2nd Queensland On-site Wastewater Treatment Symposium
Queensland University of Technology
28th October 2004

MEETING THE CHALLENGE OF MONITORING TO GET REPRESENTATIVE SAMPLES

Robert A. Patterson Ph.D.

Presented as an oral paper to

Queensland On-site Wastewater Treatment Symposium: A Practitioners' Forum
Jointly sponsored by Initiative for Sustainable Living, Queensland University of Technology and the Department of Local Government, Planning, Sport and Recreation. Held at Queensland University of Technology, 28th October 2004.

Lanfax Laboratories, PO Box W90 Armidale NSW 2350
Email: robpatte@ceinternet.com.au

Reference: Patterson, R.A. (2004) Meeting the Challenge of Monitoring to Get Representative Samples. *Queensland On-site Wastewater Treatment Symposium: A Practitioners' Forum.* Jointly sponsored by Initiative for Sustainable Living, Queensland University of Technology and the Department of Local Government, Planning, Sport and Recreation. Held at Queensland University of Technology, 28th October 2004. pp 16-19.

2nd Queensland On-site Wastewater Treatment Symposium
Queensland University of Technology
28th October 2004

MEETING THE CHALLENGE OF MONITORING TO GET REPRESENTATIVE SAMPLES

Robert A. Patterson Ph.D.
Lanfax Laboratories, PO Box W90 Armidale NSW 2350
Email: robpatte@ceinternet.com.au

ABSTRACT

The requirements for obtaining an accurate soil or water sample require consideration of sample collection, packaging, transport and analysis. Inadvertent errors in the field sampling techniques or sample containers cannot be corrected by the laboratory, irrespective of the laboratory's proficiency. Understanding the various sources of sampling error can be valuable in limiting those errors and deriving a sample that truly represents the larger mass being sampled. This paper examines several sources of error in water sampling and suggests some considerations when planning a monitoring program.

Keywords
accuracy, chain-of-custody, precision, sample collection, sample variation, soil samples, water samples

INTRODUCTION

There is often an assumption that the results of environmental monitoring can simply be made by assessing a number of discrete soil and/or water samples taken at specific sites at various times over the monitoring period. Samples are dispatched to a laboratory accredited by the National Association of Testing Authorities (NATA) and the results are returned in a couple of weeks. In many instances the Environment Protection Authority (EPA) or Health Department require a chain-of-custody form as part of the procedure. The choices of analytical methods are often left to the laboratory to conform to their accredited methods or may be dictated in regulations. Sampling may seem to be simple but there are some precautions that must be taken into account, often well before the samples are taken.

SAMPLING LOCATIONS

Perhaps the most abused component of environmental monitoring is the actual collection of the representative sample. You need to ask these questions before you attempt to take the sample - Why? Who? When? How? Where? The answer to each question will indicate the sampling method, the sample container, the time of sampling, the location of the sampling point and who is competent to take the samples.

Using Figure 1, let's look at sampling location. For a biochemical oxygen demand (BOD_5) sample from this treatment lagoon, the sample can be taken on the windward side or the leeward side, from just on the surface or at some predetermined depth.

Figure 1 Numerous locations for water sampling

Is it taken in the clear water of the pond or among the vegetative matter? It is important that a protocol be established for such sampling where significant variance can occur during the day and from day to day, or over periods of weeks or months.

SAMPLE CONTAINERS AND PRESERVATIVES

In Figure 1, you are required by an EPA licence to – "take a monthly grab sample from the discharge to the wastewater treatment facility and analyse for pH, EC, soluble phosphorus, total nitrogen and metals. What day of the week will the sample be taken? What type of container will be used? How full will the sample containers be? Do you need any preservative in the sample bottle? And so the questions go on! If you don't have valid answers then it doesn't really matter which laboratory does the analysis, the risk of sampling error remains high and accuracy or precision of measurement is irrelevant.

Table 1. Sample containers and preservation of water samples

(After AS/NZS 5667-1998)

Determinand	Type of container	Typical volume (mL)	Filling technique	Preservation	Maximum recommended holding time
Ammonia	Plastic or glass	500		Refrigerate	6 h
				Filter to 0.45um and refrigerate	24 h
BOD_5	Plastic or glass	1000	Do not pre-rinse, fill completely to exclude air	Refrigerate, store in dark	24 h
Copper	P(AW), G(AW)	100		Acidify with nitric acid to <pH 2	1 month
Phosphorus, dissolved	Plastic or glass	50		Filter to 0.45 um, refrigerate	24 h
Electrical conductivity	Plastic or glass	100	Fill completely to exclude air	None	24 h
				Refrigerate	1 month

The requirements for a soil sample are less onerous but the soil must be placed in a clean container (or plastic bag) and dispatched to the laboratory as soon as possible. In the event of a delay in sending the sample to the laboratory, it may be necessary to refrigerate or air-dry the air sample. There are specific sample preservation requirements for acid sulphate soils. It is important to check with the laboratory as to protocols they have.

Timing of sample collection

A water sample collected in Armidale on Monday afternoon, packed in an esky with an ice brick, cannot be dispatched until Tuesday, simply because there are no freight transfers out of Armidale on Mondays. By the time the sample leaves Armidale on Tuesday, 12 noon for road transport, or 5 pm for air dispatch to Sydney, the sample may be up to 24 h old and a further 24 h before receipt in the laboratory, usually about 10 am the following morning. Under these conditions the sample may not conform to AS/NZS 5667-1998 for holding period. The alternative is to collect the sample on the same day as dispatch.

A sample to be analysed for faecal coliforms is collected on Friday morning in Armidale and dispatched in a chilled container by air that afternoon. Unless the laboratory has a Saturday receipt and ability to run the 24 h test over the weekend, the sample could be three days old by Monday's return to work. Surely the timing of sample collection, subsequent dispatch and laboratory work need to be factored into the monitoring program rather than set on some arbitrary calendar date.

CHAIN-OF-CUSTODY

The value of a chain-of-custody report may have more legal standing than assessment value. A chain-of-custody report accompanies the sample, the consignee receiving a dispatch docket from the transport company. So where does the sample sit until it is collected? Could it sit in the sun? Who is the driver? Is the sample always under security? How many times does the esky change vehicles?

When the esky reaches the NATA laboratory the receiver should note that the esky is sealed and upon opening assess the condition of the sample, estimating whether the sample is at reduced temperature (chilled), at ambient temperature or at elevated temperature.

The chain-of-custody report is then completed and faxed back to the sender. So what does all this bureaucracy mean? Only that the sample has been sent and dispatched and possibly no one has tampered with the sample in the interim (if seal is intact). Obviously once the sample is received, the protocols of sample receipt and subsequent sampling conform to best management practices.

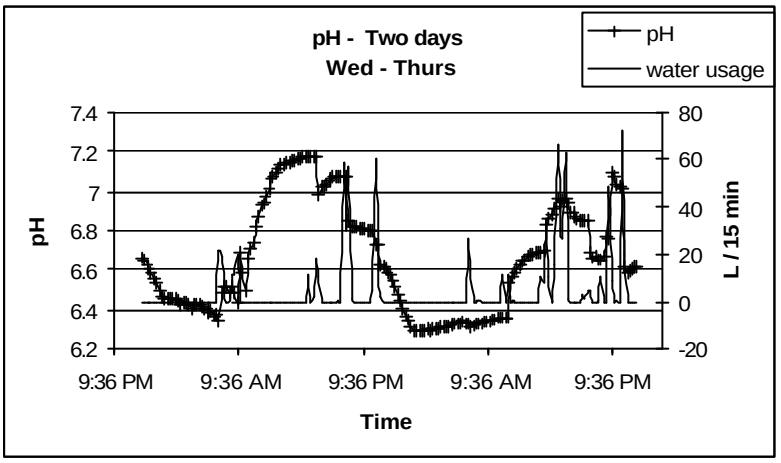

Figure 2 Daily variation in pH in septic tank

Temporal variations

While some water samples may not vary significantly throughout the day, others can change quite rapidly depending upon the upstream activities. The septic tank effluent undergoes considerable change throughout the day because of the use of water in the house. Figure 2 shows a two day measurement of pH from the outlet of a single dwelling septic tank, measurements taken at 15 minute intervals. It is clear that a grab sample may not be representative of the greater volume of water discharged from the tank,

ASSESSING LABORATORY RESULTS

There are inter-laboratory variations in the results of tests performed by different NATA registered laboratories. These differences can be accounted for by sample preparation, deterioration of sample between dispatch and analysis, operator error, and reporting error. As an example, in a recent NATA proficiency testing program (sub-program 432, December 2003) the variation in two samples tested for total phosphorus are given in Table 2. It is obvious a wide variation in results can be obtained. So how do we interpret this variation? It simply means that sending a split sample to two laboratories could derive two different values.

Table 2. Variation in results for total phosphorus across 108 participating laboratories

Analyte	Sample	No. results	Lower limit (mg/L)	Median (mg/L)	Upper limit (mg/L)	Acceptable (mg/L)	Coeff. Variation
Total Phosphorus	1	108	1.59	1.98	2.37	1.72 – 2.24	6.6%
	2	108	0.57	0.78	0.99	0.64 – 0.92	9.0%

(After: NATA, 2003)

The possible variation in total phosphorus across certified laboratories for sample 1 is from 1.72 to 2.24 mg/L (possible 13% error). Add to this the probable errors from sampling and it is clear that variations of greater than 20% are a reality. Eliminating sampling error will minimize this disparity.

CONCLUSION

There are numerous variations in sample collection, packaging, transportation and analysis that can confuse the real value of a sample, that is impinge upon the accuracy of the results. We must take all necessary steps to reduce these sources of error by having sampling protocols in place and following predetermined steps to regularly test these protocols.

REFERENCES:

AS/NZS 5667-1998 *Water Quality – Sampling Part 1*. Guidance on the design of sampling programs, sampling techniques and the preservation and handling of samples. Standards Australia and Standards New Zealand.

National Association of Testing Authorities. *Report No. 432 Waters Proficiency Testing Sub-Program 70*. NATA Sydney. Report dated December 2003

Patterson, R.A (2003) Temporal Variability of Septic Tank Effluent in *Proceedings of On-site '03 Conference: Future Directions for On-site Systems* by R.A. Patterson & M.J. Jones (Eds). Published by Lanfax Laboratories, Armidale ISBN 0-9579438-4-1, pp 305-312