, that will ensure collection of representative groundwater data (quality and levels);

- Development of a groundwater sampling and laboratory analysis plan that is appropriate for both the proposed and historical mining operations; and
- Identification of contingency measures for ongoing mine water management.

1.4 Responsible regulatory agency

The Department of Tourism Arts and the Environment (DTAE) is the principal agency responsible for assessing compliance of mining operations against environmental matters. Support to DTAE is provided by Mineral Resources Tasmania, (MRT) and Department of Primary Industries and Water (DPIW)

DPIW manage and monitor the condition of groundwater resources across Tasmania and are therefore likely to be consulted by DTAE on groundwater related issues. In addition, DPIW are responsible for issuing permits (which identify matters for environmental compliance) under the *Environmental Management and Pollution Control Act* (Tasmania) 1994 (EMPCA).

MRT provides a mineral exploration code of practice for exploration in Tasmania, which presents guidelines relating to cutting of access tracks through to management of drilling activities around exploration and mine sites and prevention of the release of oils or other fluids used during drilling into the environment. MRT are also the agency responsible for issuing of mining leases.

In Tasmania a mining lease is required under the *Mineral Resources Development Act* 1995. Tailings dam safety is handled under the *Water Management Act* 1999, which highlights in part 8 the regulations on dam construction maintenance and decommissioning. The Assessment Committee for Dam Construction (ACDC) manage this program and have to give their recommendations in any permit issued under the EMPCA. Mineral Resources Tasmania (MRT) impose rehabilitation bonds on tailings projects as they progress. Environmental management plans are required for mines under the EMPCA, whilst waste handling, rehabilitation and discharge are also covered under this Act. There are no specific regulations or tailings management guidelines for tailings storage facilities in Tasmania[1].

1.5 Report structure

At the time of preparation, limited information was available to develop a comprehensive plan; however, the groundwater management requirements for the mine site discussed in later sections of this report include the following:

- Site details (Section 2).
- Geology and Hydrogeology (Section3).
- Monitoring Infrastructure (Section 4) –

[1] http://tailings.info/guidelines.htm

  - Location and construction details of proposed groundwater monitoring wells based on a review of available hydrogeological information.

- Groundwater Sampling and Analytical Program (Section 5) –

  - Industry best practice field sampling and analytical protocols, and appropriate sampling frequency.

- Water Management Contingency Planning (Section 6) –

  - Discussion of relevant contingency plan requirements.

2 SITE DETAILS

2.1 Responsible entity

ZZL or their appointed representatives is the party responsible for implementation of the Plan. .

REM understands that ZZL are to retain ownership of groundwater management activities during the current operation and proposed expansion of the mine site.

The following information, presented as Table 2.1, is considered relevant in developing the Plan for this site. Those items not available at the time of preparation of this Plan should be considered by ZZL as it is reviewed.

2.2 Description

2.2.1 Topography

The site is located approximately 4 km west-south-west of the township of Zeehan, on the west coast of Tasmania, adjacent to Comstock Creek (Figure 1).

The surrounding topography is relatively steep with the area immediately surrounding the mine site drained by the generally south-west flowing Comstock Creek. Elevations in the north western corner of the lease reach heights of 385 m AHD; however over the majority of the lease the elevation is approximately 300 m AHD but drops steeply in the southwest corner of the lease to approximately 200 m AHD (Figure 1). McIvor Hill (360 mAHD) is a prominent high point located just west of the site (Figure 1).

A generally east-west trending topographic ridge separates the main open pit (north) from the tailings dam and polishing pond (south), as shown in Figure 2. ZZL are currently in the process of expanding the mine through the construction of an open pit and associated tailings dam and polishing pond (Figure 2).

2.2.2 Climate

Average annual rainfall is 2446 mm with a mean of 176 rain days per year[2]. Annual mean temperatures range from 6.3 ºC in winter to 15.2 ºC in summer (Bureau of Meteorology period of record 1890 to 1968). Pan evaporation data is only available from the Queenstown Bureau of Meteorology site which is some 20 km distant and considered not relevant for the topographically elevated region around the ZZL mine site.

[2] Bureau of Meteorology website http://www.bom.gov.au/

Table 2.1 Reference documentation relevant to the preparation of the Plan

Documentation	Relevance	Sighted
DTAE Industrial Regulation and Operations Section correspondence.	Correspondence from the regulator that may specify analytes and or frequency of testing.	No
Monitoring schedule of the Environmental Permit Conditions issued by DPIW.	Identification of pollution control and environmental compliance criteria as per the Environmental management and Pollution Control Act, 1994.	No
Development proposal and Environmental Management Plan (EMP), 2001 prepared by Scientists, Engineers, Managers & Facilitators (SEMF).	The EMP addresses water management issues on site and may have information relevant to managing impacts to groundwater.	No
Conceptual site water management plan developed by Dr Lois Koehnken.	This plan addresses surface water management issues which may be linked to potential management of groundwater.	No
Engineered Water Management Plan (Process Water Plan) developed by GHD.	This plan may have relevance to contingency water management issues.	No
Surface geology maps, driller's logs for the five recently installed wells (ZZ1 through ZZ5), Site plans and proposed site infrastructure.	Site geology, structural features and groundwater levels.	Yes
Geological update on the Comstock Prospect, Zeehan west Tasmania – Report.	Detailed information on geology and structural controls around site that may impact on groundwater flow direction.	Yes
Comstock Mine Water Management Plan (in preparation by SEMF).	Surface water management plan and proposed new infrastructure.	Discussed with SEMF plan outline

2.2.3 Existing infrastructure

Existing infrastructure around the mine site is presented as Figure 2. Infrastructure includes:

- the open pit in the northern portion of the site;
- a processing plant located centrally on the lease;
- tailings dam and polishing pond on the southern portion of the lease;
- underground workings (although not identified on Figure 2);
- five groundwater wells; and
- an adit which provides a direct pathway for surface water and groundwater to possibly enter Comstock Creek via the existing tailings dam and polishing pond.

2.2.4 Proposed infrastructure

In addition to the existing infrastructure, future developments at the Comstock mine site are presented as Figure 3, and includes commissioning of:

- an open cut mine on the northern part of the lease; and
- a tailings dam and contoured embankments to the southern part of the lease.

2.3 Geology and Hydrogeology

2.3.1 Site geology

The geology of the Comstock area comprises a complexly folded and faulted series of Pre-Cambrian fine grained clastics and carbonates (the Oonah Formation) overlain by a thin veneer of Quaternary clays. In general the clays are less than 5 metres thick although one drill hole (subsequently abandoned) to the west of the water storage dam intersected clay to a depth of 15 m (Figure 2). The geology and structural features are presented as Figure 4 and a schematic cross section running along a NNE-SSW axis is presented as Figure 5.

In the southern half of the lease area the Oonah Formation sediments are thrusted over Cambrian aged mafic rocks by the Tenth Legion Fault. In the northern half of the lease the Balstrup Fault has downthrown, to the north, sediments and volcanics of the overlying Crimson Creek Formation (Tear, 2005).

Tear (2005) describes the lithology with depth across the Comstock Mine Site as a succession of:

- massive sandstones and quartzites;
- interbeded to massive graphitic and carbonaceous siltstones and shales with occasional fine grained sandstone units;
- massive recrystallised dolomitic units with reefal units;
- a repeated sequence of interbedded to massive graphitic and carbonaceous siltstones and shales with occasional fine grained sandstone units;
- thick recrystallised dolomitic units with reefal units and ultramafics with associated skarns (metamorphosed dolomites); and
- interbedded siltstones and micaceous sandstones.

Additional information concerning the near surface geology has been obtained during the installation of five new groundwater wells. This information is presented in Table 2.2.

Table 2.2 Driller's Log for Monitoring Wells ZZ1 through ZZ5

Well ID	ZZ1	ZZ2	ZZ3	ZZ4	ZZ5
Clay (m bgl) [1]1	0-1.5	0-0.5	n/i [3]	0-5	0-2
Rock (m bgl)	1.5-10	0.5-10	0-10	5-10	2-10
Depth to water (m) [2]	5	4	6	7	5.5
PVC casing length (m, slotted casing length)	10 (6)	10 (6)	10 (6)	10 (6)	10 (6)

Notes:

[1](m) bgl - metres below ground level

[2] recorded immediately on completion of drilling and may not be a true equilibrated static water level (SWL)

[3] n/i - not intersected

2.3.2 Hydrogeology

Limited hydrogeological information was available for review; however, based on the geology of the site (section 2.3.1) it is inferred that groundwater will be predominantly contained within the fracture network of the associated bedrock.

Groundwater recharge is assumed to occur in the topographically elevated areas infiltrating to the bedrock as it migrates down slope. Seeps and springs may occur at the break of slope or at points along the Tenth Legion Fault; however, there is no reported occurrence of this over the site therefore groundwater discharge is assumed to occur to Comstock Creek as base flow.

Figure 6 presents the groundwater flow systems for Tasmania (source Tasmania Geological Survey Record 2003/02) and identifies that the dominant groundwater flow systems in the general Zeehan area are local flow systems in high relief folded and fractured Palaeozoic and Proterozoic rocks. Therefore, groundwater flow in the vicinity of the Comstock mine site is considered to be influenced by the local topography and faulting.

Drilling of the recent groundwater wells indicated that across the mine site the water table is typically intersected between 4 to 7 m bgl. During winter it is inferred that the water table may rise to within 1 m of ground surface.

The potentiometric surface in the fractured rock aquifer is generally assumed to be a subdued reflection of the surface topography. The inferred historical direction of groundwater flow would have been south-westerly from the topographically elevated areas towards Comstock Creek. However, the old underground workings potentially short circuit groundwater flow providing direct conduits for groundwater to flow from the site and discharge via the drainage adit into Comstock Creek (via the existing tailings dam and polishing pond). Information is not available to determine what influence the faulting may have on the movement of groundwater across the site and should be investigated further.

The thin sequence of clay recorded during the installation of the recent groundwater wells suggests that perched shallow water table aquifer systems are unlikely to develop beneath the site. However, in the area to the northwest of the mine pit, where drilling was abandoned because of a thick sequence of clay (pers. com. S. Bartel, Hydrogeologist, ZZL) perched aquifers could develop if lenses of sand are present within the clay. This may require further investigation as the mine pit is developed.

2.4 Potential groundwater receptors

A review of available information identified the following potential environmental receptors near to the Comstock mine that might be exposed to constituents of concern derived from the mine site:

- Comstock Creek – A deep mine adit in the vicinity of the main open cut is reported (pers. comm. John Sloan, SGEO) to provide a conduit for mine-site surface water discharge into Comstock Creek, and any associated aquatic ecosystems. The adit discharge point is believed to be located approximately 25m west of the main Comstock Creek line (Figure 3). However, it is unclear whether the polishing pond, located across Comstock Creek in the southern part of the mine site, would capture any upstream flow including that of the adit discharge.

- There are no reports available that identify any ecologically significant habitats or terrestrial groundwater dependent ecosystems within the surrounding area that may potentially be impacted by mining activities.

- A review of groundwater production well locations recorded on the MRT groundwater drillhole database (Figure 7) does not identify any third party groundwater users in the vicinity of the site. This is possibly due to the high rainfall along Tasmania's west coast which is likely to provide adequate surface water supplies thereby limiting the need for development of groundwater resources. Alternatively, the relatively low yields likely to be obtained from the fractured bedrock are not sufficient to support high water demand activities such as irrigated horticulture or pasture irrigation.

3 MONITORING INFRASTRUCTURE

3.1 Monitoring well location

The recently constructed groundwater wells are not suitable for inclusion in a site monitoring network because of poor completion. A total of 13 other monitoring wells, at 10 locations (three wells are nested pairs), are recommended for inclusion in a site wide environmental groundwater monitoring network as outlined below in Table 3.1 and presented as Figure 8.

Table 3.1 Proposed new monitoring well locations and rationale

Well ID	TSD [1] (m bgl) [2]	Monitoring Location Rationale
MW1a	5-10	Shallow groundwater base of polishing pond
MW1b	TBD [3]	Deeper groundwater to define potential vertical contaminant migration
MW2a	TBD	Shallow groundwater vicinity of mine adit outlet
MW2b	TBD	Deeper groundwater to define potential vertical contaminant migration at mine adit outlet
MW3a	>15	Shallow groundwater down topographic gradient of open cut
MW3b	TBD	Deeper groundwater down topographic gradient of open cut
MW4	5-10	Shallow groundwater down hydraulic gradient of tailings/polishing pond along Comstock Creek
MW5	5-10	Shallow groundwater down hydraulic gradient of tailings dam
MW6	5-10	Shallow groundwater further down hydraulic gradient of tailings dam
MW7	TBD	Shallow groundwater down hydraulic gradient of tailings dam/open cut
MW8	TBD	Shallow groundwater down hydraulic gradient of open cut in eastern depression area
MW9	TBD	Shallow groundwater in potential background location

Notes:
[1] TSD Target Screen Depth which will be based on field conditions
[2] (m) bgl metres below ground level
[3] TBD To Be Determined based on field conditions

The following information, provided by ZZL, has been referenced in siting of the new monitoring wells:

- Location of current and proposed infrastructure including the open cut, tailings dam and polishing pond (Figures 2, 3 and 4).
- Potential discharge location of deeper mine water via the drainage adit.
- Preliminary determination of potential shallow groundwater flow directions (Figure 7). In the absence of more detailed geological/hydrogeological information, particularly vertical geological profile, shallow groundwater flow is assumed to be topographically controlled.
- Understanding of interpreted geology and topography (Figures 4 and 5).

Three nested monitoring wells, i.e. two or more wells at the same location screened at different vertical depths, are recommended to delineate the vertical geological profile and determine the vertical hydraulic gradient within the groundwater system. The nested wells will also enable baseline groundwater quality to be obtained for the shallow and deeper systems.

As limited site-specific vertical geological profile information was available at the time this Plan was developed, the screen depths for the monitoring wells will need to be determined in the field during installation of the proposed monitoring wells.

For general guidance, the shallow ("a") well should be screened across the water table or where water is first encountered, which is likely to be in the weathered section found between the surficial clay and underlying bedrock. The deeper ("b") well should be screened at a depth considered representative of the deeper groundwater system, likely to be within the fractured bedrock unit. It is possible that deeper groundwater is hydraulically contiguous with the shallow water-bearing zone and that no confining layer, or deeper aquifer, exists. This will need to be carefully assessed during drilling by an experienced hydrogeologist.

3.2 Recommended monitoring well design

Groundwater wells used for the gauging of static water levels (SWLs) and samples for analytical determination of constituents of concern need to be properly constructed in accordance with relevant guidelines (LWBC, 2003).

As a guide, the minimum specifications for monitoring well construction are provided in Appendix A. Completion at surface can comprise of either casing raised above ground surface (stick-up) or finished level with ground surface (flush completion). The stick-up completion with a steel outer sleeve placed over the PVC casing (for protection) with a lockable flip top steel cap and cemented in place is the most typical method of completion.

Following installation, all wells should be surveyed to a reference datum (e.g. metres Australian Height Datum – mAHD) for both ground level (GL) and a reference point (usually a small notch cut into the PVC) on the top or protective steel cover, if fitted.

Well construction methods and specifications may vary depending on the hydrogeological conditions encountered and the following well completion is proposed based on the expected lithology at the site:

- Drilling depths for wells completed in the fractured rock are estimated to be between 10 to 15 m total depth; however, this will be dependent on the thickness of overlying clay and where groundwater is first intersected.
- The well will have deemed to have reached total depth between 3 and 6 m below the top of the first water cut in the fractured rock.
- A series of pre-collar and collar surface casings should be installed within the upper unconsolidated sequences using an auger bit.
- Drilling to the top of the fractured rock will be done using a 152 mm (6 inch) diameter hole and 152 mm DN Class 12 PVC installed and cemented to surface to stabilised the top hole and Quaternary sediments.

- 100 mm (4 inch) diameter hole will be drilled (using air hammer drilling method) in the fractured rock to the final depth and the hole will be completed with 50 mm DN Class 12 PVC to the desired depth.

- A 50 mm CN Class 12 PVC screen, will be positioned in the well from the depth at which water is cut to total depth. The screen will be Class 12 PVC with 1 mm aperture and 3-6 m in length.

- A 1.6 mm graded gravel pack will be placed to approximately 1 m above the screen and sealed with a bentonite plug.

- The remaining annulus will be cement grouted to surface.

- Approximately 300- 400 mm of casing will be left standing above ground surface, and an end cap place over the casing and a small hole drilled in the top of the end cap to enable air to escape and allow easy removal during future monitoring rounds.

- A 152 mm dia steel sleeve (stand pipe) with hinged lockable cover should be placed over the PVC casing and cemented into place.

4 GROUNDWATER SAMPLING AND ANALYTICAL PROGRAM

4.1 Sampling analysis and data quality objectives

The purpose of sampling is to collect representative groundwater samples for analytical determination of key chemical parameters by a National Association of Testing Authorities (NATA) accredited laboratory for the analyses required.

The primary Data Quality Objective (DQO) is to ensure that sampling and analyses are conducted within a rigid quality framework using established procedures and protocols to provide reliable results. An estimated quantification of the combined sampling and analytical errors associated with each result is a key outcome.

4.2 Groundwater constituents of concern

Based on the known site history outlined in previous sections and the type of ore to be mined, the main groundwater constituents of concern, in addition to salinity (TDS), major cations and anions, for the site relevant to this Plan include the following:

- Acidity (pH);
- Sulphate (SO_4^{2-});
- Turbidity;
- Nitrogen;
- Nitrogen oxide (NOX);
- Ammonium (NH_4);
- Metals including:
  - Aluminium (Al)
  - Arsenic (As);
  - Cadmium (Cd);
  - Chromium (Cr);
  - Cobalt (Co);
  - Copper (Cu);
  - Nickel (Ni);
  - Mercury (Hg);

- Lead (Pb); and
- Zinc (Zn).

Changes to the constituents of concern may be required based on regulatory agency concerns.

4.3 Groundwater quality criteria

DPIW Tasmania have adopted the ANZECC (*Australian and New Zealand Environment and Conservation Council*) 2000 water quality criteria guidelines, which have specific water quality trigger values listed, for Tasmania's freshwater ecosystems. The ANZECC trigger values for freshwater ecosystems at the 80% (species) level of protection are identified in Table 4.1 for the constituents most likely to be of concern to the regulating authorities at the Comstock Mine Site. The 80% level has been selected as it is considered that runoff from the mine site has been occurring for some period of time (prior to ZZL taking up the lease) and that any system down gradient is likely to have been highly modified because of historical site activities.

The data summarised in Table 4.1 should be used to compare the analytical results from the sampling of groundwater from the new monitoring wells to be installed. However, as the general bedrock hosts a number of minerals (e.g. zinc) groundwater levels are expected to be naturally elevated in some metals. It is therefore crucial that baseline groundwater quality data be collected for this site and the levels of the various metals should be used as the trigger values that prompt remedial management strategies. Agreement as to the trigger levels should be sought from the relevant statutory authority based on the initial background groundwater quality samples and compared against the water quality trigger values presented in Table 4.1. The trigger value to be adopted for this site should be the higher of either the representative background groundwater samples or the ANZECC 2000 guideline values.

Table 4.1 Water quality guidelines

Constituents of Concern	Aquatic Ecosystem Freshwater Criteria[1] (µg/L)
Salinity (µS/cm)	30 - 350
Total Nitrogen	450
NOx	190
Ammonium (NH^4)	415
Turbidity (NTU	2 - 25
Aluminium (pH >6.5)	150
Aluminium (pH <6.5)	-
Arsenic	360 [2]

Table 4.1 Water quality guidelines (continued)

Constituents of Concern	Aquatic Ecosystem Freshwater Criteria[1] (µg/L)
Cadmium	0.8 [2]
Chromium	40 [3]
Cobalt	-
Copper	2.5 [2]
Nickel	17 [2]
Mercury	5.4 [2]
Lead	9.4 [2]
Zinc	31 [2]

Notes:
[1] ANZECC (2000) Trigger values for freshwater ecosystems (80% level of protection).
[2] Figure may not protect key test species from chronic toxicity (this refers to experimental chronic figures or geometric mean for species)
[3] Figure may not protect key test species from acute toxicity (and chronic)

4.4 Groundwater monitoring

Ongoing monitoring shall be implemented to monitor the status of the constituents of concern in groundwater to ensure groundwater and potential receptors down hydraulic gradient of the site are not adversely impacted by elevated concentrations of these constituents as a direct result of site activities.

Groundwater monitoring and management measures are outlined in Table 4.2 below. These are listed in the order the task should be undertaken.

Table 4.2 Groundwater monitoring methodology

Activity	Details
Monitoring Objectives	The objectives are to monitor: • Groundwater quality on site and at the site boundaries to ensure no adverse impact to potential sensitive environmental receptors, including Comstock Creek, arises as a direct result of site activities.
Health and Safety	All field work conducted as part of implementation of this plan should be completed in accordance with a site-specific Health and Safety Plan. The purpose of the Health and Safety Plan is to establish personal protection standards and mandatory safe working practices to minimise health and safety risks to employees and the general public during field work.

Table 4.2 Groundwater monitoring methodology (continued)

Activity	Details
Well Surveying	Following installation all groundwater monitoring wells should be surveyed to metres Australian Height Datum (mAHD) and Easting and Northing co-ordinates logged. If future site development works necessitate a changing of monitoring well surface levels, a licensed surveyor is to be engaged to resurvey the ground surface and elevation of groundwater monitoring wells top of casing (TOC) to mAHD.
Static Water Level (SWL)	Monitoring wells will be gauged (**undertaken monthly**) for water level elevations using a calibrated water level probe, and reduced to mAHD. Water levels should be gauged from the surveyed point on the TOC. Details of the gauging dates and depths recorded are to be provided as part of reporting requirements.
Well Purging and Sampling	All groundwater monitoring wells will be purged using submersible pump and dedicated tubing prior to sampling. Low-flow (micropurge) sampling should be used to purge and sample the well (refer to appendix B for detailed procedure). Measurement of field water chemistry parameters (EC, pH, redox, Dissolved Oxygen (DO) and groundwater temperature) will be undertaken during purging and will continue until groundwater field quality parameters have stabilised. Field measurements should be recorded on appropriate forms, an example is provided in Appendix C.
Decontamination Procedure	Between each sampling event and between sampled wells, each reusable piece of monitoring equipment (e.g. water level probe, non-dedicated submersible pump) should be decontaminated according to the following procedure: • Wash with Decon 90 or similar decontaminant/water solution. • Triple rinse with clean potable water.
Sample Method and Preservation	Following stabilisation of field parameters, samples should be placed into laboratory supplied bottles containing appropriate preservatives for the selected analytes (generally all laboratory bottles for dissolved metals analysis will contain nitric acid as a preservative). Groundwater samples to be analysed for dissolved heavy metals will be filtered in the field using dedicated 0.45 micron filters for each sample prior to being placed into a pre-acidified container. Samples should be immediately chilled and stored at a temperature of 4ºC or less prior to transit to the laboratory. Appropriate Chain of Custody (COC) documentation must be correctly filled out to ensure QA/QC protocols are adhered to. An example COC form is provided in Appendix D.
Analytical Laboratories	Both a primary and secondary (QC) laboratory should be used. Both laboratories should be NATA accredited for the analyses undertaken.

Table 4.2 Groundwater monitoring methodology (continued)

Activity	Details
Analytical Program	Laboratory Analysis for the following: • pH • Salinity • Turbidity • Ammonia (NH^4), NOX • Sulphate (SO_4^{2-}) • Heavy Metals (Al, As, Cd, Cr, Co, Cu, Ni, Hg, Pb, and Zn)
Quality Assurance/ Quality Control	QA/QC samples should be collected and analysed in accordance with EPA Victoria Publication 441 (Appendix E). QA/ QC samples collected for quality control purposes during each round of groundwater sampling should include the following: • intra-laboratory field duplicates; • inter-laboratory field triplicates; 1 in 10 groundwater samples are required for intra and inter laboratory field duplicate analysis. Discussion of the laboratory and field quality assurance (QA)/quality control (QC) and analytical data validation should be included in all monitoring reports **undertaken biannually**.
Sample Nomenclature	Appropriate sampling nomenclature should be developed. As a minimum, the sample ID should be the same as the well ID. All duplicate samples should be presented to the lab 'blind' (i.e. the duplicate sample ID should contain no reference to the parent sample).
Groundwater Quality Objectives	Refer to Table 4.1

Table 4.2 Groundwater monitoring methodology (continued)

Activity	Details
Reporting	A report should be prepared following the completion of monitoring. The report should include the following: • Details of groundwater monitoring program methodology and scope of works. • Composite logs (including construction details and lithological logs) of any new or replaced groundwater monitoring wells. • Results of groundwater monitoring well levels and laboratory analysis, including NATA certified laboratory reports and chain of custody records. • Comment on laboratory and field QA/QC program and analytical data validation. • Interpretation of the data, including quality of groundwater with respect to beneficial uses and groundwater quality objectives and interpretation of groundwater elevation contours. • Conclusions and recommendations with respect to continuation or otherwise of the groundwater monitoring program.
Review	After a period where sufficient data points are collected, the monitoring frequency should be reviewed in consultation with the local regulatory oversight agency, this should not be sooner than 12 months from implementation of the Plan
Groundwater Management Objectives	Water quality guidelines consistent with protecting potential sensitive environmental receptors are presented in Table 4.1.

4.5 Abandonment of existing groundwater wells

Any decommissioning of existing groundwater monitoring wells should be undertaken in accordance with all regulatory requirements, industry relevant guidelines (LWBC, 2003) and upon obtaining a bore decommissioning license if required under local Acts for the management and protection of groundwater resources.

5 GROUNDWATER MANAGEMENT CONTINGENCY PLANNING

5.1 Groundwater monitoring

In environmental terms, the focus of the regulatory agencies will primarily be on the potential for nearby groundwater receptors (particularly sensitive environmental receptors, such as aquatic ecosystems associated with Comstock Creek) to be impacted by past, proposed and post-mining operations. As such, it is necessary for ZZL to demonstrate contingencies are in place in the event of off-site release of potential constituents of concern, in particular, heavy metals as listed in section 4.2.

The groundwater monitoring program is required to identify any significant increase in any constituents above initial background conditions. Sampling of the groundwater is proposed biannually with groundwater levels taken initially at least monthly in the first year. The frequency of sampling may reduce in subsequent years to quarterly for groundwater levels and once per year for potential constituents of concern. However, any change to the sampling frequency should be supported with sufficient evidence from the on-going sampling program and agreed to by the relevant statutory authority.

As a minimum, the analytes that should be tested for are identified in Section 4.2. However, it is possible that following discussions with the regulating authority other analytes may be identified.

Low flow sampling methods (Appendix B) are particularly suited to fractured rock aquifer systems where completion depths and standing water levels are less than 40 m below ground surface and can be employed to gain a representative sample from within the aquifer. The low flow sampling method requires less time to collect samples and large volumes do not need to be purged from the well, which potentially can create an issue concerning disposal, in order to collect a representative sample.

5.2 Trigger values

The trigger values for constituents of concern should be set at either the background groundwater quality or ANZECC 2000 freshwater ecosystem values for an 80% level of protection, whichever is the greater value of the two. If a sampling event results in a trigger value being exceeded a further round of sampling should be carried out to determine if sampling methodology or laboratory error was the cause.

In the event that the subsequent sampling event identified constituents of concern to still be greater than the adopted trigger values the contingency plan would be implemented (see section 5.3), on the basis of a specific risk assessment designed to consider specific issues.

5.3 Contingency plan

Managing acid drainage from waste rock storages

The waste rock piles are considered as possible sources of pyrite (section 1.1) and as such rainwater leaching through the waste rock storages will possibly be highly acidic. Construction of toe drains around the base of the storages with all water directed to the tailings dam will assist in managing possibly acidic water runoff. It is considered that this issue will be addressed in the surface water management plan being prepared by SEMF.

Drilling activities

Drilling activities and drill rigs have the potential to release hydraulic fluid (oils and fuel) on site. MRT guidelines identify strategies to contain the potential release of oils and hydraulic fluids. The simplest way is to ensure that hessian mats are placed beneath the drill rigs and that drilling contractors keep all fuels (44 gallon drums) on self contained spill pallets.

Leakage from tailings dam

A spill or leakage from the tailings dam may occur in one of three ways,

1. leakage through the base of the dam to underlying groundwater with eventual discharge to Comstock Creek;

2. failure of the tailings dam wall; or

3. overflow following severe rainfall events where runoff has filled the tailings dam beyond its installed capacity.

While there are no specific regulations or tailings management guidelines for tailings storage facilities in Tasmania, in the unlikely event that constituents of concern were inadvertently released from the tailings dam, the following contingency measures would be adopted:

- In the event that contamination is confirmed through subsequent sampling, ZZL would notify the relevant statutory authority.

- ZZL would engage an appropriately qualified groundwater consultant to carry out the necessary investigations (eg. groundwater sampling and laboratory analysis, risk assessment, groundwater flow and solute transport modelling) to determine the required clean up level for groundwater, assuming that the agreed trigger values are not exceeded at the lease boundary. If exceedence is predicted or identified, a groundwater recovery program should be implemented until contamination levels fall below the agreed trigger values.

- The groundwater recovery program will consist of installing a required number of recovery wells and pumping the recovered groundwater into the tailings dam for treatment.

- Pumping and treatment would continue until the sampling indicated that the constituents of concern were below the relevant trigger level.

5.4 Reporting

Reporting of sampling results would be carried out at least annually or in accordance with the operating licence conditions.

The data in the report shall consist of measured groundwater levels with time and a copy of all the relevant constituent testing, sampling methodology, chain of custody sheets and laboratory results.

6 REFERENCES

ANZECC 2000 *An Introduction to the Australian and New Zealand Guidelines for Fresh and Marine Water Quality V4.* Australian and New Zealand Environment and Conservation Council and Agriculture and Resource Management Council of Australia and New Zealand

Gurung, S. 2001. *Tasmanian Acid Drainage Reconnaissance. Report 1. Acid drainage from abandoned mines in Tasmania*. Tasmanian Geological Survey Record 2001/05.

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Vic EPA Publication 441. *A Guide to the Sampling and Analysis of Waters, Wastewaters, Soils and Wastes.* Victoria EPA March 2000, Publication 441.

Tear S. J., 2005 *Geological update on the Comstock Prospect, Zeehan, West Tasmania*. Report prepared for Zeehan Zinc Pty Ltd

7 STATEMENT OF LIMITATIONS

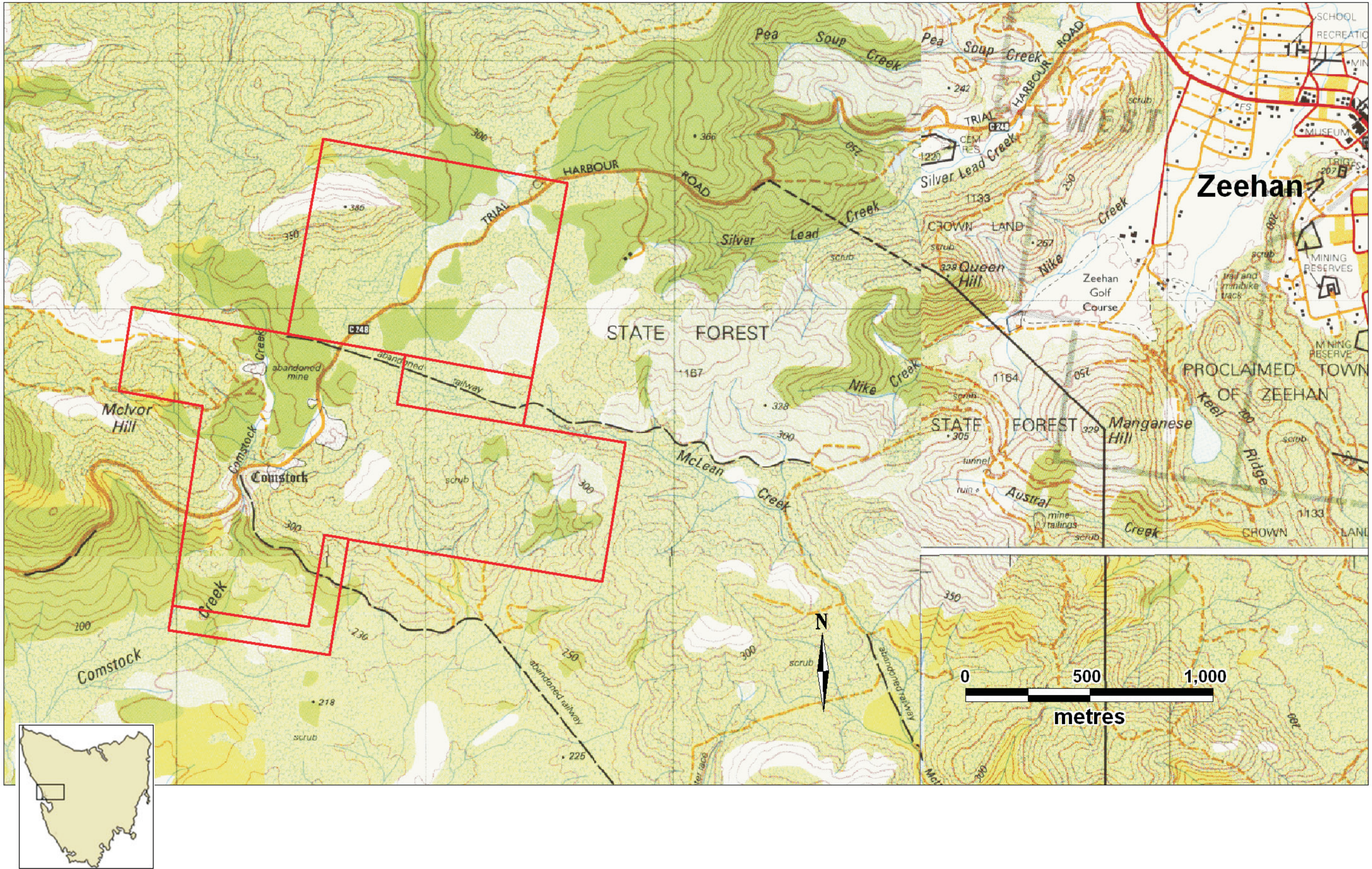
The services performed by REM have been conducted in a manner consistent with the level of quality and skills generally exercised by members of its profession and consulting practice

This report is solely for the use of Zeehan Zinc Limited and may not contain sufficient information for purposes of other parties or for other uses. Any reliance on this report by third parties shall be at such parties' sole risk.

The information in this report is considered to be accurate with respect to information provided and conditions encountered at the site at the time of investigation.

REM has used the methodology and sources of information outlined within this report and have made no independent verification of this information beyond the agreed scope of works. REM assumes no responsibility for any inaccuracies or omissions. No indications were found during our investigations that the information provided to REM was false.

Figures



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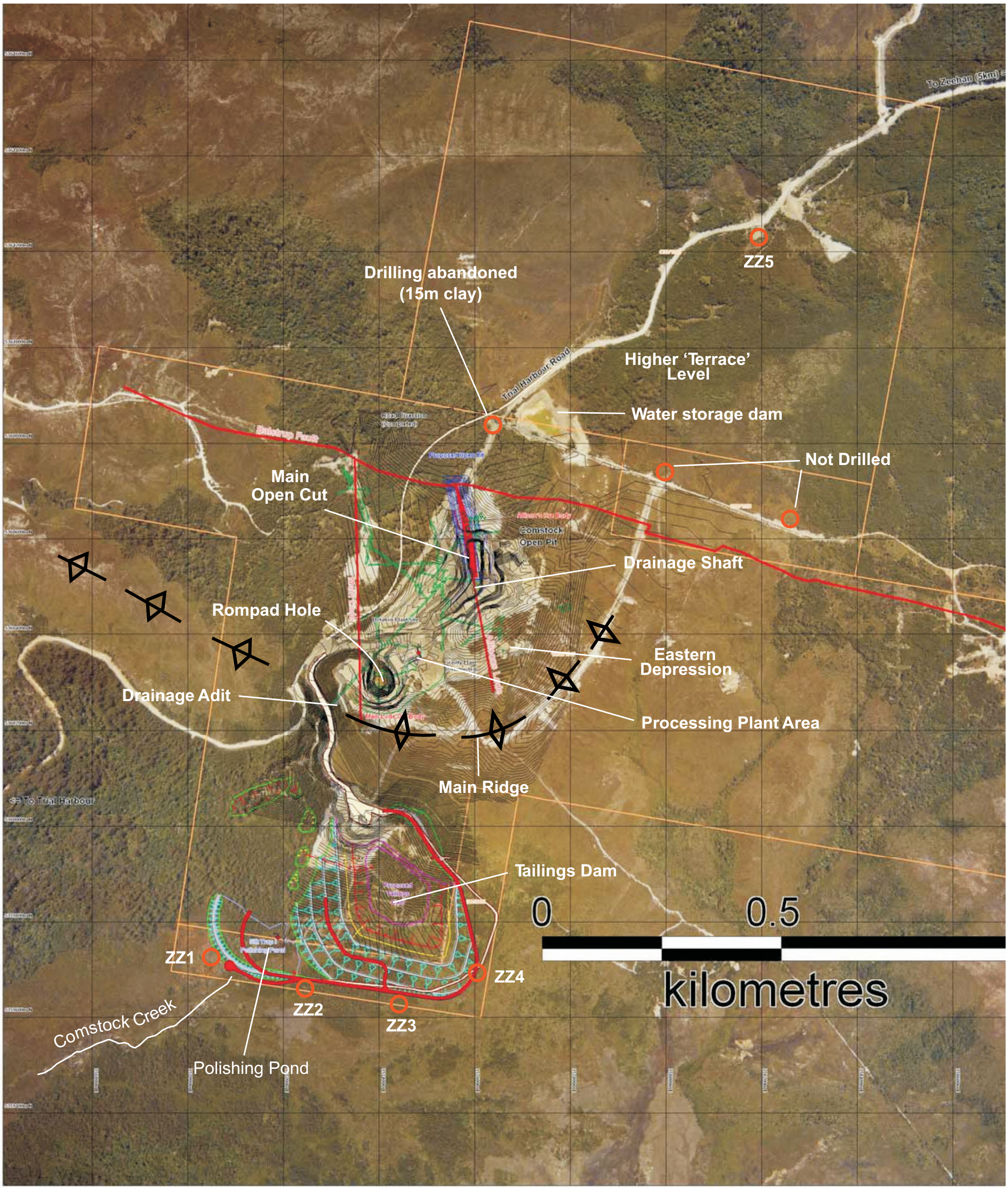
Comstock Base Site Layout – Standard Topographic Map
(courtesy of Zeehan Zinc)

FIGURE
1



	Ore Bodies (as of October 2006)		2006 Tailings Dam Road Design
	Gravity Plant		2007 Tailings Dam Road Design
	Geological Faults and Lodes		Existing Tailings Dam Road (as of April 2007)
	Old Comstock Mine Workings		Tailings Dam Staged Works
	Proposed Open Pit Extension		2 metre contour lines
	Lease Boundaries		
ZZ3	Groundwater Wells		

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Significant Site Features and
Recently Installed Groundwater Wells

FIGURE
2

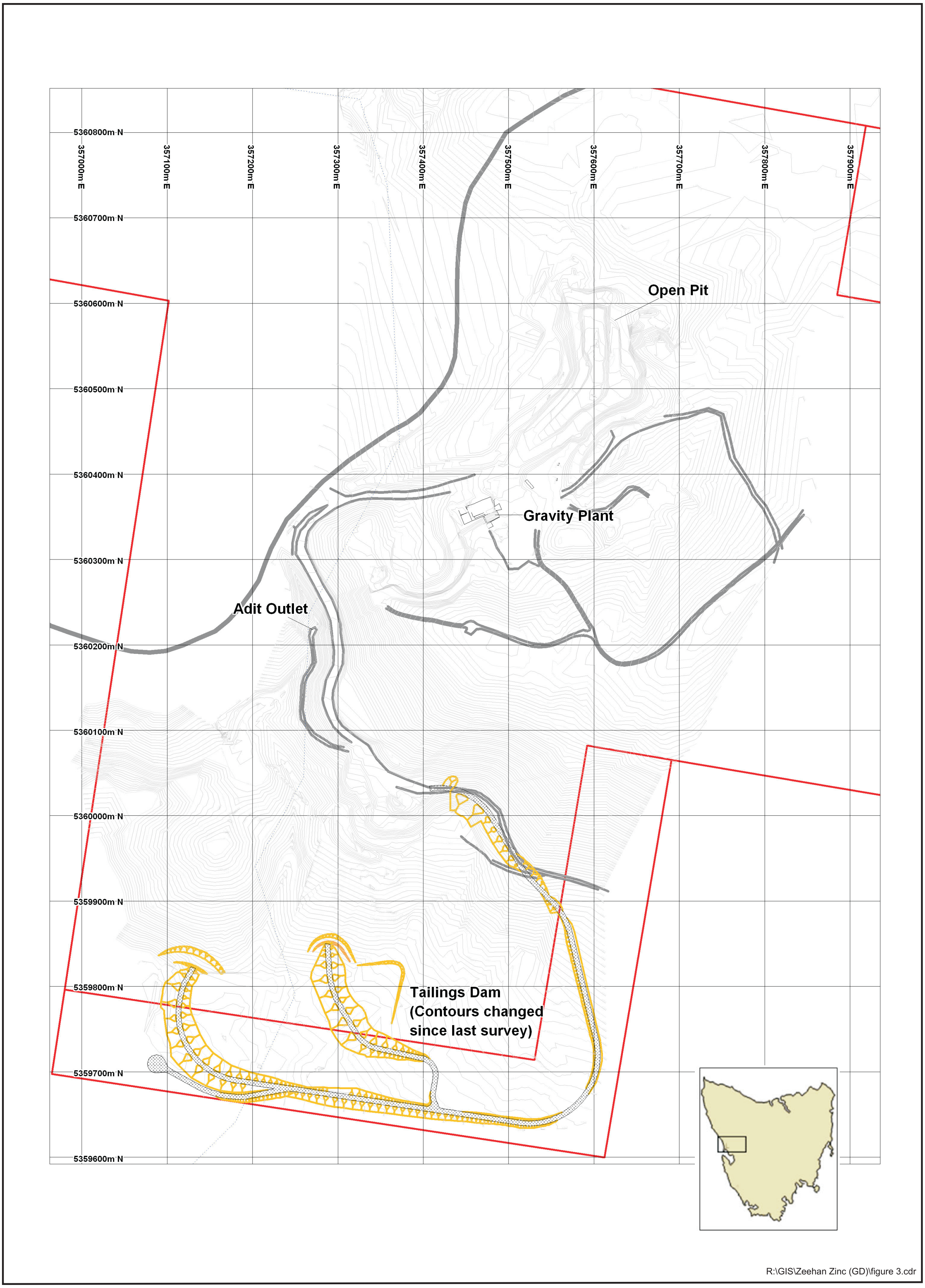

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FIGURE
3

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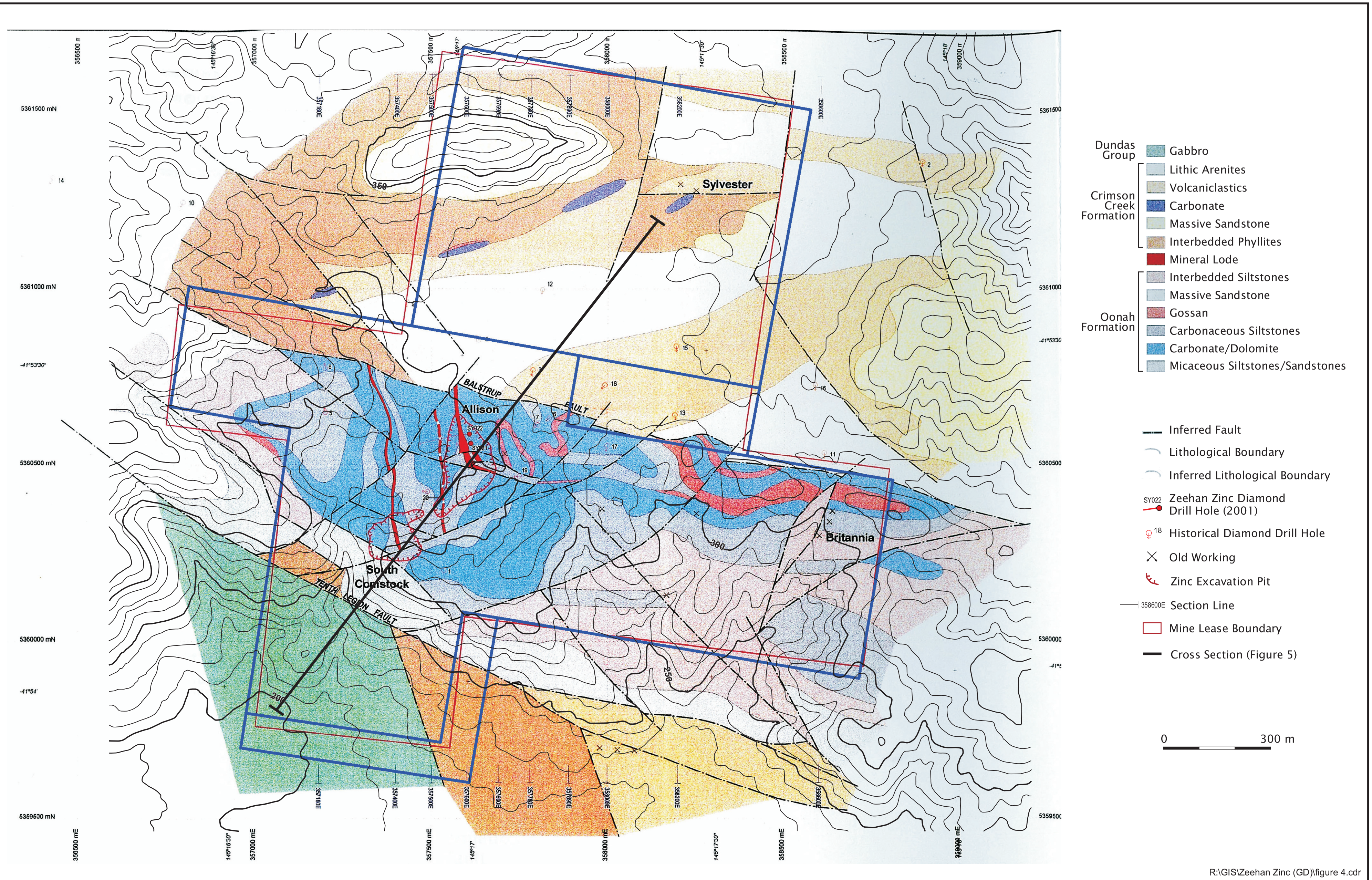
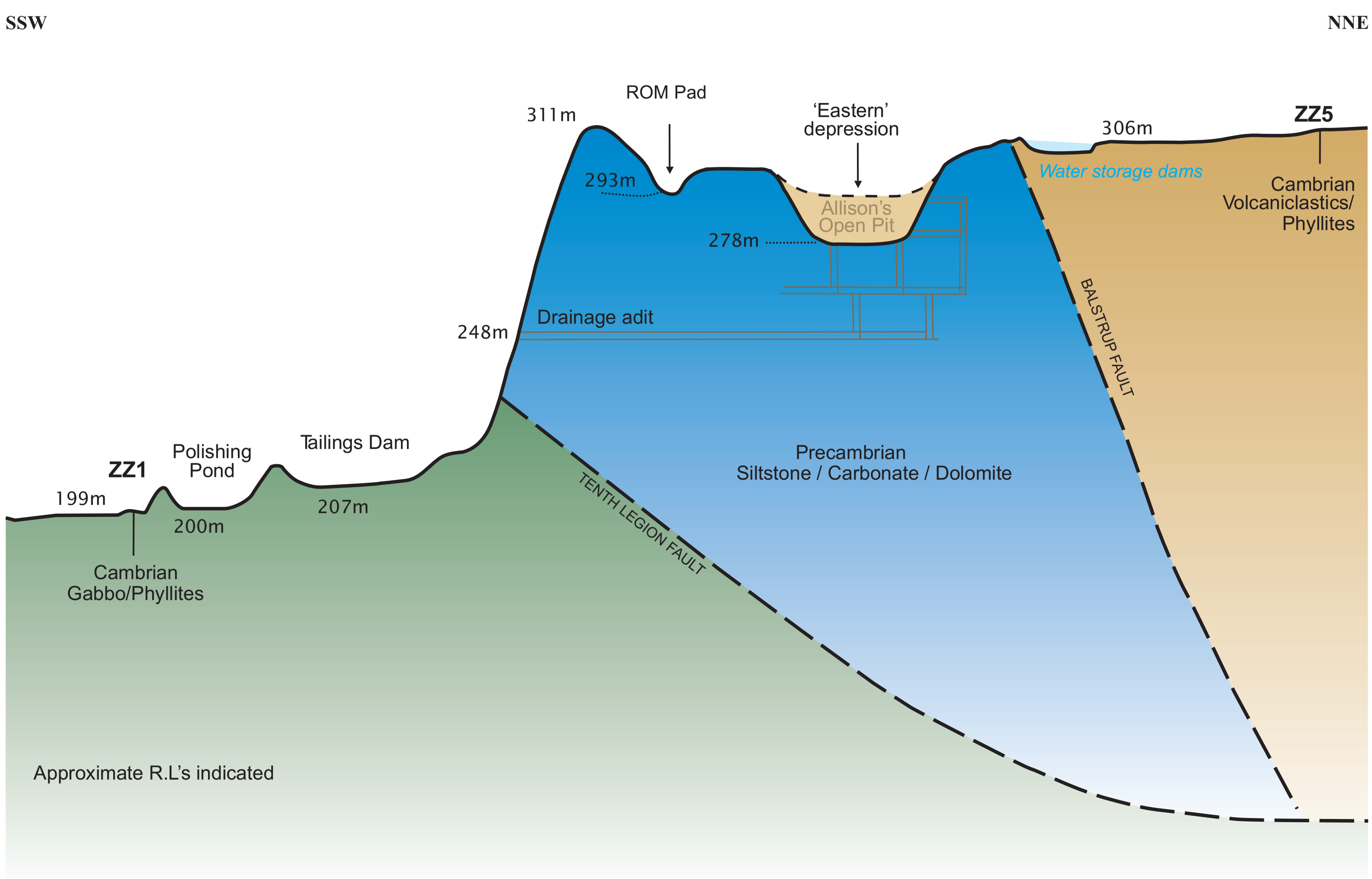
Comstock Detailed Contours (1 m from local surveys)
(courtesy of Zeehan Zinc)



Comstock Interpreted Geology with Surface Topography

FIGURE 4



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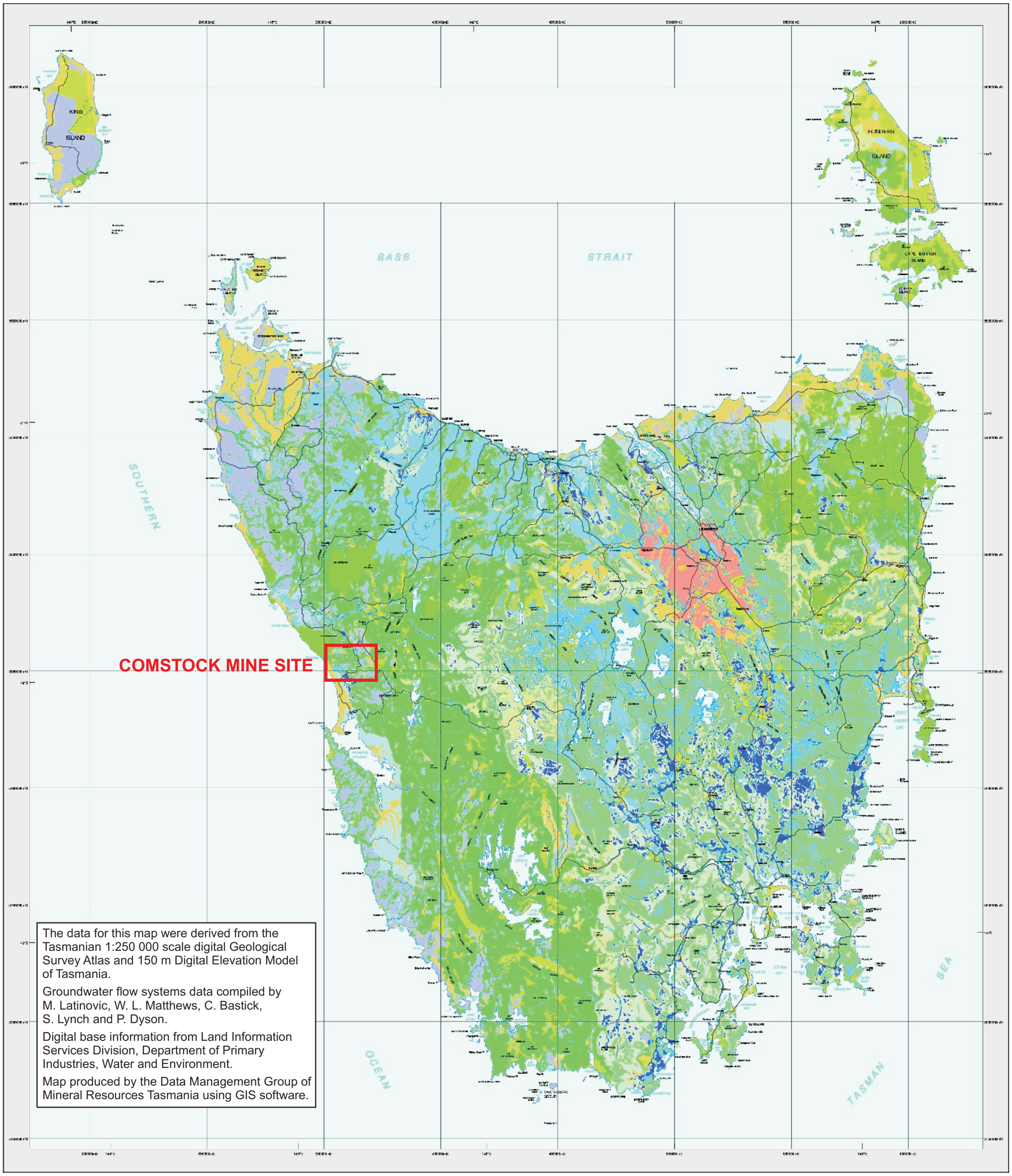
Schematic Cross Section

FIGURE 5



LOCAL FLOW SYSTEMS

- *Local flow systems in Quaternary sedimentary rocks (talus and till)*
- *Local to intermediate flow systems in Quaternary sedimentary rocks (aeolian, coastal plains and alluvium)*
- *Local to intermediate flow systems in undifferentiated Quaternary to Tertiary sedimentary rocks*
- *Local flow systems in high-relief Jurassic dolerite*
- *Local flow systems in high-relief Permian and Triassic sedimentary rocks*
- *Local flow systems in high-relief granitic rocks*
- *Local flow systems in high-relief folded, fractured Proterozoic and Palaeozoic rocks*

INTERMEDIATE FLOW SYSTEMS

- *Intermediate flow systems in Tertiary sedimentary rocks*
- *Intermediate to local flow systems in Tertiary basalt*
- *Intermediate to local flow systems in Jurassic dolerite*
- *Intermediate to local flow systems in low-relief Permian and Triassic sedimentary rocks*
- *Intermediate flow systems in low-relief folded, fractured Proterozoic and Palaeozoic rocks*

REGIONAL FLOW SYSTEMS

- *Regional flow systems in Tertiary sedimentary rocks*

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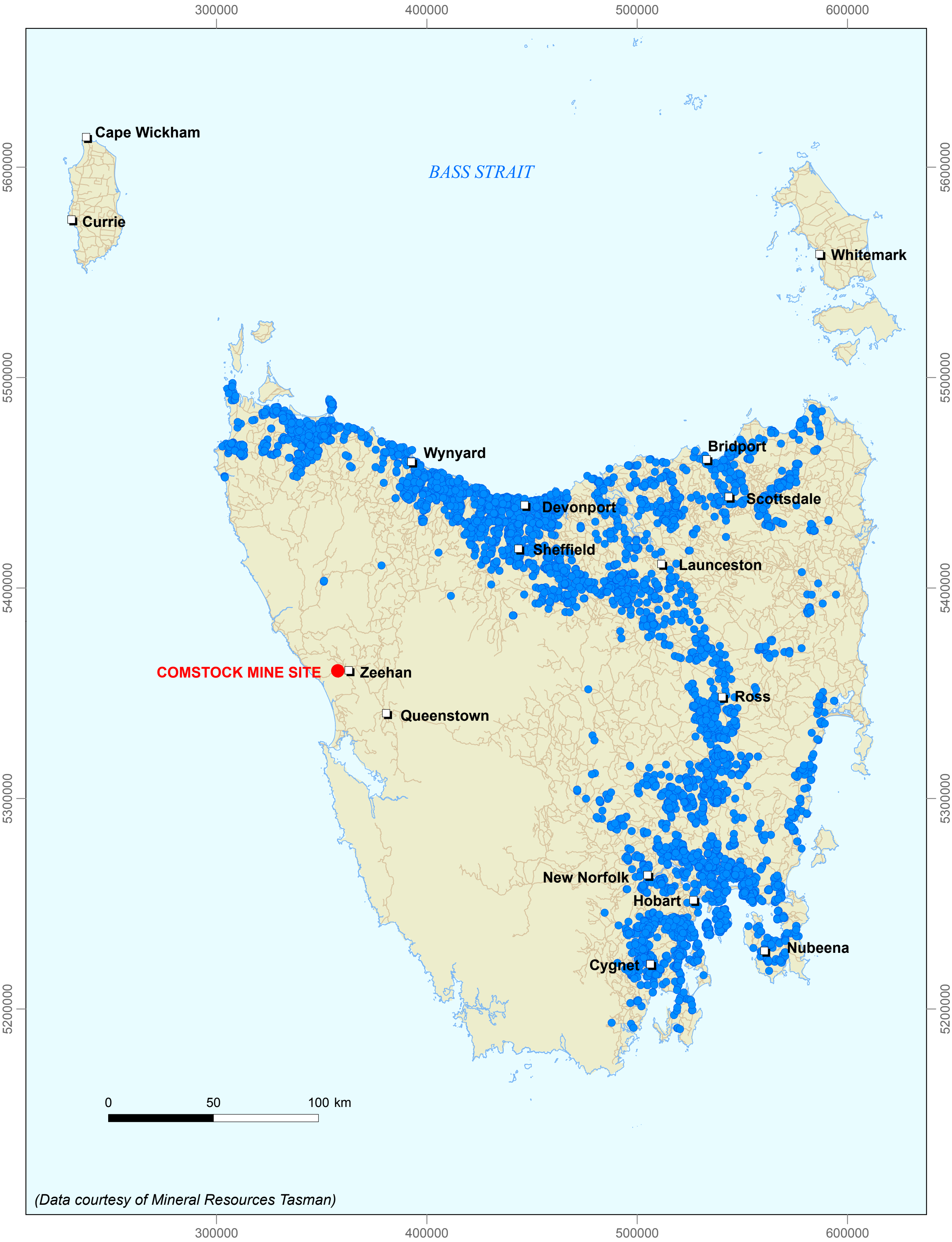
Tasmanian Groundwater Flow Systems for Dryland Salinity Planning
(courtesy of Tasmanian Geological Survey Record 2003/02)

FIGURE
6



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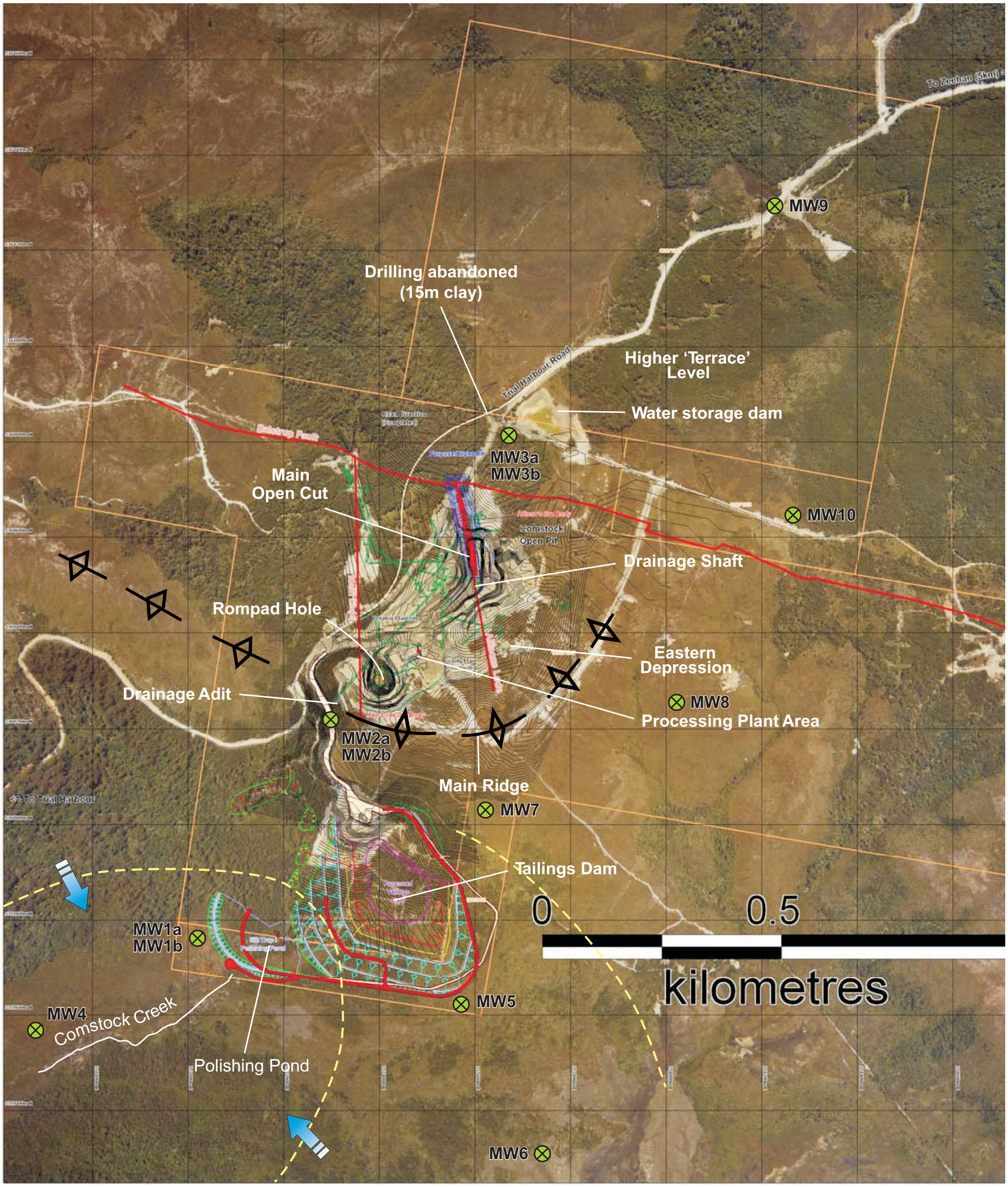
Groundwater Production Well Locations

FIGURE
7



Ore Bodies (as of October 2006)

Gravity Plant

Geological Faults and Lodes

Old Comstock Mine Workings

Proposed Open Pit Extension

Lease Boundaries

MW6 Monitoring Wells

Inferred Groundwater Flow Direction

Inferred Groundwater Contour

2006 Tailings Dam Road Design

2007 Tailings Dam Road Design

Existing Tailings Dam Road (as of April 2007)

Tailings Dam Staged Works

2 metre contour lines

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Proposed New Groundwater Monitoring Well Locations

FIGURE
8

Plates

Plate 1 Main access track eastern side of tailings dam looking SW towards Polishing Pond area.

Plate 2 View of Polishing Pond area from main track. Looking SW.

Plate 3 **Topographic ridge which separates Open Cut area on northern side from Tailings Dam/Polishing Pond area southern side. Looking NW.**

Plate 4 Monitoring bore ZZ2.

Plate 5 Monitoring Bore ZZ1. Inadequately sealed - collapse around bore collar.

Plate 6 Polishing Pond drainage outlet area. Monitoring bore ZZ1 RHS of picture.

Plate 7 Polishing Pond area. Looking SW.

Plate 8 Southern end of Tailings Dam area. Looking West. Note bedrock on far side.

Plate 9 Central Tailings Dam area. Looking West.

Plate 10 Northern Tailings Dam area. Looking NW.

Plate 11 Monitoring Bore ZZ3. Inadequately sealed - collapse around bore collar.

Plate 12 Monitoring Bore ZZ3. Surface drainage from track needs diverting.

Plate 13 Monitoring Bore ZZ4. Surface drainage from track needs diverting.

Plate 14 General view of Tailings Dam/Polishing Pond area. Looking South from main access track.

Plate 15 Monitoring Bore ZZ5 – north of Mine Site.

Plate 16 Higher 'terrace' level at northern end of mine site and E-W track. Surface water storage dams are located in this area. ZZ intended to install 3 monitoring bores along track. Installation aborted due to drilling problems as 15 m of clay was encountered. Looking NE.

Plate 17 Higher 'terrace' level at northern end of mine site and E-W track. Surface water storage dams are located in this area. ZZ intended to install 3 monitoring bores along track. Installation aborted due to drilling problems as 15 m of clay was encountered. . E-W track looking West.

Plate 18 Main Open Cut. Looking North. Drainage to main shaft just visible lower LHS.

Plate 19 Main Open Cut. Looking NW. Note old adits/shafts surrounded by safety mesh on central bench.

Plate 20 Central Western wall of Main Open Cut. Looking West.

Plate 21 Drainage Shaft in base of Main Open Cut.

Plate 22 Southern end of Main Open Cut. Looking SW.

Plate 23 Southern end of Mine site looking toward processing plant area. Eastern drainage depression centre RHS of photo. ROM pad hole upper LHS. View looking SW from main ridge which bisects site. Western extension of ridge top RHS of photo.

Plate 24 ‘Eastern’ drainage depression. Looking West from main ridge on SE side of Mine area. Surface drainage enters old shafts in base of depressions (Heather Worbey, Z.Z. pers.com.)

Plate 25 Processing Plant area. Looking SW. ROM pad hole below excavated cut at end of main ridge.

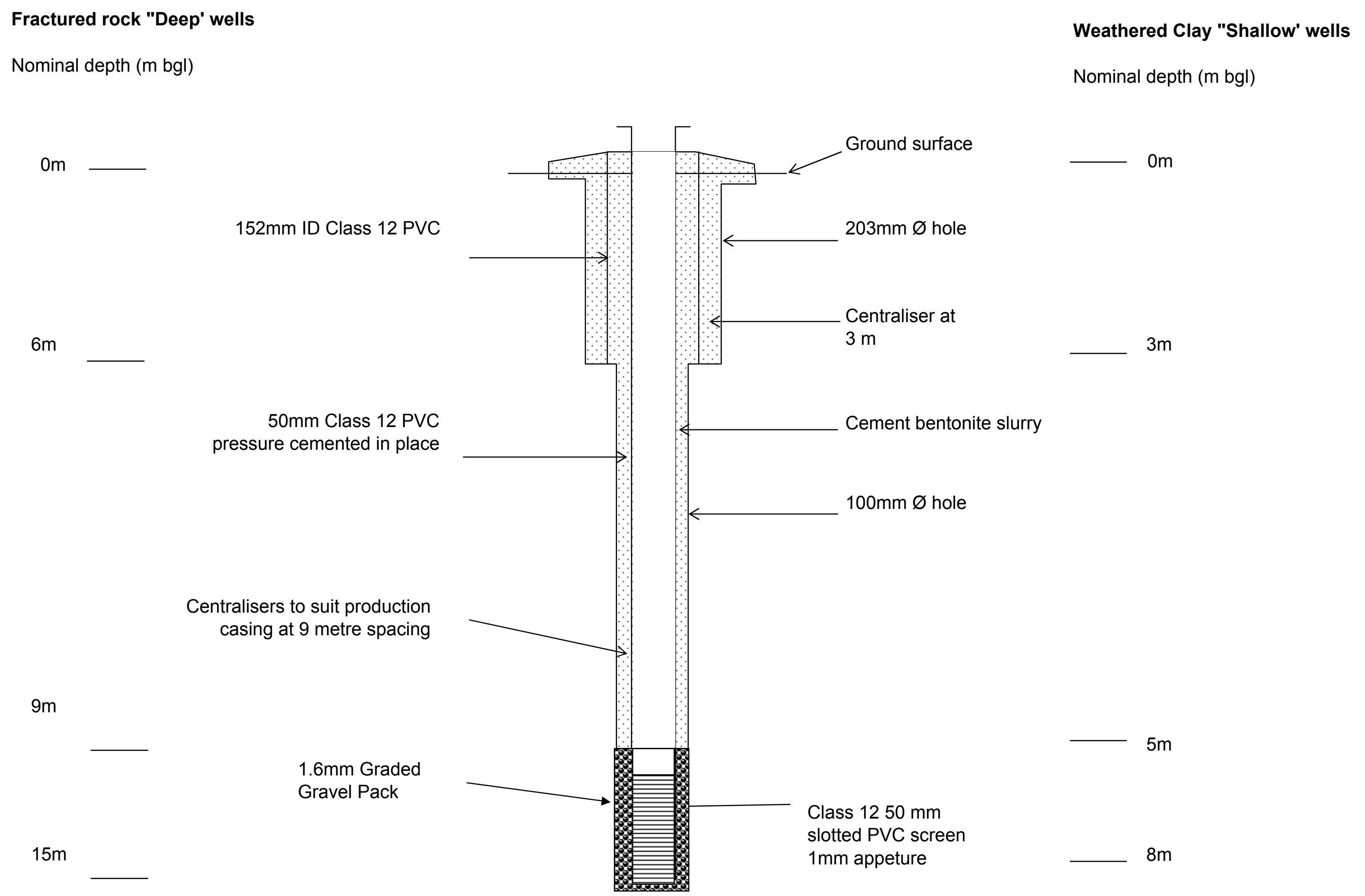
Plate 26 **ROM pad 'hole'. Southern end of Mine site. Looking SW. Apparently doesn't drain into old shafts/adits.**

Plate 27 **Drainage Adit entrance. Weir with monitoring equipment.**

Plate 28 Monitoring bore ZZ5

Appendix A

Recommended Well Construction Specifications



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Nominal well construction design

FIGURE

A.1

PROJECT AZ-01 July-02

Appendix B

Low Flow (minimal drawdown)

Groundwater Sampling Procedures

United States Environmental Protection Agency | Office of Research and Development | Office of Solid Waste and Emergency Response | EPA/540/S-95/504 April 1996

EPA Ground Water Issue

LOW-FLOW (MINIMAL DRAWDOWN) GROUND-WATER SAMPLING PROCEDURES

by Robert W. Puls[1] and Michael J. Barcelona[2]

Background

The Regional Superfund Ground Water Forum is a group of ground-water scientists, representing EPA's Regional Superfund Offices, organized to exchange information related to ground-water remediation at Superfund sites. One of the major concerns of the Forum is the sampling of ground water to support site assessment and remedial performance monitoring objectives. This paper is intended to provide background information on the development of low-flow sampling procedures and its application under a variety of hydrogeologic settings. It is hoped that the paper will support the production of standard operating procedures for use by EPA Regional personnel and other environmental professionals engaged in ground-water sampling.

For further information contact: Robert Puls, 405-436-8543, Subsurface Remediation and Protection Division, NRMRL, Ada, Oklahoma.

I. Introduction

The methods and objectives of ground-water sampling to assess water quality have evolved over time. Initially the emphasis was on the assessment of water quality of aquifers as sources of drinking water. Large water-bearing units were identified and sampled in keeping with that objective. These were highly productive aquifers that supplied drinking water via private wells or through public water supply systems. Gradually, with the increasing awareness of subsurface pollution of these water resources, the understanding of complex hydrogeochemical processes which govern the fate and transport of contaminants in the subsurface increased. This increase in understanding was also due to advances in a number of scientific disciplines and improvements in tools used for site characterization and ground-water sampling. Ground-water quality investigations where pollution was detected initially borrowed ideas, methods, and materials for site characterization from the water supply field and water analysis from public health practices. This included the materials and manner in which monitoring wells were installed and the way in which water was brought to the surface, treated, preserved and analyzed. The prevailing conceptual ideas included convenient generalizations of ground-water resources in terms of large and relatively homogeneous hydrologic *units*. With time it became apparent that conventional water supply generalizations of *homogeneity* did not adequately represent field data regarding pollution of these subsurface resources. The important role of *heterogeneity* became increasingly clear not only in geologic terms, but also in terms of complex physical,

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[2]University of Michigan

Communication · Training · Technology Support · Technology Support Project

Superfund Technology Support Center for Ground Water

National Risk Management Research Laboratory
Subsurface Protection and Remediation Division
Robert S. Kerr Environmental Research Center
Ada, Oklahoma

Technology Innovation Office
Office of Solid Waste and Emergency Response, US EPA, Washington, DC

Walter W. Kovalick, Jr., Ph.D.
Director

chemical and biological subsurface processes. With greater appreciation of the role of heterogeneity, it became evident that subsurface pollution was ubiquitous and encompassed the unsaturated zone to the deep subsurface and included unconsolidated sediments, fractured rock, and *aquitards* or low-yielding or impermeable formations. Small-scale processes and heterogeneities were shown to be important in identifying contaminant distributions and in controlling water and contaminant flow paths.

It is beyond the scope of this paper to summarize all the advances in the field of ground-water quality investigations and remediation, but two particular issues have bearing on ground-water sampling today: aquifer heterogeneity and colloidal transport. Aquifer heterogeneities affect contaminant flow paths and include variations in geology, geochemistry, hydrology and microbiology. As methods and the tools available for subsurface investigations have become increasingly sophisticated and understanding of the subsurface environment has advanced, there is an awareness that in most cases a primary concern for site investigations is characterization of contaminant flow paths rather than entire aquifers. In fact, in many cases, plume thickness can be less than well screen lengths (e.g., 3-6 m) typically installed at hazardous waste sites to detect and monitor plume movement over time. Small-scale differences have increasingly been shown to be important and there is a general trend toward smaller diameter wells and shorter screens.

The hydrogeochemical significance of colloidal-size particles in subsurface systems has been realized during the past several years (Gschwend and Reynolds, 1987; McCarthy and Zachara, 1989; Puls, 1990; Ryan and Gschwend, 1990). This realization resulted from both field and laboratory studies that showed faster contaminant migration over greater distances and at higher concentrations than flow and transport model predictions would suggest (Buddemeier and Hunt, 1988; Enfield and Bengtsson, 1988; Penrose et al., 1990). Such models typically account for interaction between the mobile aqueous and immobile solid phases, but do not allow for a mobile, reactive solid phase. It is recognition of this third *phase* as a possible means of contaminant transport that has brought increasing attention to the manner in which samples are collected and processed for analysis (Puls et al., 1990; McCarthy and Degueldre, 1993; Backhus et al., 1993; U. S. EPA, 1995). If such a phase is present in sufficient mass, possesses high sorption reactivity, large surface area, and remains stable in suspension, it can serve as an important mechanism to facilitate contaminant transport in many types of subsurface systems.

Colloids are particles that are sufficiently small so that the surface free energy of the particle dominates the bulk free energy. Typically, in ground water, this includes particles with diameters between 1 and 1000 nm. The most commonly observed mobile particles include: secondary clay minerals; hydrous iron, aluminum, and manganese oxides; dissolved and particulate organic materials, and viruses and bacteria. These reactive particles have been shown to be mobile under a variety of conditions in both field studies and laboratory column experiments, and as such need to be included in monitoring programs where identification of the *total* mobile contaminant loading (dissolved + naturally suspended particles) at a site is an objective. To that end, sampling methodologies must be used which do not artificially bias *naturally* suspended particle concentrations.

Currently the most common ground-water purging and sampling methodology is to purge a well using bailers or high speed pumps to remove 3 to 5 casing volumes followed by sample collection. This method can cause adverse impacts on sample quality through collection of samples with high levels of turbidity. This results in the inclusion of otherwise immobile artifactual particles which produce an overestimation of certain analytes of interest (e.g., metals or hydrophobic organic compounds). Numerous documented problems associated with filtration (Danielsson, 1982; Laxen and Chandler, 1982; Horowitz et al., 1992) make this an undesirable method of rectifying the turbidity problem, and include the removal of potentially mobile (contaminant-associated) particles during filtration, thus artificially biasing contaminant concentrations low. Sampling-induced turbidity problems can often be mitigated by using low-flow purging and sampling techniques.

Current subsurface conceptual models have undergone considerable refinement due to the recent development and increased use of field screening tools. So-called hydraulic *push* technologies (e.g., cone penetrometer, Geoprobe®, QED HydroPunch®) enable relatively fast screening site characterization which can then be used to design and install a monitoring well network. Indeed, alternatives to conventional monitoring wells are now being considered for some hydrogeologic settings. The ultimate design of any monitoring system should however be based upon adequate site characterization and be consistent with established monitoring objectives.

If the sampling program objectives include accurate assessment of the magnitude and extent of subsurface contamination over time and/or accurate assessment of subsequent remedial performance, then some information regarding plume delineation in three-dimensional space is necessary prior to monitoring well network design and installation. This can be accomplished with a variety of different tools and equipment ranging from hand-operated augers to screening tools mentioned above and large drilling rigs. Detailed information on ground-water flow velocity, direction, and horizontal and vertical variability are essential baseline data requirements. Detailed soil and geologic data are required prior to and during the installation of sampling points. This includes historical as well as detailed soil and geologic logs which accumulate during the site investigation. The use of borehole geophysical techniques is also recommended. With this information (together with other site characterization data) and a clear understanding of sampling objectives, then appropriate location, screen length, well diameter, slot size, etc. for the monitoring well network can be decided. This is especially critical for new in situ remedial approaches or natural attenuation assessments at hazardous waste sites.

In general, the overall goal of any ground-water sampling program is to collect water samples with no alteration in water chemistry; analytical data thus obtained may be used for a variety of specific monitoring programs depending on the regulatory requirements. The sampling methodology described in this paper assumes that the monitoring goal is to sample monitoring wells for the presence of contaminants and it is applicable whether mobile colloids are a concern or not and whether the analytes of concern are metals (and metalloids) or organic compounds.

II. Monitoring Objectives and Design Considerations

The following issues are important to consider prior to the design and implementation of any ground-water monitoring program, including those which anticipate using low-flow purging and sampling procedures.

A. Data Quality Objectives (DQOs)

Monitoring objectives include four main types: detection, assessment, corrective-action evaluation and resource evaluation, along with *hybrid* variations such as site-assessments for property transfers and water availability investigations. Monitoring objectives may change as contamination or water quality problems are discovered. However, there are a number of common components of monitoring programs which should be recognized as important regardless of initial objectives. These components include:

1) Development of a conceptual model that incorporates elements of the regional geology to the local geologic framework. The conceptual model development also includes initial site characterization efforts to identify hydrostratigraphic units and likely flow-paths using a minimum number of borings and well completions;

2) Cost-effective and well documented collection of high quality data utilizing simple, accurate, and reproducible techniques; and

3) Refinement of the conceptual model based on supplementary data collection and analysis.

These fundamental components serve many types of monitoring programs and provide a basis for future efforts that evolve in complexity and level of spatial detail as purposes and objectives expand. High quality, reproducible data collection is a common goal regardless of program objectives.

High quality data collection implies data of sufficient accuracy, precision, and completeness (i.e., ratio of valid analytical results to the minimum sample number called for by the program design) to meet the program objectives. Accuracy depends on the correct choice of monitoring tools and procedures to minimize sample and subsurface disturbance from collection to analysis. Precision depends on the repeatability of sampling and analytical protocols. It can be assured or improved by replication of sample analyses including blanks, field/lab standards and reference standards.

B. Sample Representativeness

An important goal of any monitoring program is collection of data that is truly representative of conditions at the site. The term *representativeness* applies to chemical and hydrogeologic data collected via wells, borings, piezometers, geophysical and soil gas measurements, lysimeters, and temporary sampling points. It involves a recognition of the statistical variability of individual subsurface physical properties, and contaminant or major ion concentration levels, while explaining extreme values. Subsurface temporal and spatial variability are facts. Good professional practice seeks to maximize representativeness by using proven accurate and reproducible techniques to define limits on the distribution of measurements collected at a site. However, measures of representativeness are dynamic and are controlled by evolving site characterization and monitoring objectives. An evolutionary site characterization model, as shown in Figure 1, provides a systematic approach to the goal of consistent data collection.

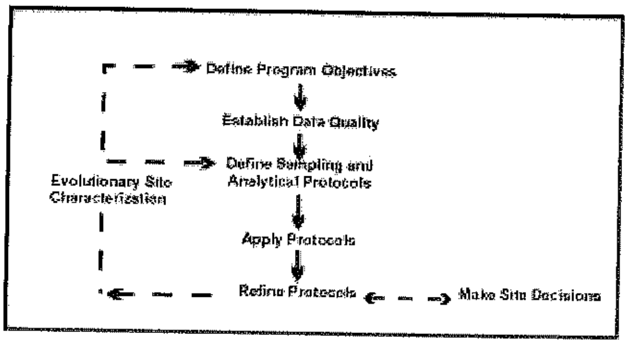

Figure 1. Evolutionary Site Characterization Model

The model emphasizes a recognition of the causes of the variability (e.g., use of inappropriate technology such as using bailers to purge wells; imprecise or operator-dependent methods) and the need to control avoidable errors.

1) Questions of Scale

A sampling plan designed to collect representative samples must take into account the potential scale of changes in site conditions through space and time as well as the chemical associations and behavior of the parameters that are targeted for investigation. In subsurface systems, physical (i.e., aquifer) and chemical properties over time or space are not statistically independent. In fact, samples taken in close proximity (i.e., within distances of a few meters) or within short time periods (i.e., more frequently than monthly) are highly auto-correlated. This means that designs employing high-sampling frequency (e.g., monthly) or dense spatial monitoring designs run the risk of redundant data collection and misleading inferences regarding trends in values that aren't statistically valid. In practice, contaminant detection and assessment monitoring programs rarely suffer these *over-sampling* concerns. In corrective-action evaluation programs, it is also possible that too little data may be collected over space or time. In these cases, false interpretation of the spatial extent of contamination or underestimation of temporal concentration variability may result.

2) Target Parameters

Parameter selection in monitoring program design is most often dictated by the regulatory status of the site. However, background water quality constituents, purging indicator parameters, and contaminants, all represent targets for data collection programs. The tools and procedures used in these programs should be equally rigorous and applicable to all categories of data, since all may be needed to determine or support regulatory action.

C. Sampling Point Design and Construction

Detailed site characterization is central to all decision-making purposes and the basis for this characterization resides in identification of the geologic framework and major hydro-stratigraphic units. Fundamental data for sample point location include: subsurface lithology, head-differences and background geochemical conditions. Each sampling point has a proper use or uses which should be documented at a level which is appropriate for the program's data quality objectives. Individual sampling points may not always be able to fulfill multiple monitoring objectives (e.g., detection, assessment, corrective action).

1) Compatibility with Monitoring Program and Data Quality Objectives

Specifics of sampling point location and design will be dictated by the complexity of subsurface lithology and variability in contaminant and/or geochemical conditions. It should be noted that, regardless of the ground-water sampling approach, few sampling points (e.g., wells, drive-points, screened augers) have zones of influence in excess of a few feet. Therefore, the spatial frequency of sampling points should be carefully selected and designed.

2) Flexibility of Sampling Point Design

In most cases *well-point* diameters in excess of 1 7/8 inches will permit the use of most types of submersible pumping devices for low-flow (minimal drawdown) sampling. It is suggested that *short* (e.g., less than 1.6 m) screens be incorporated into the monitoring design where possible so that comparable results from one device to another might be expected. *Short*, of course, is relative to the degree of vertical water quality variability expected at a site.

3) Equilibration of Sampling Point

Time should be allowed for equilibration of the well or sampling point with the formation after installation. Placement of well or sampling points in the subsurface produces some disturbance of ambient conditions. Drilling techniques (e.g., auger, rotary, etc.) are generally considered to cause more disturbance than *direct-push* technologies. In either case, there may be a period (i.e., days to months) during which water quality near the point may be distinctly different from that in the formation. Proper development of the sampling point and adjacent formation to remove fines created during emplacement will shorten this water quality *recovery* period.

III. Definition of Low-Flow Purging and Sampling

It is generally accepted that water in the well casing is non-representative of the formation water and needs to be purged prior to collection of ground-water samples. However, the water in the screened interval may indeed be representative of the formation, depending upon well construction and site hydrogeology. Wells are purged to some extent for the following reasons: the presence of the air interface at the top of the water column resulting in an oxygen concentration gradient with depth, loss of volatiles up the water column, leaching from or sorption to the casing or filter pack, chemical changes due to clay seals or backfill, and surface infiltration.

Low-flow purging, whether using portable or dedicated systems, should be done using pump-intake located in the middle or slightly above the middle of the screened interval. Placement of the pump too close to the bottom of the well will cause increased entrainment of solids which have collected in the well over time. These particles are present as a result of well development, prior purging and sampling events, and natural colloidal transport and deposition. Therefore, placement of the pump in the middle or toward the top of the screened interval is suggested. Placement of the pump at the top of the water column for sampling is only recommended in unconfined aquifers, screened across the water table, where this is the desired sampling point. Low-flow purging has the advantage of minimizing mixing between the overlying stagnant casing water and water within the screened interval.

A. Low-Flow Purging and Sampling

Low-flow refers to the velocity with which water enters the pump intake and that is imparted to the formation pore water in the immediate vicinity of the well screen. It does not necessarily refer to the flow rate of water discharged at the surface which can be affected by flow regulators or restrictions. Water level drawdown provides the best indication of the stress imparted by a given flow-rate for a given hydrological situation. The objective is to pump in a manner that minimizes stress (drawdown) to the system to the extent practical taking into account established site sampling objectives. Typically, flow rates on the order of 0.1 - 0.5 L/min are used, however this is dependent on site-specific hydrogeology. Some extremely coarse-textured formations have been successfully sampled in this manner at flow rates to 1 L/min. The effectiveness of using low-flow purging is intimately linked with proper screen location, screen length, and well construction and development techniques. The reestablishment of natural flow paths in both the vertical and horizontal directions is important for correct interpretation of the data. For high resolution sampling needs, screens less than 1 m should be used. Most of the need for purging has been found to be due to passing the sampling device through the overlying casing water which causes mixing of these stagnant waters and the dynamic waters within the screened interval. Additionally, there is disturbance to suspended sediment collected in the bottom of the casing and the displacement of water out into the formation immediately adjacent to the well screen. These disturbances and impacts can be avoided using dedicated sampling equipment, which precludes the need to insert the sampling device prior to purging and sampling.

Isolation of the screened interval water from the overlying stagnant casing water may be accomplished using low-flow minimal drawdown techniques. If the pump intake is located within the screened interval, most of the water pumped will be drawn in directly from the formation with little mixing of casing water or disturbance to the sampling zone. However, if the wells are not constructed and developed properly, zones other than those intended may be sampled. At some sites where geologic heterogeneities are sufficiently different within the screened interval, higher conductivity zones may be preferentially sampled. This is another reason to use shorter screened intervals, especially where high spatial resolution is a sampling objective.

B. Water Quality Indicator Parameters

It is recommended that water quality indicator parameters be used to determine purging needs prior to sample collection in each well. Stabilization of parameters such as pH, specific conductance, dissolved oxygen, oxidation-reduction potential, temperature and turbidity should be used to determine when formation water is accessed during purging. In general, the order of stabilization is pH, temperature, and specific conductance, followed by oxidation-reduction potential, dissolved oxygen and turbidity. Temperature and pH, while commonly used as purging indicators, are actually quite insensitive in distinguishing between formation water and stagnant casing water; nevertheless, these are important parameters for data interpretation purposes and should also be measured. Performance criteria for determination of stabilization should be based on water-level drawdown, pumping rate and equipment specifications for measuring indicator parameters. Instruments are available which utilize in-line flow cells to continuously measure the above parameters.

It is important to establish specific well stabilization criteria and then consistently follow the same methods thereafter, particularly with respect to drawdown, flow rate and sampling device. Generally, the time or purge volume required for parameter stabilization is independent of well depth or well volumes. Dependent variables are well diameter, sampling device, hydrogeochemistry, pump flow rate, and whether the devices are used in a portable or dedicated manner. If the sampling device is already in place (i.e., dedicated sampling systems), then the time and purge volume needed for stabilization is much shorter. Other advantages of dedicated equipment include less purge water for waste disposal, much less decontamination of equipment, less time spent in preparation of sampling as well as time in the field, and more consistency in the sampling approach which probably will translate into less variability in sampling results. The use of dedicated equipment is strongly recommended at wells which will undergo routine sampling over time.

If parameter stabilization criteria are too stringent, then minor oscillations in indicator parameters may cause purging operations to become unnecessarily protracted. It should also be noted that turbidity is a very conservative parameter in terms of stabilization. Turbidity is always the last parameter to stabilize. Excessive purge times are invariably related to the establishment of too stringent turbidity stabilization criteria. It should be noted that natural turbidity levels in ground water may exceed 10 nephelometric turbidity units (NTU).

C. Advantages and Disadvantages of Low-Flow (Minimum Drawdown) Purging

In general, the advantages of low-flow purging include:

- samples which are representative of the *mobile* load of contaminants present (dissolved and colloid-associated);
- minimal disturbance of the sampling point thereby minimizing sampling artifacts;
- less operator variability, greater operator control;

- reduced stress on the formation (minimal drawdown);
- less mixing of stagnant casing water with formation water;
- reduced need for filtration and, therefore, less time required for sampling;
- smaller purging volume which decreases waste disposal costs and sampling time;
- better sample consistency; reduced artificial sample variability.

Some disadvantages of low-flow purging are:

- higher initial capital costs,
- greater set-up time in the field,
- need to transport additional equipment to and from the site,
- increased training needs,
- resistance to change on the part of sampling practitioners,
- concern that new data will indicate a *change in conditions* and trigger an *action.*

IV. Low-Flow (Minimal Drawdown) Sampling Protocols

The following ground-water sampling procedure has evolved over many years of experience in ground-water sampling for organic and inorganic compound determinations and as such summarizes the authors' (and others) experiences to date (Barcelona et al., 1984, 1994; Barcelona and Helfrich, 1986; Puls and Barcelona, 1989; Puls et. al. 1990, 1992; Puls and Powell, 1992; Puls and Paul, 1995). High-quality chemical data collection is essential in ground-water monitoring and site characterization. The primary limitations to the collection of *representative* ground-water samples include: mixing of the stagnant casing and *fresh* screen waters during insertion of the sampling device or ground-water level measurement device; disturbance and resuspension of settled solids at the bottom of the well when using high pumping rates or raising and lowering a pump or bailer; introduction of atmospheric gases or degassing from the water during sample handling and transfer, or inappropriate use of vacuum sampling device, etc.

A. Sampling Recommendations

Water samples should not be taken immediately following well development. Sufficient time should be allowed for the ground-water flow regime in the vicinity of the monitoring well to stabilize and to approach chemical equilibrium with the well construction materials. This lag time will depend on site conditions and methods of installation but often exceeds one week.

Well purging is nearly always necessary to obtain samples of water flowing through the geologic formations in the screened interval. Rather than using a general but arbitrary guideline of purging three casing volumes prior to sampling, it is recommended that an in-line water quality measurement device (e.g., flow-through cell) be used to establish the stabilization time for several parameters (e.g. , pH, specific conductance, redox, dissolved oxygen, turbidity) on a well-specific basis. Data on pumping rate, drawdown, and volume required for parameter stabilization can be used as a guide for conducting subsequent sampling activities.

The following are recommendations to be considered before, during and after sampling:

- use low-flow rates (<0.5 L/min), during both purging and sampling to maintain minimal drawdown in the well;
- maximize tubing wall thickness, minimize tubing length;
- place the sampling device intake at the desired sampling point;
- minimize disturbances of the stagnant water column above the screened interval during water level measurement and sampling device insertion;
- make proper adjustments to stabilize the flow rate as soon as possible;
- monitor water quality indicators during purging;
- collect unfiltered samples to estimate contaminant loading and transport potential in the subsurface system.

B. Equipment Calibration

Prior to sampling, all sampling device and monitoring equipment should be calibrated according to manufacturer's recommendations and the site Quality Assurance Project Plan (QAPP) and Field Sampling Plan (FSP). Calibration of pH should be performed with at least two buffers which bracket the expected range. Dissolved oxygen calibration must be corrected for local barometric pressure readings and elevation.

C. Water Level Measurement and Monitoring

It is recommended that a device be used which will least disturb the water surface in the casing. Well depth should be obtained from the well logs. Measuring to the bottom of the well casing will only cause resuspension of settled solids from the formation and require longer purging times for turbidity equilibration. Measure well depth after sampling is completed. The water level measurement should be taken from a permanent reference point which is surveyed relative to ground elevation.

D. Pump Type

The use of low-flow (e.g., 0.1-0.5 L/min) pumps is suggested for purging and sampling all types of analytes. All pumps have some limitation and these should be investigated with respect to application at a particular site. Bailers are inappropriate devices for low-flow sampling.

1) General Considerations

There are no unusual requirements for ground-water sampling devices when using low-flow, minimal drawdown techniques. The major concern is that the device give consistent results and minimal disturbance of the sample across a range of *low* flow rates (i.e., < 0.5 L/min). Clearly, pumping rates that cause minimal to no drawdown in one well could easily cause *significant* drawdown in another well finished in a less transmissive formation. In this sense, the pump should not cause undue pressure or temperature changes or physical disturbance on the water sample over a reasonable sampling range. Consistency in operation is critical to meet accuracy and precision goals.

2) Advantages and Disadvantages of Sampling Devices

A variety of sampling devices are available for low-flow (minimal drawdown) purging and sampling and include peristaltic pumps, bladder pumps, electrical submersible pumps, and gas-driven pumps. Devices which lend themselves to both dedication and consistent operation at definable low-flow rates are preferred. It is desirable that the pump be easily adjustable and operate reliably at these lower flow rates. The peristaltic pump is limited to shallow applications and can cause degassing resulting in alteration of pH, alkalinity, and some volatiles loss. Gas-driven pumps should be of a type that does not allow the gas to be in direct contact with the sampled fluid.

Clearly, bailers and other *grab* type samplers are ill-suited for low-flow sampling since they will cause repeated disturbance and mixing of *stagnant* water in the casing and the *dynamic* water in the screened interval. Similarly, the use of inertial lift foot-valve type samplers may cause too much disturbance at the point of sampling. Use of these devices also tends to introduce uncontrolled and unacceptable operator variability.

Summaries of advantages and disadvantages of various sampling devices are listed in Herzog et al. (1991), U. S. EPA (1992), Parker (1994) and Thurnblad (1994).

E. Pump Installation

Dedicated sampling devices (left in the well) capable of pumping and sampling are preferred over <u>any</u> other type of device. Any portable sampling device should be slowly and carefully lowered to the middle of the screened interval or slightly above the middle (e.g., 1-1.5 m below the top of a 3 m screen). This is to minimize excessive mixing of the stagnant water in the casing above the screen with the screened interval zone water, and to minimize resuspension of solids which will have collected at the bottom of the well. These two disturbance effects have been shown to directly affect the time required for purging. There also appears to be a direct correlation between size of portable sampling devices relative to the well bore and resulting purge volumes and times. The key is to minimize disturbance of water and solids in the well casing.

F. Filtration

Decisions to filter samples should be dictated by sampling objectives rather than as a *fix* for poor sampling practices, and field-filtering of certain constituents should not be the default. Consideration should be given as to what the application of field-filtration is trying to accomplish. For assessment of truly dissolved (as opposed to operationally *dissolved* [i.e., samples filtered with 0.45 µm filters]) concentrations of major ions and trace metals, 0.1 µm filters are recommended although 0.45 µm filters are normally used for most regulatory programs. Alkalinity samples must also be filtered if significant particulate calcium carbonate is suspected, since this material is likely to impact alkalinity titration results (although filtration itself may alter the CO_2 composition of the sample and, therefore, affect the results).

Although filtration may be appropriate, filtration of a sample may cause a number of unintended changes to occur (e.g. oxidation, aeration) possibly leading to filtration-induced artifacts during sample analysis and uncertainty in the results. Some of these unintended changes may be unavoidable but the factors leading to them must be recognized. Deleterious effects can be minimized by consistent application of certain filtration guidelines. Guidelines should address selection of filter type, media, pore size, etc. in order to identify and minimize potential sources of uncertainty when filtering samples.

In-line filtration is recommended because it provides better consistency through less sample handling, and minimizes sample exposure to the atmosphere. In-line filters are available in both disposable (barrel filters) and non-disposable (in-line filter holder, flat membrane filters) formats and various filter pore sizes (0.1-5.0 µm). Disposable filter cartridges have the advantage of greater sediment handling capacity when compared to traditional membrane filters. Filters must be pre-rinsed following manufacturer's recommendations. If there are no recommendations for rinsing, pass through a minimum of 1 L of ground water following purging and prior to sampling. Once filtration has begun, a filter cake may develop as particles larger than the pore size accumulate on the filter membrane. The result is that the effective pore diameter of the membrane is reduced and particles smaller than the stated pore size are excluded from the filtrate. Possible corrective measures include prefiltering (with larger pore size filters), minimizing particle loads to begin with, and reducing sample volume.

G. Monitoring of Water Level and Water Quality Indicator Parameters

Check water level periodically to monitor drawdown in the well as a guide to flow rate adjustment. The goal is minimal drawdown (<0.1 m) during purging. This goal may be difficult to achieve under some circumstances due to geologic heterogeneities within the screened interval, and may require adjustment based on site-specific conditions and personal experience. In-line water quality indicator parameters should be continuously monitored during purging. The water quality indicator parameters monitored can include pH, redox potential, conductivity, dissolved oxygen (DO) and turbidity. The last three parameters are often most sensitive. Pumping rate, drawdown, and the time or volume required to obtain stabilization of parameter readings can be used as a future guide to purge the well. Measurements should be taken every three to five minutes if the above suggested rates are used. Stabilization is achieved after all parameters have stabilized for three successive readings. In lieu of measuring all five parameters, a minimum subset would include pH, conductivity, and turbidity or DO. Three successive readings should be within ± 0.1 for pH, ± 3% for conductivity, ± 10 mv for redox potential, and ± 10% for turbidity and DO. Stabilized purge indicator parameter trends are generally obvious and follow either an exponential or asymptotic change to stable values during purging. Dissolved oxygen and turbidity usually require the longest time for stabilization. The above stabilization guidelines are provided for rough estimates based on experience.

H. Sampling, Sample Containers, Preservation and Decontamination

Upon parameter stabilization, sampling can be initiated. If an in-line device is used to monitor water quality parameters, it should be disconnected or bypassed during sample collection. Sampling flow rate may remain at established purge rate or may be adjusted slightly to minimize aeration, bubble formation, turbulent filling of sample bottles, or loss of volatiles due to extended residence time in tubing. Typically, flow rates less than 0.5 L/min are appropriate. The same device should be used for sampling as was used for purging. Sampling should occur in a progression from least to most contaminated well, if this is known. Generally, volatile (e.g., solvents and fuel constituents) and gas sensitive (e.g., Fe^{2+}, CH_4, H_2S/HS^-, alkalinity) parameters should be sampled first. The sequence in which samples for most inorganic parameters are collected is immaterial unless filtered (dissolved) samples are desired. Filtering should be done last and in-line filters should be used as discussed above. During both well purging and sampling, proper protective clothing and equipment must be used based upon the type and level of contaminants present.

The appropriate sample container will be prepared in advance of actual sample collection for the analytes of interest and include sample preservative where necessary. Water samples should be collected directly into this container from the pump tubing.

Immediately after a sample bottle has been filled, it must be preserved as specified in the site (QAPP). Sample preservation requirements are based on the analyses being performed (use site QAPP, FSP, RCRA guidance document [U. S. EPA, 1992] or EPA SW-846 [U. S. EPA, 1982]). It may be advisable to add preservatives to sample bottles in a controlled setting prior to entering the field in order to reduce the chances of improperly preserving sample bottles or introducing field contaminants into a sample bottle while adding the preservatives.

The preservatives should be transferred from the chemical bottle to the sample container using a disposable polyethylene pipet and the disposable pipet should be used only once and then discarded.

After a sample container has been filled with ground water, a Teflon™ (or tin)-lined cap is screwed on tightly to prevent the container from leaking. A sample label is filled out as specified in the FSP. The samples should be stored inverted at 4°C.

Specific decontamination protocols for sampling devices are dependent to some extent on the type of device used and the type of contaminants encountered. Refer to the site QAPP and FSP for specific requirements.

I. Blanks

The following blanks should be collected:

(1) field blank: one field blank should be collected from each source water (distilled/deionized water) used for sampling equipment decontamination or for assisting well development procedures.

(2) equipment blank: one equipment blank should be taken prior to the commencement of field work, from each set of sampling equipment to be used for that day. Refer to site QAPP or FSP for specific requirements.

(3) trip blank: a trip blank is required to accompany each volatile sample shipment. These blanks are prepared in the laboratory by filling a 40-mL volatile organic analysis (VOA) bottle with distilled/deionized water.

V. Low-Permeability Formations and Fractured Rock

The overall sampling program goals or sampling objectives will drive how the sampling points are located, installed, and choice of sampling device. Likewise, site-specific hydrogeologic factors will affect these decisions. Sites with very low permeability formations or fractures causing discrete flow channels may require a unique monitoring approach. Unlike water supply wells, wells installed for ground-water quality assessment and restoration programs are often installed in low water-yielding settings (e.g., clays, silts). Alternative types of sampling points and sampling methods are often needed in these types of environments, because low-permeability settings may require extremely low-flow purging (<0.1 L/min) and may be technology-limited. Where devices are not readily available to pump at such low flow rates, the primary consideration is to avoid dewatering of the well screen. This may require repeated recovery of the water during purging while leaving the pump in place within the well screen.

Use of low-flow techniques may be impractical in these settings, depending upon the water recharge rates. The sampler and the end-user of data collected from such wells need to understand the limitations of the data collected; i.e., a strong potential for underestimation of actual contaminant concentrations for volatile organics, potential false negatives for filtered metals and potential false positives for unfiltered metals. It is suggested that comparisons be made between samples recovered using low-flow purging techniques and samples recovered using passive sampling techniques (i.e., two sets of samples). Passive sample collection would essentially entail acquisition of the sample with no or very little purging using a dedicated sampling system installed within the screened interval or a passive sample collection device.

A. Low-Permeability Formations (<0.1 L/min recharge)

1. Low-Flow Purging and Sampling with Pumps

   a. "portable or non-dedicated mode" - Lower the pump (one capable of pumping at <0.1 L/min) to mid-screen or slightly above and set in place for minimum of 48 hours (to lessen purge volume requirements). After 48 hours, use procedures listed in Part IV above regarding monitoring water quality parameters for stabilization, etc., but do not dewater the screen. If excessive drawdown and slow recovery is a problem, then alternate approaches such as those listed below may be better.

   b. "dedicated mode" - Set the pump as above at least a week prior to sampling; that is, operate in a dedicated pump mode. With this approach significant reductions in purge volume should be realized. Water quality parameters should stabilize quite rapidly due to less disturbance of the sampling zone.

2. Passive Sample Collection

Passive sampling collection requires insertion of the device into the screened interval for a sufficient time period to allow flow and sample equilibration before extraction for analysis. Conceptually, the extraction of water from low yielding formations seems more akin to the collection of water from the unsaturated zone and passive sampling techniques may be more appropriate in terms of obtaining "representative" samples. Satisfying usual sample volume requirements is typically a problem with this approach and some latitude will be needed on the part of regulatory entities to achieve sampling objectives.

B. Fractured Rock

In fractured rock formations, a low-flow to zero purging approach using pumps in conjunction with packers to isolate the sampling zone in the borehole is suggested. Passive multi-layer sampling devices may also provide the most "representative" samples. It is imperative in these settings to identify flow paths or water-producing fractures prior to sampling using tools such as borehole flowmeters and/or other geophysical tools.

After identification of water-bearing fractures, install packer(s) and pump assembly for sample collection using low-flow sampling in "dedicated mode" or use a passive sampling device which can isolate the identified water-bearing fractures.

VI. Documentation

The usual practices for documenting the sampling event should be used for low-flow purging and sampling techniques. This should include, at a minimum: information on the conduct of purging operations (flow-rate, drawdown, water-quality parameter values, volumes extracted and times for measurements), field instrument calibration data, water sampling forms and chain of custody forms. See Figures 2 and 3 and "Ground Water Sampling Workshop -- A Workshop Summary" (U. S. EPA, 1995) for example forms and other documentation suggestions and information. This information coupled with laboratory analytical data and validation data are needed to judge the "useability" of the sampling data.

VII. Notice

The U.S. Environmental Protection Agency through its Office of Research and Development funded and managed the research described herein as part of its in-house research program and under Contract No. 68-C4-0031 to Dynamac Corporation. It has been subjected to the Agency's peer and administrative review and has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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Figure 2. **Ground Water Sampling Log**

Project ______________ **Site** ______________ **Well No.** ____________ **Date** ____________________

Well Depth ___________ **Screen Length** _________ **Well Diameter** ________ **Casing Type** __________

Sampling Device ______________ **Tubing type** ____________________ **Water Level** ______________

Measuring Point _________________ **Other Infor** ______________________________________

____

Sampling Personnel ____

Time	pH	Temp	Cond.	Dis.O_2	Turb.	[ ]Conc			Notes

Type of Samples Collected

____

Information: 2 in = 617 ml/ft, 4 in = 2470 ml/ft: $Vol_{cyl} = \pi r^2 h$, $Vol_{sphere} = 4/3\pi\ r^3$

Figure 3. **Ground Water Sampling Log** (with automatic data logging for most water quality parameters)

Project _______________ **Site** _______________ **Well No.** _____________ **Date** _________________________

Well Depth ____________ **Screen Length** __________ **Well Diameter** _________ **Casing Type** ___________

Sampling Device _______________ **Tubing type** _____________________ **Water Level** _________________

Measuring Point ___________________ **Other Infor** ____

____

Sampling Personnel ____

Time	Pump Rate	Turbidity	Alkalinity	[ ] Conc	Notes

Type of Samples Collected

____

Information: 2 in = 617 ml/ft, 4 in = 2470 ml/ft: $Vol_{cyl} = \pi r^2 h$, $Vol_{sphere} = 4/3\pi\ r^3$

Appendix C

Groundwater Sampling Field

Data Sheet

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Bore Purging and Groundwater Sampling Data Sheet

General Information

Client:			
Job Number:		Bore Locked (Y/N)	
Project:		Well ID No.	
Location:		Chem Kit No.	
Depth to Groundwater (m-TOSC):		Well depth (m-PVC)	
Depth to Groundwater (mPVC):		Free product thickness:	
Depth to Groundwater (m-BGL):		RL from TOC:	

Weather Conditions

Rain:	Wind Direction:
Temperature:	Wind Speed:
Cloud Cover:	Upwind Activities:
Location Conditions:	

Field Comments

Other Comments and Observations: r = H =

- Bore Conditions R = h =
- Fate of Tubing, etc. (left in hole/disposal)
- Purge Volume Calculations in Liters(screened & unscreened sections) PV =

$$PV = [(H \times \pi \times r^2) + 0.2(h \times \pi \times (R^2 - r^2))] \times 1000$$

where H = height of water column (m) R = Bore Radius (m) PV =

h = thickness of saturated filterpack (m) r = PVC Radius (m)

PV =

Purging Information

Date:	Name:					
Method:	Tubing Material			Pump Depth		
Start Time:	Finish Time			Pump Speed		
Purge Volume (L)	No times purged			Total Purge Volumes (litres)		

Time	Volume Removed (L)	pH	E.C. (mS/cm)	Redox (mV)	Temp (Cels)	Appearance (Colour / Odour / Turbidity)

Purging should continue until measurements for pH are within 0.1 pH unit, EC is within 3%, Redox is within 10mV and Temperature is within 0.5 degC of the previous set of parameters.

Sampling Information

Date:		Name:
Method:	Tubing Material	Pump Depth
Start Time	Finish Time	Pump Speed

Time	Volume Removed (L)	pH	E.C. (mS/cm)	Redox (mV)	Temp (Cels)	Appearance (Colour / Odour / Turbidity)

Purger's Name:	Signature	Date	/ /
Sampler's Name:	Signature	Date	/ /
Checked by:	Signature	Date	/ /

rem

Appendix D

Chain of Custody (CoC)

Documentation

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CHAIN OF CUSTODY FORM

rem
resource and environmental management

From :
ACN:
Address:
ph: **fax:**

LAB USE ONLY	**Project No:**
ALS QUOTE NUMBER	
Job Code:	**Project Manager:**
Due Date:	
Custody seal intact?	**Sampler(s):**
Sample cold?	
Received for Laboratory by:	**Checked:**
Date:	**Date:**
Time:	

	Container Identification				
Size					
Type					
Preserv					
Analytes					

Lab identification	**Date**	**Time**	**Matrix**	**Sample Identification**	**Comments**		**Tick required analytes**				
					TOTAL						

Comments

Sheet of

Appendix E

EPA Victoria Publication 441

A guide to the sampling and analysis of waters, wastewaters, soil and wastes

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A GUIDE TO THE SAMPLING AND ANALYSIS OF WATERS, WASTEWATERS, SOILS AND WASTES

Environment Protection Authority
State Government of Victoria

March 2000

A GUIDE TO THE SAMPLING AND ANALYSIS OF WATERS, WASTEWATERS, SOILS AND WASTES

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FOREWORD

To effectively reduce risks of environmental damage, a regular program of monitoring industrial and other activities should be undertaken in which wastes are characterised, and potentially contaminated land is audited. This responsible approach should be taken whether or not it is a statutory requirement.

This publication significantly expands on the previous edition of *A Guide to the Sampling and Analysis of Water and Wastewater* by including soils, other non-gaseous environmental samples and wastes.

For quantified information, rigorous procedures, as outlined in this Guide, need to be followed to ensure that laboratory analysis accurately and reliably measures a pollutant or quality of the receiving environment.

Providing accurate and reliable measurements of environmental quality depends on a number of steps. Program and sampling design must have statistical rigour and ensure that representative samples are taken, with due consideration of the chemical behaviour and temporal and spatial distribution of the pollutant *in situ*. To maintain the integrity of the sample in the interval before it is analysed, most pollutants need to be preserved in some way to inhibit physical, chemical and biological transformations which can alter their concentration.

It is necessary for both the sampler and laboratory staff to work closely together, within the framework provided in this Guide. Any weak link between collection of the sample, its pre-treatment and storage, and the analysis, can jeopardise the integrity of the final result.

Laboratories need to establish a rigorous quality assurance system covering all their analytical procedures, as well as addressing field testing and sample collection.

This Guide establishes best practice procedures for collecting and analysing environmental samples. It should be used for statutory purposes under the *Environment Protection Act 1970*, and by any company or agency that wishes to obtain an accurate picture of the impact of its activities on the environment.

BRIAN ROBINSON
CHAIRMAN

CONTENTS

1. INTRODUCTION

Environmental samples are analysed for a range of purposes, such as to:

- determine ambient pollutant concentrations
- assess potential and known contaminated sites
- monitor effluents, trade wastes and process streams to manage performance
- identify the source and nature of accidental spills or pollution to assess their effects on the environment
- determine background levels of potential contaminants and pollutants, and
- meet statutory requirements of the *Environment Protection Act 1970* and the *Pollution of Waters by Oils and Noxious Substances Act 1986*.

The importance of obtaining representative samples, which faithfully represent a waste or element of the environment from which they are taken, cannot be underestimated. Whereas quality assurance[*] systems are well developed for laboratories, similar systems often do not encompass sample collection. Care needs to be taken in the field to ensure that samples are not contaminated during collection, and that the concentrations of analytical parameters of interest do not alter in the interval between collection and analysis.

Critical steps in any environmental monitoring program include, but are not limited to:

- determining the objectives of the monitoring program
- selecting chemical, physical or biological indicators which are relevant to the objectives of the monitoring program
- selecting the appropriate sampling equipment
- obtaining a representative sample or samples
- making and accurately recording site observations and measurements
- labelling, preserving, storing and transporting the sample correctly for analysis
- analysing the sample accurately and precisely for appropriate indicators
- reporting the result accurately and completely, and
- providing informed interpretation.

Good communication between the sampler and analyst is vital because they are mutually dependent on each other in order to produce a relevant and accurate output.

It is not possible to address all the issues that could arise in the field, and specialist advice may need to be called upon. Statisticians can provide useful advice on developing a sampling strategy to adequately represent a complex situation, while chemists, microbiologists or hydrogeologists may need to be consulted to advise on the behaviour of a pollutant in different elements of the environment.

This Guide aims to provide general direction on appropriate sampling, preservation, storage, and analytical and quality assurance procedures. It should be used for environmental monitoring programs, assessments, risk management, investigations and audits. The guidelines cover waters (including groundwaters), wastewaters, wastes and soils, but not biota. They must be used for analyses produced for the purposes of the *Environment Protection Act 1970* and the *Pollution of Waters by Oils and Noxious Substances Act 1986*, unless other procedures are approved by EPA.

This Guide is a companion publication to *A Guide to the Sampling and Analysis of Air Emissions* (EPA Publication 440).

[*] According to the International Standards Organisations (ISO), quality assurance is defined as: '...all those planned and systematic actions necessary to provide adequate confidence that a product, process or service will satisfy quality requirements.'

2. PLANNING A SAMPLING PROGRAM

Monitoring or assessment involves the collection of observations and measurements from the field for interpretation, in order to provide a reliable picture of the condition or state of a particular element of the environment.

There is no single methodology that is applicable for all monitoring and assessment needs. Therefore the design of a successful sampling strategy is dependent on firstly determining both the objectives of the program and the hypothesis to be tested. Wherever possible, an objective should be expressed as a statistically testable hypothesis.

In turn, the choice of indicators in most monitoring and assessment applications will be dictated by their capacity to reliably reflect an element of the environment to be monitored. Where characterisation or identification of pollutants is required, the choice of indicators will be dependent on the likelihood of their presence in the environment to be tested.

Any sampling program needs to be based on a good understanding of the spatial and temporal distribution of the indicator and its physico-chemical behaviour in the element of the environment being investigated. Statistical methodology should be employed to ensure that sampling locations and timing are representative of both indicator behaviour and the discharge or study area. Spatial and temporal representivity should be achieved.

Spatial representivity means that the whole study area is accurately characterised by a set of data. For elements of the environment where a pollutant's distribution is not homogeneous, a good understanding of the factors that affect this distribution will assist in developing a statistical basis for obtaining a representative picture. For example, the spatial distribution of a pollutant could be affected by spot spills onto soils. In the case of water bodies, understanding the vertical stratification in large water bodies, and the effects of mixing in flowing streams, may be important in characterising them.

Temporal representivity means that variations in time are accurately characterised by the sampling strategy selected. Examples of temporal variations include changes in industrial processes over a periodic cycle that affect effluent quality and, storm events where short term, peak concentrations of pollutants in stormwater enter natural waterways.

Composite sampling is a cost-effective means of representing study areas or flows that are heterogeneous in space or time, and is also useful as a screening tool. In composite sampling, collected samples are mixed to give an 'average' concentration. Great care needs to be taken to ensure that composites are not biased. However, if the objective of a program is to detect a 'hot spot', then composite sampling may be unsuitable because it dilutes polluted single samples, which could result in the 'hot spot' going undetected.

Some pollutants do not mix with the surrounding matrix. A good example is oil which floats on still water. If the objective is to quantify its concentration, it may prove difficult taking a representative volume of the water body. In such cases, the impact may be governed by the area covered, which needs to be estimated in the field. If, however, the objective is to characterise the nature of the oil, then skimming the oil off the water surface will suffice.

Sampling wastes stored in a drum or other storage container presents particular problems. It should not be assumed that the contents of the drum are homogeneous; the sampling strategy should take into account the nature and quantities of any distinct liquid or solid layers in the container.

In situ measurement provides a rapid and direct means of measuring certain qualities in the environment (see section 4). Where it provides relevant and reliable information, it should be used in preference to laboratory testing.

If a program objective requires pollutant loads to be calculated, accurate flow, volume or mass measurement will be required at the sampling point.

There are also practical issues that need to be addressed in designing a sampling program. They are:

- access to the area and media being sampled;
- the availability of relevant and sufficiently sensitive analytical methods; and
- the distance from, and capacity of, the analytical laboratory.

The sampling design will need to ensure that the practicalities of on-site pre-treatment and preservation (where required) are in accordance with section 3 of this Guide.

The choice of analytical methods needs to be compatible with the sampling program design. The choice should be made in full understanding of what characteristic of, or component in, the sample needs to be measured to meet the objectives of the monitoring program.

Good design will assist in determining the limit of detection and precision required which will, in turn, determine the analytical method to be used. For example, ambient heavy metal concentrations in seawater will be in the part per billion range or lower, while determining heavy metals in polluted sludge will be many orders of magnitude higher. In some instances inexpensive screening tests may be acceptable, while in other programs a high level of accuracy will be required. Methods to be used should be chosen from those presented in section 4 of this Guide.

PROGRAM DESIGN CHECKLIST

- ❑ **The key to good program design is to first determine the objectives of the sampling program and propose hypotheses to be tested.**
- ❑ **Collect background information, including:**
- **potential pollutants, their likely sources and transport mechanisms**
- **pollutant behaviour, fate and effects in the environment**
- **the beneficial uses of the receiving environment.**
- ❑ **Equipped with the program aim and background, a statistically rigorous testing program must be developed to meet the test hypotheses.**
- ❑ **Site locations, indicators, timing, frequency and analytical methods must be determined in accordance with the program objectives and hypotheses.**

3. SAMPLE COLLECTION AND TRANSPORT

The objective of sampling is to collect and present for analysis a sample that properly represents the element of the environment, waste or waste discharge of interest.

There are physical, chemical and biological processes that can affect the sample from the time it is collected to when it is analysed. To avoid or minimise the effect of these processes, it is necessary to use the appropriate sampling equipment, select the appropriate container and apply preservation methods in order to maintain the sample's integrity. Samples must also be analysed within stipulated holding time limits.

Care is required to avoid contamination of the sample during sampling, handling and transport to the laboratory.

Health and safety precautions

Safety precautions need to be taken when sampling in the field, and when handling contaminated samples and preservative chemicals. The characteristics and features of each site and sampling point need to be assessed to ensure the safety of the sampler.

The following precautions and warnings must be observed when sampling wastewaters, other wastes or heavily polluted soils, sludges or wastes that may contain harmful chemicals or bacteriological contaminants.

- Skin contact and inhalation of gases from the effluents and polluted samples must be avoided. Wearing disposable plastic gloves is advisable, and if necessary, wearing suitable protective clothing.
- For sewage effluents, hands should be washed with bactericidal soap after sampling such effluent.
- If accidental contact occurs, then rinse the exposed area thoroughly and seek medical advice. If regularly sampling or handling effluents containing sewage, appropriate inoculations should be obtained.
- For hazardous or heavily contaminated samples, the sample label should bear a warning to the analyst.
- Where necessary, designated sampling points, such as a suitable stable platform should be provided. Locations should be readily accessible, and where necessary, safety rails or roping points to which safety harnesses can be attached should be available. The sampler should be either accompanied by another person or make known their sampling location.
- When sampling wastes, care should be taken to avoid inhaling vapours that could be harmful. If necessary, appropriate respiratory protection should be worn by personnel trained in its use. Unless the ignition point of the contents or contaminants is known, precautions should be taken on the assumption that they are flammable.
- Cuts and skin abrasions should be covered with waterproof dressings.
- A suitable change of clothing should be worn during work.
- Eye protection should be used when there is a risk of material entering the eye.
- If dusts or aerosols are considered a problem then masks, conforming to Australian Standard AS 1715 (Standards Australia 1994), should be worn to prevent inhalation. Where possible, work upwind of the application process.

The degree of precaution taken and the type of protective equipment and clothing used should be commensurate with the level of risk. When in doubt, assume the worst case outcome will occur.

When preserving samples in the field, the following precautions should be observed:

- Familiarise yourself with the safety precautions relevant to the preservative(s) to be used.
- The preservation of samples should be performed on a stable surface such as the lid of a portable cooler or a paved surface in order to minimise the chances of spillage.
- Avoid contact with acids, solvents and other preservatives by wearing disposable plastic gloves and safety glasses and by avoiding the inhalation of vapours.
- Addition of acid preservative may release toxic gases such as hydrogen sulphide and hydrogen cyanide. This should always be done in a well-ventilated area, and with due care. After the acid has been added to the sample, time should be allowed for all evolved gas to be vented before placing the lid on the container.

Sampling devices

Sampling devices should be constructed of materials that have minimum interaction with, and do not contaminate, the sample. They should be designed in such a way as to minimise disturbance to the sample.

Sampling devices need to be cleaned appropriately, using the same approach used for sampling containers, as recommended elsewhere in this Guide. Sampling devices should be well cleaned between samples*, particularly when heavy contamination is suspected. In some cases, it may be necessary to collect the final rinsate for analysis, in order to demonstrate that the sampling device has been sufficiently well cleaned. Wherever possible, when sampling waters and wastewaters rinse the container with some of the material to be sampled.

It is not always possible to collect a liquid sample directly into a sample container. Where access is difficult, a scoop or bucket may be used. When a bucket is used, care must be taken to ensure the contents of the bucket remain well mixed while sub-samples are withdrawn. For deep waters, wastewaters and groundwaters, a special sampling device (for example, automatic samplers, Van Dorn bottle) may be needed to collect the sample, which is then transferred into the sample container.

Sample containers

Selecting a sample container

Containers are usually glass, polyethylene or polypropylene, and are selected based on their lack of interaction with analytical parameters. For example, glass is suitable for samples containing trace organics as leaching and adsorption are minimal. However, glass is unsuitable for sampling most trace inorganics because active sites on its surface are capable of binding inorganic ions. For some analytical parameters, fluoropolymer (PTFE) lid liners should be used.

Washing sample containers

To avoid contamination, sample containers need to be specially washed and pre-treated. Suitable containers and special instructions on washing these containers are presented in Appendix A for waters, wastewaters and groundwaters, Appendix B for soils and Appendix C for wastes. Even new containers should be washed and dried, unless specifically not recommended in this Guide.

Containers should only be washed and rinsed with high-grade reagents and solvents. These may need to be retained and submitted to the laboratory for analysis as a blank. Where reagents are added during the preservation step, a sample of the added reagents must be submitted to the laboratory for analysis as a reagent blank.

For waters, wastewaters and groundwaters, rinsing the sampling container with the sample is usually advisable. This minimises any contamination of the container that may have

* When this involves the use of detergents or solvents, the cleaning liquid should be collected and disposed of appropriately.

occurred between washing and sampling. Do not follow this procedure when:

- the analytical parameters are associated with immiscible liquids or suspended particles that will adhere to the sides of the container and may result in higher concentrations in the sample
- sampling for bacterial or other microbiological pollutants, because it is essential that the sterility of the container is maintained before use and the removal of any de-chlorinating agent must be prevented
- containers already contain preservatives (for example solvent or acid).

In the case of waters, wastewaters and wastes, it is occasionally appropriate to overfill containers, particularly when the analytical parameter is potentially oxidisable. For requirements for specific analytical parameters see Appendices B and D.

Sampling waters

Sampling and analysis plans should be devised in accordance with the requirements of Australian Standard 5667.1-12 (Standards Australia 1998a).

Where very low ambient concentrations are expected, special precautions may need to be taken to ensure samples are not contaminated. The integrity of samples must be maintained during sampling, and sources of contamination should be avoided.

Precautions for avoiding or minimising contamination are suggested below.

- Never handle the insides of containers, lids and collection vessels.
- Where preservative is required for the sample, do not allow the device used to add the preservative to make contact with the inside of the container or sample.
- Isolate buffer solutions and preservatives that could cross-contaminate samples. For example, buffer solutions can cross-contaminate water samples being collected for phosphorus analysis.
- Sample containers and chemical preservatives may need to be specially prepared and purified to ensure no cross-contamination occurs. Specialist laboratories have clean rooms to handle the analysis of such samples.

When sampling for volatile species, care should be taken to avoid losses. The sample vial or bottle should be filled gently to reduce agitation that might drive off volatile compounds. Cool the sample immediately on ice for transportation to the analysing laboratory.

Sampling surface waters

When waters are well mixed, a sample taken 100 mm below the surface, well away from the edge, may be adequate. However, deep and stratified waters may require special devices (such as a Van Dorn sampler) and careful handling techniques if the chemical species of interest is unstable. A hand or power-driven pump with an extended inlet tube may be useful to draw water from selected depths.

When sampling shallow waters, contamination of the sample from disturbed sediment should be avoided by using an extended inlet of thin tube on the sample bottle and drawing water into the bottle by suction.

To collect a sample of the surface layer for analysis, the container should be held horizontally in the water, half submerging it. To collect a sample of the water beneath a surface layer, a syringe or other device with an extended inlet tube capable of piercing the surface layer, may be appropriate, depending on the thickness of the surface layer.

In all cases, ensure that the sampling device or method does not contaminate the sample.

Sampling groundwaters

Regular testing of groundwater quality is usually done from bores. Monitoring bores should be constructed in accordance with the guidelines of the Agriculture and Resource Management Council of Australia and New Zealand (ARMCANZ 1997).

Groundwater sampling should be undertaken in accordance with *Groundwater Sampling Guidelines* (EPA 2000).

Sampling groundwaters by pumping or bailing the sample to the surface requires special precautions to avoid contamination. All equipment that either enters a bore or carries the water from the bore to the sampling container should be cleaned before each sample is taken. Special care needs to be taken for certain analytical parameters that can be affected by the presence of dissolved gases.

Sampling a waste discharge

The most representative sample of a waste discharge is from a point where the effluent is thoroughly mixed and close to the outlet from the discharging premises. For a licensed discharge, a sampling point will normally be described in the licence, and samples must always be taken from that point.

Use of automatic samplers

Automatic samplers are used to monitor diurnal variations or to collect temporal composite samples from a water body. The probe for these samplers should be placed sufficiently far from both the surface and bottom of the water body so that the sample is not affected by the presence of the air/water or sediment/water interface.

Sampling soils

Sampling and analysis plans should be devised in accordance with the requirements of the *Australian and New Zealand Guidelines for the Assessment of Contaminated Sites* (ANZECC/NH&MRC 1992) and Australian Standard 4482.1 (Standards Australia 1997a) or Australian Standard 4482.2 (Standards Australia 1999). When sampling soils for volatile contaminants, special precautions should be taken to prevent evaporative losses.

Collection of samples should be accomplished with minimal disturbance, using a coring device. The core soil sample should either be immersed into methanol in the field; or the core should be placed into a vial that will also act as a purge vessel in the laboratory. These methods have been shown to provide generally more accurate results than placement of samples into jars (USEPA 1991).

If the soils to be sampled are suspected of being acid sulfate soils or potential acid sulfate soils, the EPA Information Bulletin *Acid Sulfate Soil and Rock* (EPA 1999) provides guidance and further references on sampling and handling.

When sampling from a test pit, samples should be taken from the lowest point first to prevent cross contamination from other sampling points.

Before sampling, vegetation and other non-soil material (including rocks and concrete) should be removed by hand. Any material removed should be weighed and its description recorded.

Sampling sediments

The best locations for sampling sediments are where fine materials accumulate. These are generally confined to areas where there is little or no flow.

Sediment samples can be collected using a number of devices including grabs, scoops, corers, shovels and buckets. When sampling for organic analysis, sampling devices should be constructed from metal. Conversely, when sampling for metals, sampling devices should be constructed from plastic.

Where there is a lack of fine sediment, more than one scoop or grab sample may be necessary to obtain a sufficient amount of material. These samples should be combined and mixed well before processing for analysis.

Sampling wastes

At all times it is important that sampling is carried out so that representative samples are obtained. Sampling wastes can be difficult if the wastes are heterogeneous, contain many different types of waste, or the contamination is not evenly distributed. In these circumstances, it can be useful to keep different types of waste separate (for example by separating the phases in a multi-phase waste), or to separate different portions that contain high levels of contaminants. General guidance on sampling can be obtained from *Pierre Gy's Sampling Theory and Sampling Practice: Heterogeneity, Sample Correctness and Statistical Process Control* (Pitard, 1989) particularly when there are large amounts of waste to be sampled.

Liquid wastes should be handled according to the methods for sampling waters described above. Waste soils should be treated according to the guidelines for soils above.

For solid wastes with particle sizes greater than soils, or non-uniform particle sizes, Australian Standard 1141.3:1996, (Standards Australia, 1996) may be relevant in some cases. Wastes containing biosolids should be handled and treated according to the procedures listed in Appendix C for the individual parameters by which the wastes are to be characterised.

Preserving samples

When biological, chemical or physical changes to the sample may occur between the time it is collected and when it is analysed, it must be either chemically or physically preserved to retard such processes.

Preservation methods vary greatly in their effectiveness and should only be employed when the sample cannot be analysed within a few hours of collection. Preservation should be carried out as soon as possible after sampling.

Recommended preservation methods for waters, wastewaters and groundwaters are given in Appendix A, for soils and sediments in Appendix B, and for wastes in Appendix C.

Freezing

Water and soil samples are best frozen in small amounts sufficient for the determination of one parameter. This procedure avoids repeated thawing and re-freezing if the total analysis is spread over a number of days. Quick freezing with dry ice is recommended.

For water, wastewater and groundwater samples provide sufficient air gap in the container to allow expansion of the liquid.

Thawed samples must be mixed and allowed to reach ambient temperature before any measurements or analysis.

Cooling

Samples that need to be cooled to between 1°C and 4°C should be placed in an insulated container or icebox containing a mixture of water and ice, and checked to ensure that some ice always remains. Alternatively, a maximum/minimum thermometer can be used in the icebox to check that the temperature remained within this range during transport to the laboratory.

Acidification

For water samples, acidification to below pH 2 is used to preserve most trace metals. This reduces precipitation and sorption losses to the container walls. A sample of the acid used, which should be of analytical grade and have low metal content, must be retained for analysis as a blank by the laboratory and correction of the analytical results for any analyte present. For groundwaters, acidification should only be applied to filtered samples.

Reagent addition

Reagents may be added to samples to chemically fix the analytical parameter. Reagents added should be of high grade, and blanks provided to the laboratory so that contamination levels can be checked.

When chemicals are added to a sample to preserve or fix an analytical parameter, it is important to separate procedures for sampling, sample handling and analysis for each parameter, to minimise any risk of cross-contamination. For example, nitric acid used for container preparation and as a preservative for heavy metals analysis can contaminate samples to be analysed for nitrate. Similarly, copper sulfate used for preservation of phenols may contaminate samples for metals analysis.

For heavily contaminated samples, care needs to be taken when adding chemical preservatives that could release hazardous gases. For example, when adding acid to preserve a sample collected for a heavy metal analysis, care should be taken to ensure that the sample does not also contain high concentrations of cyanide which could result in release of hydrogen cyanide gas.

Solvent extraction

A solvent may, at times, be added to extract the analyte from its matrix. For analysis of organic pollutants such as hydrocarbons, PAHs and some pesticides, an initial on-site solvent extraction in the sample container may be necessary. Samples of the solvent and containers used should be submitted for analysis.

Field filtration

Filtration of water samples in the field may be required in the following circumstances.

- Where organic and inorganic contaminants adsorb onto suspended matter in water, wastewater and groundwater samples.
- Where the concentration of dissolved contaminants or the contaminants associated with suspended matter need to be determined.

Filtering should occur immediately after collection and the analysis conducted on the filtered liquid, the particles, or both.

Filtration can be undertaken under gravity or by applying vacuum or pump pressure.

Filters and filtering devices should be cleaned in a similar manner to sample containers, and care taken that contamination is not introduced in the field. Filters from the same batch as used in the field, and the filtering device should be provided to the laboratory so that blank levels can be determined. On-site (between sample) final rinses from filtration equipment should also be submitted to the laboratory as ‘rinsate blanks’ for analysis.

Preserving soil samples

Often soil samples are moist when collected. This moisture can accelerate microbial action, which can change the concentration of some contaminants. In these circumstances, it is recommended to store the soil at 4°C or below.

Labelling and logging

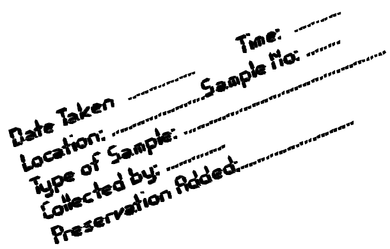
Samples should be adequately described and securely labelled at the sampling site.

The sample container must be labelled to uniquely identify the sample, and the time and location of sampling. Use a solvent based marking pen (preferably black) or similar waterproof means of marking. Any changes to a label should be initialled and dated.

The sample log must show all relevant information, including where (precise location and depth) and when (date and time of day) the sample was taken and other relevant information.

Details of preservatives added (the type, concentration before addition and quantity added) and other pre-treatment applied to the sample must be noted on the label.

An example of a label used for samples is shown below:



A submission sheet must accompany all samples when handed to the laboratory. This contains relevant information about the sample and the nature of the analyses required and is signed off by the person delivering the samples and the person receiving them.

Transporting samples

Transport of the sample to the laboratory should be done as soon as possible after sampling, and within the stipulated holding times (Appendices A, B and C).

Before and during transport, the following precautions must be taken to:

- check that container seals or caps are secured tightly to prevent leakage
- ensure sample labels remain on containers and are not damaged during transit
- store all bottles upright, and
- prevent containers from unnecessary movement during transport, and in particular ensure glass bottles are cushioned to prevent breakage.

When collecting and transporting samples, all possible sources of contamination must be avoided. A few examples are given below:

- vehicle exhausts (hydrocarbons or lead)
- airborne dusts
- ammonia solutions – including cleaning agents – must not be handled or stored in the vicinity of sampling or analytical operations
- smoking during sampling and analytical operations must be avoided –cigarette ash and smoke contain contaminants such as phosphate, nitrate, hydrocarbons, and heavy metals.

If there is concern that contamination has occurred, the sample and container should be discarded, and a fresh sample collected.

Approved samplers

Sampling requires special expertise and must be undertaken by trained people.

Whenever sampling or field analysis is undertaken, it must done within the framework of a well-documented quality system. This applies whether the analysing laboratory is also responsible for the sampling, whether a company monitoring its own wastes or wastewaters does it, or another organisation is contracted to conduct the sampling.

Preferably, sampling should be undertaken by people operating within a laboratory system accredited by the National Association of Testing Authorities (NATA) for sampling. Otherwise, people taking samples must meet the following requirements.

- Samplers must have undertaken face-to-face training by an appropriate body with experience in sampling, and be able to demonstrate that they have the knowledge and ability to safely take, preserve, store and transport samples within the requirements of this Guide. This would include programmed refresher training, with records to be kept on the nature and frequency of training provided.
- The laboratory conducting the analysis is to provide appropriately prepared sample containers and preservatives, for the analytes of interest.
- Sufficient records of the sampling are to be prepared and maintained by the samplers so that the results obtained by the laboratory can be related back to the date, time and location of sampling.

Evidence showing that the above requirements have been satisfied shall be documented.

SAMPLE HANDLING AND PREPARATION CHECKLIST

- ❑ **Ensure that there is good communication between sampling staff and the laboratory on precautions to be taken in the field.**
- ❑ **Observe all safety precautions during sampling, in particular taking care to avoid contact with contaminated samples.**
- ❑ **Ensure that the selection of sample containers, the container pre-treatment procedures (such as washing), the sample preservation procedures and the sample holding times stipulated in this Guide are followed.**
- ❑ **Ensure that, where reagents are added to the sample or the sample is filtered, blanks are collected and delivered to the laboratory for analysis of blanks.**
- ❑ **Take precautions to ensure samples are not contaminated by reagents, polluted samples or environmental sources in the field or during transport, and that samples are secured during transport to avoid damage.**
- ❑ **Complete the sample identification and description on a label attached to the sample and on the submission sheet, including any treatment of the sample undertaken in the field.**

4. ANALYTICAL METHODS AND QUALITY ASSURANCE PROCEDURES

Approved laboratories

Laboratories performing analyses should be accredited by NATA for all the tests conducted. In addition, the laboratory should be experienced and proficient at testing the types of samples, at the concentration ranges required, for the particular program.

Where testing is being undertaken for statutory purposes under the *Environment Protection Act 1970* or the *Pollution or Waters by Oils and Noxious Substances Act 1986*, NATA accreditation of the laboratory is a requirement, unless permission is given by EPA to use a non-accredited laboratory.

Approved analytical methods

Only analytical methods chosen from the approved references listed for each environmental matrix in this chapter should be used. Minor changes can be made to these methods, provided that the changes are of little consequence.

For all methods used, the laboratory needs to demonstrate that it can accurately analyse for the relevant analytes, in the types of environmental samples, and in the concentration range normally encountered. This can be done by either:

- proficiency tests, or
- checking against standard reference materials.

It is also necessary to determine the precision (both reproducibility and repeatability), selectivity, limits of detection, linearity and applicable range of concentrations when using the method.

Procedures that should be followed for method validation are available in *Requirements for the Format and Content of Test Methods and Recommended Procedures for the Validation of Chemical Test Methods* [NATA Technical Note No. 17] (NATA 1997).

For statutory testing, methods not based on any of the methods in the approved references can only be used with prior approval of EPA. Validation of the proposed procedure must be demonstrated before approval can be granted.

It is important that the analyst verifies the suitability of the procedure used for the particular sample type under investigation, before commencing the analysis.

Limits of detection and reporting

It is important that the limits of detection and reporting are reliably established before sampling and analysis are undertaken. A method for estimating the limit of detection and the limit of reporting (also known as the ‘limit of quantitation’) is provided in NATA Technical Note No. 17 (NATA 1997).

The limit of detection is defined as the lowest concentration of analytical parameter in a sample that can be detected, but not necessarily quantitated. The limit of reporting is defined as the lowest concentration of an analytical parameter that can be determined with acceptable precision and accuracy. In practice, the limit of reporting is frequently taken to be ten times the limit of detection (NATA, 1997). However, some laboratories may use limits of reporting that are five times the limit of detection (APHA 1995).

The selected methods should have appropriate detection limits for the objectives of the program. This is particularly relevant when testing ambient waters, as dissolved species are invariably at much lower concentrations than wastewaters. For instance the detection limit for lead using flame atomic absorption spectroscopy is 50 µg/L, whereas using graphite furnace atomic absorption spectroscopy it is 1 µg/L, more suitable for pristine waters. Detection limits may also be affected by interferences.

Waters, wastewaters and groundwaters

For waters, wastewaters and groundwaters methods selected from the standard references listed below* should be used.

1. American Public Health Association 1995, *Standard Methods for the Examination of Water and Wastewater.*
2. US Environmental Protection Agency 1979, *Methods for Chemical Analysis of Water and Wastes*.
3. American Society for Testing and Materials 1992, *Water and Environmental Technology*.
4. US Environment Protection Agency 1978, *Microbiological Methods for Monitoring the Environment, Water and Wastes.*
5. Department of the Environment 1994, *The Bacteriological Examination of Drinking Water Supplies*, Report on Public Health and Medical Subjects, No. 71, Method for the Examination of Waters and Associated Material.
6. Relevant Australian Standards.

Trace analysis

For analysis at very low contractions (at µg/L and below) special precautions need to be taken.

Publications such as USEPA Method 1669 (USEPA 1995) should be referred to for the specifics of sampling at trace levels. For all trace level work, sample container cleanliness must be established before sampling is undertaken. Treating a statistically significant number of containers from any batch by the relevant extraction method and analysing the extract for the analytical parameters of interest should do this.

For guidance on the installation and use of clean rooms and clean workstations see Australian Standards 1386.1–7 (Standards Australia 1989).

Trace level analysis methods for seawaters can be obtained from either *Methods of Seawater Analysis* (Grasshoff 1983), *A Manual of Chemical and Biological Methods for Seawater Analysis* (Parsons 1989) or *A Practical Handbook of Seawater Analysis* (Strickland 1974).

During sampling of seawaters, extreme care should be taken to avoid contamination of the sample by the sampling equipment or boat. The publications listed should be consulted for guidance on choice of equipment and procedures.

In situ measurements

While most of the methods cited above relate to laboratory analyses, they also include field or *in situ* measurements for selected environmental indicators.

In situ measurement provides a rapid means to assess certain aspects of water quality. It has the advantage of overcoming the possibility of contamination or change in sample composition between collection and analysis.

Common *in situ* measurements include pH, temperature, turbidity, dissolved oxygen and conductivity. Some ions, such as fluoride and sulphide can also be determined using ion selective electrodes, although their determination can be subject to matrix interferences.

Ensure field instruments are robust and reliable, and that they are capable of measuring to the appropriate level of accuracy. They must be calibrated with fresh solutions before use. pH and dissolved oxygen meters need to be calibrated before every use. This can be performed either in the laboratory or in the field. The manufacturer's instructions are the best guide for the use of any particular meter; however, meters must be calibrated according to the NATA publications *General Requirements for Registration: Supplementary Requirements:*

* The latest editions of these references at the time of publishing this *Guide* are referenced. Where they are superseded, the most recent edition should be used.

Chemical Testing (NATA 1993) and Technical Note No. 19 (NATA 1994).

The meter must be calibrated over an appropriate range for the samples analysed. If the meter is to be used over a period of several hours, periodic readings of a reference solution must be made to ensure the calibration is stable. If excessive drift is observed, readings taken over the period of drift must be discarded.

While field meters are designed to take a certain level of harsh treatment (such as knocks, vibration, extreme temperature changes), good maintenance and calibration regimes ensure that they produce reliable and accurate data.

Secondary parameters such as temperature salinity, altitude and air pressure may affect certain field measurements. For instance, dissolved oxygen readings are affected by all of the above parameters. If the field meter does not automatically measure and compensate for the secondary parameter, then this parameter must be measured, using the appropriate equipment, and a manual compensation performed. The manufacturer’s instructions should be consulted for correction factors.

Many factors may cause interference when taking field measurements. These interferences cannot be compensated for; in particular, oily films and high levels of suspended solids may cause problems. If the measurements are being taken in unusual situations, the manufacturer’s instructions should be consulted to check whether interference could occur.

Where *in situ* measurements are incorporated into a process or effluent stream to provide continuous monitoring, adequate levels of data validation through frequent calibration checks are required. The manufacturer’s instructions for the meter concerned should be consulted for the appropriate calibration method. Any calibration regime must be based on a sound knowledge of the process and the nature of the effluent stream. Guidance may be obtained from *Process Instruments and Controls Handbook* (Considine 1985).

Radioactivity measurements

Some of the references cited above include methods for the measurement of radioactivity. Other suitable methods for the measurement of gross radioactivity can be found in the international standards ISO 9696:1992 (ISO 1992a) and ISO 9697:1992 (ISO 1992b).

Soils and sediments

For the analysis of soils, *Guidelines for the Laboratory Analysis of Contaminated Soils* (ANZECC 1996) or *Test Methods for Evaluating Solid Wastes: Chemical/ Physical Methods* (USEPA 1997) should be followed. The procedures for quality control, described in the latter document, should also be followed.

For measuring radioactivity in soils, use the methods included in *Eastern Environmental Radiation Facility Radiation Procedures Manual* (Lieberman 1984).

For the analysis of acid sulfate soils or potential acid sulfate soils, EPA Information Bulletin *Acid Sulfate Soil and Rock* (EPA 1999) should be consulted.

Depending on the objectives of the program, it may be necessary to remove interstitial water from the sample by filtration. This may need to be done in the field if the contaminant equilibrium between the solid and liquid phases is dynamic.

As the nature of the soil or sediment can have a significant effect on the behaviour and environmental availability of contaminants, it is often desirable to characterise the soil type, including other relevant information such as pH, ion exchange capacity, clay content, moisture content and permeability

Determination of contaminants in soils and sediments may entail measurement of the total concentration. Alternatively, a bio-available or leachable fraction may be determined. Therefore, the digestion step is of paramount importance in determining the fraction of total contaminants present.

Often it is necessary to determine the permeability or hydraulic conductivity of a soil.

The test methods to be used will vary depending on the range of permeability values likely to be encountered and the purpose for which the measurements are being made. Test methods will, generally be applicable to either laboratory tests or field tests, but not both.

Relevant Codes of Practice, published as part of the EPA Best Practice Environmental Management Series*, contain details of tests to be used to determine soil permeability. For example, the requirements for testing soil percolation rates for septic tank installations are given in *Code of Practice-Septic Tanks* (EPA 1996).

In the absence of a relevant Code of Practice, ASTM Standard D5126–90 (ASTM, 1998) contains references to a number of field tests for soil permeability, and their applicable range of permeability values.

There are also American Society for Testing and Materials (ASTM) Standards (ASTM 1990) and Australian Standards (Standards Australia 1998b) which describe laboratory methods for testing soil permeability. There is some uncertainty about the applicability to field conditions of the results obtained from tests according to these methods. As such, these methods should be treated with some caution if field permeability is to be assessed.

In situ measurements

As for waters, a range of *in situ* measurements may be appropriate for characterising soils, for example, field soil gas measurements using a photo-ionisation analyser. Consult the section on *in situ* measurements above as similar requirements regarding use and calibration apply to waters and to soil samples.

* This series of publications is updated from time to time, and only the latest editions should be used.

Wastes

Procedures to determine total concentrations of a range of contaminants in wastes are listed in *Test Methods for Evaluating Solid Wastes. Chemical/ Physical Methods* (USEPA 1997).

There are a number of other characteristics of wastes that affect their environmental impact, and may need to be measured. They are leachability (the tendency for contaminants to be leached by rain or groundwater), flammability or ignitability, corrosivity and the amount of contained free liquids. Some of the suitable test methods are listed below.

Leachability and leachates

Leachable organics (volatile and semi-volatile), metals and anions (except cyanide) may be determined using the Toxicity Characteristic Leaching Procedure (TCLP), which is method 1311 in Test Methods for Evaluating Solid Wastes. Chemical/ Physical Methods (USEPA, 1997).

Alternatively, Australian Standard 4439.2 (Standards Australia 1997b) can be used for volatile organics, and Australian Standard 4439.3 (Standards Australia 1997c) can be used for semi-volatile organics, metals and anions.

The methods in the Australian Standards are different from the USEPA method in that a wider range of leaching reagents is allowed. All methods are designed to simulate leaching conditions in the environment to determine available pollutants. The choice of leach reagent should be based on the environmental conditions to which the wastes are, or will be, exposed .

Leachable cyanide may be determined by Method 1312, the Synthetic Precipitation Leaching Procedure (USEPA 1997) or by leaching with distilled or de-ionised water only, using the methods in Australian Standard 4439.2 (Standards Australia1997b).

Leachates collected from the environment should be analysed using the methods listed for waters and wastewaters.

Flammability and ignitability

Flammability of liquid wastes may be assessed by determining whether a flash occurs on application of a flame to sample vapours. A suitable procedure is described in ASTM Method D327–96 (ASTM 1992). 'Ignitability' is a characteristic of a waste that once ignited, burns. This characteristic can be measured using Method 1030 in *Test Methods for Evaluating Solid Wastes: Chemical/Physical Methods* (USEPA, 1997).

Corrosivity

'Corrosivity' is defined as the ability of a substance to attack human skin or plant and equipment. Often this is due to extreme acidity or alkalinity, and waste pH is normally tested. Liquid waste pH may be measured directly using a calibrated pH meter. The prescribed test for soils and solid wastes is Method 103 in *Guidelines for the Laboratory Analysis of Contaminated Soils* (ANZECC 1996). To measure corrosivity of a waste towards steel use Method 1110, 'Corrosivity Toward Steel' from *Test Methods for Evaluating Solid Wastes: Chemical/Physical Methods* (USEPA 1997).

Free liquid determination

To determine free liquid use Method 9095A: 'Paint Filter Liquids Test' in *Test Methods for Evaluating Solid Wastes. Chemical/Physical Methods* (USEPA 1997).

Volatile contaminants in soils and wastes

For determination of volatile contaminants in soils and wastes, special precautions must be taken to avoid losses during sampling, transport, storage and analysis.

As samples for volatile analysis cannot be taken from thoroughly homogenised bulk samples, small samples should not necessarily be regarded as representative of the whole material. Therefore, a sufficient number of samples should be taken to confidently obtain an accurate measure of average concentrations.

Samples taken for analysis of volatile components should be separate from those taken for other analytical parameters. This will allow for volatile analysis to be repeated, if necessary, on samples that have not been homogenised or otherwise inappropriately treated.

Volatile components should be determined using the 'purge and trap', procedure. Methods involving measurement of headspace concentrations may be less rigorous, and should only be used for screening soil samples. Use the methods outlined in *Test Methods for Evaluating Solid Wastes: Chemical/Physical Methods* (USEPA 1997) for both these procedures.

Qualitative analysis

Sometimes, it is necessary to identify components in a sample or confirm their presence prior to conducting a quantitative analysis. In such cases, a qualitative test may be used. Texts such as *Spot Tests In Organic Analysis* (Feigl and Anger 1966), *Spot Tests in Inorganic Analysis* (Feigl and Anger 1972) and *Vogel's Qualitative Inorganic Analysis* (Vogel 1996) are useful references.

Commercially available qualitative and semi-quantitative test kits may also be used. But, in either instance, the analyst must be familiar with the limitations of the method used, particularly possible interferences and what factors are likely to contribute to false positive or false negative results. Whenever qualitative tests are used, quality control should be incorporated, including a blank, at least one standard or reference material, and a spike of standard into a sample.

For solid materials that have a limited solubility, x-ray diffraction analysis (XRD) may provide useful information on the identity of compounds present in the sample. However, XRD does suffer from some limitations. Only crystalline substances will give an XRD response. Components representing less that 5% of the sample cannot be identified with any reliability. *Elements of X-ray Diffraction* (Cullity 1978) and *X-Ray Diffraction Procedures: For Polycrystalline and Amorphous Materials*

(Klug and Alexander 1974) are useful references.

Toxicity screening testing

If contaminated samples require screening tests to give an indication of their likely toxicity, the Microtox® is the recommended technique. The use of this technique is described in EPA Scientific series publication SRS 89/012 (Hinwood 1990). Other toxicity screening tests may be used if approval is obtained from EPA.

Quality assurance

A laboratory quality assurance system is a requirement of NATA accreditation, and laboratories should seek to constantly assess their competence by participating, whenever possible, in inter-laboratory proficiency programs. Additional details on quality assurance and quality control are presented in Appendix D.

Analysts receiving samples need to assure themselves that they were collected in appropriate containers and they have been preserved in a manner recommended in this Guide. A statement should be included in the report on whether there have been any departures from the requirements outlined in this Guide.

TEST METHODS CHECKLIST

- ❑ **Select the appropriate method of analysis from those approved in this Guide.**
- ❑ **For field measurements, ensure that meters are calibrated beforehand.**
- ❑ **Ensure that an adequate Quality Assurance regime is in place in the laboratory and field procedures.**
- ❑ **Report analytical data on NATA-endorsed reports, where appropriate.**
- ❑ **Analysts should include a statement in their report that samples have been collected in a manner recommended in this Guide.**

5. REPORTING AND REVIEW OF RESULTS

Analytical reports

The final product of sampling and analysis, the analytical report, must have sufficient information for the end user to make a critical evaluation of its contents. The analytical report format should comply with the NATA requirements.

The following information is usually reported with the analytical result for each parameter determined. This information is either provided by the person taking the sample or by the laboratory and should include:

- identification of the sample (include sample description, location, sample number and unique laboratory number)
- date and time of sampling
- field observations and *in situ* measurements
- field pre-treatment details, if any sample preservation procedure
- reference to analytical method used.
- date of determination
- accurate description of the parameter
- results, in the appropriate units
- notations of any deviation from the sampling or analytical procedures recommended in this Guide.

Analysts should define the quality measured and ensure reporting meets the formats required in the standard method.

The limit of detection for each analyte should be quoted with quantitative test results. Concentrations below the limit of reporting should be quoted as a ‘less than’ (<) figure.

Results are normally reported as mg/L or µg/L for concentrations in solutions, mg/kg or µg/kg for concentrations in solids and organisms/100 mL for concentrations of bacterial organisms in liquids. For radioactivity measurements, the units are Bq/L for concentrations in solutions and Bq/g for concentrations in solids.

It is preferable to report results that are not corrected for spike recovery unless a test method specifically requires analytical results to be reported after correcting for recovery (NATA 1997). A statement of the spike recovery achieved provides the maximum information on the quality of the test result to the recipient of the report.

Reviewing data

All analytical results should be reviewed on receipt by the person or organisation requesting the analysis, and action taken if abnormal or unexpected levels are detected. When reviewing data:

- compare results with those expected and query unusual results
- as a general rule duplicates should agree within 10% and spike recovery values should be between 80–120%. (If quality control results fall outside of this range, query the laboratory)
- identify problems, and
- take appropriate action to address the problems identified.

If monitoring is being undertaken as a discharge licence condition, then whenever the licence emission limits are exceeded, the breach should be reported immediately to EPA, in accordance with the licence conditions. The reasons leading to the breach and action taken to ensure future licence compliance should be included in this report.

REPORTING CHECKLIST
❑ **Analytical reports should include all relevant information**
❑ **Analytical reports should include a statement that samples have been collected in accordance with procedures recommended by this Guide.**
❑ **Detection of abnormal or unexpected concentrations or polluted samples should be reported quickly so that action can be taken to address the problem.**

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APPENDIX A: CONTAINERS, PRESERVATION AND HOLDING PERIODS FOR WATERS, GROUNDWATERS AND WASTEWATERS

Sample containers and their preparation

Selection and preparation of containers, sample pre-treatment, preservation and holding periods must comply with this Appendix, which is based, in part, on AS/NZS 5667.1:1998*. The third column lists typical volumes for a single determination, and should only be used as a guide. To determine very low concentrations that may be present in uncontaminated samples, larger volumes may be required. Typical volumes are dependent on the analytical method used, and the analyst should be consulted prior to sampling on his or her requirements. Unless otherwise stated, the requirements listed are those for quantitative determination. The analyst should always be consulted for advice on the actual sample volumes required when a choice of preservation methods exists in the Table.

Container types, preservation and maximum sample holding times

Analytical parameter	Container	Typical volume (mL)	Preservation procedure	Maximum holding period	Comments
Acidity and alkalinity	Polyethylene or borosilicate glass	500	Fill bottle to exclude air. Immediately store between 1°C and 4°C.	24 hours	Samples should preferably be analysed in the field, particularly if they contain high levels of dissolved gases.
Aluminium	Acid washed glass or acid washed polyethylene	500	Acidify with nitric acid to pH 1 to 2.	28 days	

* *EPA is grateful to Standards Australia for the permission to reproduce information presented in AS/NZS 5667.1:1998 on which this Table is, in part, based.*

Analytical parameter	Container	Typical volume (mL)	Preservation procedure	Maximum holding period	Comments
Ammonia	Polyethylene or glass	500	Store between 1°C and 4°C.	6 hours	When samples containing low levels of ammonia are encountered, special care should be taken to avoid contamination.
			Filter sample on site (0.45 µm cellulose acetate membrane filter) and store between 1°C and 4°C.	24 hours	Pressure filtering is preferred.
			Filter sample on site (0.45 µm cellulose acetate membrane filter) and freeze sample immediately upon collection.	28 days	
Antimony	Acid washed polyethylene or acid washed glass	500	Acidify with nitric or hydrochloric acid to pH 1 to 2.	28 days	Hydrochloric acid should be used for acidification if the hydride generation technique is used for analysis. Acid washed polyethylene, polycarbonate or fluoropolymer containers should be used for determinations at very low concentrations, such as encountered in uncontaminated streams and seawater.
Arsenic	Acid washed polyethylene	500	Acidify with nitric or hydrochloric acid to pH 1 to 2.	28 days	Hydrochloric acid should be used for acidification if the hydride generation technique is used for analysis. Acid washed polyethylene, polycarbonate or fluoropolymer containers should be used for determinations at very low concentrations, such as encountered in uncontaminated streams and seawater.
Barium	Acid washed polyethylene or acid washed glass	500	Acidify with nitric acid to pH 1 to 2.	28 days	
Beryllium	Acid washed polyethylene or acid washed glass	500	Acidify with nitric acid to pH 1 to 2.	28 days	

Analytical parameter	Container	Typical volume (mL)	Preservation procedure	Maximum holding period	Comments
Biochemical oxygen demand (BOD) and Carbonaceous Biological Oxygen Demand (CBOD)	Plastic or glass	1000	Fill bottle to exclude air. Store between 1°C and 4°C in the dark.	24 hours	Do not pre-rinse container with sample. Glass containers should be used for samples with low BOD (<5 mg/L). Nitrification inhibition is not to be implemented when performing the BOD test unless carbonaceous biological oxygen demand (CBOD) is required.
Boron	Polyethylene	100	Fill bottle to exclude air.	28 days	
Bromate	Polyethylene or glass	100	Store between 1°C and 4°C.	7 days	
Bromide	Polyethylene or glass	500	Store between 1°C and 4°C in the dark.	28 days	
Bromine (residual)	Polyethylene or glass	500	Store between 1°C and 4°C in the dark.	24 hours	Samples should be kept out of direct sunlight.
Cadmium	Acid washed polyethylene	500	Acidify with nitric acid to pH 1 to 2.	28 days	Acid washed polyethylene, polycarbonate or fluoropolymer containers should be used for determinations at very low concentrations, such as encountered in uncontaminated streams and seawater.
Calcium	Polyethylene	500	Fill bottle to exclude air. Fill container completely to exclude air, acidify with nitric acid to pH 1 to 2 and store between 1°C and 4°C.	7 days 28 days	Samples of water of pH > 8 or high total carbonate, taken solely for the determination of calcium, magnesium or hardness should be acidified with nitric acid. Acidification permits the determination of calcium and the other metals in the sample.
Carbamates	Solvent washed amber glass	1000	Store between 1°C and 4°C.	28 days	Extract the sample in the container as part of the sample extraction procedure. If the sample is chlorinated, for each 1000 mL of sample, add 80 mg of sodium thiosulfate to the container prior to collection.

Analytical parameter	Container	Typical volume (mL)	Preservation procedure	Maximum holding period	Comments
Carbon dioxide	Polyethylene or glass	500	Fill container completely to exclude air. Store between 1°C and 4°C.	24 hours	Determination preferably carried out in the field.
Carbon, total organic (TOC)	Amber glass with PTFE cap liner	100	Acidify with sulphuric acid to pH 1 to 2, store between 1°C and 4°C in the dark.	7 days	
Chemical oxygen demand (COD)	Glass or polyethylene	100	Fill container completely to exclude air. Acidify with sulphuric acid to pH 1 to 2 and store between 1°C and 4°C in the dark. Freeze (only if polyethylene containers are used).	7 days 28 days	Glass containers are preferable for samples with low COD (<5 mg/L).
Chloramine	Polyethylene or glass	500	Keep sample out of direct sunlight.	Begin analysis within five minutes of sample collection.	Analysis should be carried out in the field.
Chlorate	Polyethylene or glass	500	Store between 1°C and 4°C.	7 days	
Chloride	Polyethylene or glass	100	None required.	28 days	
Chlorine (residual)	Polyethylene or glass	500	Keep sample out of direct sunlight.	Begin analysis within five minutes of sample collection.	Analysis should be carried out in the field.

Analytical parameter	Container	Typical volume (mL)	Preservation procedure	Maximum holding period	Comments
Chlorine dioxide	Polyethylene or glass	500	Keep sample out of direct sunlight.	Begin analysis within five minutes of sample collection.	Analysis should be carried out in the field.
Chlorite	Polyethylene or glass	500	Store between 1°C and 4°C.	24 hours	
Chlorophyll	Polyethylene or amber glass	Filter on site	Filter and snap freeze filter paper in the dark. Store in the dark between 1°C and 4°C.	28 days 24 hours	Samples should be filtered at the time of collection. The volume filtered will depend largely on the amount of particulate matter present and expected chlorophyll concentrations. Filters must not be touched with fingers and all sample handling apparatus must be kept free of acids, as this causes degradation of chlorophylls to phaeophytins. Filter and process promptly upon reception at the laboratory and ensure minimum exposure to light. Use polyethylene containers only when snap freezing sample filters.
Chromium (total)	Acid washed polyethylene or acid washed glass	500	Acidify with nitric acid to pH 1 to 2.	28 days	Acid washed polyethylene, polycarbonate or fluoropolymer containers should be used for determinations at very low concentrations, such as encountered in uncontaminated streams and seawater.
Chromium (VI)	Acid washed polyethylene or acid washed glass	500	Store between 1°C and 4°C.	24 hours	Acid washed polyethylene, polycarbonate or fluoropolymer containers should be used for determinations at very low concentrations, such as encountered in uncontaminated streams and seawater. Sample containers should be thoroughly rinsed after acid washing to ensure there is no residual nitric acid present.

Analytical parameter	Container	Typical volume (mL)	Preservation procedure	Maximum holding period	Comments
Cobalt	Acid washed polyethylene or acid washed glass	500	Acidify with nitric acid to pH 1 to 2.	28 days	Acid washed polyethylene, polycarbonate or fluoropolymer containers should be used for determinations at very low concentrations, such as encountered in uncontaminated streams and seawater.
Coliforms (total)	Polyethylene or glass, sterile and containing pre-sterilised sodium thiosulfate solution sufficient to give 100 mg/L in preserved sample	500	Store between 1°C and 4°C.	6 hours	Do not rinse container before taking sample. Leave approximately 2 cm head space. In exceptional circumstances, such as sampling in a remote location, a holding period of up to 24 hours is acceptable.
Colour	Polyethylene or glass	500	Store between 1°C and 4°C and in the dark.	48 hours	
Conductivity	Polyethylene or glass	100	Fill container completely to exclude air. None required. Fill container completely to exclude air. Store between 1°C and 4°C.	24 hours 28 days	Preferably on site or *in situ*. The meter must be calibrated prior to use.
Copper	Acid washed polyethylene or acid washed glass	500	Acidify with nitric acid to pH 1 to 2.	28 days	Acid washed polyethylene, polycarbonate or fluoropolymer containers should be used for determinations at very low concentrations, such as encountered in uncontaminated streams and seawater.
Cyanide	Polyethylene or glass	500	If no interfering compounds are present, then add sodium hydroxide solution to pH ≥ 12. Store between 1°C and 4°C in the dark.	24 hours	If hydrogen sulphide is present it can be removed by adding cadmium nitrate after adjusting the pH of the sample to pH ≥ 12. If oxidising agents are present, add ascorbic acid. Excess ascorbic acid has been added when a starch iodide paper fails to turn blue on contact with the sample.

Analytical parameter	**Container**	**Typical volume (mL)**	**Preservation procedure**	**Maximum holding period**	**Comments**
E. coli	Plastic or glass, sterile and containing pre-sterilised sodium thiosulfate solution sufficient to give 100 mg/L in preserved sample	500	Store between 1°C and 4°C.	6 hours	Do not rinse container before taking sample. Leave approximately 2 cm head space. In exceptional circumstances, such as sampling in a remote location, a holding period of up to 24 hours is acceptable.
Fluoride	Polyethylene	500	None required.	28 days	
Hardness	Polyethylene	200	Fill bottle to exclude air. Immediately store between 1°C and 4°C or acidify with nitric acid to pH 1 to 2.	7 days	Water samples of high pH (pH > 8) or high total carbonate taken solely for the determination of hardness, calcium or magnesium should be acidified with nitric acid.
Herbicides (acidic)	Glass with PTFE cap liner	1000	Acidify with hydrochloric acid to pH 1 to 2 and store between 1°C and 4°C. Do not completely fill container.	14 days	If residual chlorine is present, add 80 mg sodium thiosulfate per 1000mL of sample.
Herbicides (non-acidic)	Amber glass with PTFE cap liner	1000	Store between 1°C and 4°C.	7 days	If residual chlorine is present, add 80 mg sodium thiosulfate per 1000mL of sample.
Herbicides (glyphosate)	Polypropylene	1000	Store between 1°C and 4°C in the dark.	14 days	If residual chlorine is present, add 80 mg of sodium thiosulfate per litre of sample.
Hydrazine	Glass	500	Acidify with 100 mL of concentrated hydrochloric acid for every litre of sample and store in the dark.	24 hours	

Analytical parameter	Container	Typical volume (mL)	Preservation procedure	Maximum holding period	Comments
Hydrocarbons,	Solvent rinsed glass with PTFE faced liner	500	Solvent extract on site with the appropriate solvent where practical.	Analyse as soon as possible but within 7 days	If residual chlorine is present, add 80 mg sodium thiosulfate per 1000mL of sample. Store in an area free of solvent fumes.. For purge and trap analysis collect samples in duplicate in 40 mL vials with PFTE faced septum Store in an area free of solvent fumes.
		80	Fill container to completely exclude air and store between 1°C and 4°C.	Analyse as soon as possible but within 24 hours	
		80	Fill container to completely exclude air and acidify to pH 1 to 2 with hydrochloric acid and store between 1°C and 4°C.	Analyse as soon as possible but within 7 days	. .
Hydrocarbons (qualitative identification)	Solvent washed glass with PTFE cap liner	500	Do not completely fill container. Acidify with sulphuric or hydrochloric acid to pH 1-2. Store between 1°C and 4°C.	7 days	Do not pre-rinse container with sample. This procedure may also be suitable for unreactive hydrocarbon derivatives.
Hydrocarbons (halogenated)	Solvent rinsed glass with PTFE cap liner	250	Fill container to completely exclude air and acidify to pH 1 to 2 with hydrochloric acid and store between 1°C and 4°C.	Analyse as soon as possible but within 7 days	If residual chlorine is present, add 80 mg sodium thiosulfate per 1000mL of sample. For purge and trap analysis collect samples in duplicate in 40 mL vials with PFTE faced septum Store in an area free of solvent fumes.
Iodide	Polyethylene or glass	500	Store between 1°C and 4°C.	28 days	
Iodine	Glass	500	Store between 1°C and 4°C in the dark.	24 hours	

Analytical parameter	Container	Typical volume (mL)	Preservation procedure	Maximum holding period	Comments
Iron (II)	Acid washed polyethylene or acid washed glass	500	Fill container completely to exclude air. Acidify with hydrochloric acid to pH 1 to 2.	24 hours	Do not use nitric acid to wash sample containers.
Iron (total)	Acid washed polyethylene or acid washed glass	500	Acidify with nitric acid to pH 1 to 2.	28 days	
Lead	Acid washed polyethylene or acid washed glass	500	Acidify with nitric acid to pH 1 to 2.	28 days	Acid washed polyethylene, polycarbonate or fluoropolymer containers should be used for determinations at very low concentrations, such as encountered in uncontaminated streams and seawater.
Lignins and tannins	Glass	250	Store between 1°C and 4°C.	7 days	
Lithium	Polyethylene	500	None required.	28 days	If samples for lithium are also to be determined for other metals they can be acidified without effecting the analysis.
Magnesium	Polyethylene	500	Fill bottle to exclude air. Fill bottle to exclude air. Acidify with nitric acid to pH 1 to 2 and store between 1°C and 4°C.	7 days 28 days	Water samples of high pH (pH > 8) or high total carbonate taken solely for the determination of magnesium, calcium or hardness should be acidified with nitric acid.
Manganese	Acid washed polyethylene or acid washed glass	500	Acidify with nitric acid to pH 1 to 2.	28 days	Acid washed polyethylene, polycarbonate or fluoropolymer containers should be used for determinations at very low concentrations, such as encountered in uncontaminated streams and seawater
Mercury	Acid washed borosilicate glass	500	Immediately acidify the unfiltered sample to pH <2 with nitric acid and add potassium dichromate to give 0.05% m/V final concentration.	28 days	For contaminated waters more oxidant may be required. Reference should be made to the analyst for further instruction. Acid washed fluoropolymer or borosilicate containers with a fluoropolymer lined lid should be used for determinations at very low concentrations, such as encountered in uncontaminated streams and seawater.

Analytical parameter	Container	Typical volume (mL)	Preservation procedure	Maximum holding period	Comments
Molybdenum	Acid washed polyethylene or acid washed glass	500	Acidify with nitric acid to pH 1 to 2.	28 days	Acid washed polyethylene, polycarbonate or fluoropolymer containers should be used for determinations at very low concentrations, such as encountered in uncontaminated streams and seawater
Monocyclic aromatic hydrocarbons (MAHs)	Solvent rinsed glass with PTFE faced liner	500	Fill container to completely exclude air. Acidify to pH 1 to 2 with hydrochloric acid and store between 1°C and 4°C.	Analyse as soon as possible but within 7 days	If residual chlorine is present, add 80 mg sodium thiosulfate per 1000mL of sample. Store in an area free of solvent fumes. For purge and trap analysis collect samples in duplicate in 40 mL vials with PFTE faced septum. If the sample is chlorinated, for each 40 mL of sample add 3 mg of sodium thiosulfate. Store in an area free of solvent fumes.
Nickel	Acid washed polyethylene or acid washed glass	500	Acidify with nitric acid to pH 1 to 2.	28 days	Acid washed polyethylene, polycarbonate or fluoropolymer containers should be used for determinations at very low concentrations, such as encountered in uncontaminated streams and seawater.
Nitrate	Polyethylene or glass	500	Store between 1°C and 4°C. Filter on site (0.45 µm cellulose acetate membrane filter) and freeze sample immediately upon collection.	24 hours 28 days	
Nitrite	Polyethylene or glass	200	None required. Freeze sample immediately upon collection.	Analyse in the field 48 hours	
Nitrogen (all forms)					See individual entries under Ammonia, Nitrogen (Kjeldahl), Nitrate and Nitrite.
Nitrogen (Kjeldahl)	Polyethylene or glass	500	Store between 1°C and 4°C. Freeze sample immediately upon collection.	24 hours 28 days	The sample may be acidified with sulphuric acid to pH <2 if required for other analyses.

Analytical parameter	Container	Typical volume (mL)	Preservation procedure	Maximum holding period	Comments
Nitrogen (total)	Polyethylene or glass	500	Store between 1°C and 4°C. Freeze sample immediately upon collection.	24 hours 28 days	
Odour	Polyethylene or glass	500	Store between 1°C and 4°C.	6 hours	
Organic carbon (total)					See Carbon, total organic (TOC)
Oxygen, dissolved (DO)	Polyethylene or glass	300	None required.	On site or *in situ*	Excessive turbulence should be avoided to minimise oxygen entrainment. The meter must be calibrated on the day of use and preferably checked after measurements.
Pesticides (carbamates)					See entry under Carbamates
Pesticides (nitrogen-containing, organo-chlorine and organo-phosphate)	Solvent washed glass with PTFE cap liner	1000 to 3000	Do not completely fill container. Store between 1°C and 4°C.	7 days	Solvent extract on-site with the appropriate solvent where practical. Extract the sample in the container as part of the sample extraction procedure. If residual chlorine is present, add 80 mg sodium thiosulfate per 1000mL of sample.
pH	Polyethylene or borosilicate glass	100	None.	Determine *in situ*	The meter must be calibrated on the day of use and preferably checked after measurements.
Phenolic compounds	Solvent washed glass (amber) with PTFE cap liner	1000	Store between 1°C and 4°C in the dark. Do not completely fill sample container.	24 hours	Do not pre-rinse container with sample. Oxidising agents such as chlorine may be neutralised by the addition of excess sodium arsenite or iron (II) sulfate prior to acidification. If residual chlorine is present, add 80 mg sodium thiosulfate per 1000mL of sample. Sulphur dioxide or hydrogen sulphide may be removed by briefly aerating the acidified sample.

Analytical parameter	Container	Typical volume (mL)	Preservation procedure	Maximum holding period	Comments
			Acidify to pH 1 to 2 with orthophosphoric acid, hydrochloric acid or sulphuric acid. Store between 1°C and 4°C and store in dark.	21 days	
Phosphate (ortho or dissolved)	Polyethylene or glass	50 to 300	Filter on site (0.45 µm cellulose acetate membrane filter). Store between 1°C and 4°C. Filter on site (0.45 µm cellulose acetate membrane filter) and freeze upon collection.	24 hours 28 days	

Analytical parameter	Container	Typical volume (mL)	Preservation procedure	Maximum holding period	Comments
Phosphate (total)	Polyethylene or glass	300	Store between 1°C and 4°C. Freeze immediately upon collection. Acidify with sulphuric or hydrochloric acid to pH 1 to 2 and store between 1°C and 4°C in the dark.	24 hours 28 days 28 days	The use of the acid preservation method should not be used for the persulfate oxidation method of analysis.
Polychlorinated biphenyls (PCBs)	Solvent washed glass with PTFE cap liner	1000 to 3000	Store between 1°C and 4°C in the dark. Do not completely fill sample container.	7 days	Do not pre-rinse container with sample. Extract on-site, where practical, in the container as part of the sample extraction procedure. If residual chlorine is present, add 80 mg sodium thiosulfate per 1000mL of sample.
Polycyclic aromatic hydrocarbons (PAHs)	Solvent washed glass with PTFE cap liner	1000	Store between 1°C and 4°C in the dark. Do not completely fill sample container.	7 days	Do not pre-rinse container with sample. Extract on-site, where practical, in the container as part of the sample extraction procedure. If residual chlorine is present, add 80 mg sodium thiosulfate per 1000mL of sample.
Potassium	Polyethylene	500	None required. Acidify with nitric acid to pH 1 to 2.	28 days 28 days	Acidification permits the determination other metals in the sample.
Radioactivity (specific forms)					See Table 2 in AS/NZS 5667.1:1998.
Radioactivity, α and β activity (gross)	Polyethylene or glass	1000	Acidify with nitric acid to pH 1 to 2. Fill container to exclude air.	28 days	

Analytical parameter	Container	Typical volume (mL)	Preservation procedure	Maximum holding period	Comments
Selenium	Acid washed polyethylene or acid washed glass	500	Acidify with nitric or hydrochloric acid to pH 1 to 2.	28 days	Acid washed polyethylene, polycarbonate or fluoropolymer containers should be used for determinations at very low concentrations, such as encountered in uncontaminated streams and seawater.
Silica (reactive)	Polyethylene	200	Store between 1°C and 4°C. Filter in the field (0.45 µm cellulose acetate membrane filter) and store between 1°C and 4°C.	24 hours 28 days	 Turbid river samples should be filtered in the field (0.45 µm cellulose acetate membrane filter).
Silver	Acid washed polyethylene (wrapped in foil) or acid washed amber glass	100	Acidify with nitric acid to pH 1 to 2.	28 days	Acid washed polyethylene, polycarbonate or fluoropolymer containers should be used for determinations at very low concentrations, such as encountered in uncontaminated streams and seawater.
Sodium	Polyethylene	500	None required. Acidify with nitric acid to pH 1 to 2.	28 days 28 days	 Acidification permits the determination of other metals in the sample.
Solids (dissolved)	Polyethylene or glass	500	Store between 1°C and 4°C. Fill container to exclude air.	24 hours	Also known as ‘filtrable residues’ and ‘total dissolved solids’ or TDS.
Solids (suspended)	Polyethylene or glass	500	Store between 1°C and 4°C.	24 hours	Also known as ‘non-filtrable residues’ and ‘suspended solids’ or SS.
Solids (total)	Polyethylene or glass	500	Store between 1°C and 4°C.	24 hours	
Sulfate	Polyethylene or glass	200	Store between 1°C and 4°C.	7 days	
Sulphide (dissolved)	Polyethylene	50 by pipette	Add 10 mL copper-DMP reagent.	12 hours	
Sulphide (total)	Polyethylene or glass	500	None required. Completely fill bottle without aeration.	Determine on site	

Analytical parameter	**Container**	**Typical volume (mL)**	**Preservation procedure**	**Maximum holding period**	**Comments**
			Fix samples immediately on site by adding 2 mL of 10% (m/v) zinc acetate solution per 500 mL of sample. Store between 1°C and 4°C.	7 days	
Sulfite	Polyethylene	1000	Fix in the field by addition of 10 mL of 2.5% EDTA solution per 1 L.	7 days	
Surfactants (anionic)	Glass rinsed with methanol	500	Acidify with sulphuric acid to pH 1 to 2, fill container to exclude air and store between 1°C and 4°C. Add 40% formaldehyde solution to give 1% (v/v) final concentration and store between 1°C and 4°C.	48 hours 96 hours	Glassware should not previously have been washed with detergent.
Surfactants (cationic)	Glass rinsed with methanol	500	Fill container to exclude air and store between 1°C and 4°C.	48 hours	Glassware should not previously have been washed with cationic detergent.
Surfactants (non-ionic)	Glass rinsed with methanol	500	Fill container to exclude air. Add 40% formaldehyde solution to give 1% (v/v) final concentration and store between 1°C and 4°C.	28 days	Glassware should not previously have been washed with detergent.
Temperature	None required		Not applicable.	Determine *in situ*	

Analytical parameter	Container	Typical volume (mL)	Preservation procedure	Maximum holding period	Comments
Tin	Acid washed polyethylene or acid washed glass	500	Acidify with nitric acid to pH 1 to 2.	28 days	Acid washed polyethylene, polycarbonate or fluoropolymer containers should be used for determinations at very low concentrations, such as encountered in uncontaminated streams and seawater
TOC					See entry for Carbon, total organic
Total dissolved solids (TDS)					See entry for Solids (dissolved)
Total solids					See entry for Solids (total)
Total suspended solids (TSS)					See entry for Solids (suspended)
Toxicity (by Microtox®)	As for the suspected toxicant	200	Store between 1°C and 4°C.	As for the suspected toxicant	
Trihalomethanes	Solvent washed glass vial with PTFE faced septum	100	Fill container to exclude air.	14 days	If residual chlorine is present, for each 40 mL of sample add 3 mg of sodium thiosulfate.
Turbidity	Polyethylene	100	None required. Store between 1°C and 4°C in the dark.	On site 24 hours	
Uranium	Acid washed polyethylene or glass	500	Acidify with nitric acid to pH 1 to 2.	28 days	Acid washed polyethylene, polycarbonate or fluoropolymer containers should be used for determinations at very low concentrations, such as encountered in uncontaminated streams and seawater
Vanadium	Acid washed polyethylene or glass	500	Acidify with nitric acid to pH 1 to 2.	28 days	Acid washed polyethylene, polycarbonate or fluoropolymer containers should be used for determinations at very low concentrations, such as encountered in uncontaminated streams and seawater

Analytical parameter	Container	Typical volume (mL)	Preservation procedure	Maximum holding period	Comments
Zinc	Acid washed polyethylene or glass	500	Acidify with nitric acid to pH 1 to 2.	28 days	Acid washed polyethylene, polycarbonate or fluoropolymer containers should be used for determinations at very low concentrations, such as encountered in uncontaminated streams and seawater

APPENDIX B: CONTAINERS, PRESERVATION AND HOLDING PERIODS FOR SOILS AND SEDIMENTS

Sample containers and their preparation

The requirements are taken from Table 3.1 of ANZECC *Guidelines for the Laboratory Analysis of Contaminated Soils* (1996)*. Unless otherwise specified, samples should be stored refrigerated between 1°C and 4°C.

The analyst should always be consulted for advice on the actual sample sizes required.

Container types, preservation and maximum sample holding times

Analytical parameter	**Container**	**Preservation procedure**	**Maximum holding period**	**Comments**
Acid sulfate soils	Plastic bag	Exclude as much air as is possible from the bag and seal. Freeze the sample in the field using dry ice or a portable freezer.	24 hours for submission to the laboratory 14 days for analysis	Drying of the sample at 80°C – 85°C must commence as soon as possible after reception at the laboratory. If the presence of monosulphides is suspected, the sample must be freeze-dried.
Asbestos	Glass or LDPE	Store between 1°C and 4°C.	48 hours	Polypropylene containers are unsuitable.
Bromide (water soluble)	Polyethylene or glass	None.	7 days	Air dry
Carbon, organic	Glass	Store between 1°C and 4°C in the dark.	7 days	Air dry
Cation exchange capacity and exchangeable cations	Acid washed polyethylene	None.	6 months	Air dry
Chloride (water soluble)	Polyethylene or glass	If field moist, store between 1°C and 4°C.	7 days	Field moist or air dry

Analytical parameter	**Container**	**Preservation procedure**	**Maximum holding period**	**Comments**
Cyanide	Polyethylene or glass	Store between 1°C and 4°C in the dark.	7 days	Field moist
Electrical conductivity	Polyethylene or glass	None.	7 days	Air dry
Fluoride	Polyethylene	If moist, store between 1°C and 4°C.	7 days	Field moist or air dry
Leachable metals and semi-volatile organics	As for the analytical parameter of interest (see below)	As for the analytical parameter of interest.	No preservatives to be added prior to leaching. Metals 6 months Anions 7 days Hydrocarbons (including Total Petroleum Hydrocarbons and PAHs) 14 days Pesticides, organochlorine 14 days Pesticides, other 14 days Phenolics 14 days Polychlorinated biphenyls 28 days Other 14 days	As for the analytical parameter of interest (see below).
Leachable volatile organics	As for the analytical parameter of interest	Store between 1°C and 4°C in the dark.	7 days	
Mercury	Acid washed polyethylene	Store between 1°C and 4°C in the dark.	28 days	Field moist
Metals (except mercury)	Acid washed polyethylene	If moist, store between 1°C and 4°C.	6 months	Field moist or air dry
Moisture content	Polyethylene or glass (As for the analytical parameter of interest)	Store between 1°C and 4°C.	7 days, and on the same day as sample extraction for other analytical parameters.	Field moist
Net acid generating potential				See entry for acid sulfate soils

Analytical parameter	**Container**	**Preservation procedure**	**Maximum holding period**	**Comments**
Organics, semi-volatile	Solvent rinsed glass	Store between 1°C and 4°C in the dark.	14 days	Field moist
Organics, volatile	Solvent rinsed glass	Store between 1°C and 4°C in the dark.	14 days	Field moist
pH	Polyethylene or glass	None.	7 days	Air dry
Sulfate	Polyethylene or glass	If moist, store between 1°C and 4°C.	7 days	Field moist or air dry
Sulphide	Polyethylene or glass	Add sufficient 1 molar zinc acetate to fully cover soil surface and allow minimal headspace. Store between 1°C and 4°C.	7 days	Field moist
Sulphur – total	Polyethylene or glass	If moist, store between 1°C and 4°C.	7 days	Field moist or air dry

APPENDIX C: CONTAINERS, PRESERVATION AND HOLDING PERIODS FOR CONCENTRATED LIQUID WASTES, SLUDGES AND SOLID WASTES, OTHER THAN SOILS AND SEDIMENTS

Where the sample is being collected to determine a specific component, the following containers and sample handling procedures should be followed. Other procedures apply when the sample is being collected for a general identification (See the second Table, at the end of this Appendix).

Additional details on sampling for soils and sediments can be obtained from USEPA Publication: *Test Methods for Evaluating Solid Waste: Volume 1A Laboratory Manual Physical/Chemical Methods,* USEPA Publication No SW-846, Third Edition, Final Update III (1997)), or its latest update.

Aqueous trade wastes should be handled in accordance with the requirements set out in Appendix A.

Analytical parameter	Container	Preservation procedure	Maximum holding period
Antimony	Acid washed polyethylene or acid washed glass	For solid samples, store between 1°C and 4°C. For liquid samples, acidify to pH<2 with nitric acid.	6 months 6 months
Arsenic	Acid washed polyethylene or acid washed glass	For solid samples, store between 1°C and 4°C.	6 months
		For liquid samples, acidify to pH<2 with nitric acid.	6 months
Asbestos	Glass or LDPE	Store between 1°C and 4°C.	6 months
Barium	Acid washed polyethylene or acid washed glass	For solid samples, store between 1°C and 4°C. For liquid samples, acidify to pH<2 with nitric acid.	6 months 6 months
Cadmium	Acid washed polyethylene or acid washed glass	For solid samples, store between 1°C and 4°C. For liquid samples, acidify to pH<2 with nitric acid.	6 months 6 months

Analytical parameter	Container	Preservation procedure	Maximum holding period
Carbon, total organic (TOC)	Polyethylene or glass (glass is preferable)	For liquid samples, acidify to pH < 2 using sulphuric acid or hydrochloric acid. Store between 1°C and 4°C in the dark.	28 days
Chloride	Polyethylene or glass	None.	28 days
Chromium (total)	Acid washed polyethylene or acid washed glass	For solid samples, store between 1°C and 4°C. For liquid samples, acidify to pH<2 with nitric acid.	6 months 6 months
Chromium (VI)	Polyethylene or glass	For solid samples, store between 1°C and 4°C. For liquid samples, store between 1°C and 4°C.	28 days until extraction and 4 days after extraction. 24 hours
Copper	Acid washed polyethylene or acid washed glass	For solid samples, store between 1°C and 4°C. For liquid samples, acidify to pH<2 with nitric acid.	6 months 6 months
Cyanide	Polyethylene or glass	For solid samples, store between 1°C and 4°C in the dark. For liquid samples, if oxidising agents are present add an excess of 0.6 g ascorbic acid per litre (excess ascorbic acid has been added when a starch iodide paper fails to turn blue on contact with the sample) and adjust pH>12 with 50% sodium hydroxide. Store between 1°C and 4°C in the dark.	7 days 14 days
Dioxins and furans	Solvent washed glass with PTFE-lined cap	For solid samples, store between 1°C and 4°C.	14 days until extraction and 40 days after extraction

Analytical parameter	Container	Preservation procedure	Maximum holding period
	Solvent washed amber glass with PTFE-lined cap	For liquid samples, store between 1°C and 4°C. If residual chlorine is present, add 80 mg sodium thiosulfate per 1000mL of sample.	30 days until extraction and 45 days after extraction
Hydrocarbons (halogenated)	Solvent washed glass with PTFE-lined cap	For solid samples, store between 1°C and 4°C.	14 days until extraction and 40 days after extraction
	Solvent washed amber glass with PTFE-lined cap	For liquid samples, store between 1°C and 4°C. If residual chlorine is present, add 80 mg sodium thiosulfate per 1000mL of sample.	7 days until extraction and 40 days after extraction
Lead	Acid washed polyethylene or acid washed glass	For solid samples, store between 1°C and 4°C.	6 months
		For liquid samples, acidify to pH<2 with nitric acid.	6 months
Mercury	Acid washed polyethylene or acid washed glass	For solid samples, store between 1°C and 4°C.	28 days
		For liquid samples, acidify to pH<2 with nitric acid.	28 days
Metals (except mercury and chromium (VI))	Acid washed polyethylene or acid washed glass	For solid samples, store between 1°C and 4°C.	6 months
		For liquid samples, acidify to pH<2 with nitric acid.	6 months
Nitrate	Polyethylene or glass	For liquid samples, store between 1°C and 4°C.	48 hours
Polychlorinated biphenyls (PCBs)	Solvent washed glass with PTFE-lined cap	For solid samples, store between 1°C and 4°C.	14 days until extraction and 40 days after extraction
	Solvent washed amber glass with PTFE-lined cap	For liquid samples, store between 1°C and 4°C.	7 days until extraction and 40 days after extraction
Pesticides and herbicides (organochlorine)	Solvent washed glass with PTFE-lined cap	For solid samples, store between 1°C and 4°C.	14 days until extraction and 40 days after extraction

Analytical parameter	Container	Preservation procedure	Maximum holding period
	Solvent washed amber glass with PTFE-lined cap	For liquid samples, store between 1°C and 4°C.	7 days until extraction and 40 days after extraction
Pesticides and herbicides (organophosphate)	Solvent washed glass with PTFE-lined cap	For solid samples, store between 1°C and 4°C.	14 days until extraction and 40 days after extraction
	Solvent washed amber glass with PTFE-lined cap	For liquid samples, adjust the samples to pH 5-8 using sodium hydroxide or sulphuric acid.	7 days until extraction and 40 days after extraction
pH	Polyethylene or glass	None.	For solid samples 7 days
	Polyethylene or glass	None.	For liquid samples 6 hours
Phenols	Solvent washed glass with PTFE-lined cap	For solid samples, store between 1°C and 4°C.	14 days until extraction and 40 days after extraction.
	Solvent washed amber glass with PTFE-lined cap	For liquid samples, store between 1°C and 4°C. If residual chlorine is present, add 80 mg sodium thiosulfate per 1000mL of sample.	7 days until extraction and 40 days after extraction
Phthalate esters	Solvent washed glass with PTFE-lined cap	For solid samples, store between 1°C and 4°C.	14 days until extraction and 40 days after extraction
	Solvent washed amber glass with PTFE-lined cap	For liquid samples, store between 1°C and 4°C.	7 days until extraction and 40 days after extraction
Polycyclic aromatic hydrocarbons (PAHs)	Solvent washed glass with PTFE-lined cap	For solid samples, store between 1°C and 4°C.	14 days until extraction and 40 days after extraction.
	Solvent washed amber glass with PTFE-lined cap	For liquid samples, store between 1°C and 4°C. If residual chlorine is present, add 80 mg sodium thiosulfate per 1000mL of sample.	7 days until extraction and 40 days after extraction
Residues, volatile	Polyethylene or glass	Store between 1°C and 4°C.	7 days

Analytical parameter	Container	Preservation procedure	Maximum holding period
Selenium	Acid washed polyethylene or acid washed glass	For solid samples, store between 1°C and 4°C.	6 months
		For liquid samples, acidify to pH<2 with nitric acid.	6 months
Sulfate	Polyethylene or glass	For solid samples, store between 1°C and 4°C.	6 months
		For liquid samples, store between 1°C and 4°C.	28 days
Sulphide	Polyethylene or glass	For solid samples, fill the surface of the solid with 1 M zinc acetate until moistened. Store between 1°C and 4°C and store headspace free.	6 months
		For liquid samples, add 4 drops 1 M zinc acetate per 100 mL, adjust pH to >9 using 6 M sodium hydroxide. Fill bottle completely and stopper with minimum aeration. Store between 1°C and 4°C.	7 days
Zinc	Acid washed polyethylene or acid washed glass	For solid samples, store between 1°C and 4°C.	6 months
		For liquid samples, acidify to pH<2 with nitric acid.	6 months

Where the sample is being collected for a general identification, then the following procedures should be followed.

Analytical parameter	Container	Preservation procedure	Maximum holding period
Concentrated wastes	Glass with a fluoropolymer cap	Store at 1°C and 4°C.	14 days
Aqueous samples	Glass with a fluoropolymer cap	Store at 1°C and 4°C and adjust pH <2 with hydrochloric acid.	7 days

Analytical parameter	**Container**	**Preservation procedure**	**Maximum holding period**
Solids and sludges	Glass with a fluoropolymer cap	Store at 1°C and 4°C.	7 days

APPENDIX D: QUALITY ASSURANCE SYSTEMS

Quality assurance procedures are mandatory for NATA accreditation. The recommended methods (see Chapter 4) contain detailed guidance on appropriate QA/QC systems, and these should be followed.

The terms ‘quality assurance’ (QA) and ‘quality control’ (QC) are often confused. In terms of laboratory analysis activities, they are defined below.

Quality assurance

Quality assurance (QA) is all of the actions, procedures, checks and decisions undertaken to ensure the accuracy and reliability of analysis results. For example: routine procedures ensure proper sample control, data transfer, instrument calibration; proper decisions are required to select and properly train staff, select equipment and analytical methods; and day-to-day judgments result from regular scrutiny and maintenance of the laboratory system.

Any of the following publications could be used in developing a QA program:

1. Australian and New Zealand Environment and Conservation Council, *Guidelines for the Laboratory Analysis of Contaminated Soils*, Chapter 2 (ANZECC 1996).
2. American Public Health Association, *Standard Methods for the Examination of Water and Wastewater*, Method 1020 (APHA 1995).
3. US Environment Protection Agency, *Test Methods for Evaluating Solid Waste*, SW-846, Chapter 2 (USEPA 1997).
4. National Association of Testing Authorities, *Guide to Development of a Quality System For a Laboratory* (NATA 1995a).

Quality control

Quality control (QC) is those parts of QA which serve to monitor and measure the effectiveness of other QA procedures compared with previously decided objectives. These may include measurement of the quality of reagents, cleanliness of apparatus, accuracy and precision of methods and instrumentation, and reliability as implemented daily in the laboratory.

For more information, readers are referred to documentation available from NATA. In particular, Technical Note No. 23 (NATA, 1995b).

QC procedures

Analysts should implement the following QC steps with each analytical batch, or with each twenty samples, whichever is the smaller.

Analysis blank – determination of the contribution to the analytical signal by reagents, glassware, etc. The contribution measured should be subtracted from the gross analytical signal for each analysis, before calculation of each sample’s measured concentration.

Replicate Analysis – repeated analysis of at least one sample from the batch.

Laboratory Control Samples – comprise a control matrix (for example deionised or tap water) or a replicate portion of a sample under analysis, fortified with components representative of the analytical parameter class. Recovery check portions should be fortified at concentrations that are easily quantified, but within the range of concentrations expected for real samples.

Surrogate Spikes – known additions to each sample, blank and matrix spike or reference sample of compounds that are similar to the analytical parameters of interest in terms of:

- extraction,
- recovery through clean-up procedures,

and

- response to chromatographic or other determination,

but which:

- are not expected to be found in real samples,
- will not interfere with quantification of any analytical parameter of interest,

and

- may be separately and independently quantified.

Surrogate spikes are added to the analysis portion before extraction. The purpose of surrogates is to provide a means of checking that no gross errors leading to significant analytical parameter losses have occurred at any stage of the procedure.

In the case of organic analyses, the surrogate spike compounds may be deuterated, alkylated or halogenated analogues, or structural isomers of compounds under analysis. They should be added for each analysis by chromatographic analysis.

Internal Standards – are added to samples after all extraction, clean-up and concentration steps. The addition is a constant amount of one or more compounds with similar qualities to surrogate compounds.

The purpose of internal standards is to check the consistency of the analytical step (for example, injection volumes, instrument sensitivity and retention times for chromatographic systems) and provide a reference against which results may be adjusted in case of variation.

Use of internal standards is required for chromatographic analysis of organics.

Reference Materials **–** are homogeneous materials that have been rigorously characterised by several different procedures. They may be prepared in-house or obtained from commercial suppliers. Reference materials should be certified and traceable to a recognised authority. A reference material of comparable matrix should be analysed with each batch of samples.

QC records

Records of the results of QC procedures should be maintained to establish method reliability, confidence intervals for analysis results, and trends in precision and accuracy. NATA accreditation means that analytical methods and QA systems are regularly reviewed. However, no QA system is perfect. As the user of the service, any organisation having analyses performed is entitled to question the analytical service regarding methods and QA procedures.