Measurement Uncertainty in Laboratory Test Results

Understanding what your results really mean…

Overview

- General Factors Influencing Data Variability
- Measurement Uncertainty
- How is MU minimized in the Laboratory?
  - Analytical Methods
  - Laboratory QA/QC
  - Data Reporting
- Data Interpretation
  - Chloroform
  - BOD

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Measurement Uncertainty (MU)

How to Ensure Reliable Laboratory Results

In order to understand the reliability of laboratory results and ultimately, what they mean, it is important to understand what affects the "variability" of a number, and what steps need to be taken to maximize the "representative-ness" of the data in the context of the site.

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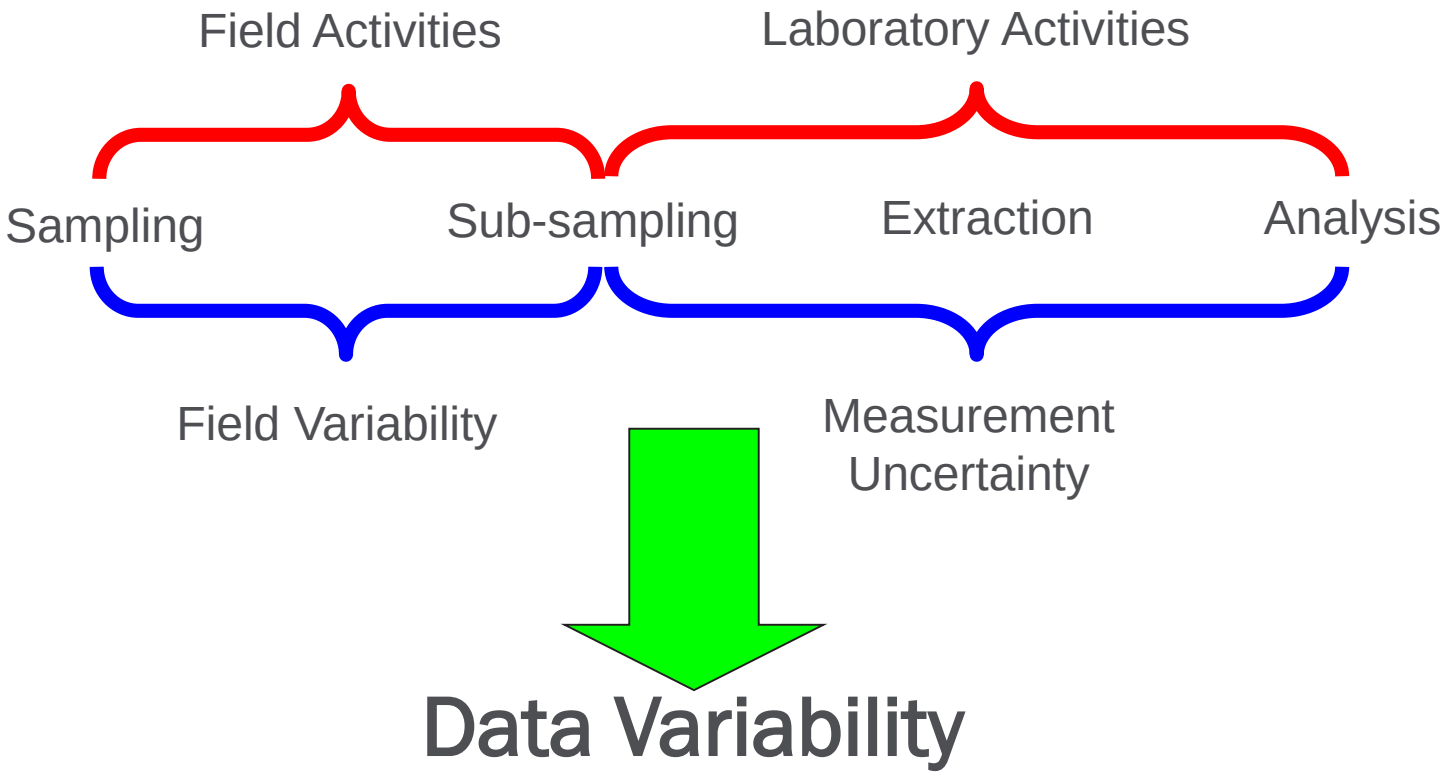
Factors Affecting Data Variability



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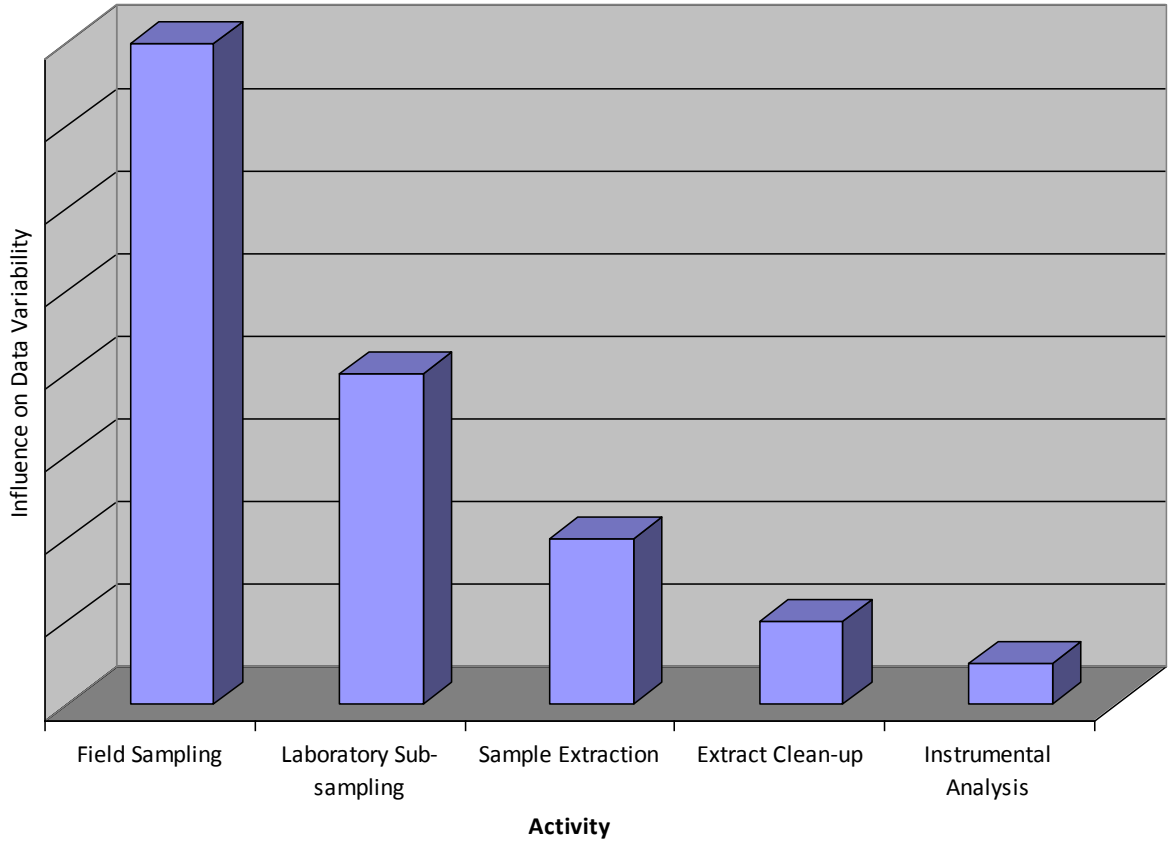

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Definition Measurement Uncertainty

*A parameter associated with the result of the measurement, that characterizes the dispersion of the values that could be reasonably attributed to the measurand.**

* ISO *Guide to the Expression of Uncertainty in Measurement*

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Definition of Measurement Uncertainty
(…in English)

It's a value that gives an idea of variability within a set of measurements that is specific to a sample or group of samples…

or

"…a ± value specific to the result"

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Approaches to Estimating MU

Simple (but with limitations)

$$\sigma \times \text{factor}$$

where,
σ = standard deviation

More Robust

$$U_c = MBlkLT + k * [\sqrt{\{s_0^2 + (\theta c)^2\}}]$$

where,
U_c = expanded uncertainty at concentration c
MBlkLT = mean positive long term method blank value
k = coverage factor (dependent on no. of data point)
S_0 = standard deviation at “zero” concentration
θ = combined relative standard uncertainty
C = measured concentration of analyte in the sample

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Measurement Uncertainty (MU)

Note…

The ability to evaluate and calculate measurement uncertainty is a ***requirement of ISO Standard 17025***

Caveat:

MU reported by the laboratory represents the variability resulting from the lab testing only.

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Possible Sources of MU in the Laboratory

Source	Impact
Sample Homogenization	▪ Poor reproducibility
Representative sub-sampling	▪ Poor reproducibility ▪ Limited data “representativeness”
Reagent purity	▪ Potential contamination or background interference
Sample matrix effects	▪ Interference (e.g. low bias due to oil) ▪ Raised detection limits due to dilution
Instrument effects ▪ Instrument maintenance ▪ Calibration (e.g. solvent standards vs matrix matched standards)	▪ Data bias if instrumentation not optimized ▪ Low bias if solvent-based standards used in calibration
Instrumentation used (e.g. ECD vs MS)	▪ Data variability
Computational effects (e.g. how many and which Aroclors were used to calculate “total”)	▪ Data variability

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Minimizing Measurement Uncertainty

Analytical Methods

- All lab methods are well documented in Standard Operating Procedures (SOP)
- SOPs are based on recognized methods developed by APHA/AWWA/WEF, USEPA, MOE or Environment Canada
- All methods used are validated and verified to meet or exceed the performance specifications of the recognized method

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Quality Management System

QC Sample	Definition	Metric
Laboratory Reagent Blank	Laboratory reagent water put through the entire analytical process; measure of contamination from the lab	Absolute concentration of analyte
Laboratory Control (Spike) Sample	Reagent water or clean reference soil/oil spiked with known amount of target analyte; measure of extraction/analytical efficiency	% Recovery of analyte
Laboratory Duplicate (Split) Sample	Field sample split at the laboratory and processed as two unique samples; measure of analytical reproducibility	Relative Percent Difference (RPD)
Surrogate Spike	Representative analyte (not naturally occurring) that has been added to processed sample, prior to instrumental analysis;	% Recovery of surrogate compound
Matrix Spike	Actual sample (expected to be clean) spiked with known amount of target analyte	% Recovery of analyte

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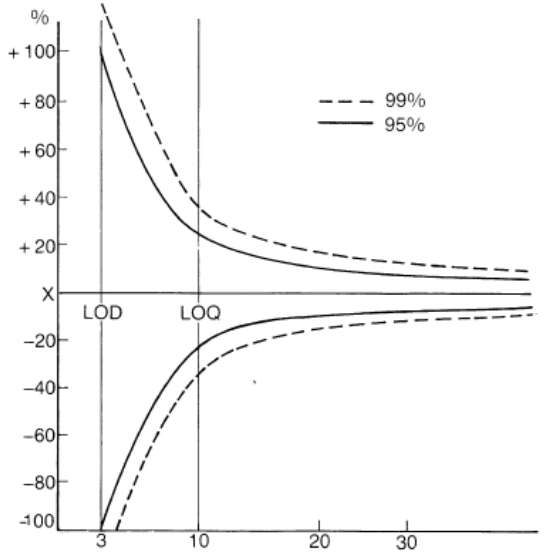
Interpretation of Low Level Data

- As data approach the limit of detection, variability increases
- Variability in analytical results increases as concentrations approach the limits of detection or the upper end of the system's linear range.



LOD ~ 3 x S.D.

LOQ ~ 3 x LOD or ~ 10 x S.D

What this means is that the level of confidence in the value reported at or above the LOQ (RDL) is much higher than the level of confidence reported at the LOD (MDL)

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Reporting Limit (RL)

Maxxam sets a "reporting limit" or "estimated quantitation limit" at 1-10X the statistical MDL for the following reasons:

- More confidence in results when "hits" are detected
- For many compounds there is no need to see 1000X lower than the applicable criteria – only causes headaches
- Significantly reduces false positives
- Accounts for varying MDLs for multiple instruments running the same test, and annual MDL studies (otherwise our MDLs would change constantly!)

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Data Reporting: *What does "<" mean?*

- Results reported as "<" or "less than" indicate that the analyte of interest could not be reliably quantified above the reporting detection limit (RDL)

- Does not necessarily mean 'zero'.

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Data Reporting: *Significant Figures*

What are significant figures?

- Significant figures are the digits in a number (e.g. a test result) that are "meaningful"
- These numbers typically provide the data user an indication of the precision of a measurement
- It is important to understand, when "rounding" a value that important information is not lost (over rounding) nor is the precision of a value overstated (too many significant figures).

Too few significant digits cause information to be lost and perhaps, limit the utility of a result, and too many significant digits is considered bad style in numerical reporting – showing a lack of understanding of precision.

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Measurement Uncertainty Applied to Typical Water Tests

("What do the results mean?")

Chloroform

Chloroform Concentration	Measurement Uncertainty	What it means…
1	10%	0.9 – 1.1 ug/L
10	9%	9.9 – 10.9 ug/L
100	9.4%	91 – 109 ug/L
1000	94%	910 – 1100 ug/L

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Biochemical Oxygen Demand (BOD)

BOD	Measurement Uncertainty	What it means…
2	28%	1.4 – 2.6 mg/L
200	25%	150 – 250 mg/L
2000	24%	1500 – 2500 mg/L
20000	24%	15000 – 25000 mg/L

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Suggestions for Improvement in the Field

- Robust field quality assurance program
  - No hard and fast rules to field quality assurance…dependent upon acceptable risk
  - Documented in a QAPP
    - Defined data quality objectives (DQOs)
    - Defined field and laboratory quality assurance programs, specific to the project

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Suggestions for Improvement in the Field

- Reproducibility:
  - Field duplicates (must be homogeneous “splits”)
- Sample/Cross contamination:
  - Field blanks (“environment” blanks, rinse or equipment blanks, etc.)
- “Representativeness”:
  - Statistically significant sampling of the location
  - Different locations

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QUESTIONS