Applying Principles of Measurement Uncertainty (MU) to Remediation Monitoring

Phil Heaton, P.Chem.
Maxxam Analytics Inc.

Phil.Heaton@maxxamanalytics.com

Abstract

- *Analytical data is frequently used to monitor remediation projects. Response to remediation techniques is measured by plotting decreasing contaminant concentrations over extended periods of time. In some cases, end points are predicted based on extrapolation of analytical data to predict target concentrations or theoretical endpoints. The accuracy of the estimates of remediation endpoints is predicated on the quality and quantity of data used to prepare the extrapolation. Measurement uncertainty (MU) can contribute to the overall quality of the data as well as the accuracy of the estimates of remedial endpoints. Measurement uncertainty can be estimated for all analytical parameters by using replicate data and statistical techniques. Quantification of analytical measurement uncertainty has been regulated in Canadian environmental laboratories since 2003. This presentation will discuss extending the concept of measurement uncertainty to include field replicates and multiple sampling events. Inclusion of these variables provides options for applying measurement uncertainty boundaries or confidence limits to estimates of remediation effectiveness and prediction of remediation endpoints. The paper includes descriptions of the statistical techniques and how they can be applied to remediation projects. The paper will also include a discussion and examples of measurement uncertainty components such as accuracy, repeatability, reproducibility and confidence intervals.*

Outline

- What is Measurement Uncertainty (MU)?
- Evolution of MU within Canadian Environmental Laboratories
- Reporting and interpretation of MU
- Analytical measurements in remediation monitoring
- Impact of MU on the decision process
- Components of MU
- Increasing confidence
- Field impacts on measurements - examples
- Expanding MU to include field duplicates
- “Fit For Purpose”
- Summary

What is Measurement Uncertainty and how is it applied?

- Measurement uncertainty (MU) acknowledges that no measurements can be perfect.
- MU is a parameter that describes the expected range of the combined errors.
- MU associated with remediation monitoring is critical for process control and prediction of end-points.
- MU associated with compliance monitoring measurements is critical for risk assessment and regulatory compliance.

Evolution of Measurement Uncertainty in Canada

- Canadian environmental laboratories are accredited to international standard ISO 17025.
  - ISO17025: General Requirements for the Competence of Testing and Calibration Laboratories
- ISO 17025 includes a requirement for the ability to report MU.
- Several approaches exist for the estimation of MU.
  - Statistical approaches are the most common and are usually defensible.
- Audits that included MU began in 2002 and became mandatory in 2003.

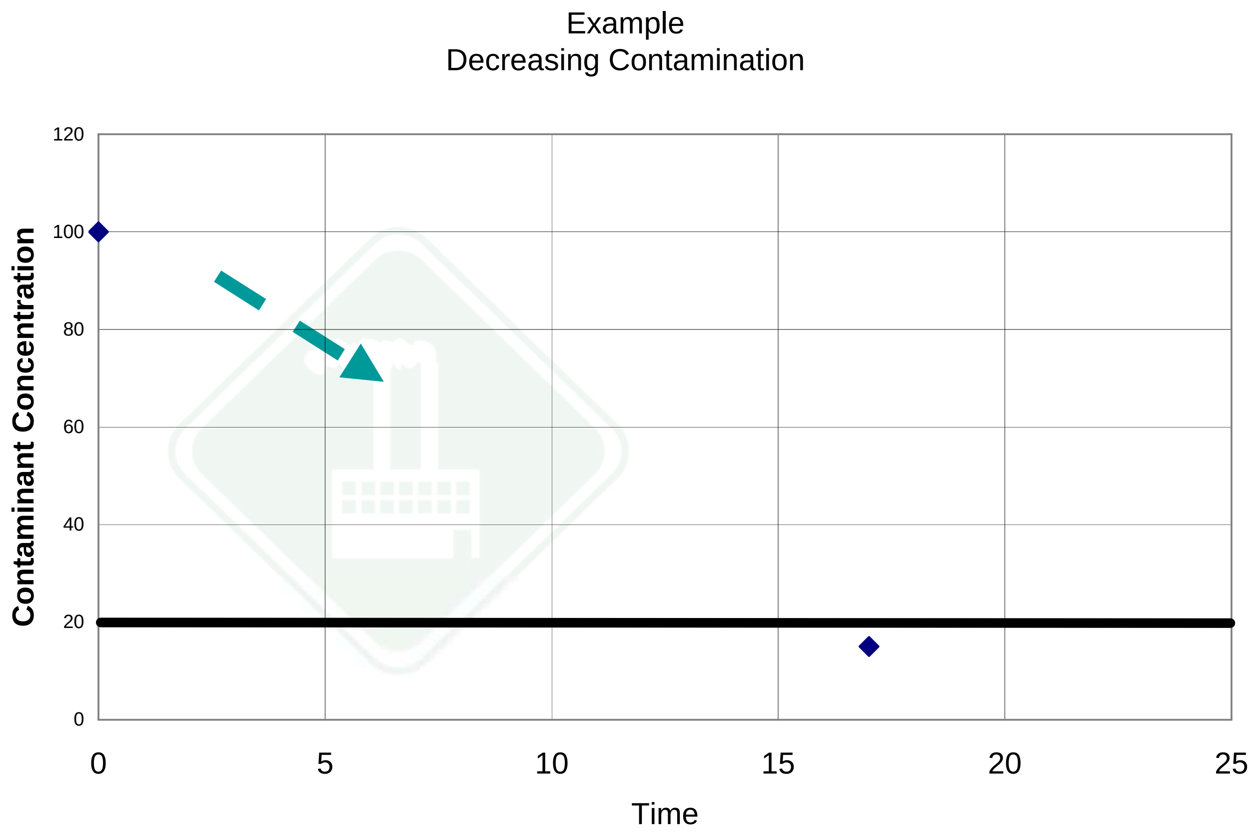
Reporting and Interpretation of Measurement Uncertainty

Maxxam ID		720977			
Sampling Date		02/02/2005			
	Units	Sample #1	MU	DL	QC Batch

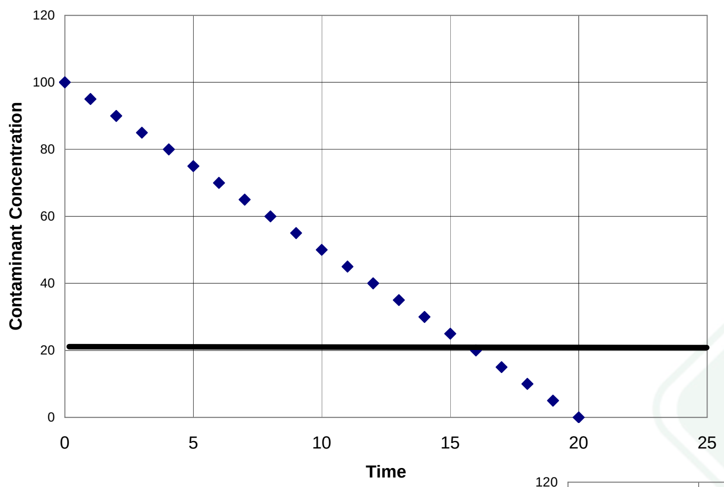
Nutrients					
Total Ammonia (N)	mg/L	12.2	+/- 1.2	0.01	688392
Total Kjeldahl Nitrogen	mg/L	23.1	+/- 3.2	0.05	688391
Total Phosphate (P)	mg/L	2.91	+/- 0.25	0.003	689719

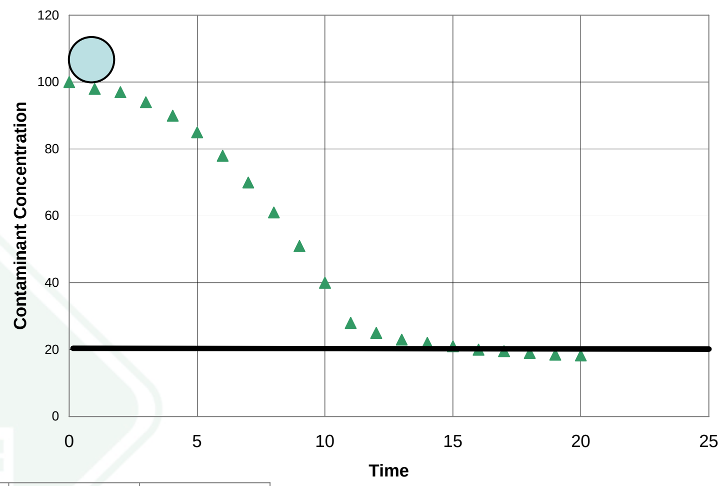
Applying Analytical Measurements to Remediation Projects

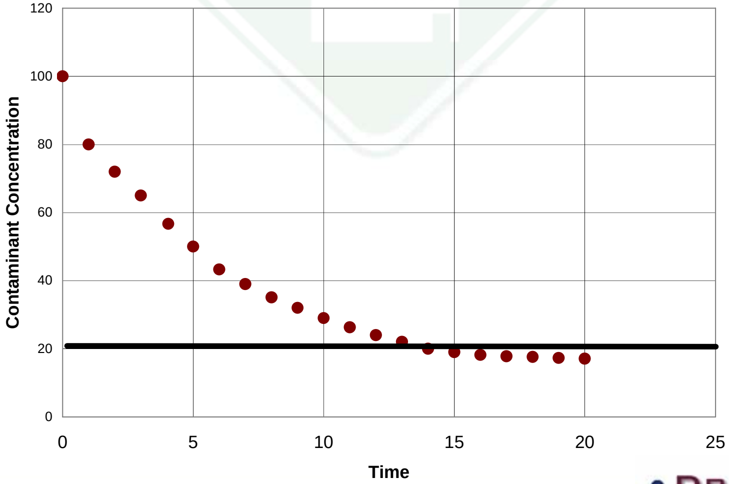
- Analytical measurements are required to monitor the performance of remediation projects
- Typically the expectation is that contamination will decrease over time.
- In some cases increasing concentrations are desired (i.e. recovery wells or vapour monitoring)



Analytical measurements are required to develop models and understand behavior

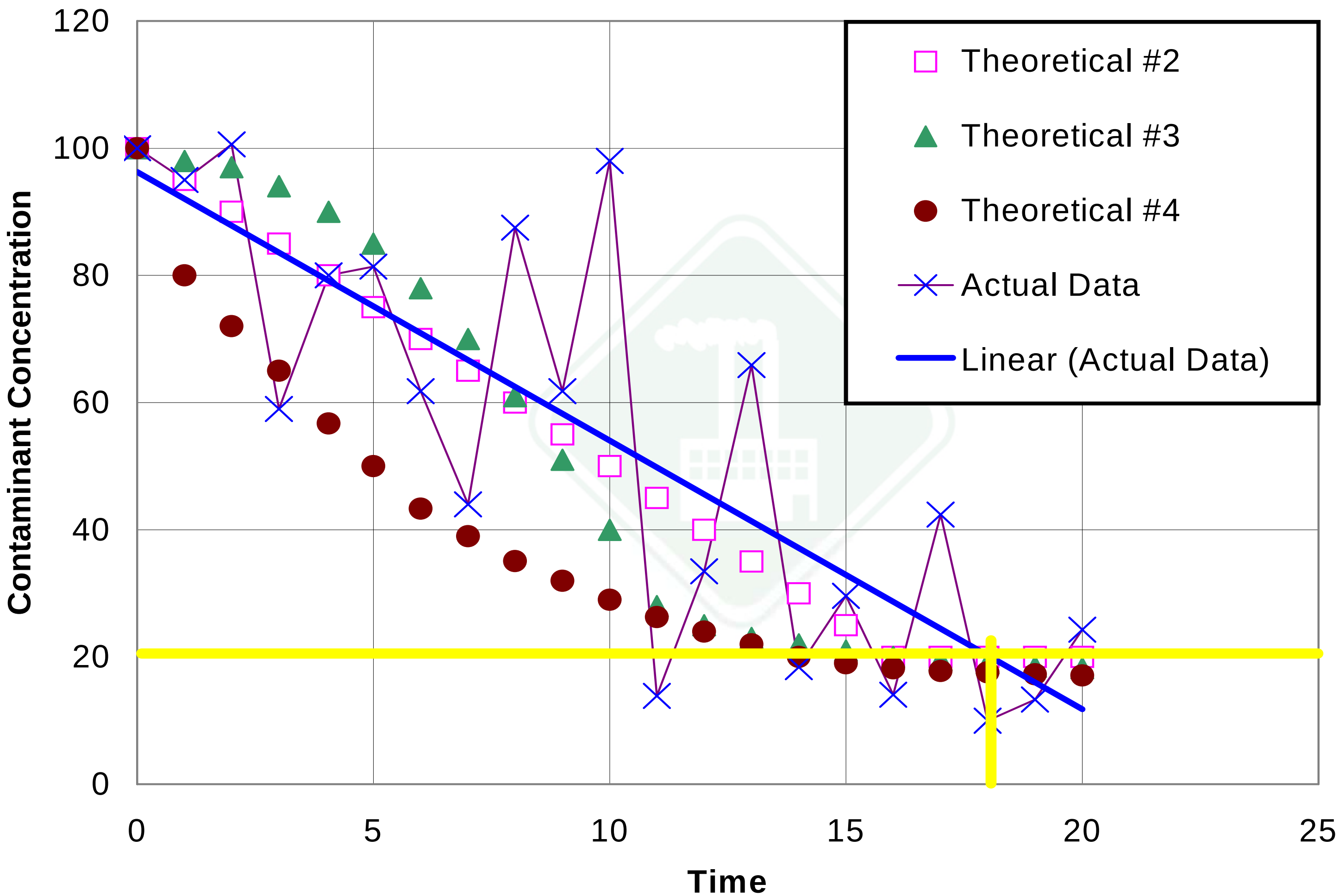




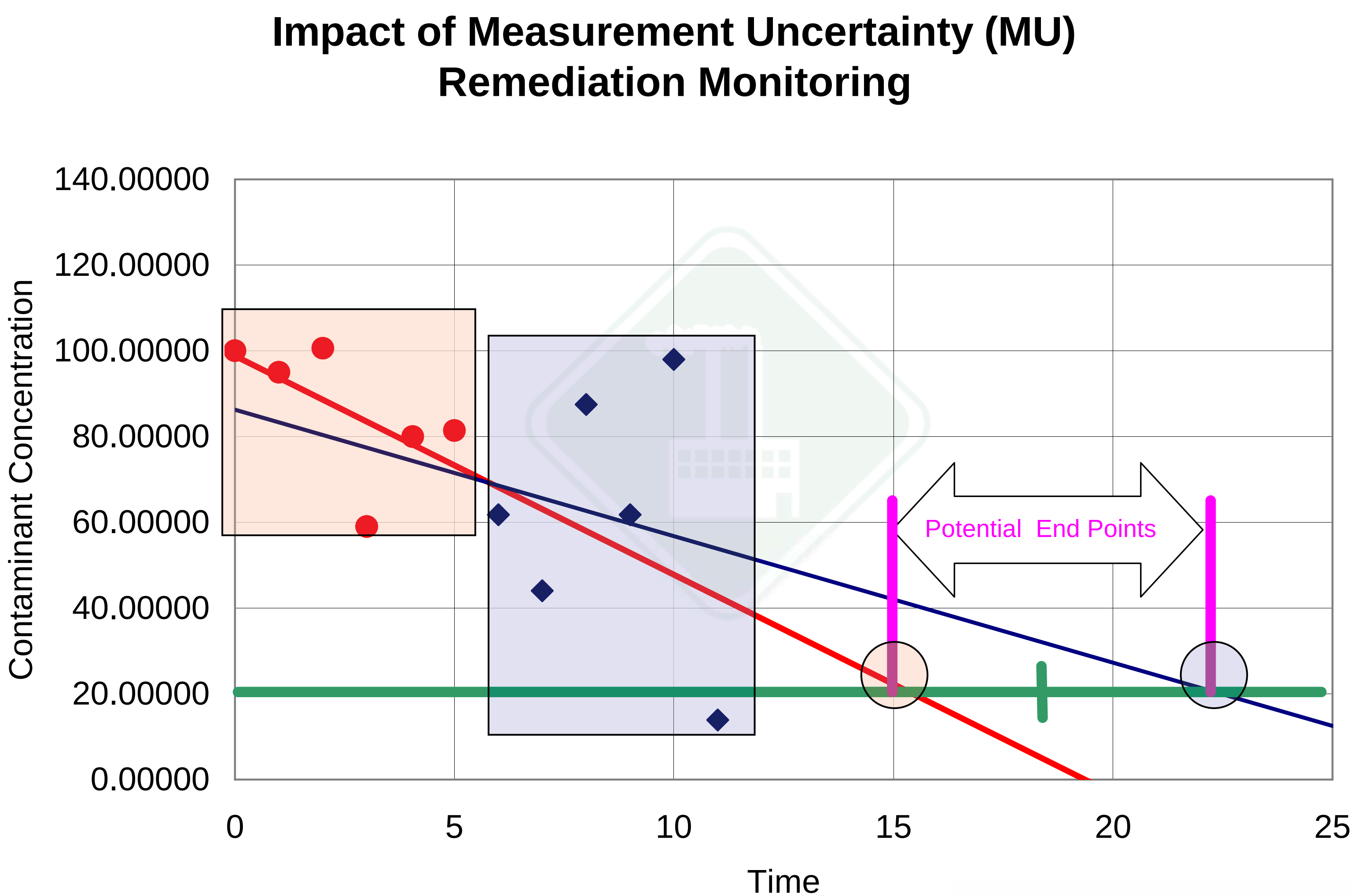


“All models are wrong… some are useful.”

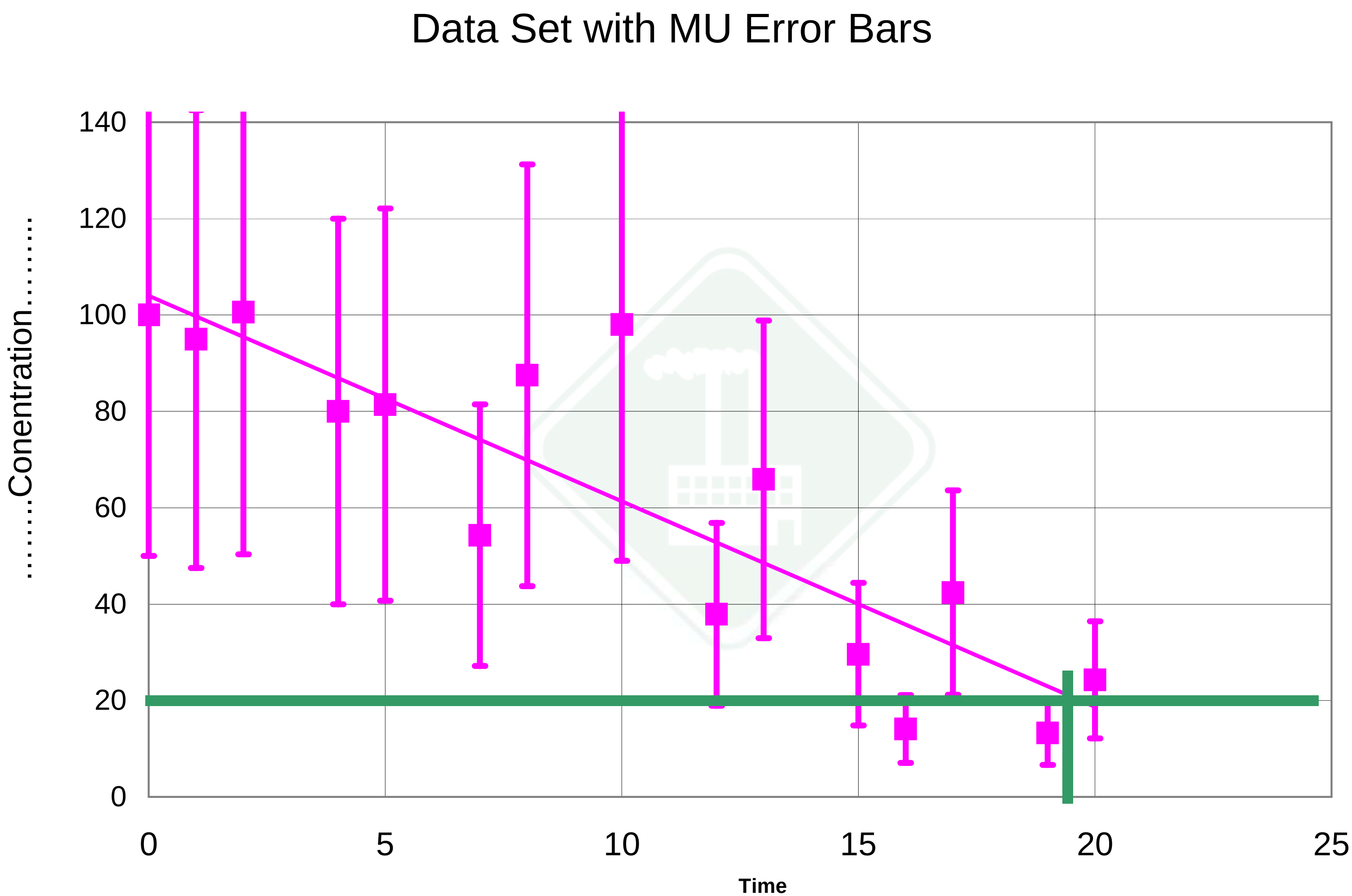
-George Box-



Impact of Measurement Uncertainty



Impact of Measurement Uncertainty

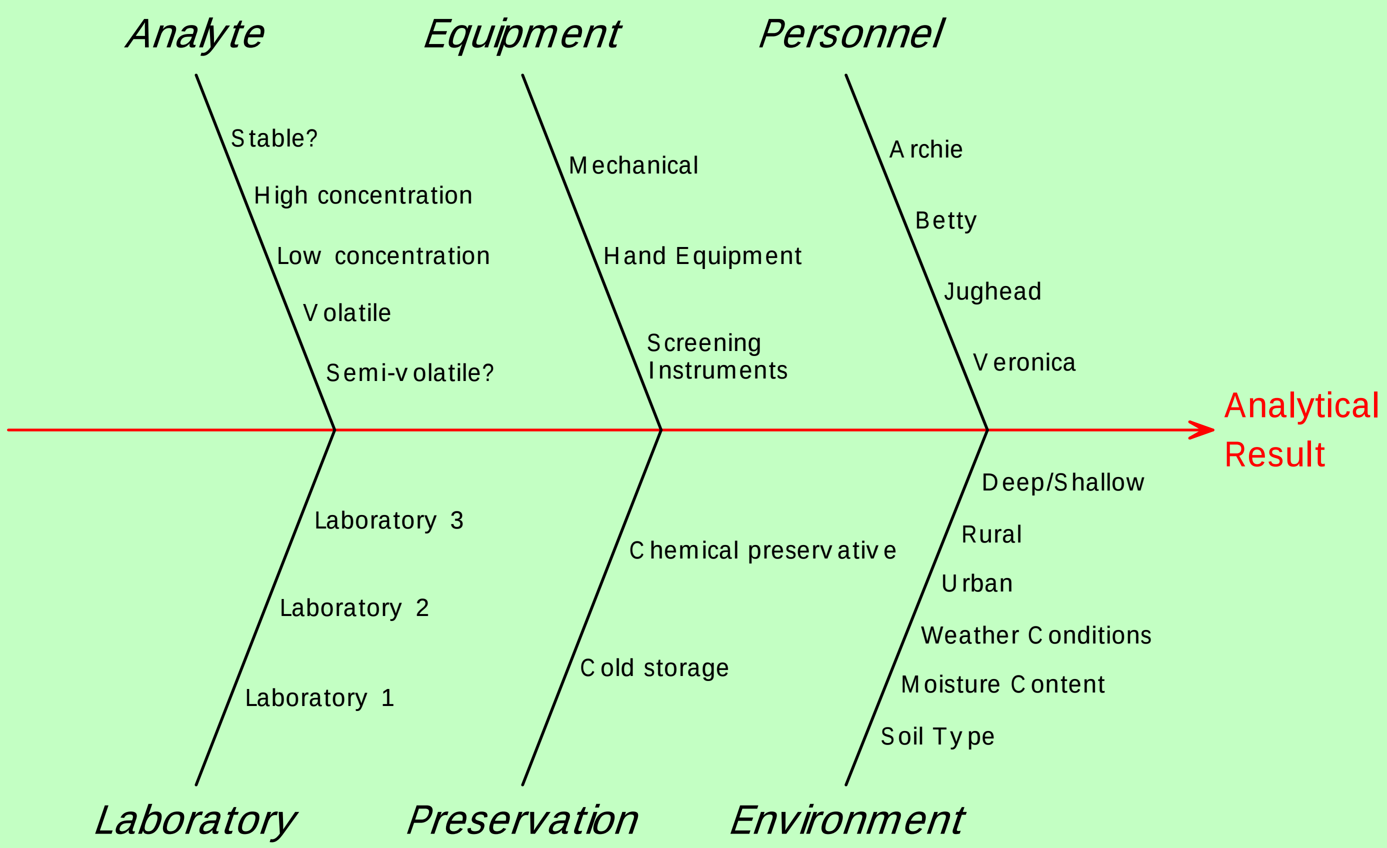


ENVIRONMENTAL SERVICES

Maxxam Analytics Inc

Determining Measurement Uncertainty

Contributions to Measurement Uncertainty



Calculating MU

- Combined Uncertainty (u_c) is calculated by combining all of the uncertainty sources into a single value

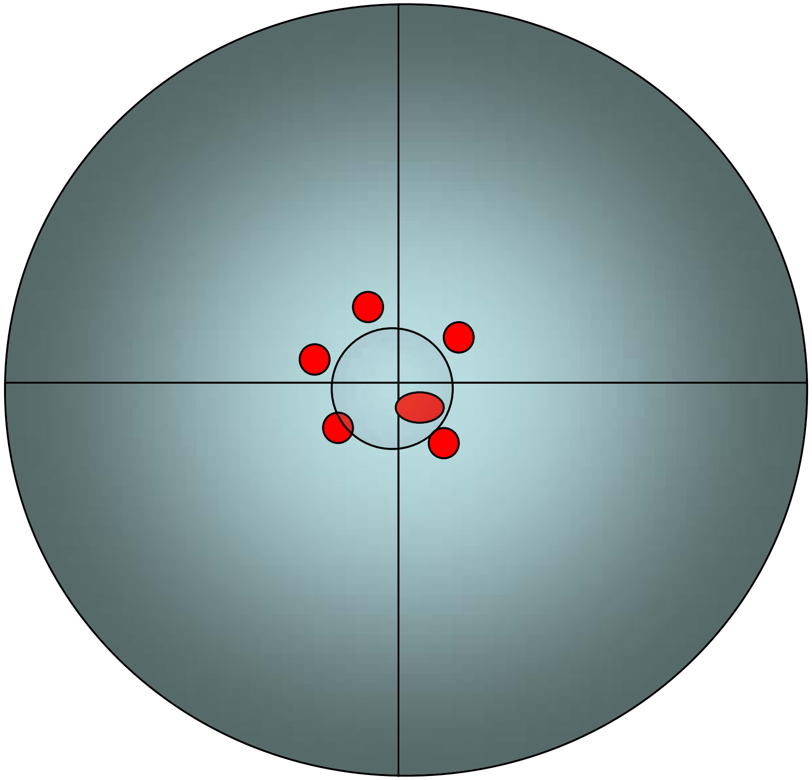
$$u_c = \sqrt{(u_{precision})^2 + (u_{bias})^2}$$

- Expanded Uncertainty (U) utilizes a coverage factor, k = 2, to provide a confidence of 95%.

$$U = 2x\,u_c$$

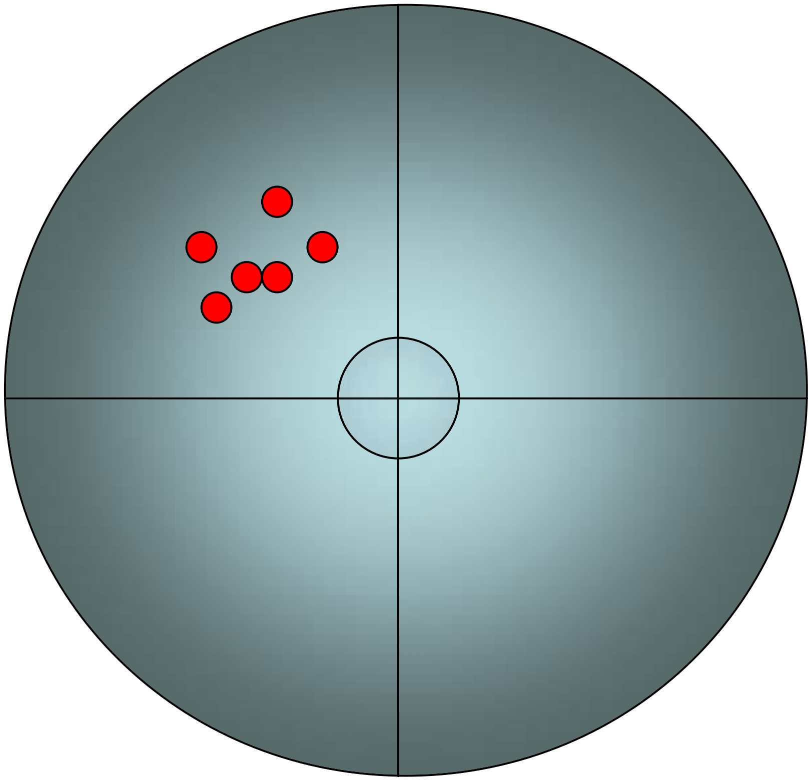
Accuracy

- Accuracy refers to the variation of experimental data to a known or consensus value



Precision

- Precision refers to the amount of scatter associated with a data set



Increasing Confidence

- The most common confidence levels are 90% and 95%.
- The general formula used to describe confidence intervals is shown in the equation below:

$$\bar{x} \pm z^{*} \frac{\sigma}{\sqrt{n}}$$

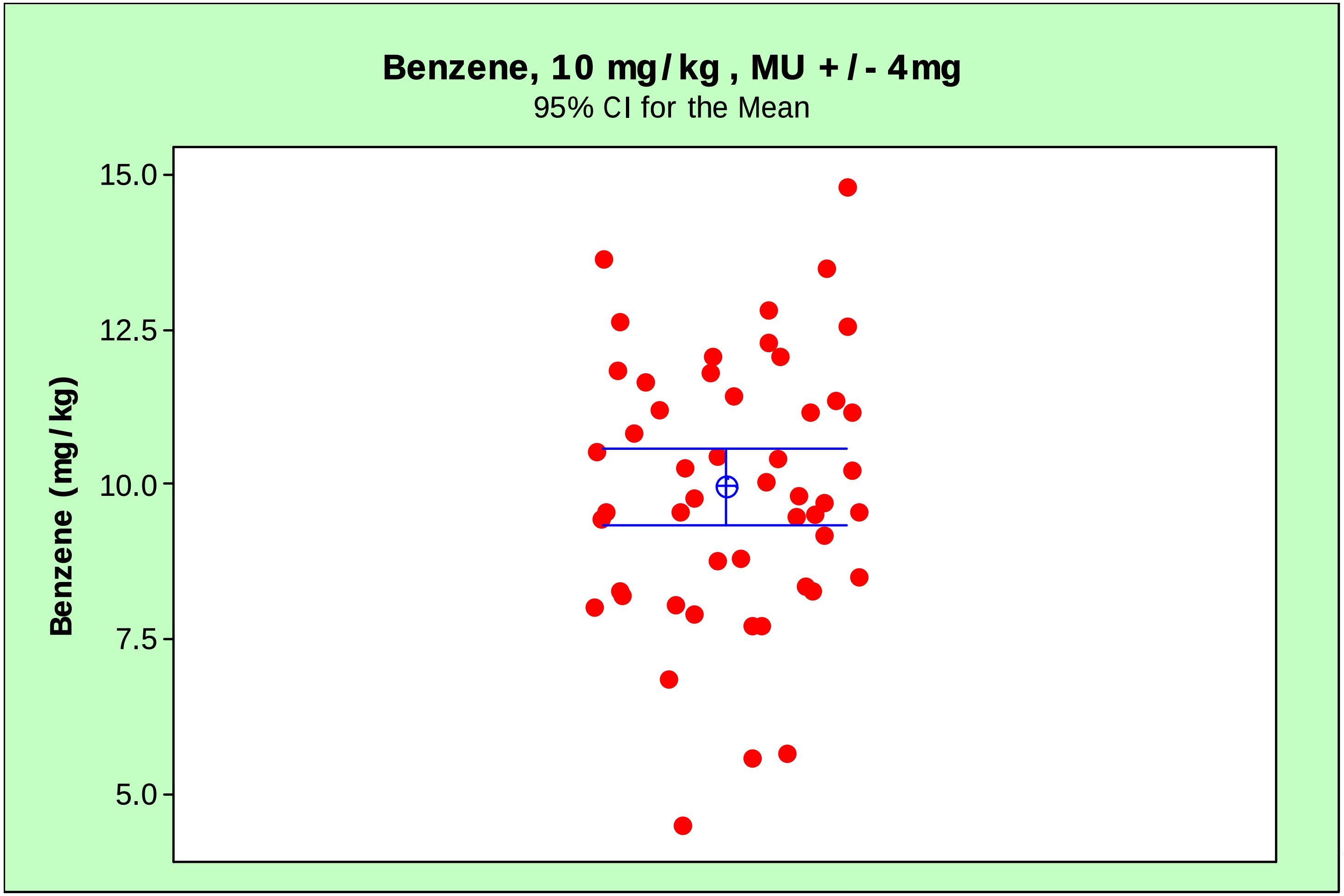
Where $\bar{x}$ equals the mean value found over n observations. σ represents the standard deviation of the data over the long run. z is the standardized normal value and can be found in tables or more often is calculated by computer software .*

n = number of samples

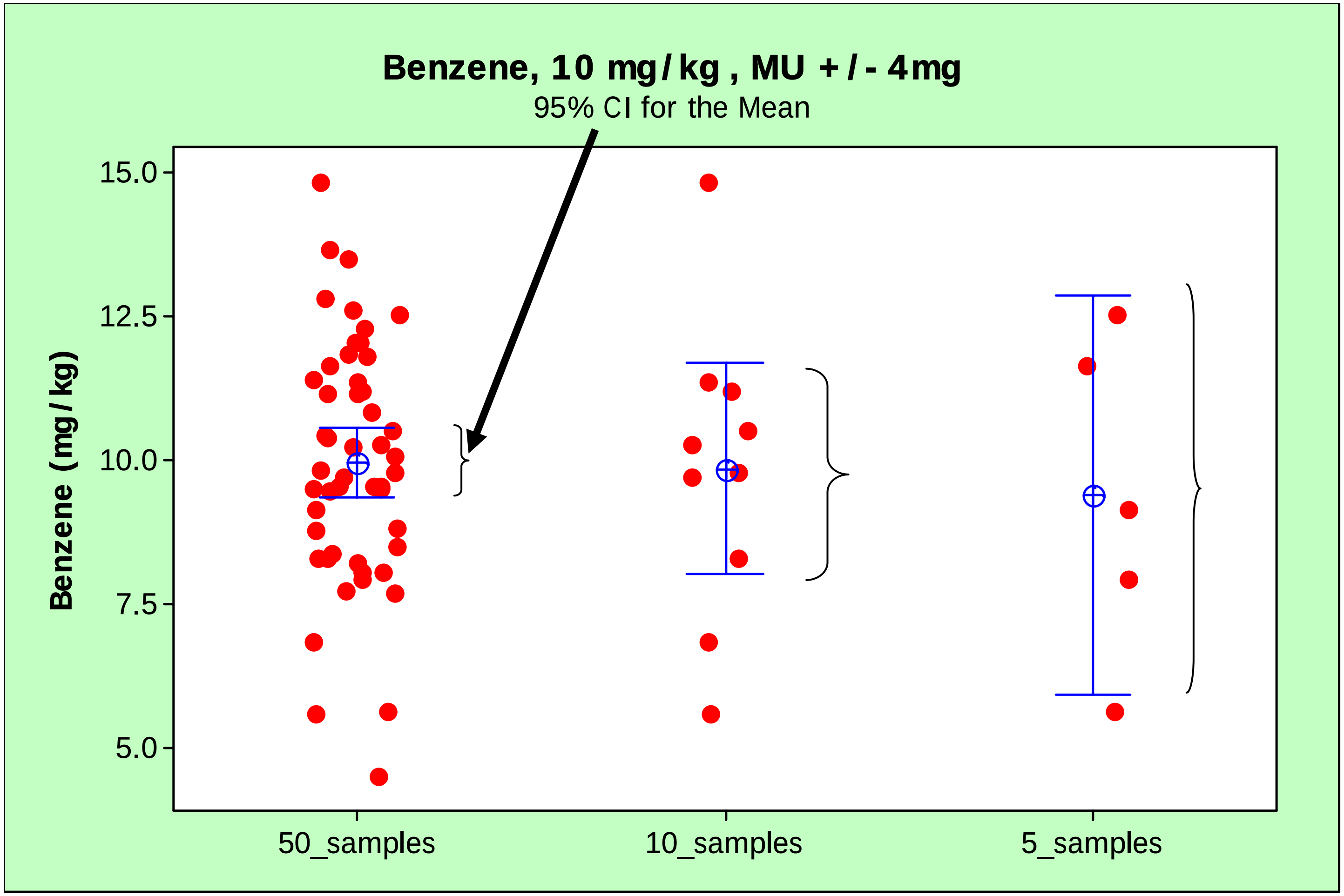
Implies that we can increase confidence by increasing the number of samples collected

Examples of Measurement Uncertainty in Environmental Monitoring

50 samples

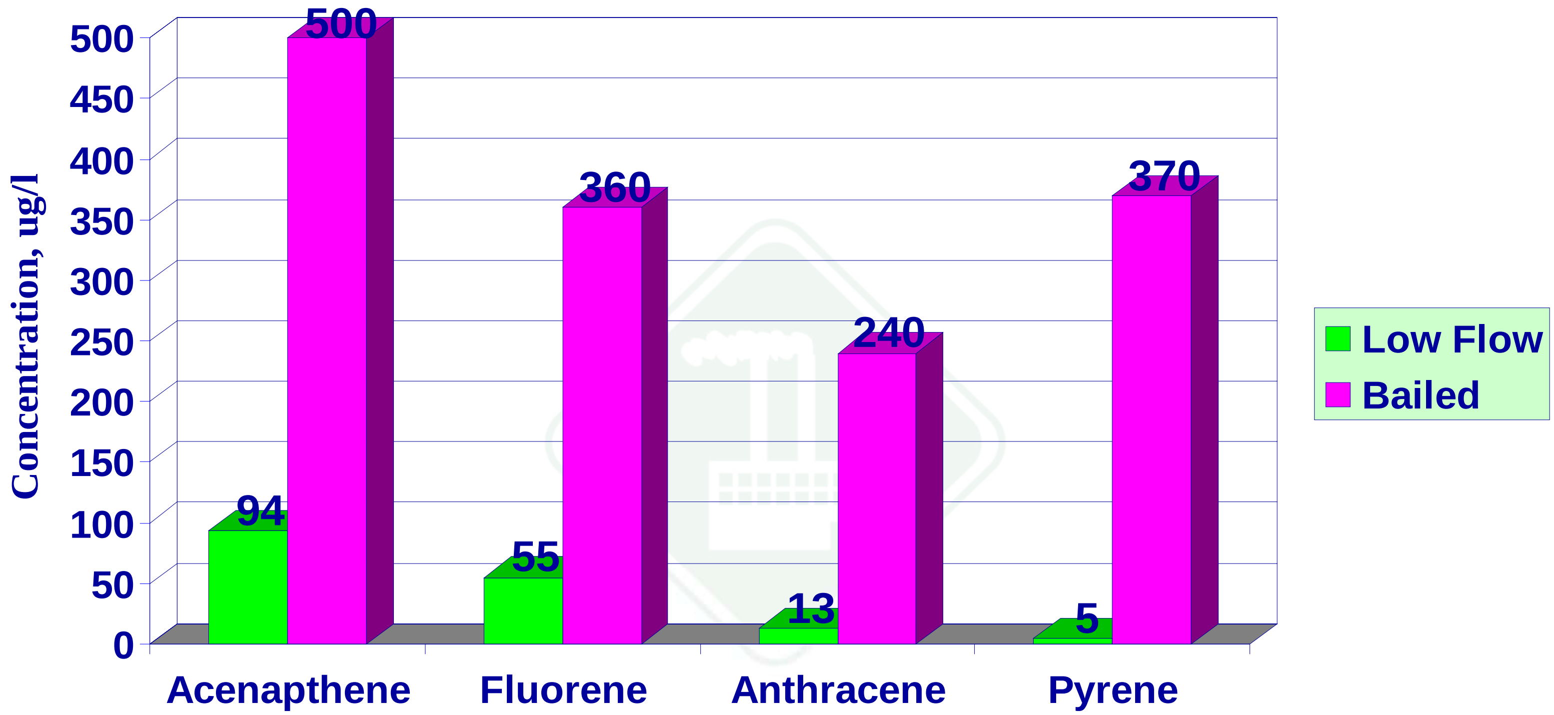


Impact of # of data points on confidence interval



Effect of turbidity on PAH values

(From MacFarlane, et al., 1992)



High sample turbidity results in artificially high PAH concentrations, while low-flow samples represent the true mobile contaminant load.

From: Low-Flow Ground Water Sampling: Theory to Application, David Kaminski, QED Environmental Systems Inc.

Effect of turbidity on PAH values

(From MacFarlane, et al., 1992)

Sampling method	Low-flow pump	Open-top bailer	Open-top bailer
Sample type and Turbidity	**Unfiltered 0.5 NTU**	**Unfiltered > 100 NTU**	**Filtered, 0.45μ 0.6 NTU**
Lead	2	29	2
Aluminum	57	5490	84
Cobalt	9	44	11
Copper	9	22	19
Iron	21	4920	7
Manganese	2	899	3
Nickel	12	33	29
Vanadium	7	31	13

Turbidity can have a significant effect on the concentrations of metals in unfiltered samples. The values from turbid samples that have been filtered can be measurably higher or lower than values from low turbidity samples.

From: Low-Flow Ground Water Sampling: Theory to Application, David Kaminski, QED Environmental Systems Inc.

Repeatability

- Repeatability (r) is a performance measure for results that are obtained with the same method on identical test items in the <u>same laboratory</u> by the same operator over a short interval of time
  - *What are the equivalent conditions that could be applied to "Field Repeatability" (r_f)?*
    - *Same field sampler?*
    - *Same sampling equipment?*
    - *Short interval of time?*
    - *Same preservation techniques*

Reproducibility

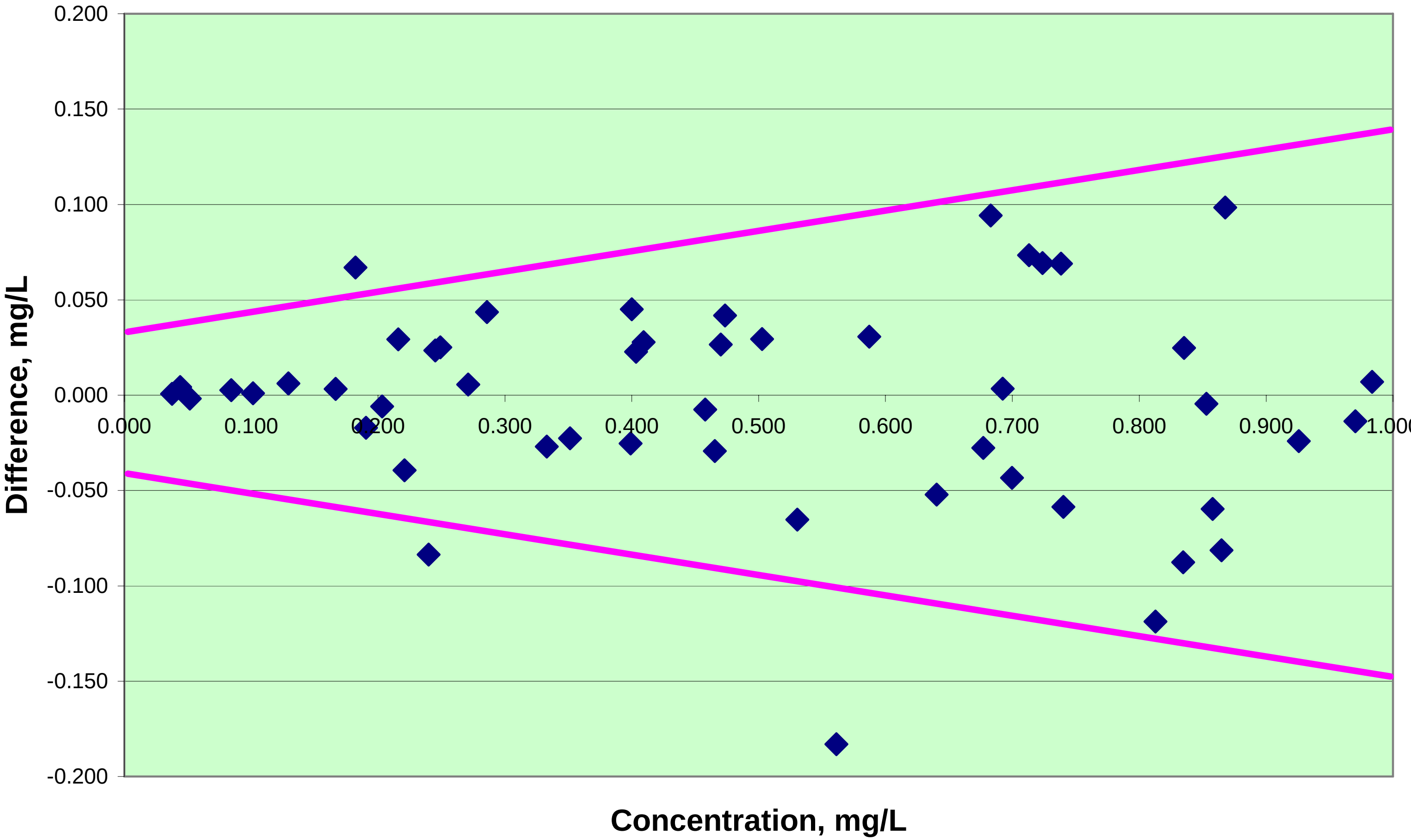
- Reproducibility (R) is a performance measure for results that are obtained with the same method on identical test items in <u>different laboratories</u>.
  - *What are the equivalent conditions that could be applied to "Field Reproducibility" (R_f)?*
    - *Different field sampler?*
    - *Different sampling equipment?*
    - *Different sampling techniques?*
    - *Different preservation techniques?*

Using Duplicates to Estimate Measurement Uncertainty

Sample #	Original	Dupicate	Mean	Difference	%RSD
1	0.351	0.374	0.363	-0.023	6.2
2	0.271	0.265	0.268	0.006	2.1
3	0.399	0.424	0.412	-0.025	6.1
4	0.677	0.705	0.691	-0.028	4.0
5	0.813	0.932	0.872	-0.119	13.6
6	0.044	0.040	0.042	0.004	10.0
7	0.740	0.799	0.769	-0.059	7.6
8	0.221	0.260	0.241	-0.039	16.4
9	0.458	0.465	0.462	-0.007	1.6
10	0.409	0.381	0.395	0.028	7.0
11	0.530	0.596	0.563	-0.065	11.6
12	0.101	0.100	0.101	0.001	1.0
13	0.853	0.857	0.855	-0.004	0.5
14	0.167	0.163	0.165	0.003	2.0
15	0.333	0.360	0.346	-0.027	7.8
16	0.700	0.743	0.721	-0.043	6.0
17	0.465	0.495	0.480	-0.029	6.1
18	0.182	0.156	0.169	0.067	39.6
19	0.473	0.432	0.453	0.042	9.2
20	0.926	0.950	0.938	-0.024	2.6
Mean range				**%**	**8.1**
Reproducibility standard deviation				**% s(R)**	**7.1**

Using Duplicates to Estimate Measurement Uncertainty

Phosphate in Water, Duplicate Samples



Using Field Duplicates and Multiple Sampling Events to Estimate Measurement Uncertainty

- One possible approach is to directly use the reproducibility standard deviation (s_R) obtained from field duplicate results. In this case u_c is approximately equal to s_R

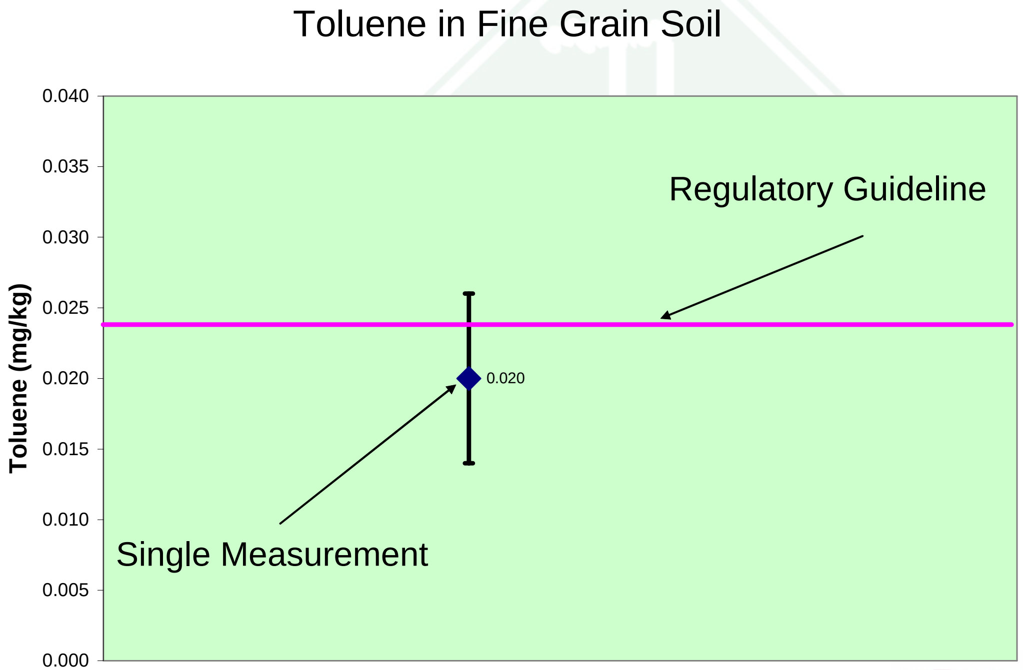
- Example: Phosphate in Water, single result = 0.50 mg/L
  - Previous number of duplicates, n = 20
  - $u_c \sim s_R$ = 7.1%
  - Measurement uncertainty = $U = 2 \times u_c$ = 14.2%

    ==➔ *a possible duplicate range of 28%*

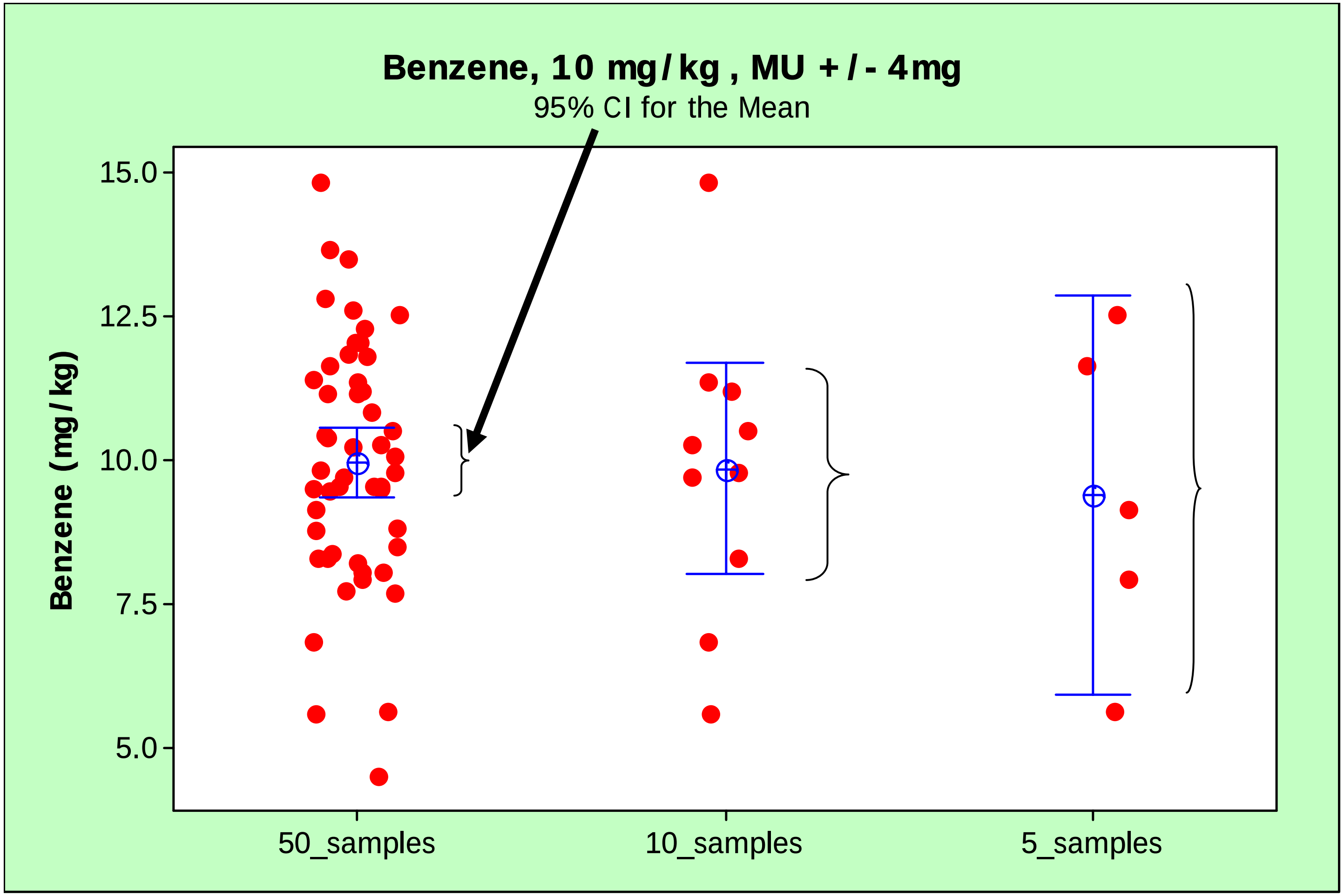
  - Result = 0.50 mg/L +/- 0.07

Fit for Purpose

- For a measurement to be “Fit for Purpose” it must provide the end user with sufficient accuracy and precision.
  - The end user or client must decide if the MU is within tolerance for the application.
    - Example: An analytical result meets the regulatory guideline by approximately 10% (i.e. 90% of guideline value). However the MU associated with a single measurement is +/- 30% at the guideline concentration.
      - A single measurement may not be fit for purpose.



Impact of # of data points on confidence interval



Summary

- Laboratory MU excludes field duplicates. Uses laboratory duplicates
- Ideally MU should include both precision and accuracy components
- Quantifiable MU can aid in the understanding of environmental remediation processes.
- MU can be a useful parameter when concentrations approach regulatory guidelines.
- MU estimates can be obtained from existing duplicate data.
- MU should be fit for purpose.
- Multiple measurements can reduce M.U.

QUESTIONS

Phil Heaton

Maxxam Analytics Inc.

Phil.Heaton@maxxamanalytics.com