Water quality assessment - issues from a laboratory management perspective

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Abstract
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WATER QUALITY ASSESSMENT – ISSUES FROM A LABORATORY MANAGEMENT PERSPECTIVE

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ABSTRACT

This paper considers issues relating to the measurement of water quality parameters in the laboratory, especially an external (usually commercial) laboratory. Many organizations now use testing laboratories for water quality measurements, a process that has advantages and some limitations. The interaction between the testing laboratory and the organization requiring the data is crucial, and this paper looks at some aspects where a full appreciation of the role of each partner is important. These include limits of detection and reporting, measurement uncertainty, sample storage and preservation times, and various quality control procedures.

INTRODUCTION

Water quality is hard to define specifically as the determination of good quality depends very much on the water user. Nevertheless, assessment of water quality will normally involve measurement of some combination of physical, chemical and biological parameters. While a number of measurements can be completed in the field or at the sampling site, many require samples to be analysed in the laboratory. Some organizations carry out such analyses within their own facilities, but many others send the waters samples to an external (usually commercial) laboratory. This use of external laboratories has the advantage that there is no need to employ professional and technical staff, purchase and maintain what is often expensive equipment, and the costs involved can usually be accurately determined in advance. A typical commercial laboratory will receive hundreds of samples per day and is set up to handle most of these in a routine way, with appropriate accreditation in place, and well-established methods and quality control procedures.

The pressure is continuously on laboratories to produce high quality information with an ever-increasing set of guidelines and standards being introduced to the assessment of the environment (including water quality). Guidelines are established to guide decisions on limitations of use for water, and are often presented as ranges of values (triggers) where actions are required. It is important to note that guideline values do not often account for any uncertainty in the measurement of a parameter and the legal interpretation of results may not therefore be straightforward. For example, if a parameter has a guideline value of 10 units and a laboratory determines that a sample has a value of 10.5±1 units, does this sample fall within the guideline? This issue is one that will need further consideration by those responsible for developing guidelines and for the legal interpretation of them.

Competition amongst laboratories maintains constant commercial pressure to minimise costs but to maximise quality and service. Dramatic improvements in these aspects have been driven by technological change, particularly with instrumentation, as well as quality systems and data handling capabilities. Concurrent with this, the number and rigour of guidelines and standards for environmental assessment have generally increased. To some degree these trends are related. The ANZECC 2000 Guideline default values for metals in freshwater, that were significantly lower than the ANZECC 1992 values, were introduced as a result of improved research into the response of biota to metals, of changes in the philosophy of the guidelines, and also because of the widespread availability of multi-element parts per billion instrumentation such as Inductively Coupled Plasma Mass Spectrometers (ICP-MS). Laboratory technology and operational changes effect how we evaluate ecological change and the health of the environment.

A final introductory point to note is that laboratories only analyse the samples provided to them. Many will advise on sample collection and provide appropriate containers and advice on sample handling, but it is important to be aware of the variability of natural water bodies and the sampling may be the step in the whole process that limits the overall quality and utility of the information gained from the sampling and analysis exercise. A fuller discussion of this important area can be found in the relevant Australian Standard (AS, 1998) and related publications.

This paper examines several issues that frequently arise in discussions between environmental measurement laboratories and their customers, including costs, uncertainty in results, limits of detection and reporting, quality control of data, preservation and storage of samples.

Costs
Laboratory costs associated with testing water samples can vary enormously, and the costs are often not directly related to the purchase price of the major equipment used, as other issues like level of technical skill, use of expensive materials and extent of sample pre-treatment are also important. For example, pesticide analyses are usually around $60-80 per sample where the major equipment (GC/MS) costs about $100,000, while a discrete nutrient analyser costs about $80,000, with analyses costing about $15-25 per nutrient, and for metals in water using a ICP-MS costing $250,000 enables analyses to be completed at about $5-8 per element per sample. Laboratories often give attractive rates for customers who use their services regularly and provide large numbers of samples in a batch. Other factors affecting costs are the required turn-around time, detection limit requirements and, occasionally, difficult sample matrices.

Detection Limits
In reporting the results of analyses, analysts will often provide information on detection limits, but it is important to note that different limits may be reported. Data users should be check which ‘detection limit’ is provided with the laboratory report if this is important for their interpretation. The Method Detection Limit (MDL) is usually derived from analyzing 7 replicates, and is the minimum concentration of an analyte that can be measured and reported with 99 percent confidence that the analyte concentration is greater than zero as determined by a specific laboratory. The Practical Quantitation Limit (PQL) is normally 5 x the MDL, and represents a concentration able to be detected by good laboratories during routine conditions. The PQL is also called the Limit of Reporting (LOR), (Estimated Quantitation Limit) EQL, (Limit of Quantitation) LOQ, (Minimum Quantitation Limit) MQL.

PQLs often have to be raised when dealing with real and complex samples rather than individual component solutions. Examples where this is often necessary include matrix interference of salt for metals, high sulfur for organochlorines, and highly coloured waters when analyzing for nutrients. PQLs may also be raised depending on the dilution required.

Duplicates
The use of duplicates is common in good analytical assessments. In this a sample is split into two and each separate is analyzed, and the results assist in method performance assessment. The frequency of duplicate analyses is 1 per 10 samples or process batch. The Relative Percentage Difference (RPD) (also called relative percent precision) is used to assess what difference between duplicates is acceptable.

\[ RPD = \frac{\text{highest} - \text{lowest}}{\text{average}} \times 100 \]

If the RPD is less that 5 x PQL, e.g., for chloride, duplicates gave 1 mg/L and 5mg/L (RPD-133%) when the PQL was 1 mg/L – any duplicate result between 1 and 5 mg/L is acceptable. On the other hand, if any RPD is greater than 5 x PQL, e.g., chloride values of 55 mg/L and 85 mg/L (RPD = 43%), any RPD between 0-50% is acceptable. There may be exceptions to these guidelines and laboratory supervisors have some discretion.

Matrix Spikes and Surrogates
Matrix spikes are components added to samples to monitor method performance and determine if matrix interferences exist, e.g., Al interference in F analyses. Spikes must be added to the samples before any digestion or extraction procedures are initiated. The recommended frequency of use is 1 per 20 samples or process batch. Acceptable recoveries are in the range 70 – 130% inorganics/metals, 60 – 140% most organics. Failed spikes (i.e., unsatisfactory recoveries) may not necessarily be bad news – they tell a story. For example, charcoal in soil sample may adsorb a PAH spike indicating that PAH concentrations as measured for that soil may not be representative. When spikes are used, they should only be reported to the client on whose samples the spikes were used (i.e., never report another clients spikes).

Surrogates are analytes whose chemical behaviour is similar to that of the target compound(s) but which are not normally found in the environment, that are added to samples to determine the performance of a given procedure. They are added in known quantities and provide an extra check increasing the confidence in the result. Surrogates must be added before any extraction is initiated, and the acceptance recovery range is generally 60-140% for most organics.

Laboratory Control Samples and Blind Duplicates
Laboratories attempt to evaluate their performance and provide confidence in the results by using control samples; these can be either a reference material (the answers for which have been rigorously determined) or a blank spike. Such controls should be analyzed every 20
samples or process batch. They are also valuable as a backup if interferences prevent a matrix spike from working.

Users of analytical laboratories can also assess performance with regard to their samples. This can be facilitated by splitting samples and submitting the separate batches to different laboratories. National Environment Protection Measures (NEPM) for contaminated soil samples recommend that this be done for one in every 20 samples where the samples are split in the field at the time of sampling and submitted simultaneously to 2 laboratories. The difference between primary and secondary laboratories should generally be <30% (recommended by NEPM), but there are exceptions.

Another way of assessing performance is to submit blind replicates to the laboratory, i.e., a sample is split on site during sampling and the separate samples are sent to the laboratory with different sample codes. The duplicates should be from the same sampling point, removed from the ground/water in a single action, and mixed well. NEPMs recommend that this be done for about 1 sample in 20. It is important that the testing laboratory does not know the identity of any blind duplicated submitted.

**Measurement Uncertainty (MU)**

The international vocabulary of basic and general terms in metrology considers measurement uncertainty (MU) as 'A parameter associated with the result of a measurement that characterises the dispersion of the values that could reasonably be attributed to the measured quantity – or basically – how sure is the laboratory of the result?' It is a range containing the 'true value' with a stated level of confidence. For example, if a laboratory is testing soil samples for lead and has a MU of 10%; if a particular sample on testing gives a result of 20 ppm, then the laboratory is 95% confident that the concentration of Pb is somewhere between 18 and 22 ppm.

The MU depends on the matrix and PQL. For example, the MU for organochlorine pesticides is about 80% when the measured value is about 0.001 ppm, but this drops to 15% when the measured value is about 0.1 ppm. A small MU indicates that the result is relatively reliable, but with larger MUs, caution should be exercised in the interpretation of the result. The biggest contributor to MU is often the sampling.

**Preservation and Storage Times**

Many components of natural samples change with time after sampling due to evaporation, chemical reactions, adsorption onto the walls of containers, etc. It is therefore very important to sample correctly and preserve the samples in such a way that such changes are minimized in the period between sampling and analysis. Appropriate preservation techniques can extend the time that samples can be held between sampling and analysis without significant change in the analyte of interest. Different agencies (e.g., USEPA, APHA, ANZECC, Australian Standards, NEPM) recommend different preservation techniques and storage times. For example, for BTEX in water, the Australian Standard recommends a maximum storage time of 7 days, while USEPA and APHA recommend 14 days. It is important that storage times should allow for the time required by the laboratory to carry out the tests.

Holding times can vary enormously e.g., for chlorine in waters the time is 15 minutes while for iron(II) it is recommended that samples be tested on site or quickly acidified to pH<2 with no headspace in the sample bottle and analysed within 24 hours. Other samples can be held for several months without loss of integrity. Some other preservation and holding time details are given in Table 1.

In the development of water quality sampling/testing programs, early discussions between the data user and the laboratory to be used to generate the data will avoid significant issues in the design of the whole sampling and testing regime that could lead to later difficulties in data analysis and interpretation.

<table>
<thead>
<tr>
<th>Test</th>
<th>Volume (mL)</th>
<th>Preservation</th>
<th>Recommended Holding Time</th>
<th>Reference*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkalinity</td>
<td>100</td>
<td>Cool to 4°C</td>
<td>14 days</td>
<td>APHA</td>
</tr>
<tr>
<td>Chlorophyll-a</td>
<td>500</td>
<td>Freeze</td>
<td>28 days</td>
<td>APHA</td>
</tr>
<tr>
<td>Cyanide</td>
<td>50</td>
<td>pH-12 (NaOH) + cool to 4°C</td>
<td>14 days</td>
<td>APHA</td>
</tr>
<tr>
<td></td>
<td></td>
<td>+ dark</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fluoride</td>
<td>20</td>
<td>Nil</td>
<td>28 days</td>
<td>AS</td>
</tr>
<tr>
<td>Hexavalent Cr</td>
<td>100</td>
<td>Cool to 4°C</td>
<td>1 day</td>
<td>AS</td>
</tr>
<tr>
<td>Microorganisms</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Metals</td>
<td>50</td>
<td>pH&lt;2 (HNO₃)</td>
<td>6 months</td>
<td>USEPA</td>
</tr>
<tr>
<td>N-ammonia</td>
<td>20</td>
<td>Site filter and freeze</td>
<td>28 days</td>
<td>AS</td>
</tr>
<tr>
<td>N-nitrate</td>
<td>20</td>
<td>Site filter and freeze</td>
<td>28 days</td>
<td>AS</td>
</tr>
<tr>
<td>N-Nitrite</td>
<td>20</td>
<td>Cool to 4°C</td>
<td>2 days</td>
<td>APHA</td>
</tr>
<tr>
<td>N-total</td>
<td>120</td>
<td>Freeze</td>
<td>28 days</td>
<td>AS</td>
</tr>
<tr>
<td>Phosphorus-T</td>
<td>50</td>
<td>Freeze</td>
<td>28 days</td>
<td>AS</td>
</tr>
<tr>
<td>Phosphate</td>
<td>20</td>
<td>Filter and freeze</td>
<td>28 days</td>
<td>AS</td>
</tr>
<tr>
<td>Sulfate</td>
<td>100</td>
<td>Cool to 4°C</td>
<td>28 days</td>
<td>APHA</td>
</tr>
</tbody>
</table>


**CONCLUSIONS**

The use of ‘external’ or ‘commercial’ laboratories is now an integral part of the water quality assessment programs of many agencies. These laboratories carry out large numbers of analyses for numerous components in waters from many different sources. The results produced are widely used in water use planning decisions. Most laboratories have well-established procedures in place for controlling the quality of their work, but those requesting the analyses also play an important role by ensuring that sampling has been carried out in an appropriate way and that samples have been properly handled and stored prior to delivery to the laboratory. It is also good for water quality assessors to set in place their own quality control procedures. Strong cooperation between laboratories and their clients will ensure that accurate and reliable data is used in the assessment and management of the quality of our water resources.
REFERENCES


THE ROLE OF THE SOUTHERN RIVERS CATCHMENT MANAGEMENT AUTHORITY IMPROVING THE HEALTH OF WATERWAYS IN SOUTHERN NSW

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ABSTRACT

The Southern Rivers Catchment Management Authority (SRCMA) is one 13 authorities established by the New South Wales government in 2004 to enhance the management of natural resources in the State. The region covered by the SRCMA is more than 29,000 km² and extends from Stanwell Park to the Victorian border and inland to Braidwood, Bombala and Jindabyne. This paper presents a brief overview of the Authority’s Catchment Action Plan priorities with respect to water quality, and some indication of targets. Several case studies are also outlined.

INTRODUCTION

The Southern Rivers Catchment Management Authority (SRCMA) is one 13 authorities established by the New South Wales government in 2004 to enhance the management of natural resources in the State. The SRCMA operates within a region that covers more than 29,000 km² and extends three nautical miles offshore. It is bounded by Stanwell Park to the north, and includes all coastal catchments south from there to the Victorian border. It extends westward to include the catchments of the Snowy, Genoa and Shoalhaven Rivers. Cities and towns in the region include Wollongong, Shellharbour, Kiama, Nowra, Ulladulla, Braidwood, Bateman’s Bay, Moruya, Narooma, Bermagui, Bega, Merimbula, Bombala and Jindabyne (Figure 1).

About 450,000 people live in the region, but as the region is a popular tourist attraction, the population almost doubles during the summer holiday season. Population levels are trending strongly upwards in most of the coastal settlements as identified in the South Coast Regional Strategy (NSW Department of Planning, 2007 B).